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Mapping the feasibility of lignocellulosic biorefinery routes: the relevance of system modelling in life cycle assessment

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MAPPING THE FEASIBILITY OF LIGNOCELLULOSIC BIOREFINERY ROUTES: THE RELEVANCE OF SYSTEM MODELLING IN LIFE CYCLE ASSESSMENT

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Mapping the feasibility of lignocellulosic biorefinery routes: the relevance of system modelling in life cycle assessment

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Abstract

Human induced climate change has caused an escalation of the alterations observed in the climate with consequences that are destabilizing not only the climate, but also water systems, land and ultimately the Earth’s biodiversity. Every chain reaction derived from climate change is bound to be worsened by an intensification of carbon emissions that have already caused warming up to 1.1ºC from pre-industrial levels. Surpassing the 1.5 ºC warming barrier, would signify the trigger of permanent impacts and irreversible consequences in vulnerable areas.

To reach climate goals it will be key to support the development of sustainable biorefineries. Biorefineries integrate processes that convert a biomass feedstock into a range of biochemicals, biofuels and bioenergy. This defossilization of the production industry, together with negative emission technologies like carbon capture and storage (CCS) and carbon capture and utilization (CCU) have been defined as essential contributors to curb the climate crisis. Wood is an attractive raw material that has been highlighted in recent years as an outstanding source for the production of sugars and platform chemicals, materials and bioproducts with high added value. In this context, the concept of second generation biorefinery, based on the exploitation of lignocellulosic raw materials, stands out as a firm candidate to be addressed within the framework of sustainable industrial development. Biorefineries are evolving systems that have great potential to replace traditional alternatives based on the exploitation of fossil resources.

The main objective of this thesis is to determine, environmentally, the weaknesses and strengths of different production routes framed in the scope of a second generation biorefinery. Environmental impacts will be compared with traditional or chemical routes and areas of improvement will be proposed based on the result of the environmental study. The backbone of this thesis is the analysis of renewable carbon opportunities to reach climate neutrality goals and objectives beyond that. This analysis is based in the life cycle assessment (LCA) methodology. Detailed LCAs are performed to support the development of recommendations and best practices in regulations and standards.

Chapter 2 analyzes the environmental impact of biorefineries as systems for the production of sugars. This chapter provides a comparative analysis of the production of first and second-generation sugars, with an overview of the downfalls and benefits of each configuration for a varied range of biomass types. In Chapter 3 the evaluation of a second-generation biorefinery system is accomplished from cradle to gate. The use of residual lignocelluloses, the application of organosolv fractioning and the eco-efficiency concept were key focal points in the evaluation. In Chapter 4 bioethanol is the focal product of the lignocellulosic biorefinery. The second generation biorefinery system is analyzed in a cradle to wheel perspective in this case. Going beyond, if the

CO_2 emissions of the biorefinery process are captured and stored permanently underground, the biorefinery production system has the potential of delivering a carbon negative fuel. Chapter 5 has the objective of evaluating a route for the production of furandicarboxylic acid from hydroxymethyl furfural. These are lignocellulosic intermediates potentially used for the production of bioplastics like polyethylene furanoate. Chapter 6 introduces the environmental assessment of enzyme production through LCA. The future of a well-integrated sustainable bioeconomy will most probably involve the deployment of processing routes based on biocatalysis. In Chapter 7 an integrated route for the production of lignocellulosic succinic acid is analyzed including the utilization of lignocellulosic wastes from the pulp and paper industry and the utilization of CO_2 as raw material from emitting point sources of other industrial plants (CCU). The consequential LCA modelling perspective was considered appropriate for this case study, to evaluate the integration effect environmentally.

This thesis aims to evidence whether the decarbonization of the chemical industry will be possible with biobased systems that involve the use of second-generation biomass. This decarbonization will have a greater potential if CCS or CCU systems are deployed as well. However, the burden shifting to other areas of protection has been a common denominator in the biorefinery systems evaluated. Thus, the recommendations derived from this thesis are that, not only climate impacts should be considered in the drafting of policies, guidelines, standards, binding regulations or environmental product declarations. These guidelines and standards should clearly reflect the need to evaluate other impact categories such as the ones analyzed throughout this thesis. The intrinsic complexity of biorefinery systems make also crucial to consider other methodological alternatives in LCA. These should involve prospective evaluations, absolute sustainability assessments, assessments including the temporality of carbon emissions within the methodology, and a more frequent use of consequential LCA.

KEYWORDS

life cycle assessment, biorefinery, wood, carbon capture and storage, carbon capture and utilization, bioproducts, biofuels, enzymes

Resumo

O cambio climático inducido polo home provocou unha escalada das alteracións observadas no clima con consecuencias que están a desestabilizar non só o clima, senón tamén os sistemas hídricos, a terra e, en última instancia, a biodiversidade. Todas as reaccións en cadea derivadas do cambio climático veranse agravadas por unha intensificación das emisións de carbono que xa provocaron un quecemento de ata 1,1ºC respecto dos niveis pre-industriais. Superar a barreira do quecemento de 1,5ºC, significaría o desencadeamento de impactos permanentes e consecuencias irreversibles nas zonas máis vulnerables. Neste punto de inflexión, as medidas de adaptación para facer fronte aos efectos do cambio climático volveríanse gradualmente menos eficaces. As partes asinantes do acordo de París ratificaron o obxectivo de manter o aumento da temperatura global moi por baixo dos 2ºC, e preferiblemente limitar o aumento a 1,5ºC. Isto levou á necesidade de crear estratexias de descarbonización e redución do uso de recursos fósiles, co obxectivo de alcanzar cero emisións netas. Unha redución drástica e sostida das emisións de gases de efecto invernadoiro podería mellorar rapidamente a calidade do aire, estabilizando as temperaturas de aquí a 2050.

Para alcanzar os obxectivos climáticos, será clave apoiar o desenvolvemento de novas biorrefinarías sustentables e facer efectiva a aplicación de tecnoloxías de emisións negativas, en liña coa Estratexia de Bioeconomía da Unión Europea. As biorrefinarías integran procesos que converten unha materia prima —biomasa— nunha serie de produtos bioquímicos, biocombustibles e bioenerxía. Esta redución de recursos fósiles na industria de produción, xunto coas tecnoloxías de emisións negativas como a captura e o almacenamento de carbono e a captura e utilización de carbono, definíronse como contribuíntes esenciais para frear a crise climática.

A hipótese que se manexa como base é que os procesos desenvolvidos no marco de biorrefinarías e tecnoloxías de emisións negativas, son esenciais para a descarbonización da industria química. Con todo, esta redución das emisións de carbono debe demostrarse mediante os métodos adecuados, non só pola natureza nova dos procesos implicados no desenvolvemento da bioeconomía, senón que tamén pola súa complexidade nalgúns casos. A columna vertebral desta tese é a análise das oportunidades do carbono renovable para alcanzar os obxectivos de neutralidade climática e mesmo o potencial de alcanzar emisións negativas. Esta análise baséase na metodoloxía de análise do ciclo de vida (ACV). Probar esta hipótese é un dos principais obxectivos da tese. Farase a través da análise ambiental dunha serie de casos no marco das biorrefinarías de segunda xeración. Estes sistemas son sistemas propensos a causar efectos negativos noutras áreas de protección ambiental: 'bio' non sempre é sinónimo de sustentable. O efecto do desprazamento da carga ambiental será avaliado nos casos de estudo propostos.

Doutra banda, aínda que o ACV é o método máis adecuado para cuantificar os beneficios e desvantaxes destes procesos, as suposicións metodolóxicas deben ser coidadosamente comprobadas e estudadas. Algunhas das complexidades do ACV dos sistemas de biorrefinaría residen na súa natureza multifuncional, a captación de carbono bioxénico na fase de crecemento das materias primas e o potencial desprazamento da carga a outras categorías de impacto, como se mencionou. Ademais, na maioría dos casos, os procesos implicados nas cadeas de produción de biorrefinarías non se desenvolveron a escala industrial aínda. Moitos dos procesos son probas de concepto, a escala piloto ou laboratorio, o que reduce a dispoñibilidade de datos primarios. Por iso, recoméndase realizar ACV detallados para promover o desenvolvemento consistente de recomendacións e mellores prácticas en regulamentos, normas, estudos, etc. que, en moitos casos na actualidade, non proporcionan un enfoque uniforme. Como resultado, outro obxectivo desta tese foi profundar nos enfoques metodolóxicos do ACV para sistemas bioxénicos.

O **capítulo 1** presenta unha visión xeral das motivacións desta tese. O seu obxectivo é contextualizar a situación climática actual, que segue sendo crítica. O último informe do *Intergovernmental panel on climate change* (IPCC) é un *código vermello para a humanidade* e puxo en manifesto a necesidade de evolucionar cara a cadeas de produción biolóxica, tecnoloxías de emisións negativas e sistemas de mitigación. E aínda que estamos nun punto de inflexión, reverter a situación aínda é posible. A segunda parte desta introdución é unha revisión do concepto de biorrefinaría. En concreto, as biorrefinarías de segunda xeración, que serán o centro dos sistemas estudados nesta tese. Nesta introdución, unha breve visión xeral da metodoloxía ACV mostra a súa estrutura e as recomendacións principais para a súa correcta aplicación.

O **capítulo 2** analiza o impacto ambiental das biorrefinarías como sistemas de produción de azucres. Un dos primeiros procesos da cadea de produción da biorrefinaría é o pretratamento da biomasa para liberar as súas principais fraccións. Os compoñentes como os azucres, dispoñibles nas biorrefinarías de primeira e segunda xeración, son a base para a produción de múltiples produtos de valor engadido. Con todo, tamén son produtos finais na industria alimentaria. Este capítulo ofrece unha análise comparativa da produción de azucres de primeira e segunda xeración, cunha visión xeral das desvantaxes e beneficios de cada configuración para unha gama variada de tipos de biomasa.

Neste capítulo conclúese que os futuros sistemas de produción deberían tender a explotar as fraccións residuais da agricultura e a silvicultura para substituír aos combustibles fósiles co potencial de proporcionar produtos sustentables de valor engadido. Os sistemas de primeira xeración para a produción de azucres, en xeral, presentan mellores resultados que os de segunda xeración, especialmente nas categorías de quecemento global, escaseza de fósiles e impacto na toxicidade humana. Aínda que os sistemas de produción de azucre de primeira xeración implican unha tecnoloxía máis madura, as prácticas de cultivo coa produción e o uso de fertilizantes seguen tendo un impacto significativo en categorías como a eutrofización mariña e de auga doce e a acidificación terrestre. Este non é o caso nos sistemas de segunda xeración, que presentan cargas relacionadas sobre todo co procesamento da madeira para a delignificación, que adoitan traducirse en procesos química ou enerxéticamente intensivos e nun uso menor ou nulo de fertilizantes. A sección augas arriba da cadea de valor das biorrefinarías é relevante, debido aos procesos de pretratamento implicados sobre todo para a biomasa lignocelulósica.

Os resultados ambientais suxiren que é necesaria unha maior optimización dos procesos de hidrólise encimática para reducir o consumo enerxético global destas operacións de procesamento lignocelulósico. Algúns sistemas específicos para a produción de azucres lignocelulósicos son comparables dende o punto de vista ambiental e mesmo resultan en menos impacto que a produción de azucres a partir de cultivos como o trigo. Cabe esperar que, no futuro, a industria azucreira convencional pase a formar parte do concepto de biorrefinaría multipropósito, producindo produtos de alto valor engadido xunto co produto primario. A produción de azucres a partir de cultivos azucreiros deberíase priorizar en lugar de cultivos con contido de amidón. As lignocelulosas ofrecen boas oportunidades para obter azucres de grao químico se as tecnoloxías e os pretratamentos evolucionan.

No **capítulo 3** lévase a cabo a avaliación dun sistema de biorrefinaría de segunda xeración dende o berce ata a porta. O uso de madeira residual, a aplicación do fraccionamento Organosolv e o concepto de ecoeficiencia foron os puntos crave da avaliación. O obxectivo principal era analizar o impacto ambiental dunha instalación de biorrefinaría que produce múltiples produtos. Así, neste capítulo, discútese o concepto de multifuncionalidade no ACV —as biorrefinarías son, por definición, sistemas multifuncionais. As recomendacións actuais de ACV deberían ter en conta a natureza deste tipo de sistemas para evitar ofrecer conclusións insuficientes e recomendacións que dependen das suposicións do estudo.

En termos xerais, os puntos conflitivos da biorrefinaría lignocelulósica son as seccións de materia prima e pulpeo, así como a produción de enerxía de consumo propio. Estes puntos críticos son diferentes dependendo a categoría de impacto analizada. A comparación de resultados entre diferentes sistemas é complexa no caso dos sistemas lignocelulósicos, debido á cantidade limitada de datos dispoñibles e ás suposicións. Por iso, a introdución do concepto de ecoeficiencia e a exemplificación a través de diferentes escenarios de biorrefinaría é clave para a optimización do proceso. As configuracións de biorrefinaría que son máis ecoeficientes son as que teñen unha mellor integración e un mellor aproveitamento da materia prima que se traduce na produción dunha gama múltiple de produtos de alto valor engadido. A optimización do sistema de biorrefinaría estudado debería centrarse en estudar as posibilidades dunha maior optimización enerxética para lograr a plena integración da planta.

Mentres que o capítulo 3 centrábase na biorrefinaría como instalación multifuncional, no **capítulo 4** o bioetanol é o produto central. Neste caso, o sistema de biorrefinaría de segunda xeración analízase desde a perspectiva do berce á roda. O bioetanol pode utilizarse como substituto da gasolina en vehículos reducindo o impacto climático global. De feito, se as emisións de CO_2 do proceso de produción de bioetanol fosen capturadas e almacenadas permanentemente en depósitos baixo terra, o sistema de produción da biorrefinaría ten o potencial de ofrecer un combustible de emisións negativas de carbono. Conceptualmente, isto significaría que un coche de pasaxeiros que circula utilizando o bioetanol producido con captura de carbono, potencialmente non emitiría CO_2, senón que o recuperaría da atmosfera. O ACV resulta moi útil neste caso, xa que permite avaliar todas as etapas do ciclo de vida para valorar cuantitativamente se esta hipótese pode chegar a ser certa e baixo que circunstancias.

Como resultado concluíuse que os biocombustibles con captura de carbono reducen a pegada de carbono en comparación á gasolina convencional. Estas reducións son maiores se se utiliza electricidade baixa en emisións de carbono e/ou biomasa como fonte de calor no proceso. Os combustibles con maior contido de bioetanol teñen o potencial de producir emisións negativas. En particular, cun combustible E85, podería alcanzarse un balance neto de -2,74 kg de CO_2 eq por cada 100 km percorridos, considerando a rede eléctrica media europea. As redes eléctricas cunha maior proporción de enerxía renovable (por exemplo, en Suíza, Francia ou Noruega) duplicarían as emisións netas negativas alcanzadas (-5,01 kg de CO_2 eq/100 km en Noruega).

A localización xeográfica das biorefinarías con captura convértese nun aspecto crave na produción de biocombustibles con emisións netas negativas. O ideal é que a biorrefinaría sitúese preto de redes eléctricas máis renovables, preto da biomasa usada como materia prima e preto das zonas de almacenamento xeolóxico de CO_2. Na práctica, atopar un emprazamento adecuado pode ser un reto porque estes recursos tenden a estar dispersos xeograficamente. É posible que se prefiran localizacións próximas á fonte de biomasa, o que requirirá unha infraestrutura de tubaxes para a captura que aínda están por desenvolver. Neste tipo de sistemas pódense conseguir importantes beneficios ambientais en categorías de cambio climático e esgotamento de recursos fósiles. Estes sistemas tamén provocan un desprazamento da carga empeorando outras categorías de impacto.

En xeral, o concepto de bioenerxía con captura e almacenamento de carbono, aplicado ás biorrefinarías de segunda xeración, ofrece excelentes oportunidades para reducir a pegada de carbono de frotas de vehículos particulares. Isto é unha vantaxe moi convinte na transición cara a un sistema de mobilidade que sexa neutro en carbono ou mesmo carbono-negativo.

O **capítulo 5** continúa cos produtos procedentes da madeira, mediante o concepto de biorrefinaría. Este capítulo ten como obxectivo avaliar unha ruta para a produción de ácido furandicarboxílico (FDCA) a partir de hidroximetil furfural (HMF). Trátase de produtos intermedios lignocelulósicos potencialmente utilizados para a produción de bioplásticos como o furanoato de polietileno. A produción de produtos que poden ser precursores de bioplásticos ofrece un gran potencial para a estratexia de descarbonización. A produción de produtos químicos a partir de biomasa lignocelulósica inclúe procesos que aínda están en fases preliminares de desenvolvemento. É necesario analizar estes procesos novos, para alcanzar non só a ruta máis optimizada desde o punto de vista económico, senón tamén a mellor alternativa ambientalmente viable. A simulación mediante Aspen Plus deste proceso e o ACV permitiron comparar dúas opcións para a separación do produto final: a cristalización e a destilación. A cristalización presentou unha pegada ambiental significativamente menor.

Doutra banda, la produción de HMF e FDCA segue requirindo disolventes convencionais como o diclorometano, que prexudican a saúde e o medio ambiente. Polo tanto, a futura investigación de rutas para a produción de FDCA debería incluír o estudo de disolventes e catalizadores máis respectuosos co medio ambiente. Tamén debería considerarse a posibilidade de reducir os requisitos enerxéticos, especialmente en consonancia cos obxectivos europeos de descarbonización, nos que debería favorecerse a electricidade renovable.

Este estudo demostra que os produtos químicos baseados na biomasa non contribúen necesariamente á sustentabilidade ambiental. O proceso de transformación de biomasa é moi relevante para conseguir resultados ambientalmente sustentables. Deberían estudarse rutas, desde a perspectiva de ACV, para a produción de FDCA a través de encimas, para avaliar o potencial de ofrecer mellores resultados que as rutas catalíticas.

O **capítulo 6** presenta a avaliación ambiental mediante ACV da produción de encimas. O futuro dunha bioeconomía sustentable ben integrada implicará moi probablemente o despregamento de rutas de procesamento baseadas na biocatálise. A integración dos procesos encimáticos no marco da biorrefinaría será unha parte clara deste futuro. Os biocatalizadores, por exemplo as encimas, adoitan producirse en baixas cantidades en rutas de produción moi especializadas. Isto pode significar que o seu impacto, mesmo para baixas cantidades de produto, é moi elevado. Por outra banda, a avaliación detallada dos procesos de produción de encimas nas biorrefinarías en poucas ocasións inclúese nos estudos de ACV con detalle. Isto dificulta a posibilidade de extraer conclusións sólidas para estas novas rutas. Este capítulo ofrece un estudo detallado da produción de encimas oxidantes que poderían utilizarse para a produción encimática de FDCA.

A produción de encimas mediante procesos de produción a escala laboratorio non optimizados e altamente especializados revela que o consumo de electricidade é un dos principais puntos conflitivos medioambientalmente. Cando estes procesos se escalan, os químicos como materias primas para a formulación do medio de cultivo son o principal contribuínte ao impacto ambiental. Este estudo confirmou que a avaliación dos impactos ambientais de procesos de produción industriais, a través de datos de experimentos a escala de laboratorio, incorrería en erros significativos. Necesítanse procedementos adecuados de escalado para estimar os resultados ambientais a escala industrial a partir de datos de laboratorio. Os resultados do ACV a escala de laboratorio poden ser válidos como punto de referencia preditivo para establecer os obxectivos de optimización máis apropiados.

As diferenzas atopadas nos resultados de encimas diferentes que poderían realizar unha función similar, mostran a necesidade de incluír estes e outros biocatalizadores dentro dos límites do sistema nas avaliacións ambientais de biorefinarías. A investigación futura debe centrarse no desenvolvemento de bases de datos, con datos primarios, que inclúan a produción de varias encimas a diferentes escalas.

No **capítulo 7** estúdase unha hipotética ruta integrada para a produción de ácido succínico lignocelulósico mediante ACV. Esta integración inclúe a utilización dos residuos lignocelulósicos da industria da pulpa e o papel e a utilización do CO_2 como materia prima obtida de fontes puntuais emisoras doutras plantas industriais (captura e utilización de carbono). Este capítulo pretende analizar as perspectivas de redución neta das emisións de carbono na produción de ácido succínico e comparalas cos métodos de produción habituais. Con todo, a procura de oportunidades para a utilización do carbono renovable aumenta a complexidade do proceso e as interaccións con sistemas adxacentes. O ideal é avaliar o efecto e as consecuencias de decisións tomadas que poidan producir cambios na cadea de produción existente. Para iso, a diferenza doutros capítulos desta tese, neste utilizouse o ACV consecuente. Esta perspectiva de modelado examinouse xunto co ACV atribucional, para analizar as conclusións que poden extraerse a través de cada unha delas. O uso do ACV consecuente será cada vez máis relevante nos crecentes marcos de descarbonización e biorrefinaría.

Os resultados do ACV, especialmente de sistemas complexos, presentan unha gran dispersión que conduce a unha toma de decisións problemática. Moitas veces, a necesidade de facer suposicións obstaculiza a posibilidade de chegar a ditas conclusións. Isto leva a profesionais do ACV e outras partes interesadas a non poder tomar decisións en canto á selección da mellor alternativa desde o punto de vista ambiental.

Cando se considera a captura de carbono —para o seu almacenamento ou utilización— a complexidade da contabilización de emisións e fluxos técnicos aumenta a incerteza e a dispersión das conclusións. Aínda que non é adecuado para todos os sistemas, neste caso, o ACV consecuente proposto clarificou á análise das alternativas de produción de ácido succínico. O enfoque atribucional mostra resultados que parecen axustarse ao estado da arte na literatura, mostrando melloras do 41% na pegada de carbono do produto cando se compara coa alternativa fósil. Con todo, o ácido succínico procedente de residuos da industria de papel e CO_2, non mostra melloras con respecto á alternativa convencional producida con biomasa.

A utilización das emisións de CO_2 como recurso (é dicir, carbono renovable) presenta resultados prometedores para a redución da pegada de carbono cando se analiza o sistema mediante un enfoque sinérxico mediante ACV consecuente. No enfoque consecuente, as proxeccións do próximos 20 e 40 anos do mercado de ácido succínico mostran o gran potencial do ácido succínico producido con captura e utilización de carbono. A produción de ácido succínico ten unha serie de efectos, empezando pola redución das emisións de CO_2 en industrias emisoras como a do cemento ou a do bioetanol. Esta gran mellora da pegada de carbono prodúcese á conta de empeorar outras categorías de impacto, como os indicadores relacionados coa toxicidade ou o uso do chan.

Por último, o **capítulo 8** ofrece unha visión xeral das principais conclusións e recomendacións. Tamén se ofrece unha perspectiva de futuros traballos e áreas de interese. Como se puxo de manifesto nesta tese, a descarbonización da industria química será posible con sistemas de base biolóxica que impliquen o uso de biomasa de segunda xeración. Esta descarbonización será máis factible se se despregan tamén sistemas de captura e almacenamento ou utilización de carbono. Con todo, o desprazamento da carga a outras áreas de protección tamén foi un denominador común nos sistemas de biorrefinaría avaliados.

Unha das recomendacións derivadas desta tese é que, non só os impactos climáticos deben ser considerados na elaboración de políticas, directrices, normas, regulamentos vinculantes, declaracións ambientais de produtos, etc. Estas directrices e normas deberían reflectir claramente a necesidade de avaliar outras categorías de impacto como as analizadas ao longo desta tese como a eutrofización, o esgotamento da capa de ozono, a toxicidade, o uso do chan, o consumo de auga, etc.

Estas mesmas recomendacións, regulamentos, normas e mellores prácticas non proporcionan, polo momento, un enfoque uniforme en termos de recomendacións metodolóxicas claras para os ACV. Estas normas deberían regular que suposicións deben recomendarse en escenarios específicos. Isto permitirá comparar de forma coherente os resultados e as conclusións do ACV de diferentes estudos sen necesidade de remarcar continuamente a necesidade de ser cauteloso á hora de sacar conclusións sobre as comparacións realizadas. En definitiva, os sistemas reguladores deben ser conscientes da necesidade de uniformidade, de recomendacións metodolóxicas claras e baseadas no coñecemento e da necesidade de proporcionalas en función do sistema estudado. Os sistemas de biorrefinaría son un bo exemplo diso, xa que necesitarían un marco propio.

Esta tese mostrou a necesidade de considerar formas alternativas de aplicar a metodoloxía do ACV. Máis concretamente, a modelaxe debería proporcionar unha perspectiva máis holística para os sistemas de biorrefinaría que implican tanto a liberación como a captación de CO_2 a través do ACV consecuente. Na implantación de novas liñas de produción e sistemas de biorrefinaría, os estudos tamén deberían incluír a avaliación de escenarios futuros a través de avaliacións prospectivas. Tamén sería recomendable considerar outros métodos para a cuantificación dos impactos a través da metodoloxía do ACV. En concreto, os métodos de sustentabilidade ambiental absoluta permitirían avaliar os sistemas con respecto á situación ambiental actual e a biocapacidade da Terra, para diferentes categorías. Cada categoría de impacto neste método representa a marxe de espazo operativo para a Terra. Os procesos analízanse con respecto a esta marxe de funcionamento, podendo entender cuantitativamente se son sustentables para manterse dentro da marxe no que a humanidade pode seguir desenvolvéndose e prosperando para as xeracións vindeiras sen sufrir danos. Estes modelos alternativos deben considerarse como un complemento dos estudos atribucionais, as avaliacións de sensibilidade e outras consideracións metodolóxicas.

1

Introduction

> *"What you do makes a difference, and you have to decide what kind of difference you want to make."*
>
> Jane Goodall

Chapter 1 Summary

Human induced climate change has caused an escalation of the alterations observed in the climate with consequences that are, and will continue to destabilize not only the climate, but also water systems, land and ultimately the Earth’s biodiversity. Every chain reaction derived from climate change is bound to be worsened by an intensification of carbon emissions that have already caused warming up to 1.1ºC from pre-industrial levels. Surpassing the 1.5 ºC warming barrier, would signify the trigger of permanent impacts and irreversible consequences in vulnerable areas. From this point, adaptation measures to cope with the climate change effects become gradually less effective. The signing parties in the Paris agreement have ratified the goal to keep the rise in global temperature to well below 2ºC, and preferably limit the increase to 1.5ºC. This has led to the need of decarbonization and defossilization strategies aiming to reach net zero emissions. Strong and sustained reductions in greenhouse gas emissions could quickly make air quality better, stabilizing temperatures by 2050.

To reach climate goals, enabling the development of new sustainable biorefineries in line with the Bioeconomy Strategy of the European Union and negative emission technologies will be key. Biorefineries integrate processes that convert a biomass feedstock into a range of biochemicals, biofuels and bioenergy. This defossilization of the production industry, together with negative emission technologies like carbon capture and storage and carbon capture and utilization have been defined as essential contributors to curb the climate crisis.

Due to the novelty of processes involved in the pathways towards a bioeconomy, the hypothetical environmental sustainability of such processes should be confirmed through the appropriate methods. The backbone of this thesis is the analysis of renewable carbon opportunities to reach climate neutrality goals and beyond. This analysis is based in the life cycle assessment methodology. Detailed life cycle assessments should be performed to support the development of recommendations and best practices in regulations and standards.

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1.1. “CODE RED FOR HUMANITY”: CLIMATE TIPPING POINTS

The Earth’s temperature has been naturally and regularly oscillating, approximately for the past 3 million years. Over this period, the climate has bounced from deep Ice Ages, with low concentrations of CO_2, to warmer transition epochs, with peaks of CO_2 concentration in the atmosphere. These natural temperature cycles of the world correspond to complex Earth system dynamics influencing the radiation balance of the planet. Changes in the Earth’s orbit or the sun (incoming radiation), alterations in the albedo (fraction of solar radiation that is reflected), or the long wave energy radiated back to space influence the radiation balance (Jansen et al., 2007). The current Interglacial period —the Holocene— dating approximately 12,000 years back (Figure 1.1), is a warmer transition epoch characterized by the proliferation of the human species, agriculture, the settlement of communities and ultimately a large population growth, energy use increase, and technological advances of today’s day and time (Steffen et al., 2018).

This very human activity, growing exponentially, has caused an escalation of the alterations observed in the climate, which, for the first time are attributed to human activity rather than natural events. The consequences will be a potential departure from the natural cyclic climate changes, destabilizing not only the climate, but also the Earth’s biodiversity. Human-induced climate change has given rise to a new proposed geological epoch —the Anthropocene (Figure 1.1). Anthropogenic activity now measures up to biogeophysical changes, giving rise to potential trajectories of the Earth system crossing planetary thresholds into a non-reversible state (Crutzen, 2002; Steffen et al., 2018). Many scientists consider the beginning of the Anthropocene in the 18th century, catalyzed by the beginning of the Industrial revolution. One of the drivers of climate change is the rapid growth of population, which has quadrupled from the 19th century. This major circumstance has been the core reason of the increased consumption of resources, water use, fertilizers, fossil fuels as a base for the current manufacturing scheme (Steffen et al., 2011).

There has been an unprecedent rise of temperatures in just 150 to 200 years of 1.07ºC above pre-industrial levels. The atmospheric CO_2 concentration annual average has risen from 280 ppm in 1800 to a contemporary 410 ppm (IPCC, 2021). These increases due to an unlimited growth of the greenhouse gas emissions, have led and will continue to lead to catastrophic events overthrowing the atmosphere and biosphere balance. Some of these are intensified by changes in the land (e.g., deforestation) and aerosols which have led to changes in the albedo, potentiating global warming effects (Winckler et al., 2019). The accelerated melting of polar glaciers has reduced the reflection of the incoming sun radiation, tipping over from being a self-cooling system to being an inductor of global warming (Zhang et al., 2021). The rise of sea level, shifts in rainfall patterns (flooding or drought), catastrophic climate events and climate extremes are the results (IPCC, 2021; Steffen et al., 2011).

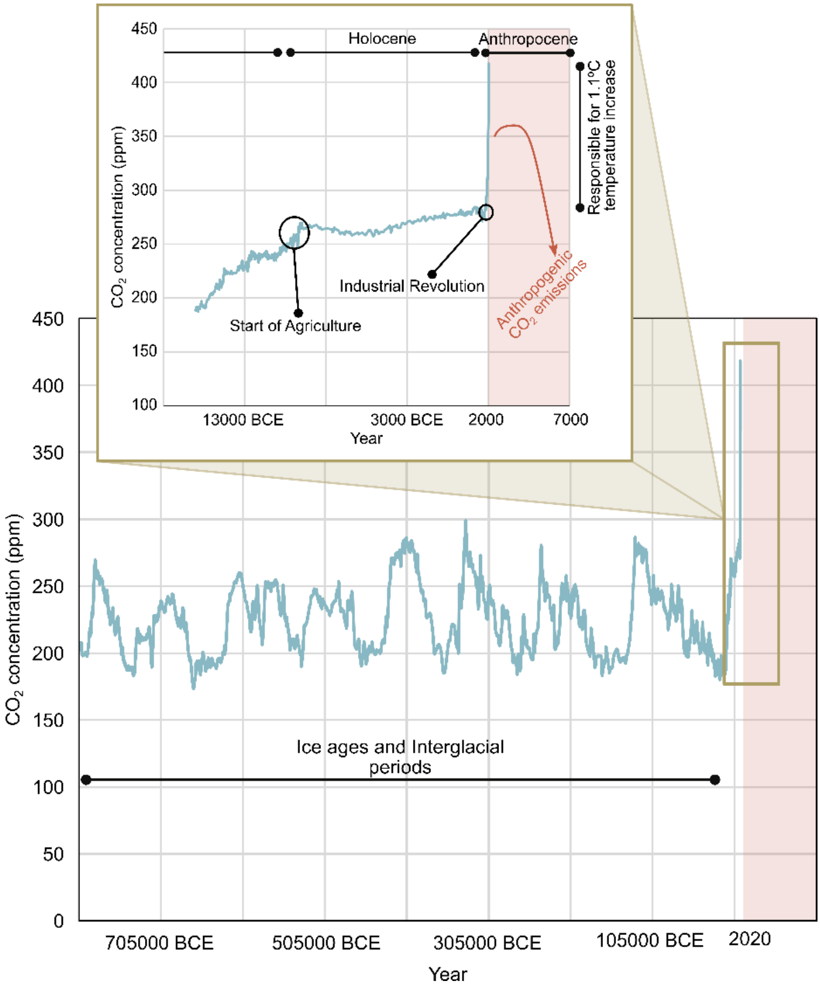


Figure 1.1 Long-term trends of global atmospheric CO_2 concentration in parts per million. Periodic oscillations are consistent with temperatures leading to ice ages and interglacial periods. BCE: Before Current Era. Data from (Ritchie et al., 2020)

However, global warming is not a standalone issue caused by anthropogenic activity. Everything in the Earth is connected, if one system crosses its tipping point, it increases the probability of other systems crossing their stable thresholds, unleashing irreversible changes (Lenton and Williams, 2013). For instance, there has been a progressive increase of deforestation, due to an increased need for agricultural activities, mining and urbanization of land. The savannization and urbanization process incurs in a release of huge amounts of carbon into de atmosphere (Ekblad and Bastviken, 2019;

Mitchard, 2018). In turn it also reflects in a decrease of the biodiversity of animal and plant species (de Chazal and Rounsevell, 2009).

Together with the climate, having a diverse range of species is another base of our civilization. Biodiversity in natural ecosystems and their conservation play a critical role in the coevolution of the biosphere and consequently the atmosphere, hydrosphere, lithosphere, etc. A healthy biodiversity is intertwined with the maintenance of water quality, the regulation of moisture recycling with tropical and temperate forests, the control of pests, the maintenance of water quality, among many other vital roles for the planet's resilience (Folke et al., 2021). An example of the importance of biodiversity is directly related with the ability to upkeep food security. A failure to ensure pollination of food crops would translate in a 5-8% loss of the global crop production, requiring drastic measures of expansion of agricultural land to offset the shortage, or an intensification of pesticide production (Potts et al., 2016). The effects of land use on species, for instance, has been estimated to exacerbate approximately by 15% the abundance of species (Johnson et al., 2017). It has been estimated that the rate of extinction of species is of about 100 to 1,000 times of what should be considered sustainable (Rockström et al., 2009).

In water ecosystems, a relevant problem that has been arising with the growth of agriculture is eutrophication. Nitrogen and phosphorous are essential nutrients used in fertilizers. However, the exponential growth of food crops and the sometimes-overestimated need of fertilizers has produced a runoff of these nutrients from land to water bodies (Grizzetti et al., 2021; Withers et al., 2014). Fixation of nitrogen gas to ammonia (Haber Bosch process) is one of the most relevant processes worldwide, which has allowed the efficient expansion of food production (Glibert, 2020). Furthermore, the production of non-food products have been estimated to account around 35-38% of global eutrophication (Hamilton et al., 2018). This excess of nutrients in water produces an overgrowth of algae, with blooms on the surface of water that block sunlight, produce strong odors, and reduce the oxygen concentration in deeper layers. The reduction of oxygen concentrations concatenates effects such as the change of composition at the bottom of the waterbodies, and the existence of hypoxic zones prompting fish and shellfish mortality (Wurtsbaugh et al., 2019).

Continuing with water ecosystems, the increase of CO_2 emissions by fossil combustion and deforestation, has also caused an increase of the carbon dioxide absorbed by oceans. Oceans absorb about a quarter to a third of the total CO_2, which causes an acidification of seawater, due to the formation of hydrogen and bicarbonate ions from the aqueous CO_2 (Findlay and Turley, 2021). It is estimated that a 30% increase of hydrogen ions has decreased the ocean pH approximately 0.1 units from preindustrial levels (Doney et al., 2020). With current trends of fossil contamination, it is likely that a 60% increase of acidity of ocean's water is reached by 2100, with respect to preindustrial levels. The acidity affects especially the coral reefs in marine water — the rates of calcification decrease markedly, consequently decreasing their ability to grow (as well as that of other species needing carbonate for growth). Changes in ocean temperature have been estimated to range from 0.1ºC to 0.5ºC per decade since 1971 (Findlay and Turley, 2021). Corals have been increasingly dying due to thermal bleaching, as a consequence of this temperature rise directly impacting marine biodiversity (Erez et al., 2011).

The deposition from the atmosphere of acidifying substances such as sulfur oxides, nitrogen oxides, ammonia in the soil causes a decrease in the pH of the soil. This decrease of pH causes the decline of species. Soil acidity, causes changes in nutrient regulation, directly affecting plants and decreasing the yield of crops (Gade et al., 2021).

Industrialization has also prompted the generation of a wide range of other areas of concern related to emerging contaminants. These range from the release of persistent organic pollutants to microplastics present in water, soil and air. Microplastics are generally present in the environment as a result of the solar degradation of plastic waste, its breakdown, from waste incineration, and other sources like powders, microbeads or raw materials to produce plastics. The exposure to humans and other organisms, through ingestion or contact, are a direct threat to the respiratory, neural and digestive systems among others, being their bioaccumulation a serious threat (Wang et al., 2021). Persistent organic pollutants are another threat to human and ecosystems health, due to their accumulative and persistent nature. These include pesticides, dioxins, furans, polychlorinated biphenyls, chlorinated naphthalene, etc. In particular, halogenated persistent pollutants offer a marked resistance to degradation reactions. Many of these chemicals are endocrine disruptors or affect the reproductive system, among other potential effects (Alharbi et al., 2018). Heavy metals (i.e., lead, arsenic, cadmium, nickel, mercury) also have an accumulative nature, and their concentration in the environment (waters, soils) has been derived from their release during mining and extraction from their respective ores and posterior utilization in industrial processes, urban vehicle traffic, electroplating industries, steel industries, tanneries, and others (Ali et al., 2019; Fu and Xi, 2020).

The ozone layer in the stratosphere absorbs harmful ultraviolet radiation, avoiding the damage to human skin and to plants and crops. Changes in the ozone concentration in the layer, can influence the Earth's temperature and climate (Langematz, 2019). In the 80s a great decay of the total ozone was observed over Antarctica (Farman et al., 1985). It was found that the higher concentrations of substances such as chlorofluorocarbons (CFCs) and their substitutes, halons and very-short-lived substances (VSLS) emitted from industrial activity (refrigerants, aerosol sprays, styrofoam packaging, solvents) accelerated the destruction of ozone in the stratosphere which happened at a higher rate than that of its formation (Chipperfield et al., 2020). The situation, prompted the rapid mobilization of different countries, deriving in the Montreal Protocol in 1987 (UN environment programme: Ozone Secretariat, 2020). This agreement had the objective of limiting the increase of ultraviolet radiation, through regulatory limits on ozone depleting substances. The Montreal Protocol was ratified by all United Nations (UN) member states, and has allowed to revert the thinning of the ozone layer, reducing depletion by 20% (Petrescu et al., 2018). Ozone depleting gases are also global warming agents, which has potentially also prevented an even higher than 1.1ºC increase in temperature. It is expected that if the actions prompted by the Montreal Protocol are maintained, the concentrations of ozone depleting gases could be phased out completely in the second half of the 21st century (Neale et al., 2021).

The Montreal Protocol is a great example of political action and collaborative regulation that has led to significant improvements of a problem that, otherwise, would have reached its tipping point. Along these lines, the Kyoto Protocol, in 1997 was an international treaty that presented commitments to reduce greenhouse gas emissions. The gases to which it applied were carbon dioxide, methane, nitrous oxide, hydrofluorocarbons, perfluorocarbons, sulfur hexafluoride, nitrogen trifluoride and nitrogen trifluoride (United Nations, 1997). The document had legally binding obligations of limits and reductions, with two periods of applicability from 2008-2012 and 2013 to 2020. One relevant characteristic is that it addressed the emission problem as a global issue requiring collective action and collaboration. It was estimated that the protocol was effective in reducing emissions of the signing parties by about 7% of their expected trajectory (Maamoun, 2019).

To be able to maintain climate protection measures from the Kyoto Protocol, the Paris agreement was adopted in 2015, to set specific targets for limiting global warming below 2ºC from pre-industrial levels of 1750, pursuing the 1.5ºC limit. Signing countries (195 countries) have set their own reduction targets (Nationally determined contributions, NDCs) according to this agreement, requiring an economic and social transformation (United Nations, 2015). With the adoption of the Paris Agreement, the Intergovernmental Panel on Climate Change (IPCC) has provided a series of reports on different greenhouse gas emission pathways, reflecting different warming scenarios. The IPCC also provides contextualization of different approaches to the problem from the scientific perspective.

The last IPCC report, released in 2021 (IPCC, 2021) depicted the actions that have led to already irreversible changes, and what are some achievements needed to curb some of the consequences. From the IPCC reports series, this last one has been the most pessimistic one, depicting that every chain reaction derived from climate change is bound to be worsened by an intensification of carbon emissions. The report determines connections between climate change and current humanitarian crises, food insecurity, water scarcity, premature deaths, etc. For the already visible effects, it proposes adaptation measures. However, surpassing the 1.5 ºC barrier, would signify the trigger of permanent impacts and irreversible consequences in vulnerable areas (i.e., polar, coastal). From this point, adaptation measures to cope with the climate change effects become gradually less effective. In 2018, the IPCC report delivered a likely timeline for reaching the 1.5ºC from 2030 to 2052 (Intergovernmental Panel on Climate Change, 2018). However, in 2021, it was reported that crossing the 1.5ºC boundary would happen in the early 2030s (IPCC, 2021).

IPCC projections help us understand different model scenarios that correspond to possible future climates. It is a way to gauge what possible situations we can end up in, depending on the measures taken now, since it is uncertain how fast, at which rate and with how much volume emissions will be reduced (Figure 1.2). Scenarios range from stopping emissions and embracing carbon removal technologies to fossil fuel burning without limits. If CO_2 emissions remain at current levels, declining to zero around 2050, a temperature increase between 1 and 2.6ºC could be expected depending on anthropogenic drivers and socio-economic assumptions. If emissions are doubled from current levels, at lower or higher rates, scenarios of temperature increase are 2-4.5 ºC respectively. If very high levels of greenhouse gas emissions are reached, scenarios range from 3-7ºC and 5-8.5ºC (IPCC, 2021).

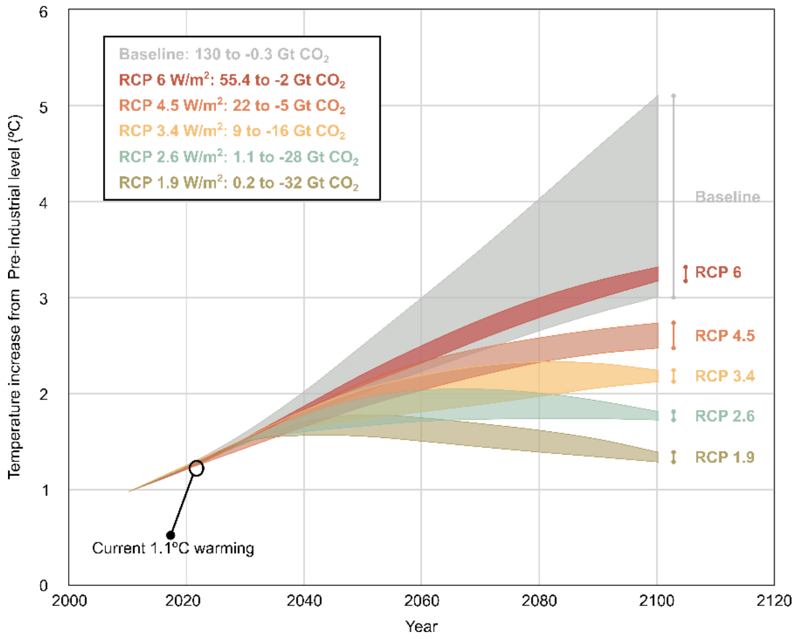


Figure 1.2 IPCC projections for warming scenarios (temperature rise in ºC expected by the end of the century). Scenarios are grouped by Representative Concentration Pathways (RCPs), which represents different levels of radiative forcings reached due

to greenhouse gases and other radiative forcings that may occur. Data from (Riahi et al., 2017)

In the range of 5 to 8ºC warming, the level of the oceans is expected to rise from 2 to 7 m, not being able to rule out up to 15 m in cases of very high emissions. For warmings of 1 to 2.6ºC the sea level rise is projected in a range of 0.5 to over 3 m. If one drought used to occur once in a decade, with today's climate this is multiplied by 2. For scenarios of >2ºC, droughts are multiplied by 3.1, and for scenarios >4ºC by 5.1. Tropical cyclones are bound to increase more than 30% in proportion if temperatures surpass the 4ºC increase (IPCC, 2021). The report specifies that the window for action is narrowing. The conclusion is that we are not in track to achieve a climate resilient future.

In terms of the European Union, member states have set targets to achieve the goals of the Paris Agreement , through the legally binding European Climate Law (European Commission, 2021). They have proposed a reduction of at least 55% of net greenhouse gases with respect to 1990 by 2030, aiming at reaching climate neutrality by 2050. These measures are part of the European Green Deal, which is based on a series of strategic goals mainly sustained on a few pillars: encouraging energy efficiency, promoting cleaner energy through the deployment of renewable sources, incorporating clean mobility systems and harnessing the potential of low-emission technologies (e.g., use of second or third-generation biofuels). The objective is to reach an economic growth that is dissociated from the intensive use of resources, through significant investment. In the short term European strategy, some other key targets are reaching at least a 32% share of renewable energy and 32.5% improvement of energy efficiency by 2030 (General Secretariat of the European Council, 2014).

To curb global greenhouse gas emissions the overall picture from different sectors should be well understood. Reversing the effects of global warming will not be achieved by focusing in only one specific sector, but with the collaborative effects in several. Overall, about 40 billion tons of CO_2 are released yearly in the world due to human made activities (IPCC, 2021). About 73% of global greenhouse gas emissions are derived from energy. Agriculture, forestry and land use account for 18.4% of greenhouse gas emissions. Direct emissions from industrial processes contribute to the climate impacts with 5%. Waste (wastewater and landfill) contributes with a 3% share to the global emissions (Ritchie et al., 2020).

Energy includes electricity, heating and transport (both particular and industry use). Within energy use, industry's share is approximately 24%. The iron and steel and chemical and petrochemical industries are the highest contributors. Direct emissions from transport are 16% of the total global emissions. This share does not include the indirect emissions from the manufacture of vehicles. Road transport represents almost 12% of the transport sector emissions, while aviation represents almost 2% (Ritchie et al., 2020).

In 2022 it is estimated that the likely remaining carbon budget —net amount of CO_2 that can still be emitted by human activities— to limit global warming to 1.5ºC is 120 Gt of carbon, which is 420 Gt of CO_2. This implies that if the remaining carbon budget is exceeded, this will result in an overshoot of the increase of global temperature over 1.5ºC, or the need to actively be globally carbon neutral and remove CO_2 from the atmosphere to draw temperatures back to the desired level. To limit global rise of temperatures to 2ºC the remaining carbon budget is 770 Gt CO_2. The temperature thresholds correspond to a timebound of 11 and 20 years approximately from 2020. Reaching net zero CO_2 emissions by 2050 would entail strong sustained reductions of greenhouse gas emissions, cutting an average of 1.4 Gt CO_2 every year (Friedlingstein et al., 2021).

To help companies target their reduction goals, initiatives like the Science Based Targets initiative allow companies to drive climate action in the private sector by enabling the setup of a framework for reduction targets in line with governmental agreements (Science Based Targets initiative, 2021). Being the objective to stay well below 2ºC warming, phasing out fossil resources in favor of embracing renewable and biobased resources and energy are in the epicenter of current research.

1.2. RENEWABLE CARBON FEEDSTOCK: BIOBASED SYSTEMS

The foreseeable depletion of fossil fuels demands a change in the present productive and economic structure. Strict emission targets will unquestionably derive in a limit of fossil fuel extraction. Models have predicted that about 58% of oil, 56% of fossil methane gas, and 90% of coal should remain in the ground in 2050 to keep global warming within 1.5ºC. Oil and gas production must decline globally by 3% every year until 2050. Accomplishing this would require the rapid deployment of renewable and clean technologies and concluding fossil fuel-based projects that are planned (Welsby et al., 2021). In recent decades, it has been shown that the growth of the humankind footprint has created a major gap between the ecological footprint and the Earth's biocapacity, with a sustained overshoot over the past 50 years. Current production and consumption pathways are prompting a consumption that is way over the resources available yearly (Global Footprint Network, 2018; Jóhannesson et al., 2018). In this context, it is clear that the current progression is far from sustainable and there is an impending need to phase out the use of fossil resources to meet carbon budgets.

The development of an alternative industrial scheme is necessary to reduce the dependency on fossil resources in favor of renewable biological resources. Within this framework, the concept of biorefinery emerges as an alternative to oil-based refineries and the extraction of oil, coal, etc. It requires the development of new processes through research, pilot plants and the scale up to the industrial environment (Elvnert, 2009). As a result of this alternative, an increasing proportion of chemicals, plastics, fuels and electricity are expected to come from biomass in the forthcoming decades. Because of its broad scope and the different drivers behind it, the sustainability of bioeconomy is expected to address important challenges in relation to social, economic and environmental aspects. Within this bioeconomic framework, not only biomass will be at the forefront of sustainability. Also, technological advances in the bioindustry sector, such as the implementation of enzymatic processes, will need to come hand in hand with the exploitation of biomass resources. But furthermore, solutions involving negative emission technologies (NET) such as the carbon capture and utilization (CCU) and carbon capture and storage (CCS), will support reaching climate neutral goals (Bauer et al., 2022; Tatarewicz et al., 2021).

In 2015 the European Commission provided a compilation of 94 bioproducts (fuels, chemicals and polymers) made from sugar platforms, most of which are in the research and development stage. The mapped production pathways were presented discussing opportunities and barriers in their upscale and the policy improvements needed to incentivize their production (E4tech et al. 2015). In Europe, the “Bioeconomy Strategy” (European Commission 2012) was launched as an action plan to guide the European Union towards the application of sustainable resources. Governmental bodies in Europe through multiple initiatives for bio-economy aim to achieve three main objectives: achieving low carbon processes, optimizing the use of raw materials and resources through efficient technologies, and establishing a competitive niche for bioproducts in the market (Scarlat et al., 2015).

In 2021, the European Commission released the European Union Biorefinery outlook to 2030. The document aims to support and facilitate the development of new sustainable biorefineries in line with the Bioeconomy Strategy of the European Union. The report highlights the importance of biochemicals and biomaterials as a key piece of the circular biobased economy, Europe’s transition to a climate neutral economy, and the importance of biorefineries as prompters of food security. In Europe 300 biorefineries are currently deployed at commercial or pilot scale. The current European supply of biorefinery products is estimated to be around 4.6 million tonnes. The supply is estimated to grow to about 7.7 million tonnes in 2030 if there is a favorable world economy and supporting policies are implemented. This, together with the financial support to biorefinery investments, and an increase in the price of oil could have a very positive impact in saving an estimated amount of 3.5 million tonnes of greenhouse gas emissions, and the substitution of 5.6 million tonnes of naphtha (Platt et al., 2021).

1.2.1. Biomass and biorefineries

Biomass has always been available for the production of energy and materials, but its importance endured a less relevant status when, at the end of the 19th century, oil reserves started to be exploited as a direct consequence of the Industrial Revolution (Höök and Tang, 2013). The secondary role that biomass has taken is very likely to change in the coming years. Biomass is mostly organic matter, classified as woody biomass, herbaceous and agricultural biomass, aquatic plants, animal and human biomass wastes, contaminated biomass and industrial wastes (Kumar and Verma, 2021; McKendry, 2002). Other potential feedstock for biorefineries is CO_2, providing diverse opportunities as renewable carbon, such as utilization in fermentative conversions into chemicals providing beneficial carbon fixation pathways (Liu et al., 2020). The global supply of biomass —considering agriculture and forestry— is estimated at almost 12 billion tonnes of dry matter annually. Agricultural crops represent 61% of the total, while forestry 39% (Popp et al., 2021). One of the limitations towards the exploitation of biomass is its secure availability. Although biomass is abundant, a large proportion is destined to food and feed, and the amount of arable land is limited. However, there is a great variety of potential feedstocks in the biobased universe, resulting in very adaptable and versatile supply chains (Platt et al., 2021). The production approaches and end use of bioproducts is also very flexible. Destining arable land to crops and forestry has added benefits such as enhancing biodiversity and providing natural carbon storage. Additionally, there is a surplus of marginal lands that can be used for biomass growth without hindering the growth of food crops (Yang et al., 2021).

Biorefineries integrate processes that convert a biomass feedstock (or multiple) into a range of biochemicals (chemicals, materials), biofuels and bioenergy (power, heat). The core idea of a biorefinery is analogous to that of oil refineries, being both multi-product systems (Figure 1.3). Biorefineries however should engage in considering sustainability criteria, to compensate for low efficiencies in biomass conversion processes. Overcoming these low efficiencies and limitations in regarding the considerable capital investment required, will allow a step towards the phase out of fossil resources (King, 2010; Platt et al., 2021).

The history of the existing corn wet-milling industry can be seen as an example of how the biorefinery of the future will evolve. Initially, the corn wet milling industry produced starch as the main product. As technology developed and the need for higher value products fostered the growth of the industry, the product portfolio expanded from starch derivatives such as glucose and maltose syrups to high fructose corn syrup. Subsequently, fermentation products derived from starch and glucose such as citric acid, gluconic acid, lactic acid, lysine, threonine and ethanol were included in the production scheme. Many other by-products such as corn gluten, corn oil, corn fibre and animal feed are currently being produced. Refineries based on lignocellulosic biomass are undergoing a similar evolution in which the product portfolio is expanding from basic wood fractions (lignin, hemicellulose and cellulose) to the production of higher value added bioproducts (Lynd et al., 2005).

There are increasing examples of biotechnology-based chemicals and materials: ethylene and isobutanol, polymers such as polylactic acid (PLA), polyethylene (PE), polyhydroxyalkanoate (PHA), enzymes, flax and hemp-reinforced composites, all of which are produced from biological feedstocks (Kamm and Kamm, 2004). There is still a substantial gap between the willingness to pay for these products and their production cost. However, the demand of biobased products can grow potentially from 3 to 10% each year until 2030 (Platt et al., 2021).

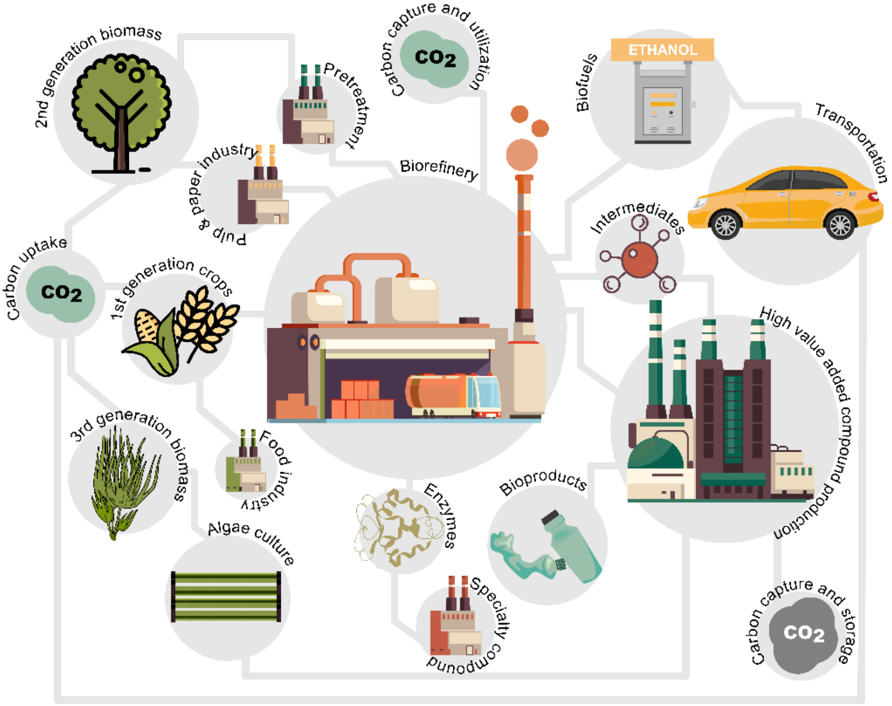


Figure 1.3 Concept of biorefinery which integrates a variety of processes that convert biomass feedstock into a range of biochemicals, biofuels and bioenergy. Multiple biobased products and intermediate chemicals may be obtained from the biorefinery pathway highlighting the multifunctional and interconnected nature of these systems.

1.2.1.1. Feedstock-based biorefinery configurations

The value chain of a biorefinery is built around two relevant entities: the type of feedstock used and the separation process of the different products. Within the biorefinery, different types of biomasses can be used for industrial purposes: energy crops and forestry biomass, agricultural food and feed, crop residues, aquatic plants, animal wastes and other waste materials including those from food and feed processing (Eaglesham et al., 2000). Taking the supply chain of polylactic (PLA) as an example, sugar-based biomass (e.g., sugar cane, sugar beet, etc.) is used as a substrate to obtain lactic acid or lactides. These lactides eventually form the basis of PLA, which can be sold as such and/or used to produce other consumer end products (Dornburg et al., 2006).

Authors suggest the existence of four different biorefinery configurations that have been defined according to the type of feedstock they intend to exploit: first, second, third and fourth generation biorefineries. The biomass to be processed affects the viability of the technologies to be used in each case (Thongchul et al., 2022).

- First generation biorefineries

The use of agricultural resources in industry was first proposed in the 18th century with the development of technologies for corn refining. This achievement marked the first step towards the evolution of the biorefinery approach. Until the conquest of the lead position by crude oil as the primary fuel in the industrialization process of the 19th and 20th centuries, extensive exploitation of biomass was mainly linked to the use of agricultural resources (Kamm et al., 2016).

Today, first-generation biorefineries are facilities that exploit edible crops such as grains, sugar, starch or oilseeds. First generation biomass typically contain sugar, starch and oil (Thongchul et al., 2022). Some of the most common food crops processed in biorefineries are maize, wheat, triticale, sorghum, rice, sugar cane, sugar beet, cassava, soybean, oil palm and rapeseed (Cassman and Liska, 2007). In Europe and North America, most bioethanol is produced from maize and wheat (Vohra et al., 2014).

However, it is recognized that the production of first-generation sugars implies the need for large quantities of feedstocks available at an uncompetitive price; conventional crops could not meet the potential global demands for biofuels to counteract declining fossil fuel reserves, mainly because of potential competition with food and feed markets, which also generates widespread social controversy (Sarkar et al., 2012).

Edible crops provide a high sugar content, which in turn leads to increased production yields of sugar-derived products (e.g., bioethanol). The challenge for first-generation biorefineries is to be able to exploit crops without causing potential damage to food security, arable land or land-use change (Gnansounou and Pandey, 2017). From these drawbacks, other feedstocks have been further analyzed as a prospect to contribute to the decarbonization of industry.

- Second generation biorefineries.

Agro-industrial residues, non-edible crops and forestry products present opportunities to avoid the use of food-based feedstock in biorefineries. Within the scope of second-generation biorefineries, different raw materials such as grass, straw, hemp, forest biomass or harvest residues from crops can be included (Stuart and El-Halwagi, 2014).

Second generation biorefineries go beyond the use of food as fuel. The use of crops that produce woody by-products or crops not intended for food production in biorefineries, avoids a speculative increase of food prices (Hatti-Kaul, 2010). Current research trends focus on lignocelluloses and feedstocks that provide lignin, hemicellulose and cellulose fractions. Some identified barriers of second-generation biomass are its more challenging fractionation, the energy needed for product separation, biological and chemical inhibition. Better integration of the entire process chain should be accomplished, to compensate the capital investment needed, requiring new technologies and facilities (E4tech et al., 2015; Thongchul et al., 2022).

One of the potential challenges faced by this category of biorefineries is the potential diversion of arable land use from food production to energy production. This is the case of energy crops, an option that avoids the use of food as a raw material for bioenergy production, but requires land-use change (Harris et al., 2015). To avoid this concern, a conceivable option would be to transform biomass fractions that have a minimal impact on the use of water, fertilizers, herbicides, machinery, as well as land-use change. Lignocellulosic by-products or waste fractions from crop cultivations that would have no other application are some potential examples.

The opportunities arising from the use of unprofitable fractions of lignocellulosic biomass make it possible to increase the intrinsic value of the raw material by producing several high added value chemicals from wastes (Tomei and Helliwell, 2016). Second generation biorefineries are good examples of biorefineries that can include a variety of processes, platforms, products and process both virgin and recycled biomass feedstocks (Platt et al., 2021). However, the pre-treatment of lignocellulosic biomass is as an essential requirement to retrieve the value-added platforms. Due to the recalcitrant nature of wood and lignocelluloses —complex polymer-like structure— the pre-treatment implies an intensive use of energy and materials for delignification (separation of the main fractions of wood). The complex structure of wood, in which cellulose is integrated within the hemicellulose and lignin network, tends to obstruct and prevent its conversion into monomeric sugars through hydrolysis and fermentation (Kamm and Gruber, 2006).

To deploy second generation biorefineries it is necessary to develop effective pre-treatment methods previously reducing the size of wood when necessary (Himmel et al., 2007). Pre-treatments can be based on mechanical, physical, chemical and/or biological methods (Table 1.1). The selection of the pre-treatment method plays a critical role in the transformation of lignocellulosic biomass in a viable and cost-effective way (Kautto et al., 2013). Pre-treatment technologies for lignocelluloses have been considered one of the costliest processes for second generation biorefineries (Harmsen et al., 2010). The main objectives of pre-treatment technologies are to improve the yields of hexoses and pentoses in downstream processing by ensuring lignin recovery. Some drivers to the optimization of these kind of processes are to decrease costs in the size reduction of biomass, to minimize energy and chemical requirements, to be flexible enough to process different lignocellulosic feedstock and to reduce waste production (Alvira et al., 2010).

Table 1.1 Lignocellulosic biomass pre-treatments. Adapted from Prasad et al. (2016)

Pre-treatment category	Methodology
Physical	Wet milling
	Dry milling
	Grinding
	Microwave
Chemical	Alkaline hydrolysis
	Acid pre-treatment
	Organosolv process
	Ozonolysis process
	Wet oxidation
Biological	Fungal degradation
Physicochemical	Steam explosion
	Ionic liquids
	Catalyzed steam explosion
	Ammonia fiber explosion
	Liquid hot water

Among the pre-treatment techniques for wood fractionation, organosolv pre-treatment has been found to have the advantage of using solvents that can be easily recovered while obtaining high quality lignin (Alvira et al., 2010). During the process, an organic solvent mixture with inorganic acid catalysts (HCl or H_2SO_4) is used to break down the internal structure of lignin and hemicellulose. The most common organic solvents used are methanol, ethanol, acetone, ethylene glycol, triethylene glycol and tetrahydrofurfuryl alcohol (Chum et al., 1988). Organic acids can also be used as catalysts during the process. At high temperatures (above 200°C), the addition of catalyst is unnecessary for delignification but leads to a high yield of xylose (Aziz and Sarkanen, 1989). Once the reaction is complete, it is necessary to recover the solvent for reuse, as it may inhibit the subsequent stages of enzymatic hydrolysis and fermentation phases (Wei Kit Chin et al., 2020).

Recovering the large amounts of lignin present in wood through pulping processes is relevant because of its potential as a fuel for heat and electricity production (Kleinert and Barth, 2008). Recent studies have shown that due to its high quality, organosolv lignin offers different applications as a substitute for phenolic resins or polyurethane compounds (Pandey and Kim, 2011). Besides lignin, many other co-products can be recovered and produced from cellulose and hemicellulose including sugars, acetic acid or furfural. Cellulose and hemicellulose can be hydrolyzed enzymatically to C6 and C5 sugars. These sugars can be further transformed, offering opportunities for the production of a wide range biofuels and biobased chemicals (E4tech et al., 2015).

Although the use of organosolv as a pre-treatment may benefit the production of co-products, its practice has been assumed to be more complex and costly than other methods, due to the high energy consumption in distillation and safety costs and the potential risks of fire and explosion (Zheng et al., 2009). In views of cushioning the high costs of production of organosolv pulp, an attempt should be made to recover all possible products at subsequent stages of processing.

- Third generation biorefineries

Third generation biorefineries use aquatic biomass such as algae to produce, mainly, biodiesel or vegetable oil due to their high oil content (Faraco, 2013). Algae and microalgae are considered a very promising feedstock as they require CO_2 for their growth, which can counteract greenhouse gas emissions through fixation. Moreover, this feedstock does not compete directly with other crops for arable land, as it is grown in photobioreactors or raceway ponds (Gavrilescu, 2014).

Algae growth rates and reactor design should be optimized to maximize production to allow efficient conversion to protein, carbohydrates and lipids. However, the bottleneck of marine biorefinery is the harvesting and subsequent extraction. The potentiality of third generation biorefineries is increasing, due to the multiple efforts towards technological advances, as well as the possibility of not only producing biodiesel, but also other products such as ethanol, hydrogen, liquid fuels, methane and high value products (pigments, antioxidants, carotenoids, proteins). In terms of sustainability, algae biorefineries potentially present strengths over the feasibility of reusing nutrient-rich wastewater instead of saline water (Martín and Grossmann, 2013).

- Fourth generation biorefineries

Some authors propose the inclusion of an additional category of biorefineries for those systems that exploit raw materials that do not belong to any other category (Demirbas, 2010; Gavrilescu, 2014; Haddadi et al., 2017; Stuart and El-Halwagi, 2014). In the case of fourth generation biorefineries, the main feedstocks are waste fractions, such as municipal waste. These biorefineries follow a circular economy approach, using waste that is difficult to manage and has the potential to produce biofuel.

Fourth generation biorefineries potentially include facilities for the treatment of feedstocks that are not directly related to crop cultivation, use of arable land or production of marine feedstock. Rather, they are intended for the valorization of waste fractions such as those from vegetable oils, food industry and even sewage sludge. These new-generation biorefineries may not follow the standard structure of a biorefinery plant and may be combined with wastewater treatment plants or industries to produce valuable products from waste and therefore manage such waste on-site

(Haddadi et al., 2017). An example of the fourth-generation biorefinery concept is the production of polyhydroxyalkanoate from primary and secondary sludge in wastewater treatment plants (Morgan-Sagastume et al., 2014; Mosquera-Corral et al., 2017).

1.2.1.2. Product-based biorefinery configurations

Some biorefineries have fixed processes that produce a permanent portfolio of products, while other configurations can produce multiple products flexibly. The flexibility of the facility to use a blend of biomass feedstocks also influences the possibility to produce a variety of products by combining technologies (Kamm and Kamm, 2004).

One of the objectives of a biorefinery is to obtain products in concentrations that make purification or recovery economically feasible (Mosier et al., 2005). In fact, some authors (Boisen et al., 2009) argue that a biorefining facility should intrinsically not be limited to the production of a single high value added bioproduct and that biobased raw materials should be used as efficiently as possible.

Therefore, we can find that a wide range of biobased products can be obtained depending on the production targets of the biorefinery and technology readiness level (TRL) of the downstream processes. On the other hand, the layout of the plant may vary depending on whether the main production objective is to obtain mainly bioenergy/biofuels or high added value products. In any way, biorefineries are viewed, in most cases as complex systems with multi-production perspectives. Not all plausible products that can be obtained from the biorefinery route have equally developed TRL, the same market size or equal potential market forecasts. Listed below are some of the possible products manufactured in biorefineries (E4tech et al., 2015; Platt et al., 2021):

- Basic biobased building blocks. These are the main starting materials obtained from biomass used for the manufacture of other chemical compounds. They are the main fractions of biomass: lignin, hemicellulose, cellulose, glucose, fructose, galactose, xylose, arabinose, ribose, lactose, sucrose, maltose (E4tech et al., 2015).
- Platform and fine biochemicals. These products are mostly intermediates, converted from biomass building blocks, to produce, for example methane, formic acid, ethanol, acetic acid, glycolic acid, lactic acid, propionic acid, succinic acid, xylitol, levulinic acid, furfural, hydroxymethyl furfural (HMF), citric acid, 2,5-furandicarboxylic acid (FDCA), lipids, 1,4-butanediol, ethyl acetate, cyrene, ethylene, isobutanol, caprolactam (Jong et al., 2012).
- Biopolymers. This category mostly includes polymers that are derived from biobased intermediates, being either biodegradable or non-biodegradable. Some examples include polyamide (PA), polyethylene (PE), polyethylene terephthalate (PET), polyethylene glycol (PEG), polyvinyl alcohol (PVA), polyvinyl chloride

(PVC), polystyrene (PS), polyhydroxyalkanoates (PHA) (Hussein and Al-khafaji, 2021).

- Biomaterials, which may include foams, composites, fibres, bioplastics and films (manufactured from biopolymers) (E4tech et al., 2015).
- Biofuels and bioenergy. This category includes energy derived from any fuel originated in biomass. Some examples are biodiesel, vegetable oil, synthesis gas, alkanes, biogas, biobased methanol, bioethanol, bioalcohol, etc.(Lee and Shah, 2013).

1.2.2. Negative emission technologies in the biorefinery pathway

The utilization of biomass as renewable carbon, in the biorefinery context, provides advantages like the quicker replaceability of resources or the uptake of CO_2 from the atmosphere during its growth. Biomass is carbon neutral, due to the natural carbon cycle, in which carbon is naturally exchanged between terrestrial biomes and the atmosphere through photosynthesis. However, biorefinery processes do not necessarily imply carbon neutrality, because of the impact of their processing technologies (Dhillon and Wuehlisch, 2013).

Experts say that reaching climate neutrality will not be possible, unless the carbon cycle is closed (Singh et al., 2021). While fossil fuels are being exploited, a great amount of CO_2 is released. This carbon emissions cannot be counteracted by the natural carbon cycle alone, or through the implementation of biorefineries and renewable technologies. In this context, carbon dioxide removal (CDR) technologies are essential for the mitigation of climate change according to the latest Mitigation Report from the IPCC (IPCC, 2022).

According to predictions, the carbon budget will be exhausted within this decade if emissions are not compensated by CDR. These technologies apply the gross removal of CO_2. Carbon removal can be done through afforestation and reforestation, which involves restocking previously depleted forests or planting trees in areas that have not been forested for the past years. Soil carbon sequestration provides means for the removal of CO_2 through the improvement of management practices that increase the carbon sequestration in soil organic matter. Enhanced weathering implies the stimulation of rock decomposition and the increase of cation release. This produces alkalinity, which enhances atmospheric CO_2 uptake. However, it also comes with side effects affecting ecosystems and agricultural productivity (Terlouw et al., 2021).

Direct air carbon capture and storage (DACCS) captures CO_2 from air through the use of solid or liquid sorbents. The concentrated CO_2 stream is subsequently stored underground (Mcqueen et al., 2021). CCS is the process of capturing CO_2 from emitting industries before they are released to the atmosphere. Captured emissions can, as well, be stored permanently underground in geological sites or aquifers (Martin-

Roberts et al., 2021). Bioenergy with carbon capture and storage (BECCS) works under the same concept. The processes from which emissions are captured are biobased factories. This implies that, not only carbon neutral biomass has been processed, but also direct carbon emissions are captured, potentially converting the process into a negative emission system (Hanssen et al., 2020).

CCU involves the production of valuable chemicals and products through the utilization of captured CO_2. CO_2 is used as a raw material in a biorefinery, playing an important role in the reduction of the dependency on fossil fuels. CO_2 falls under the renewable carbon category of raw materials, potentially uncovering an additional category of biorefinery raw materials (Garcia-Garcia et al., 2021). Studies suggests that CCU will be an indispensable element of future biorefineries (Liu et al., 2020; Sharifzadeh et al., 2015).

1.3. QUANTIFYING ENVIRONMENTAL SUSTAINABILITY

The main objective of biorefineries is to produce chemicals and products that are not fossil resource intensive. This aims to potentially provide a production system that is more environmentally sustainable than the business-as-usual (BAU). However, due to the novelty of processes involved in the pathways towards a bioeconomy, the hypothetical environmental sustainability of such processes should be confirmed through the appropriate methods. Specially because, in most cases, a great capital investment would be required. In order to evaluate the benefits from biobased systems, the full life-cycle of the products or system should be analyzed. Quantification standards for the evaluation of environmental sustainability of biobased products should be implemented and deployed appropriately (Platt et al., 2021).

Among existing management tools, life cycle assessment (LCA) can be highlighted as one of the most used and reliable methodologies to systematically quantify the environmental impact of a product or activity over its life cycle. This means that LCA is englobed under the life cycle thinking philosophy, a framework that takes a holistic view of the production and consumption of a product or service and assesses its impacts to the environment. A product life cycle, as shown in Figure 1.4, can begin with the extraction of raw materials from natural resources in the ground and the energy generation. Materials and energy are then part of production, packaging, distribution, use, maintenance, and eventually recycling, reuse, recovery or final disposal (Mazzi, 2020).

LCA helps to consistently quantify the pressures that production systems or goods exert on the environment, the trade-offs and areas of improvement. It is a standard methodology (ISO 14040, 2006; ISO 14044, 2006) developed as a result of a series of guidelines and trends kicked off during the 60s. The application of LCA to biorefinery systems should be taken with careful attention, optimizing it systematically and providing guidelines for truthful assessments that are methodologically sound

(Katakojwala and Mohan, 2021). LCA allows to have measurable science-based impacts (order of magnitude), hotspots of systems, and to analyze improvement actions. These capabilities (Figure 1.4) are beneficial to find improvement opportunities within a business, for product development, policy making, strategic planning, marketing and communication and decision making (Muralikrishna and Manickam, 2017).

1.3.1. Sustainable awakening and life cycle assessment

If we focus in environmental sustainability, many refer to the 60s as the decade of sustainable awakening. Specifically, the publication in 1962 of the book “Silent Spring” marks for many the trigger of the modern environmental movement. Rachel Carson was an American biologist well known for her studies on environmental pollution and the natural history of the sea. Silent Spring (Carson, 1962) became one of the most influential books in the modern environmental movement and provided the impetus for tighter control of pesticides (Lear, 1993). Many say that, indirectly, this event triggered the creation of the Environmental Protection Agency in 1970 (Dunn, 2012).

Already in 1969, Coca-Cola® carried one of the first versions of what can be considered today as the foundation of LCA. However, at the time, the study was known as Resource and Environmental Profile Analysis (REPA). Coca-Cola® wanted to analyze the environmental impact of their beverage containers, to assess which production process had the greatest releases to the environment. They quantified the raw materials and fuels used, as well as the environmental impact of the manufacturing processes. The study consisted of a comparative analysis between returnable glass bottles, aluminum and plastic alternatives (Hunt and Franklin, 1996). This study created a consciousness of the need for environmental knowledge for both internal planning purposes and for public relations. Today, the environmental impact of packaging is a big concern for many companies, and the environmental dimension is increasingly accounted for. But back then in 1969, the environmental assessment scene was not comparable to today (Desole et al., 2022).

In the 70s, the oil crisis and concerns about population growth led to environmental movements in many countries. The study “The Limits to Growth” summarized that outlook in 1972. For this publication, a Massachusetts Institute of Technology team produced the global model "World3", providing the basis for the publication. The book reported a study of long-term global trends in population, economics, and the environment (Meadows et al., 1972). It made headlines around the world and began the controversial debate about the limits of the Earth's capacity to support unlimited human economic expansion (Turner, 2008).

In this context of debate, the Society of Environmental Toxicology and Chemistry (SETAC) was founded in 1979. The purpose was to have an assembly for interdisciplinary communication among environmental scientists, biologists, chemists, toxicologists, as well as managers and engineers or other experts interested in environmental issues. SETAC was and continues to be concerned about global environmental issues and is committed to recommend and assure environmental integrity through science (SETAC, 2004).

In 1987 the “Brundtland Report” called for a strategy that aimed to unite economic development and the environment, described by the now-common term sustainable development. Sustainability was defined as the development (the growth) that meets the needs of the present without compromising the ability of future generations to meet their own needs (World Commission on Environment and Development, 1987). The concept of sustainable development, from the publication of the report, became predominantly used in international agreements, literature and treaties (Klarin, 2018).

Since the 1980s, an unprecedented increase of the demand for ecological studies occurred. Continuing with this trend, the 90s was considered as the decade of standardization and development of the LCA methodology. The objective was to uniformize and give a framework to the multitude of LCA studies arising without quality management and mechanisms for the assurance of excellence. In the 90s the SETAC forum was a key contributor for LCA standardization (Klöpffer, 2006). The term LCA was first mentioned after a SETAC workshop for debate and discussion on REPA. The output was an LCA Guideline: 'A Code of Practice'. The guideline reaffirmed essential points from earlier workshop reports and focused on the general structure. Although with a slightly different wording, the structure of LCA is very similar to today’s definition. There were several components to the structure, highlighting the importance of the first component 'Goal definition and scoping'. Other components were ‘Valuation’, 'Classification' and 'Characterization' (SETAC, 1993).

Also in the 90s, the Society for the Promotion of life cycle analysis (SPOLD) was founded. It was an association that wanted to create a file format that would help mold LCA data into a better management tool (Klöpffer, 1997). The SPOLD format for data was the result obtained and was meant to be implemented in LCA software for the exchange of more reliable data inventories. The original SPOLD format was created in 1997 but was later replaced in 1999 with a newer version. The SPOLD format was then replaced by the EcoSPOLD, which was later integrated in LCA (Erixon and Agren, 1998; Meinshausen et al., 2016). In 1997, the International Organization for Standardization (ISO) guidelines were stablished, building on the foundation accomplished by SETAC, and publishing a series related to LCA methodology, guidelines and framework (ISO 14040, 2006; ISO 14044:2006/Amd.1:2017, 2017; ISO 14044, 2006).

1.3.2. Life cycle assessment methodology highlights

The LCA methodology is based on four main phases: goal and scope definition, life cycle inventory, life cycle impact assessment and interpretation (Figure 1.4). In the first step of the study, the definition of the goal and scope is essential to clearly stablish the basis of the impact study. The life cycle inventory phase is one of the most time-consuming phases of the study and consists of the compilation of mass and energy data (inputs and outputs) of the process within the defined scope. The inventory of the system under assessment is a result of the interactions between the production system and the environment system. The impact assessment phase is the stage at which every environmental burden related to an input or output of the process is assigned to a different environmental impact category, to understand its nature, magnitude and significance. The interpretation phase is an iterative approach that aims to draw conclusions based on the findings of an LCA. The main objective is to qualify and check the conclusions by drawing links between the goal and scope decisions and their limitations and strengths (ISO 14040, 2006).

Within the goal and scope definition, the intended application and reasons for conducting the assessment, the functional unit (FU), the system boundaries, allocation procedures, assumptions and limitations should be clearly reported. The FU provides a reference flow and function to which inventory data are normalized. The FU should be carefully selected to allow comparisons and draw meaningful conclusions (ISO 14044, 2006). Attention should be paid to the selection of FU since decision-making strategies may depend heavily on it. The FU should not only represent a number and a unit. It involves the specific circumstances of the study under which such number and unit make sense. For instance, some studies refer to a time frame, geographical location or composition value.

The system boundary describes which unitary processes are included within the system evaluated. The stages and boundaries selected for the study, as well as the omissions considered, should be identified and explained in this scope definition phase. Linking to life cycle thinking, the cradle to grave, cradle to gate, gate to gate or cradle to cradle perspectives define the nature of the system boundary. It is helpful to describe the systems using process flows diagrams that show where the unitary process begins with raw materials and ends with the management of the final products. It is important to note that the selection of system boundaries may be influenced by the availability of data on processes such as end-of-life or waste management (ISO 14040, 2006; Omrany et al., 2021).

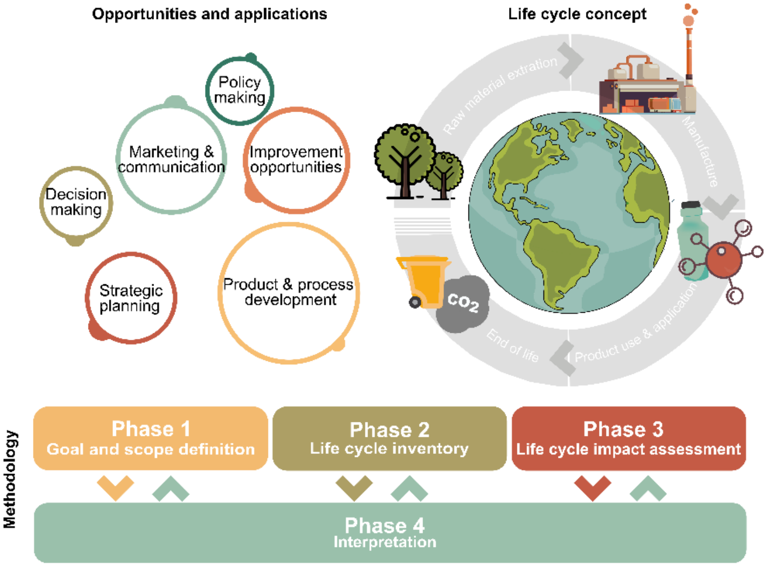
In the life cycle inventory phase, data of systems provides the basis for an environmental evaluation that should be representative of specific processes or products (ISO 14040, 2006; Suh and Huppes, 2005). Data quality and completeness of inventories influence the reliability of the LCA results. When primary data is available for foreground systems, background process data is often implemented as well through the use of literature or database information (secondary data) (Ciroth, 2021).

In the life cycle impact assessment phase, the method selected to perform the environmental evaluation determines the characterization factors that describe the interactions between elementary flows in the system and environmental consequences. The method is usually implemented through specialized software and provides a set of impact categories for the collective environmental description of inventories. Some commonly used methods are CML (Gabathuler, 2006), ReCiPe (Huijbregts et al., 2016), USETox (Rosenbaum et al., 2008), AWARE (Ansorge and Beránková, 2017), etc.. The planetary boundary method differs from traditionally developed methods in that it provides a framework to determine the absolute sustainability of systems. This can be achieved by calculating which share of the safe operating space of the world is occupied by the system under study. It is a framework to determine the absolute effect of the system to the Earth systems (Ryberg et al., 2018).

Among the impact categories, the most frequently used is the global warming potential in all its variants (climate change, greenhouse gas emissions). It is without a doubt one of the most important ones to quantify and measure the defossilization of production systems. In fact, environmental sustainability studies for biorefinery systems often focus exclusively on determining this environmental category. However, there is a relevant need to include other set of indicators that can help determine whether a system would incur in burden shifting. Other impact categories of importance are ozone depletion, acidification, land use, eutrophication and toxicity (Martin et al., 2018).

On another note, there are two types of LCAs: attributional and consequential. Most LCA of biorefineries follow the attributional approach which attributes a share of the potential environmental impacts to the product or the system. However, the consequential approach has the objective of analyzing the environmental consequences of a decision. These are two differing approaches; however, their separate dimensions help to answer different questions in terms of the environmental effect to the Earth system (Ekvall, 2019; Schaubroeck et al., 2021).

The novelty of some biorefinery systems and the specificities of the LCA study in terms of goal, FU, system boundaries, modelling approach etc. make recommendable to perform sensitivity assessments. Studying the sensitivity of certain variables allows to acquire a full picture of the pitfalls and advantages of the system (Wei et al., 2015).



ISO 14040:2006

Figure 1.4 Life cycle concept, life cycle methodology phases as determined by the ISO 14040 standard and opportunities and potential applications of life cycle assessment as a method to quantify the environmental sustainability

1.4. THESIS ROADMAP AND OBJECTIVES

The hypothesis for novel processes involved in the pathways towards a bioeconomy —biorefinery systems and NETs— is that they are essential for the decarbonization and defossilization of the chemical industry. However, this reduction in carbon emissions should be proved through the appropriate methods. They are systems also prone to come with negative effects to other environmental protection areas: ‘bio’ is not always synonym of sustainable. Proving this hypothesis is one of the main objectives of this thesis. It will be done through the environmental analysis of a series of second generation biorefinery case studies.

On the other hand, although LCA is the most appropriate method to quantify the benefits or downsides to these processes, the methodological assumptions should be carefully checked and implemented. Some complexities in LCA of biorefinery systems lie within their multifunctional nature, the biogenic carbon uptake in the upstream of feedstocks and the burden shifting to other categories of impact. Also, in most cases, the processes involved in biorefinery value chains are not deployed at large scale. Many of the processes are proof of concepts, pilot scale or laboratory scale, which narrows down the availability of primary data. Detailed LCAs should be performed to support the development of recommendations and best practices in regulations and standards, which are not providing, in many instances, a uniformized approach. Another objective of this thesis is to delve into the methodological approaches of LCA in biobased systems. The structure of the document is summarized below (Figure 1.5).

Chapter 1 has presented an overview of the motivations behind this thesis. Its aim was to contextualize the current climate situation, which continues to be critical. The latest IPCC report is a code red for humanity and has highlighted the need to shift towards biobased value chains, NETs and mitigative systems. And while we are at a breaking point, reversing the situation is still possible. The second part of this introduction has gone over the concept of biorefineries. Specifically, second generation biorefineries will be the focus of the systems studied through this thesis. A consistent robust methodology such as LCA has been the way forward for the detailed evaluation of these biorefinery processes. In this introduction, a brief overview of the methodology allowed to have a basis for each of the LCA studies analyzed in the thesis.

Chapter 2 evaluates the environmental impact of biorefineries as systems for the production of sugars. One of the first processes in the biorefinery value chain is the pretreatment of biomass to release its main fractions or building blocks. Building blocks like sugars, available from first and second-generation biorefineries, are the basis for the production of multiple value-added products. However, they are, as well, end-products in the food industry. This chapter provides a comparative analysis of the production of first and second-generation sugars, with an overview of the downfalls and benefits of each configuration for a varied range of biomass types.

In **Chapter 3** the evaluation of a core second-generation biorefinery system is accomplished from cradle to gate. The use of residual lignocelluloses, the application of organosolv fractioning and the eco-efficiency concept were key focal points in the evaluation. The main objective was to analyze the environmental impact of a biorefining facility producing multiple products. Thus, in his chapter, the concept of multifunctionality in LCA is discussed —biorefineries are, by definition, multifunctional systems. Current modern LCA recommendations should consider the nature of studied systems to avoid providing narrow conclusions and assumption-dependent recommendations.

While the focus of Chapter 3 was the biorefinery as a facility, in **Chapter 4** bioethanol is the focal product. The second generation biorefinery system is analyzed in a cradle to grave perspective in this case. Bioethanol can be used as substitute of gasoline in vehicles reducing the overall climate impact. Going beyond, if the CO_2 emissions of the biorefinery process are captured and stored permanently underground (CCS), the biorefinery production system has the potential of delivering a carbon negative fuel. Conceptually this would mean that, while a passenger-car drives utilizing bioethanol produced capturing emissions, CO_2 would be *recovered* from the atmosphere rather than emitted. LCA becomes very useful in this case, since it allows to assess all the life cycle stages to evaluate quantitatively whether this hypothesis can become true and under which circumstances.

Chapter 5 continues with the focus on products from lignocelluloses in the biorefinery approach. This chapter has the objective of evaluating a route for the production of FDCA and HMF. These are lignocellulosic intermediates potentially used for the production of bioplastics like polyethylene furanoate (PEF). The production of biobased alternatives of materials such as plastics provides great potential for the defossilization strategy. However, the production of platform and specialty chemicals for the development of biobased value chains is still in its infancy. Processes and units have to be analyzed to not only provide the most economically optimized route, but also the best environmentally feasible alternative.

Chapter 6 introduces the environmental assessment of enzyme production through LCA. The future of a well-integrated sustainable bioeconomy will most probably involve the deployment of processing routes based on biocatalysis. The integration of enzymatic processes within the biorefinery framework will be a clear part of this future. However, biocatalysts, like enzymes, are usually produced in low quantities in highly specialized production routes. This can mean that their impact, even for low quantities of product is very high. On the other hand, the detailed evaluation of enzyme production processes in biorefineries is seldom included in LCA studies. This hinders the possibility of drawing sound conclusions for these novel routes. This chapter provides a detailed study of the production of oxidative enzymes which could potentially be used for the enzymatic production of FDCA.

In **Chapter 7** a hypothetical integrated route for the production of lignocellulosic succinic acid is analyzed with LCA. This integration includes the utilization of lignocellulosic wastes from the pulp and paper industry and the utilization of CO_2 as raw material from emitting point sources of other industrial plants (CCU). This chapter aims to analyze the prospects for net reductions of carbon emissions in the production of succinic acid and benchmark them against BAU production methods. However, finding opportunities for the utilization of renewable carbon increases the complexity of the process, and the interactions with adjacent value chains. Optimally, the effect of introduced decisions in an already existing value chain should be evaluated. To do this, to the contrary of other chapters in this thesis, consequential LCA was used. This modelling perspective has been examined together with attributional LCA, to analyze the conclusions that can be drawn through each. The use of consequential LCA will become increasingly relevant in the growing decarbonization and biorefinery frameworks.

Chapter 8 summarizes the main findings of each chapter, providing an overview of the main conclusions and recommendations. An outlook for future work and areas of interest is provided as well.

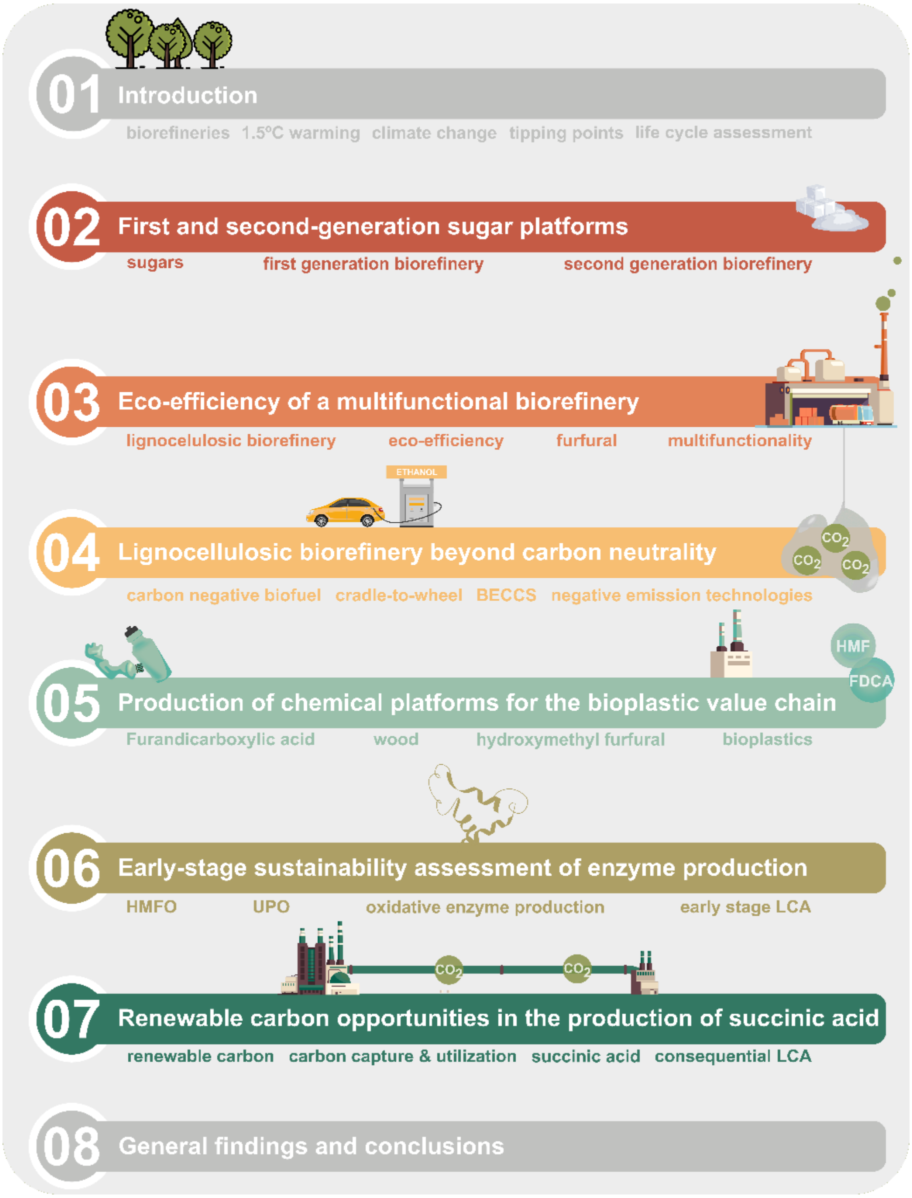


Figure 1.5 Thesis roadmap and main keywords for each chapter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2

First and second-generation sugar platforms

> *"A person who never made a mistake never tried anything new."*
>
> Albert Einstein

Chapter 2 Summary

In recent years, there has been a great movement towards the generation of knowledge related to the biorefinery concept. First-generation biorefineries bear the stigma of using arable land and edible crops for fuel instead of as sources of food and feed. However, second-generation biorefineries have not reached the level of full technical feasibility. Bearing in mind the objective of sugar production from sugar, starch, or lignocellulosic raw materials, the purpose of this chapter is to review and assess the environmental impact of first- and second-generation biorefineries, considering as an example for the comparative evaluation, the production of sugar fractions from crops (starch and sugar crops), and lignocellulosic biomass (hardwood and softwood). The characterization results were obtained using the ReCiPe 1.1 model, implemented through the SimaPro 9.0 software. Both production systems are inherently different and have strengths and weaknesses that must be carefully analyzed. The resulting environmental profile shows that the silviculture of wood implies lower impacts than cropping activities in most impact categories. In general, this study suggests that first-generation systems are environmentally burdened by the use of fertilizers, which have a significant impact on categories such as marine and freshwater eutrophication and terrestrial acidification, while second-generation systems are limited by the intensive processing steps needed for delignification, typically involving the use of chemicals and/or energy. Life cycle assessment in early stages of the production of biobased building blocks, rather than on the manufacture of biofuels or bioplastics, allows the precise identification of the environmental loads that may be influencing the overall environmental profile of a biorefinery. Subsequent chapters of this thesis will dive into the study of the biorefinery as an entity for the production of specialty chemicals and biofuels, which will allow to provide a complete environmental analysis of the lignocellulosic biorefinery framework.

This chapter under the consent of the publisher was redrafted after: S. Bello, I. Salim, G. Feijoo, M.T. Moreira, Inventory review and environmental evaluation of first- and second-generation sugars through life cycle assessment, Environ. Sci. Pollut. Res. 28 (2021) 27345–27361. doi:10.1007/s11356-021-12405-y. More information about this publication can be found in Annex I.

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2.1. FIRST- AND SECOND- GENERATION SUGAR PLATFORMS

The optimization of cropping systems and arable land are increasingly becoming a key factor in the supply of food and feed to a growing world population. Wheat and maize have been, for millennia, one of the most essential crops of major civilizations. These raw materials continue to be one of the leading staple crops, with an average world production of 771 million tonnes and 1.13 billion tonnes of wheat and maize in 2017, respectively (FAOSTAT, 2017). The exploitation of sugar beet, is a relatively recent activity, which began in the 19th century (Draycott, 2006). World production of sugar beet amounts to 301 million tonnes, with Europe accounting for more than 40% of this production. Wheat, maize, sugar beet and sugar cane are considered first-generation crops, as they are mainly used for food and feed. Sugar beet and sugar cane are two of the most relevant crops for sugar production market worldwide (Svatoŝ et al., 2013). However, in line with recent advances in the field of first generation biorefineries, crops may yield fermentable sugars as platforms for the production of biofuels and bioproducts, emerging as a controversial food and fuel competition (Bakker et al., 2013; Kathage et al., 2016; Tomaszewska et al., 2018).

Research on the exploitation of second-generation biomass (i.e., wood or lignocellulosics) has been intensified in hopes of finding different perspectives in the production of sugar platforms that may substitute the use of crops for biofuels. Lignocelluloses are compounds rich in cellulose, which in turn can be hydrolyzed to glucose. Second-generation sugars arise as a feasible option of valorizing lignocellulosic fractions. On the other hand, if the production of sugars from second-generation raw materials were to be eco-efficient, i.e., environmentally and economically sustainable, they could have the potential to be sold at low environmental rates of emission and compete in the well-established sugar market (Kamm et al., 2016).

The European Union recorded an average price for white sugar of 443 €/t in March 2022, and in 2021-2022 the total world production was 174 million tonnes (European Commission, 2022). The largest sugar producing countries in Europe were France, Germany and Poland in 2020-2021 (European Association of Sugar Manufaturers, 2021). As expected, second generation feedstocks do not currently contribute to the bulk production of sugars. Nevertheless, there are feasible opportunities to be explored to diversify the resources from which platform and specialty chemicals (i.e., sugars) are produced and, subsequently, to alleviate the impact of overexploitation of certain natural resources.

In the growing context of bioeconomy, interest in the application of life cycle assessment (LCA) in biorefinery systems has augmented. Some studies have applied the LCA methodology to understand the environmental burdens of agricultural systems, focusing on food and feed (Boone et al., 2016; Fallahpour et al., 2012; Fantin et al., 2017; Klenk et al., 2012; Noya et al., 2015). However, most of the literature focuses on the final product, such as ethanol (Buratti et al., 2008; Collins et al., 2014; Muñoz et al., 2014) and to a lesser extent, has applied LCA to account the environmental sustainability of fermentable sugars (Moncada et al., 2018; Renouf et al., 2008).

Renouf et al. (2008) studied the life cycle environmental implications of first-generation sugar-crops. The authors highlight the environmental advantages of sugar cane in global warming, energy consumption and acidification, with the disadvantages in water use and eutrophication categories. Again, within the framework of first-generation feedstocks, Tsiropoulos et al. (2013) have analyzed the energy demand and greenhouse gas emissions associated with corn glucose. Their results explore the variability of impacts when different approaches are adopted in the LCA model. Other authors have studied the impact of wood-to-sugar conversion technologies, focusing on the implementation of new techniques to increase enzyme availability, such as enzymatic hydrolysis. This is relevant in relation to the development of second-generation systems for the exploitation of biomass, in which often the use and manufacture of enzymes is an environmental hotspot of the process (Morales et al., 2017).

This chapter aims to be a contribution to the state of the art on sugar-producing biorefineries evaluated from the environmental perspective. The scope of this evaluation is the production of sugars not only as a final product (food) but also as a platform for the production of relevant biochemicals and bioplastics more profitable than bioethanol. In second generation biorefineries most LCA evaluations have been conducted with the target of identifying the environmental profile of bioethanol production (Parajuli et al., 2017; Raman and Gnansounou, 2015); conversely, this study aims to focus its attention on the upstream section of any biorefining plant.

Thus, one of the main objectives of this work is to provide a comprehensive review of both first and second-generation systems for the production of sugars through different technologies. The analyzed scenarios will be compared by means of the LCA methodology to depict where the main source of impacts is located, as well as to provide insight into the comparability of sugars from crops and wood, and how the transition to biomass that is not in competition with food for the production of biofuels may be accomplished. However, the direct comparison of such systems is not free of uncertainty. While the assumptions made throughout the study are specified, and the decisions are unified to the best of our capacities, the use of databases for background data as conglomerated markets of average inventories makes the uncertainty of the study a key consideration. Thus, the Monte Carlo simulation will be computed for the midpoint impact categories. Finally, the economic-environmental nexus of the scenarios addressed will be analyzed, to have an overall view of the potential to substitute or complement the first-generation sugar production market with other resources, especially in view of the increased demand of sugars for biorefinery value chains in the production of biochemicals and biofuels.

2.2. METHODS

The main objective implemented through LCA is to analyze in detail the input and output flows in the target production process, and to quantitatively translate those flows into environmental impacts. Furthermore, a stochastic approach was included, through Monte Carlo uncertainties, as well as the economic viewpoint through the evaluation of eco-efficiency in the life cycle perspective. In accordance with ISO 14045 (2012), the concept of eco-efficiency acknowledges the consideration of environmental factors along with the value of the system to stakeholders.

2.2.1. Goal and scope

In this work, the environmental strengths, and weaknesses of first- and second-generation biorefineries were investigated, considering the production of sugar fractions from crops (maize, sugar beet and wheat), hardwood (beech, eucalyptus, birch and poplar) and softwood (spruce and pine) biomass. There are few studies that emphasize the environmental sustainability of sugars as an intermediate platform for the production of bioproducts. Therefore, this assessment has been directed to the study of the ways in which two intrinsically different systems (i.e., first- and second-generation biomass refining) perform for the production of the same type of product —sugars—environmentally.

The environmental analysis was carried out in a cradle-to-gate perspective. The selection of the functional unit (FU) is relevant because a biorefinery is, by definition, a multi-product facility, which normally involves the production of a wide range of biochemicals or bioenergy. Since the objective is to compare the production of sugars from different sources, the FU selected is 1 kg of sugar (either hexoses, pentoses or a sugar mixture depending on the scenario). Although the type of biomass is critical, it is even more relevant the pre-processing of such biomass and its transformation to sugars. The main objective of the study is to have a comparison of two main blocks, first and second-generation biomass, thus crops and wood, respectively to produce sugars (identical function of the system). This is reflected in the FU of the study, since environmentally comparing, for instance, 1 kg of maize and 1 kg of wood is not feasible and would be a biased comparison. However, comparing 1 kg of sugar obtained either from maize or from wood is reasonable. The multiproduct nature of biorefineries was addressed by means of implementing allocation procedures in LCA calculations. Other co- or by-products that may be obtained during the sugar production process were accounted for as secondary streams and an allocation of the impacts were performed to them alongside with the sugars. In some cases, due to the nature of the scenarios, the production of sugars is the main activity of the process, while in others, sugars come as an extra stream in the production of further processed products, i.e., bioethanol. The effect of these technicalities was addressed through a sensitivity analysis on the type of allocation (mass versus economic).

The geographic scope of the study comes determined by the location of the cropping and forest lands in each scenario in European countries (Figure 2.1). The geographic location of the biomass-growth sites was considered as the location of the sugar processing refineries as well (which is relevant in background processes such as the electric mix for energy supply) with a maximum transport distance of the biomass of 100 km. Sugar cane in Australia was an extra first-generation scenario included in the Supplementary Information in Annex II, due to its importance in the sugar production industry. However, it was not included here since the geographic scope would have been vastly extended by including Australia, possibly incurring in greater uncertainty.

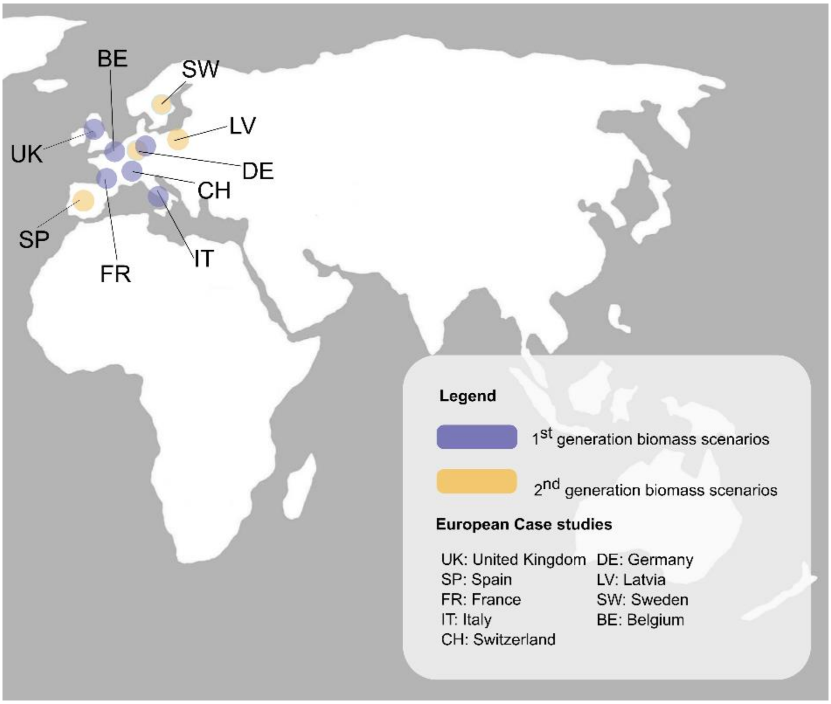

Figure 2.1 Geographic scope of the study. Location of cropping and forestry land for biomass growth

2.2.2. System boundaries

The following subsections provide a description of the system boundaries, including the identification of systems and processing units that contribute to the purpose of sugar production. The processes involved in the production of first- and second-generation sugars, although heterogeneous in bibliography, share the need of pre-treatment and posterior hydrolysis or saccharification and purification unitary operations (Figure 2.2). The selection of scenarios was based on case studies that were either exclusively first-generation or second-generation biomass processing. Therefore, scenarios including exploitation of lignocellulosic wastes along with grain were not considered.

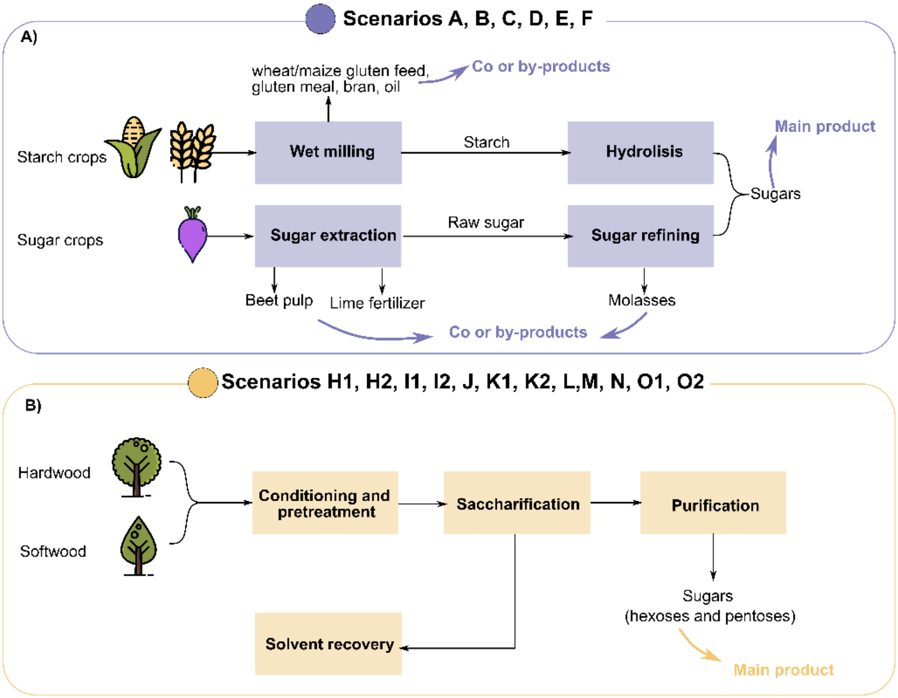

Figure 2.2 System boundaries for the general configurations under study. A) Generic view of the production of sugars from first generation biomass (starch and sugar crops such as maize, wheat, sugar beet). B) Generic view of the production of sugars from second generation biomass (soft and hard woods)

An overview of every case study considered in the assessment is provided in Table 2.1, including geographical location of the crop or forest-based biomass, the main sugar-product(s) obtained, the pre-treatment alternative for biomass processing and the main bibliographic references.

Table 2.1 Scenarios considered based on the feedstock, location, and pre-treatment method.

Scenario	Feedstock	Product	Country	Pre-treatment	Reference
		First generation scenarios			
A	wheat grain	glucose	Germany	wet milling	1, 2, 3
B	maize grain	glucose	Italy	wet milling	1, 2, 4
C	sugar beet	sucrose	United Kingdom	hot water diffusion	2
D	wheat grain	glucose	Switzerland	wet milling	1, 3
E	maize grain	glucose	Belgium	wet milling	2, 5
F	sugar beet	sucrose	France	hot water diffusion	2, 6
		Second generation scenarios			
H_1	beech	glucose	Germany	organosolv	7, 9
H_2	beech	hemicellulose	Germany	organosolv	7, 9
I_1	spruce	glucose	Sweden	organosolv	8, 10, 11
I_2	spruce	hemicellulose	Sweden	organosolv	8, 10, 11
J	eucalyptus	combined pentoses and hexoses	Spain	dilute acid	12, 13, 14
K_1	eucalyptus	pentoses	Spain	dilute acid	12, 13, 14
K_2	eucalyptus	hexoses	Spain	dilute acid	12, 13, 14
L	spruce	hemicelluloses syrup (C5)	Sweden	organosolv-steam explosion hybrid	10, 11, 15
M	birch	hemicelluloses syrup (C5)	Latvia	organosolv-steam explosion hybrid	15, 16
N	pine	concentrated sugar syrup	Latvia	reductive catalytic fractionation	17, 18, 19, 23
O_1	poplar	glucose, xylose	Spain	ionic liquid	20, 21, 22
O_2	poplar	hemicellulose	Spain	ionic liquid	20, 21, 22

1 (Mustafa et al., 2007)
2 (Renouf et al., 2008)
3 (Achten and Acker, 2015)
4 (Noya et al., 2015)
5 (Boone et al., 2016)
6 (Muñoz et al., 2014)
7 (Kautto et al., 2013)
8 (Moncada et al., 2018)
9 (Bello et al., 2018)
10 (González-García et al., 2009a)
11 (González-García et al., 2009b)
12 (Kuo and Yu, 2020)
13 (González-García et al., 2012)
14 (Morales et al., 2015b)
15 (Mesfun et al., 2019)
16 (Kuka et al., 2020)
17 (Kuka et al., 2019)
18 (Tschulkow et al., 2020)
19 (Liao et al., 2020)
20 (González-García et al., 2010)
21 (Baral and Shah, 2012)
22 (Righi et al., 2011)
23 (Snowden-Swan et al., 2016)

2.2.2.1. First generation system boundaries

The first-generation sugar production system (Figure 2.2A) was inventoried in a cradle (agriculture) to gate (glucose production) perspective, as mentioned above. In this chapter, six scenarios were considered for agriculture of first-generation feedstocks: wheat grain in Germany and Switzerland, maize grain in Belgium and Italy sugar beet in United Kingdom and France. The aforementioned case studies include the most common agricultural activities, from field preparation, sowing, application of fertilizers and pesticides, and harvesting of crops. In relation to agriculture, the management and yield of these crops vary considerably from one region to another and depend on many variables such as soil type, climate, and crop varieties. Sugar beet, wheat and maize crops also generate valuable residues, namely beet leaves, maize stover and wheat straw (Bakker et al., 2013; Muñoz et al., 2014; Tenorio, 2017).

There are many pathways to produce bioproducts from a sugar platform. The sugar industry, which uses first-generation crops (starch and sugar crops) as raw material, is well established in the market, and has qualified research and technology, unlike second-generation raw materials. In the case of wheat or maize grains, they must first be converted into starch through a wet milling process, and then enzymatic hydrolysis. In the wet milling process, the grain is soaked in water to facilitate the separation of its starch and gluten components. The milling phase generates valuable by-products that are commonly used in the food and feed industry, such as wheat gluten, meal and bran, for wheat grain processing; and maize gluten, meal and oil, for maize grain processing (Anex and Ogletree, 2006; OECD, 2003). The gluten fraction is valued as a by-product, while the enzymatic hydrolysis stage breaks down starch into glucose with the use of enzymes (Arifeen et al., 2009).

In the case of sugar crops, sugar is extracted by diffusion using hot water, diluting the sugar contained in the beet root in the water. This water is called raw juice and is purified with the use of lime and then evaporated to produce sucrose (Duraisam et al., 2017). Sugar beet processing also offers valuable by-products such as beet pulp, molasses, and lime fertilizer. Except for lime-based fertilizer, which is an inorganic substance, molasses by-products and beet pulp are usually valued for animal feed and human consumption. However, molasses can also be used as fermentable sugars to produce biofuels or bioproducts, as well as beet pulp, which is a raw material rich in lignocellulose, with the potential to be converted into glucose.

2.2.2.2. Second generation system boundaries

Overcoming wood recalcitrance by pre-treatment processes is key in the production of sugars from the hemicellulose and cellulose fractions in second generation systems (Figure 2.2B). For the second-generation case studies, eight scenarios were considered, including seven different types of wood. Each wood-type was considered to be processed through a different pre-treatment, allowing to explore a wide range of feasible alternatives. In some cases, the hemicellulose fraction of the wood yielded pentose sugars and the hexoses (i.e., glucose), which were considered as a sugar-product and involved in the allocation procedures.

Kautto et al. (2013) proposed a configuration (scenario H_1, H_2) that includes the process units involved in the ethanol organosolv pulping as well as the downstream units for the valorization of pulp and liquor. The feedstock of the process is residual beech woodchips cultivated in Germany and the plant under assessment has a capacity to process 660,000 t/year of dry wood. The wood is fractionated with ethanol (50% v/v) and sulfuric acid as catalyst and 180°C. The process also includes the recovery of ethanol, hemicellulose conditioning, enzymatic hydrolysis, and energy production from a cogeneration unit. The main products obtained are glucose, lignin, and hemicellulose.

The system for glucose production from softwood presented by Moncada et al. (2018) is a case study in which the authors consider a plant with a capacity of 1000 kt of dry spruce wood in Sweden (González-García et al., 2009a, 2009b) per year (scenario I_1, I_2). The wood pre-treatment method was based on the Organosolv process. The plant consists of four main sections: conditioning of spruce chips and organosolv fractionation, lignin precipitation and recovery, solvent recovery and recycling and finally pulp stripping and enzymatic hydrolysis. The main outputs of this process are the main sugars stream (hexoses, i.e., scenario I_1), lignin, furfural and hemicellulose derived sugars (scenario I_2).

Kuo et al. (2020) considered the processing of eucalyptus woodchips through dilute acid pretreatment. Wood from eucalyptus forests in Spain was considered as feedstock (González-García et al., 2012; Morales et al., 2015b). In scenario J, their most simplified configuration in which a mixture of hexoses and pentoses is obtained as the main product was considered. After the delignification through dilute acid (using sulfuric acid), the slurries were hydrolyzed enzymatically, washed, and filtered. Residual water from the sugars stream was evaporated. In the second configuration (scenarios K_1, K_2) the mixed sugars stream is filtered in a step previous to the hydrolysis unit to obtain a refined hexoses sugar fraction (scenario K_1) and a pentoses fraction (scenario K_2). In this case, there is a sugar loss which exits the system with the wastewater to treatment. Vapor emissions were considered to be mostly water-based in both scenarios and not included in the inventory.

In the case of scenarios L and M, a more realistic approach to sellable, marketable lignocellulosic sugars was considered. In these scenarios, sugars are obtained in a biorefinery value chain as a side-stream from a bioethanol-producing facility. In this case a hybrid organosolv-steam explosion pretreatment was carried out, using ethanol as the organic solvent. Simultaneous saccharification and fermentation yield ethanol. Lignin was another recovered product after further separation and solvent recovery. The main sugars fraction in this case is pentose-based, from the hemicellulose fraction of wood since the hexoses were mostly utilized in the fermentation to bioethanol. In these scenarios more residual wood was processed in a combined heat and power plant, to produce all the electricity and utilities needed for the process, therefore no energy inputs were considered in the inventory (Mesfun et al., 2019). In scenario L, spruce from Swedish forests was the wood type (González-García et al., 2009a, 2009b) considered, while for scenario M, birch silviculture activities in Latvia (Kuka et al., 2020) were accounted for.

For the processing of pine silviculture activities in Latvia (Kuka et al., 2019), the pretreatment process considered was a reductive catalytic fractionation (scenario N) to yield concentrated sugar syrup (mainly pentoses) (Tschulkow et al., 2020). In this case, the concept of the system under study lies in a lignin-based approach in which such product is the focus of the fractionation process. Reductive catalytic fractionation implements the depolymerization with a ruthenium on carbon catalyst in the presence of hydrogen and methanol. The subsequent steps include the recovery of methanol and separation units that make lignin oligomers and monomers and a sugar-rich pulp the main products obtained.

Finally, scenarios O_1 (hexose sugars) and O_2 (pentose sugars) deal with the fractionation of Spanish poplar wood (González-García et al., 2010) with an ionic liquid, 1-ethyl-3-methylimidazolium chloride (Baral and Shah, 2012; Righi et al., 2011). The greatest fraction of hemicellulose and part of the cellulose are converted to sugars; non-converted fractions are also further transformed to sugars in an enzymatic hydrolysis unit. The ionic liquid is recovered and reused within the system boundaries. The main products from this scenario are separate streams of hexose (scenario O_1) and pentose (scenario O_2) sugars.

2.2.3. Life cycle inventory

Inventories were retrieved from bibliographic studies, listed in Table A1 through Table A20 of the Supplementary Information in Annex II. Each scenario was built with a few premises, to allow for the greatest possible harmonization in data collection. It was ensured that biomass pretreatment and sugar production were feasible for each of the cultivated raw materials, especially when the inventory data was compiled from different publications. The inventories included all inputs and outputs of mass and energy required to produce sugars, as comprehensively as possible. To the possible extent, efforts were made to have the production of sugars as outputs (rather than intermediate products) directly mentioned in the selected literature, thus eliminating from the possible studies those which had as their sole objective the production of biofuels.

Note the dispersion of data types in literature going from differing types of biomass, for both first and second-generation scenarios, to different pretreatment alternatives. For instance, in silviculture activities, while some authors rely on providing energy-based data (González-García et al., 2009b) for machinery in each operation (e.g. MJ consumed), others use fuel-based data for the fuel use in that machinery (Kuka et al., 2019). In all scenarios the land occupation for agriculture and forest was considered. Nonetheless, in most cases it was considered that land has been long term occupied by forest plantations and agricultural activities respectively, which leaves out of the scope of this study the consideration of land use changes.

This assessment did not consider the additional recovery of agricultural residues for wheat straw and maize stover. Nevertheless, agricultural residues for sugar beet pulp are potential fertilizers. Diffuse emissions from the application of fertilizers and machinery emissions were considered in the implemented inventories. Transport of biomass to the processing plant was assumed to be 100 km by lorry for all scenarios.

Background processes for the production of chemicals, fuels, and other ancillary activities were included within the system boundaries. Data for background processes was included through the ecoinvent 3.5 database (Wernet et al., 2016). The inventories of the scenarios considered are presented in Table A1 through Table A8 for the production first generation sugars and in Table A9 through Table A20 for the production of second-generation sugars in the Supplementary Information (Annex II).

2.2.4. Allocation factors

As the production of these sugars from first and second generation raw materials generates valuable by-products and co-products, the implementation of allocation was considered as recommended in the literature (European Commission, 2017). The allocable products depend on what each system produces (output-based). Therefore, first generation systems are prone to the production of hexoses, and the by-products are those of the residual fractions or valorized products from further processing. For second generation systems, the most common co-products obtained with hexose and pentose sugars were lignin, and further converted chemicals (e.g., ethanol). Although scenarios converting sugars to ethanol were avoided whenever possible, it was found that the main objective of the literature was the conversion of those sugars to ethanol, leaving very few studies to the conversion to sugars.

As a first approach, mass allocation was considered because of the uncertainty and volatility of the price of sugars. However, economic allocation was also considered as an alternative, in order to analyze the potential differences of both perspectives in the LCA methodology. The allocation factors (i.e., economic and mass allocation) considered in the study are presented in Table 2.2 and Table 2.3. The objective will be to assess the sensitivity of the results to both types of allocation.

Table 2.2. Mass and economic allocation factors considered for first generation scenarios (A-F)

Scenario	Products	Quantity (kg)	Mass allocation (%)	Price (€/kg)	Revenue (€)	Economic allocation (%)
B, E Maize	Glucose from maize starch	1000.00	72.73	0.30	300.00	71.84
	Corn oil	27.00	1.96	0.90	24.30	5.82
	Gluten feed	268.00	19.49	0.16	42.88	10.27
	Gluten meal	80.00	5.82	0.63	50.40	12.07
A, D Wheat	Glucose	1000.00	66.23	0.50	500.00	78.20
	Wheat bran	260.00	17.22	0.12	31.20	4.88
	Vital gluten	110.00	7.28	0.78	85.80	13.42
	Wheat gluten feed	140.00	9.27	0.16	22.40	3.50
C, F Sugar beet	Beet sugar	1000.00	51.36	0.42	423.00	76.35
	Beet pulp	651.00	33.43	0.16	101.56	18.33
	Calcium carbonate	295.00	15.15	0.10	29.50	5.32
	Residual fraction	1.10	0.06	0.00	0.00	0.00

Table 2.3. Mass and economic allocation factors considered for second generation scenarios (H-O)

Scenario	Products	Quantity (kg)	Mass allocation (%)	Price (€/kg)	Revenue (€)	Economic allocation (%)
H Beech	Glucose	388.40	61.96	0.24	$9.22\cdot10^{1}$	72.51
	Hemicellulose	83.20	13.27	0.20	$1.66\cdot10^{1}$	13.08
	Lignin	155.30	24.77	0.12	$1.83\cdot10^{1}$	14.41
I Spruce	Glucose	$4.53\cdot10^{4}$	15.15	0.43	$1.97\cdot10^{4}$	32.66
	Furfural	$1.51\cdot10^{3}$	0.50	0.90	$1.36\cdot10^{3}$	2.26
	Lignin	$2.41\cdot10^{4}$	8.06	0.63	$1.52\cdot10^{4}$	25.24
	Hemicelluloses	$1.20\cdot10^{5}$	40.10	0.20	$2.40\cdot10^{4}$	39.84
	Non-converted solids	$1.08\cdot10^{5}$	36.18	0.00	0.00	0.00
J Eucalyptus	C5+C6 mixed solution	416.10	100.00	0.28	$1.15\cdot10^{2}$	100.00
K Eucalyptus	hexoses	52.56	13.79	0.29	$1.51\cdot10^{1}$	11.71
	pentoses	328.50	86.21	0.35	$1.14\cdot10^{2}$	88.29
L Spruce	Hemicellulose	$2.20\cdot10^{7}$	15.07	1.00	$2.20\cdot10^{7}$	21.37
	Lignin	$8.10\cdot10^{7}$	55.48	0.63	$5.10\cdot10^{7}$	49.56
	Ethanol	$4.30\cdot10^{7}$	29.45	0.70	$2.99\cdot10^{7}$	29.07
M Birch	Hemicellulose	$2.80\cdot10^{7}$	16.47	1.00	$2.80\cdot10^{7}$	23.05
	Lignin	$8.10\cdot10^{7}$	47.65	0.63	$5.10\cdot10^{7}$	42.00
	Ethanol	$6.10\cdot10^{7}$	35.88	0.70	$4.25\cdot10^{7}$	34.95
N Pine	Oligomers (lignin-based products)	$1.77\cdot10^{3}$	10.64	1.75	$3.10\cdot10^{3}$	29.34
	Monomers (lignin-based products)	$1.08\cdot10^{3}$	6.49	1.75	$1.89\cdot10^{3}$	17.91
	Sugar pulp (C6)	$1.38\cdot10^{4}$	82.86	0.40	$5.57\cdot10^{3}$	52.75
O Poplar	Hemicellulose solution	$9.44\cdot10^{4}$	80.45	2.42	$2.29\cdot10^{5}$	70.40
	Glucose and xylose (main product)	$2.29\cdot10^{4}$	19.55	4.19	$9.63\cdot10^{4}$	29.60

2.2.5. Life cycle impact assessment approach: methodology

In this environmental evaluation, the classification and characterization phases were undertaken within the Life Cycle Impact Assessment phase. The ReCiPe 1.1 hierarchist method (Huijbregts et al., 2016) was used. Using the SimaPro 9.0 software, the inventories were translated into environmental impacts. The following midpoint impact categories were selected to environmentally describe the systems under study: global warming (GW), ozone depletion (OD), ozone formation (OF), terrestrial acidification (TA), freshwater eutrophication (FE), marine eutrophication (ME), freshwater ecotoxicity (FET), marine ecotoxicity (MET), human toxicity (HT), water consumption (WC), land use (LU) and fossil scarcity (FS).

An uncertainty analysis of the scenarios under study was conducted through the Monte Carlo simulation module in the SimaPro software. The input parameters were considered as the available data uncertainties of inventoried processes in the ecoinvent database (Wernet et al., 2016). The distribution of the samples was lognormal. The Monte Carlo analysis was run for 2000 iterations at a 95% significance level.

On the other hand, the economic perspective in the assessment was considered through the implementation of an eco-efficiency evaluation. Eco-efficiency may be defined as the capability of processes to meet economic and environmental targets simultaneously. For the purpose of this study, the environmental dimension of the scenarios will be described through the GW impact category, while the economic dimension will be represented by a range of sugar production cost (minimum to maximum values). The sugar pricings were mostly considered as the minimum and maximum bibliographic values of the sugar selling price retrieved from techno-economic assessments. Minimum and maximum sugar production costs are presented in Table A21 provided in the Supplementary Information (Annex II). The price of sugar wheat considered to be double the price of wheat starch (Salim et al., 2019). In the cases in which hemicellulosic sugars are produced, for the maximum production cost it was considered that they had the potential to be converted to xylitol, with the high added value and production cost implied (Mountraki et al., 2017).

2.3. RESULTS AND DISCUSSION

In order to provide a complete outline of the environmental impacts derived from each of the systems studied, the environmental profile will be presented and discussed in depth for 4 representative impact categories (GW, LU, WC and FS) while the results of the rest of impact categories are provided in the Supplementary information (Figure A1 and Figure A2). In the second part of this section, the economic implications of the LCA results, and the study of what effect economic allocation may have in the results are discussed.

2.3.1. Environmental profile of first- and second-generation sugars

Characterization results were obtained for the 15 considered scenarios including first and second generation biorefineries and producing both pentose and hexose sugars applying mass allocation. Here, we directly compare the environmental performance in the GW, WC, LU and FS impact categories (Figure 2.3). These represent areas of climate protection directly related with a potential influence from cropping and silviculture systems and biorefining. The rest of impact categories analyzed in the scope of this chapter may be found in Figure A1 (OD, TA, FE, ME) and Figure A2 (OF, FET, MET, HT) in Annex II.

Figure 2.3 displays, as well, the standard deviation calculated through Monte Carlo which presents the uncertainty of the results. Results differentiate among first and second-generation scenarios, and present both the impacts from the biomass silviculture or cropping activities and the impacts from the processing of biomass to produce 1 kg of sugars. They are heterogeneous: the environmental profile of sugars is directly dependent on the specific set of processing conditions.

In the case of GW, the variability of impacts is slightly higher for second generation scenarios (in the range of 0.20-2.50 kg CO_2 eq. than for first generation (0.34-1.30 kg CO_2 eq.). The best-case scenario is found for scenario I, producing hemicellulosic sugars from spruce through Organosolv. The most carbon-intensive scenario is also a second-generation sugar (glucose) produced from eucalyptus (scenario K_1, K_2) through dilute acid pretreatment. Specifically, scenario K_2 presents, as well, the greatest standard deviation, probably in light of the intensive use of steam and the impact of the production of enzymes in the system as well as markets for chemical production. Excluding outliers such as the acid pretreatment scenarios (J, K_1 and K_2) and the ionic liquid scenarios (O_1 and O_2) in which energy and chemicals are intensive in the processing of biomass, in the rest of scenarios, second generation sugars present GW results in the range or lower than first generation sugars. In fact, scenarios H_1, H_2 (organosolv from beech), I_1, I_2 (organosolv from spruce) present 35 and 40% improvement from the best first-generation scenario (B, glucose from maize in Italy) in GW. Scenario N (reductive catalytic fractionation from pine) is better than 5 out of 7 first generation scenarios.

The variability of impacts is higher in second generation scenarios because of the diversity of pre-treatments available in the studied alternatives. Improvement in these systems it is rather a question of optimizing the pretreatment technologies and giving answer to the recalcitrance challenge. This is the step forward needed for the full deployment of second generation biomass, which has been proven to be less burdening in the area of cultivation and growth (Zheng et al., 2009).

WC is the impact category with the greatest uncertainties, with standard deviations overshooting the actual mean values of impact in scenarios D, L and M. The water consumption processes that affect scenario D are mostly irrigation demands for sowing. However, for scenarios L and M, most of the impacts in this category are derived from the water intensive use in enzyme production (usually through fermentation). In scenarios L and M, enzymes are used for simultaneous saccharification and fermentation in the organosolv-steam explosion hybrid, and have been defined as a potential hotspot of biorefinery systems (Singh et al., 2010).

LU has been found to be more intensive in the case of spruce, birch, and pine, for the lignocelluloses, and for wheat in the case of first-generation sugars. The LU impact category is, as well, the only one in which silviculture becomes the hotspot of the scenario. Interestingly enough, an area of 1 m^2 of occupation for agricultural purposes contributes to this impact category around 3 times more than every m^2 of land occupied for forestry purposes. The higher results in this category for the lignocellulosic-based scenarios could be due to the sugar/biomass ratio in each system. The sugar yield in lignocelluloses is mostly lower than that of sugar crops, meaning that the volume of lignocellulosic biomass needed to yield the sugars would be higher.

FS shows that most energy self-sufficient second generation biorefineries (with cogeneration systems within their boundaries (scenarios H, I, L, M) are the way forward. Fossil fuel scarcity is directly related to the use of crude oil, natural gas, or coal, either directly or indirectly (e.g., for the production of chemicals). Therefore, energy-intensive systems, especially when the production of electricity heavily relies on non-renewable sources, will increase their contribution within the FS impact category. Clean energy systems that contribute to the decarbonization or resources used in the production of energy (natural gas, fossil fuels) are key for the reduction of the carbon intensity of the process. The processing of poplar wood through ionic liquids achieves the highest impacts in the FS impact category, due to the use of fossil-based chemical intensive production of the ionic liquid.

In the case of first-generation sugars, the cropping activities (i.e., the use of agricultural machinery, production and application of fertilizers, irrigation when needed, emissions) represent over 58% of the burden in all scenarios. For wood, the silviculture presents always less than 25% of the impacts when analyzing GW. This trend is paralleled in WC and FS for all scenarios. However, in LU, as mentioned, the burdens from forest land occupation shift the hotspot to the silviculture section. LU is almost negligible for pretreatment and processing of wood subsystem.

Among first generation scenarios, the sugar production systems with the worst environmental profile are scenarios A and D, which use wheat as feedstock. The result is consistent for three out of four impact categories displayed in Figure 2.3 and for the rest of impact categories, in the Supplementary Information. In starch crops such as wheat, the sugars are not as readily available as in sugar crops, implementing the need to include unit operations such as hydrolysis, making these crops not as suitable for sugar extraction.

The OD category (Figure A1 in Annex II) is the impact category that shows the greatest differences between first- and second-generation systems. In this category for all scenarios studied, second generation systems present better environmental results than first generation systems. This is due to the direct emissions to air from the application of fertilizers (diffuse emissions) and from the fuel burning in agricultural machinery, specially of dinitrogen monoxide in most first-generation scenarios.

Nitrogenous substances cause the effect of eutrophication on marine ecosystems (ME). Looking at the ME impact category (Figure A1 in Annex II), it is clear that substances contributing to the environmental profile in first-generation systems involve the use of nitrogenous substances in their production such as fertilizers, whereas second-generation systems do not appear to be so dependent. In fact, in this impact category, second generation systems present satisfactory results when compared to sugar production from crops, especially scenario D (glucose from wheat in Switzerland). On the contrary, FE (Figure A1 in Annex II), is affected by phosphorus-derived compounds, which has an effect derived from the processing of biomass in second generation biorefineries. Specifically, through the use of chemicals such as potassium phosphate (in scenarios O) or the production of enzymes in scenarios L and M.

It should be noted that, depending on the geographical location of the cropping activities, the results may vary. Variations could, for example, happen in terms of transport distances. In the case studies considered in this assessment, the transport distances were the same for all scenarios due to the lack of primary data. Ideally, sugar production plants would be as close as possible to the origin of the biomass. However, in real systems, transport distances would vary depending on the crop and the processing location. This would probably influence emissions from transport and fuel use, which are mainly represented within the GW, OF and FS impact categories.

Likewise, the location also determines the soil type and fertility or the climate and weather, which influence relevant parameters such as the yield and crop and the type of farming practices (Iizumi and Ramankutty, 2015). Rainfall, for instance, has an impact on the amount of irrigation water needed and emissions to water produced at the cropping locations. For example, phosphorous emissions to water are calculated taking into account factors such as the type of land use, the type of fertilizer, drainage or soil properties (Bengoa et al., 2015). An increase in phosphate emissions would probably have an impact on the FE impact category, while any change in ammonia, nitrates, total nitrogen, etc. will influence the ME category to a greater extent. Climatic conditions and more specifically, rainfall have an impact on other relevant issues such as soil loss through water erosion, as presented in the study of Panagos et al. (2015).

The environmental results of the systems studied have a generic influence derived from the use of energy from specific country electricity mixes. The electrical mix yields variable carbon emissions depending on the way the electricity is produced. Countries with a mix that depends heavily on coal-based power production, such as Poland, contribute more to the GW impact categories, while countries such as Finland, which have power production systems based on cleaner energy systems, would reduce total carbon emissions (Bello et al., 2019). For each scenario, the corresponding electricity country mix of the country in which the biomass was cultivated was selected.

In most cases, it is usual that average chemical markets (from databases such as ecoinvent) are used for the calculation of impacts in background processes (i.e. clusters of specific chemicals that include the inventory averaged for regionalized groups, such as Europe, the World, etc.) making uncertainty higher for those impact categories mostly affected by these chemicals such as toxicity impact categories (both ecotoxicity and human toxicity) as it can be observed in Figure A2 in the Supplementary Information (Annex II).

In all, the heterogeneity of results shows the importance of performing LCA to draw valuable insight when the objective is to favor environmental optimization for case-specific situations. Nevertheless, this study is valuable as an approach to establish a benchmark of the most common pretreatment technologies and crops, as a direct comparison, in which the efforts of data compilation and processing have been made.

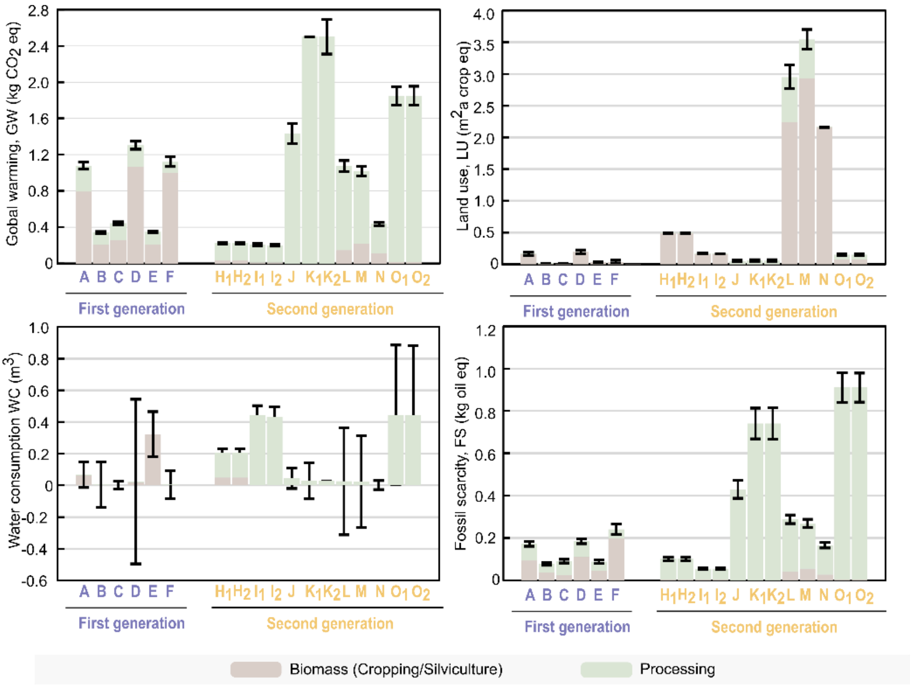

Figure 2.3 Environmental impact in global warming (GW), water consumption (WC), land use (LU) and fossil scarcity (FS) impact categories per kg of sugar produced at the gate of the system and standard deviations obtained through Monte Carlo simulation of the inventoried data for each scenario assessed. Scenarios A-F include first generation biomass processing and scenarios H_1-O_2 include second generation biomass processing

2.3.2. The economic outlook of LCA results: eco-efficiency perspective.

In this section the effect that the type of allocation (mass or economic) has in the results will be explored (Figure 2.4). The allocation factors (in Table 2.2 and Table 2.3) show that, along with the sugars produced, other co-products and by-products are, in all cases, obtained. The difference between first- and second-generation co-products is mainly their economic value. For first generation by-products, beet pulp, bran or gluten feed are some examples of co-products. On the other hand, co-products such as lignin or furfural can be obtained in second generation biorefineries. The latter have a high potential within the current bioeconomy and constitute a relevant base for the production of other high value-added products (Biddy et al., 2016).

In Figure 2.4 the relative contribution of all scenarios is presented. For GW, in relative terms, scenarios K_1 and K_2 were the worse alternatives (eucalyptus processed through dilute acid pretreatment) when mass allocation was performed. However, when economic allocation was performed, the worse scenario shifted to be scenario G (sucrose from sugarcane) displayed in the Supplementary Material file, followed by scenario O_1 (glucose from poplar). In this case, when directly comparing the economic revenue potentially obtained from both cases, sugars (obtained after dilute acid pretreatment) have far more economic value in the market than steam (co-product from the sugarcane processing facility), making the allocation factors shift the conclusions of the assessment from the GW perspective. Also, note that dilute acid pretreatment (scenarios J, K) is the only case in which the products are exclusively sugars (no lignin, or furfural), resulting as the worst-case in most comparisons since all impacts are assigned to the sugars.

This same shift happened again for the OF impact category. Performing mass allocation, the worst scenarios were O_1 and O_2 (poplar pre-treated with ionic liquids). In the case of ionic liquid pre-treatments, the production of the ionic liquid is chemical intensive. In this case, only pentose and hexose sugars share the burdens.

In the FET impact category (Figure A2 in Annex II), while for mass allocation, scenario E (glucose from maize in Belgium) is the worst scenario, with economic allocation, scenario O_1 (glucose from poplar) is the most burdening scenario. Maize yields a series of co-products from which gluten feed and gluten meal are responsible for 10 and 12% of the impacts respectively when the system is economically allocated.

Note that the use of economic allocation methods may be viewed as controversial, since environmental outcomes would be linked to prices and market fluctuations. The variability of sugar prices is also another disadvantage of considering this type of impact distribution, linked to the fact that second-generation sugars do not yet have a fixed market value. Other studies have performed LCA analysis on sugars considering the mass allocation of their products. While in this impact assessment the allocation of impacts to second generation sugars were fairly variable, with values from 15 to 60%, Moncada et al. (2018) considered allocation factors ranging from 40 to 70% in the system dealing with wood biomass. For maize, the allocation factor for sugars in this study was calculated at around 72%, which is close to the value of 67% reported in literature (Moncada et al., 2018).

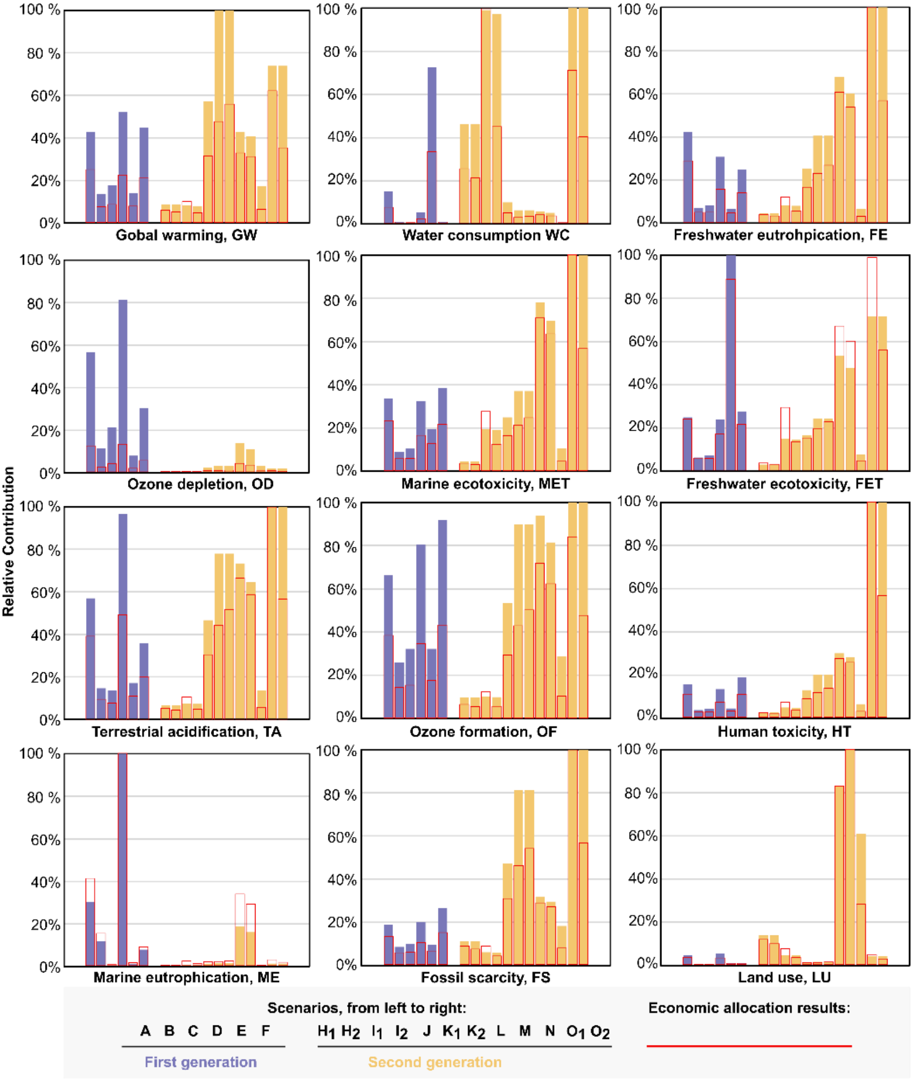

Figure 2.4 Comparative environmental profiles (in %) per kg of sugars produced from first (scenarios A-F) and second generation (scenarios H_1-O_2) biomass considering mass allocation and economic allocation (outlined results in red) for global warming (GW), water consumption (WC), freshwater eutrophication (FE), ozone depletion (OD), marine ecotoxicity (MET), freshwater ecotoxicity (FET), terrestrial acidification (TA), ozone formation (OF), human toxicity (HT), marine eutrophication (ME), fossil scarcity (FS) and land use (LU).

In cases such as this study, in which multiple product systems with great variability among them is present, further research should focus on the possibility of evaluation through consequential LCA rather than attributional LCA. Consequential LCA would allow to analyze the changes directly related to the potential shift from the production of sugars from first- to second- generation biomass. Another methodology to consider within attributional LCA is system boundary expansion, in which the system boundaries under study should be expanded to consider all products (from bioethanol to gluten meal or lignin) from both first- and second-generation systems. System expansion would allow avoiding all allocation procedures; however, the limits of data availability make it a less feasible option.

Through the analysis carried out in this study it can be seen that, first of all, increasing the usability or exploitability of raw materials will reduce the impact of biorefinery systems, when allocation methodologies are applied to calculate environmental results. Conventional sugar production can be environmentally competitive when environmentally burdensome processes, e.g., cultivation activities, are alleviated by increased exploitation of high value-added products (e.g., succinic acid) from products harvested in systems that have already proven to be profitable (Alexandri et al., 2019). However, the production cost of second-generation sugars remains a burden compared to starch-based sugars, which are based on more mature technologies (Cheng et al., 2019a). Therefore, the need to work on cost-effective biorefinery systems for lignocellulosic biomass through technologically efficient systems is fundamental.

The production cost dimension was analyzed in this study through an eco-efficiency indicator (Figure 2.5). Eco-efficiency is a good way of simultaneously considering two relevant variables for the assessment. In Figure 2.5 pentose and hexose sugars were depicted separately due to the highest variability (probably due to uncertainty in the market) of hemicellulosic sugars.

In the case of hexoses, when analyzing the results, the whole cluster of scenarios is near the most eco-efficient section of the graph. For optimal eco-efficiency scores, what should be hoped for, is that the cost of sugar production is minimized, while also minimizing the environmental impact, in this case, depicted as GW. The scenarios that fall below the average and achieve the best eco-efficiency score are C, B, E and H_1 when considering the minimum production cost of their range. These are scenarios of sugar beet, maize (Italy and Belgium) and beech processed through Organosolv. Scenario K1 is the less eco-efficient scenario, falling in the quadrant of the graph in which environmental and economic attributes are the highest. This translates into recommendations to optimize scenario K (eucalyptus treated with dilute acid) both technologically and environmentally. This production optimization would need to transform it into a factory closer to the biorefinery concept (more similar to scenarios

H or I), in which other bioproducts are obtained along with sugars, to exploit to the best possible extent the woody biomass.

The hemicellulosic sugars present more disperse eco-efficiencies, displaying variability in production cost and performance. Hemicellulosic sugars (pentoses) are exclusively obtained from lignocelluloses, thus, a wider range of possibilities for pretreatment translate into more scattered GW. Also, in this study, the potential processing of pentoses to xylitol was considered in the economic perspective and depicted as the higher value in the range of production-cost for all scenarios. In these cases, a higher production cost is mostly related to further need of processing. K and O scenarios, again, appear as the less eco-efficient alternatives. For pentoses, scenario N (pine pretreated through reductive catalytic fractionation) is in the quadrant of the graph in which values present lower GW and production costs than the average (more eco-efficient).

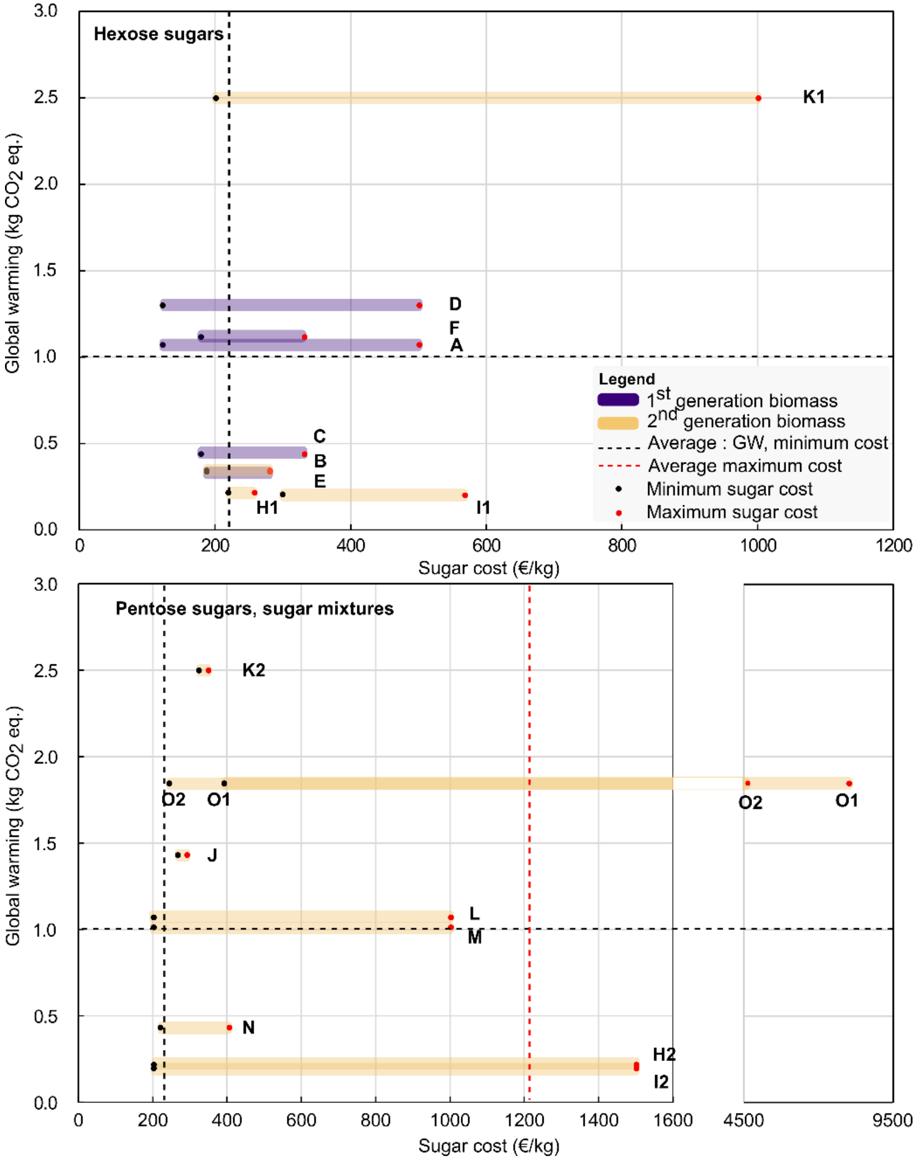

Figure 2.5 Ecoefficiency indicator as function of global warming (GW) for the environmental performance and range of sugar costs (€/kg) for first generation (A-F) and second generation (H_1-O_2) scenarios.

2.4. CONCLUSIONS

Trends show that, in the future, production systems will be geared towards replacing conventional raw materials (e.g., fossil fuels). The exploitation of residual fractions from agriculture and forestry has great potential to provide sustainable value-added products. In light of this, sugar production systems based on first- and second-generation raw materials were analyzed through LCA. Overall, the results from this assessment show a great variability of the impact of sugars. This variability depends mostly on the type of biomass, the type of pre-treatment and the co-products obtained. Methodologically, it depends mostly on the allocation method. This study suggests that, while first-generation sugar production systems are a much more mature technology, cultivation practices with fertilizer production and use have a significant impact on categories such as ME, FE and TA. This is not the case for the second-generation systems which present burdens related to mostly the processing of wood for delignification, which usually translate into chemically or energetically intensive processes. Further research is needed to optimize enzymatic hydrolysis processes and the overall energy consumption of lignocellulosic processing operations. Based on the environmental results obtained, the production of second-generation sugars is environmentally comparable and even less burdensome in some cases than the production of sugars from crops such as wheat. It can therefore be expected that in the future the conventional sugar industry will be adjusted to become biorefineries producing high value-added products. Biorefineries are systems with great potential to become low-carbon production systems. However, to the knowledge of the authors, LCA has been implemented on many occasions in bioethanol-producing biorefineries, with little focus on the upstream section of the value chain. Evaluating through LCA the processes involved in the fractionation and pre-treatment of biomass aims to contribute to the state-of-the art knowledge on the environmental profile of biorefineries. The supplementation of the sugar market with lignocellulosic raw materials should not be viewed as an interest to substitute the traditional sugar production from crops. In fact, such production for food-grade sugars should be maintained according to the results in this study (with sugar crops rather than starch crops). However, lignocelluloses provide good opportunities for fuel or chemical-grade sugars, as the technologies and pretreatments evolve. So far, it has not been possible to establish a clear position on which are the best available technologies from the environmental point of view for the production of sugars from first- or second- generation biomass. This may be possible when more primary data becomes available for evaluation.


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Eco-efficiency of a multifunctional biorefinery

"We are running the most dangerous experiment in history right now, which is to see how much carbon dioxide the atmosphere can handle before there is an environmental catastrophe."

Elon Musk

Chapter 3 Summary

The exploitation of lignocellulosic materials with the aim of producing high value-added products will potentially counteract concerns such as depletion of fossil resources intimately related to the exponential population growth and consequential boost of industrial activity. This chapter focuses on the assessment of an integrated process based on organosolv fractionation of residual beech woodchips, with the objective of implementing concepts such as circular economy or process integration. The life cycle assessment (LCA) methodology and the eco-efficiency concept allow for a holistic analysis of sustainability. The environmental assessment was conducted in a cradle-to-gate perspective and a functional unit of 1 kg woodchips entering the biorefining facility. Eco-efficiency grants comparability of scenarios that have different production targets. Two potential biorefinery set-ups were considered differing on the produced bio-products and downstream steps included within system boundaries. The first scenario considered a somewhat preliminary biorefinery achieving the pre-treatment and conversion of wood into basic platform chemicals such as glucose, hemicellulose and lignin that do not undergo additional processing. The second scenario conveys a somewhat more advanced facility. Consideration was given to the possibility of further conversion to more specialized and higher value-added bioproducts, such as furfural and bioethanol. The results show that the pre-treatment of biomass together with the energy demands of the process and enzyme production constitute the hotspots of the system. Analyzing the system by means of the ecoefficiency indicator demonstrates that broadening the multi-production spectrum of a biorefinery provides better results when production volume and processing steps fit environmental and techno-economical requirements. While the production of bioethanol from wood biomass is a relevant topic, the main focus of this chapter is to analyze the biorefining facility, rather than the footprint of specific fuels and chemicals in a cradle-to-gate perspective.

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OUTLINE

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3.1. INTRODUCTION TO SECOND GENERATION BIOREFINING AND PURPOSE

The exploitation of lignocellulosic materials with the aim of producing biofuels and high added value products, is a trend that has been ventured in recent years. Under the premise of exploiting alternative resources, which, in one or another way would positively impact on environmental sustainability, forestry-based biomass becomes an interesting alternative (Limayem and Ricke, 2012).

Chapter 3 delves into the assessment of a well-integrated process, based on organosolv fractionation of residual woodchips further processed within a second generation biorefinery or lignocellulosic biorefinery. Most of the renewable ethanol market is based on feedstocks such as maize, wheat, sugar beet and other cereals. However, the lignocellulosic raw materials present favorable results in terms of the output/input energy ratio, lower cost and high ethanol yields, which together with their high availability in locations with temperate and tropical climates, make this raw material potentially advantageous (Sánchez and Cardona, 2008). It has been estimated that it is feasible to produce bioethanol from lignocelluloses in a range of 442-491 billion liters per year (Balat, 2011; Saini et al., 2015). In comparison, world bioethanol production has been estimated at 95 billion liters in 2015 (Zabed et al., 2017). This demonstrates the high potential for almost completely replacing the production of first-generation biofuels with second-generation biomass sources, for the sake of minimizing environmental impacts.

On another note, it has been demonstrated that one of the critical points in relation to the biorefining process of wood-based raw material is the pre-treatment stage. In fact, it is one of the processing steps with the greatest costs in biorefinery facilities. In the last decade, several technologies have been reported in literature covering a wide range of categories: physical, biological, chemical and physico-chemical pre-treatments. The intended purpose of pretreatment technologies is the efficient fractionation of lignocellulose into its basic components: cellulose, lignin and hemicellulose. After efficient fractionation, the resulting streams should contain high value-added compounds in concentrations that make purification or recovery economically feasible (Mosier et al., 2005). Some pretreatment alternatives include wet oxidation (Martín et al., 2007), steam explosion (Jacquet et al., 2015), dilute acid pretreatment (Humbird et al., 2011), ionic liquid pretreatment (Brandt et al., 2011), ozonolysis (Travaini et al., 2016), biological pretreatment (Sindhu et al., 2016) or organosolv digestion. As previously stated, this chapter focuses on an LCB that uses organosolv digestion as the fractionation technique. Authors such as Viell et al. (2013) or Laure et al. (2014) have demonstrated the economic viability of organosolv as a fractionation technique in wood biorefineries.

Industrially, some companies have adopted the approach of demonstrating the viability of the biorefining process through pilot and demo-scale implementation. Lignol Innovations in Canada (Arato et al., 2005), has installed a plant facility (Lignol

Biorefinery Technology) with a capacity of 100 metric tons/day of dry wood. The demonstration plant constitutes an integrated biorefinery producing ethanol and other added value products such as lignin and furfural, xylose or acetic acid. The Lignol pre-treatment step is an ethanol-based organosolv fractionation.

CIMV (Compagnie Industrielle de la Matière Végétale), in France, has developed laboratory and pilot facilities, adequate for processing wheat straw or other agricultural residues as feedstock. Organosolv fractionation using acetic and formic acids (Snelders et al., 2014) allows relatively mild conditions for the pre-treatment of the feedstocks (atmospheric pressure and maximum temperature of 110°C).

Abengoa Bioenergy New Technologies (ABNT) has also developed a demonstration plant in Spain with a capacity to process 70 t/d of feedstock. The plant processes wheat straw along with other agricultural residues. One of the main features is the use of enzymatic hydrolysis together with steam explosion as the biomass pre-treatment method (De Wild et al., 2014).

The Fraunhofer-Zentrum für Chemisch-Biotechnologische Prozesse (Fraunhofer CBP) in Germany has developed a pilot-scale facility that processes up to 70 kg of dry hardwood per batch. The pretreatment of wood is performed with ethanol based organosolv fractionation and the main products obtained are glucose, lignin and xylose (Laure et al., 2014).

The viability of second generation biorefineries on a commercial scale is based on a few pillars. On the one hand, economic and technical feasibility: the facility must produce benefits in an efficient way and be technologically achievable. In the case of lignocellulosic biorefineries, the multi-product approach is favorable to this first premise. On the other hand, if the plant is versatile, the availability of feedstock is not a constraint for production. Therefore, under this assumption, the objective must be to design biorefineries with the capacity to process multiple types of raw materials.

In this context, the objective in exploiting alternative resources as raw materials, is based on determining whether it is feasible to show strengths within the environmental sustainability pillar. The purpose of this chapter is to assess the environmental sustainability of a large-scale simulated lignocellulosic biorefinery producing bioethanol alongside high added value platform chemicals trough the life cycle assessment (LCA) methodology (ISO 14040, 2006). The state of the art regarding LCB proves that the concept of biorefining is not a novelty in itself. However, the aim of this chapter is to go beyond general considerations and address the sustainability of intensive biomass exploitation through LCB. Some authors (Boisen et al., 2009) suggest that a biorefining facility will probably not be limited to the production of just one high value added bioproduct. Therefore, the aim of this study is to address a simple hypothesis. If the production scope of a lignocellulosic biorefinery is broadened, is sustainability really improved?

Three main representative cases have been identified to address the research question. Firstly, the so-called Biorefinery 1.0 was considered as a somewhat conventional biorefinery. This facility achieves the pretreatment and conversion of wood into basic products such as glucose, hemicellulose and lignin that do not undergo additional processing. The study of lignocellulosic sugars was addressed in depth in Chapter 2. The objective of this chapter is to analyze the differences among sugar-platform production and the following scenarios: Biorefinery 2.0 and Biorefinery 2.5 which convey a somewhat more advanced facility. The conversion to more specialized platforms and higher value-added bioproducts, such as furfural and bioethanol would theoretically uphold the concept of designing for the resource efficiency principle. However, whether this ultimately would result in higher sustainability must be analyzed through quantitative science-based calculations based in LCA.

3.2. METHODS

3.2.1. Goal and scope

The function of the system under study is the use of lignocellulosic biomass to produce bio-products with marketable added value. The aim of the environmental study, performed in accordance with the LCA methodology, is to determine the process subsystems that significantly affect the overall environmental performance of the system. Hence, it is expected that the result of the study will identify the process hotspots in the biorefinery and their root cause.

The functional unit considered was the processing of 1 t/h of hardwood chips in the biorefinery facility. It seems consistent to select a feedstock-based functional unit, as the process is characterized by its multiple-output nature. On the other hand, one of the objectives of this study is to benchmark three main plant schemes, Biorefinery 1.0, Biorefinery 2.0 and Biorefinery 2.5, with increasing number of produced bioproducts. Bearing in mind that each biorefinery has distinct outputs, the selection of the raw material input as a functional unit ensures consistency throughout the study.

The production scheme was assessed through a cradle-to-gate approach. It is a perspective that allows us to consider the processes from the extraction of feedstock up to the plant gate, that is, the products obtained, ready for the market.

3.2.2. System boundary definition

This section is intended to provide a generic description of the production system. To address the research question, several plant configurations were considered through the conception of case studies. The subsystems described below do not necessarily belong to all the case studies. The specificities of the system boundaries regarding each case study are defined in Table 3.1.

The generic system comprises all the process units involved in the ethanol organosolv pulping process, as well as the downstream units for the valorization of pulp and liquor, respectively. The feedstock of the process, as already mentioned, is residual beech woodchips supplied by a sawmill. The plant under assessment has a capacity to process 83.3 t/h of dry wood.

The foreground system includes process units that are the direct object of the lignocellulosic biorefinery. To provide meaningful results in terms of the process sections that will be inferred in more environmental loads, the system under study is divided into nine subsystems (SS). described below. Figure 3.1 depicts a block diagram of the plant identifying the system boundaries, and subsystems. Note that the figure addresses the most complete view of the LCB, including all possible subsystems considered in this study. Specific boundaries of every case study are reported in Table 3.1.

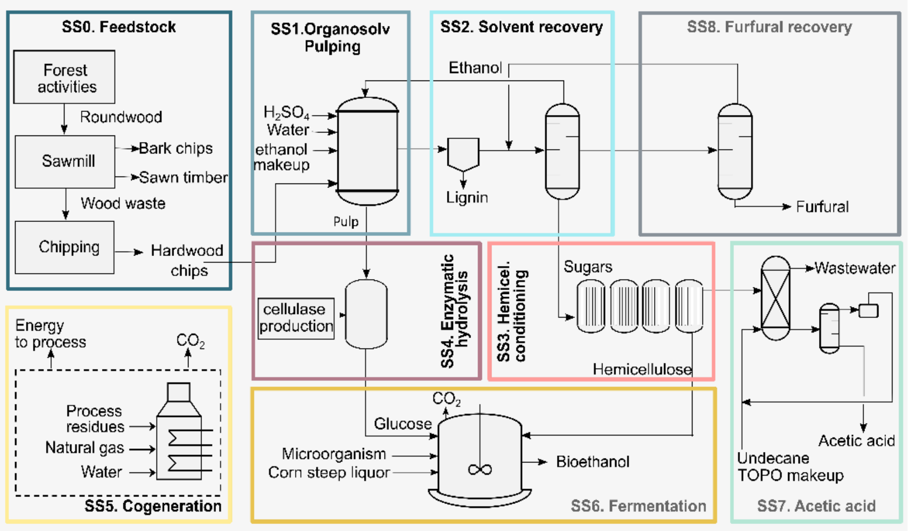

Figure 3.1 System boundaries of the lignocellulosic biorefinery to produce glucose, hemicellulose, lignin, bioethanol, acetic acid, lignin and furfural. Subsystems (SS) are defined with reference to process units in the plant.

SS0.Feedstock comprises forest activities for wood exploitation, sawmill activities and chipping. These process sections and subsystems are implemented within the main subsystem. Feedstock production data have been adapted from other studies. SS0.1 includes activities ranging from soil preparation (use of fertilizers) to wood extraction (González-García et al., 2014). SS0.2 includes the sawmilling activities carried out to produce three main products: sawn timber, bark chips and residual wood (Werner et al., 2007). Residual wood is the feedstock considered for the purpose of this study.

The pre-processing of residual wood to prepare the feedstock for organosolv pulping is considered as SS0.3. Pre-processing activities include chopping of wood as physical pre-treatment to obtain woodchips of a suitable size for further processing (Laschi et al., 2016). All the environmental burdens derived from this subsystem were allocated to this residual wood.

SS1. Organosolv pulping. The process is based on the digestion of wood chips with ethanol (50% v/v) and 1.25% sulfuric acid at 180°C for 60 min. The pulp is washed with water and ethanol solution and pumped through a screen to the enzymatic hydrolysis stage (SS4). The liquor is further hydrolyzed to obtain sugar monomers. Heat and a fraction of ethanol are recovered prior to SS2 operations (Kautto et al., 2013).

SS2. Solvent recovery. The SS1 liquor is diluted to an ethanol concentration of 15% (v/v) and cooled to 50°C to promote lignin precipitation. After lignin precipitation, ethanol is recovered by distillation and recycled to SS1 (Kautto et al., 2013).

SS3. Hemicellulose conditioning. After solvent recovery, the liquor (sugar solution) is sent to a four-effect evaporation train. Low molecular weight soluble lignin (LMW) is easily separated after evaporation and has no added value, so it is burned in the boiler (SS5). The aqueous stream is further subjected to liquid-liquid extraction with furfural, to separate the residual LMW lignin and other organic residues. Lastly, the addition of ammonia allows to adjust pH to 5 before fermentation in SS6 (Kautto et al., 2013).

SS4. Enzymatic hydrolysis. Conversion to glucose from cellulose and hemicellulose is feasible through the use of an enzyme cocktail, mainly cellulase with a minor percentage of hemicellulases, allowing a partial conversion of unreacted hemicellulose to hemicellulosic sugars. This process takes place in an enzymatic reactor at 48°C and a residence time of 84 h (Kautto et al., 2013). On-site enzyme production is included in this subsystem (Dunn et al., 2012; Heinzle et al., 2006).

SS5. Electricity and heat cogeneration. The biorefinery needs significant energy input. The operation of a boiler is considered to meet the demands of steam and electricity, using biogas, WWT sludge, bark and all the organic waste from the different subsystems. In this way, it is possible to valorize the different waste streams. The contribution of natural gas as an external energy source is also considered necessary to balance energy demand (Kautto et al., 2013).

SS6. Fermentation to ethanol. The streams from the enzymatic hydrolysis and the diluted hemicellulosic sugar are used as culture medium for the fermentation stage, using *Zymomonas mobilis* as microorganism. In addition, corn liquor and diammonium phosphate are added as nutrient sources. After obtaining a sufficient volume of inoculum, the main fermenter of the process is operated with culture medium with a composition similar to that of the inoculum train (Kautto et al., 2013).

SS7. Acetic acid recovery. It is possible to recover the fraction of acids (acetic and formic) from the condensates obtained in the evaporator train (SS3). For this purpose, a liquid-liquid extraction (in a mixer-settler column) with triocyphosphine oxide (TOPO) in undecane is used. Undecane and TOPO are used in a closed circuit, however, for the purpose of LCA, 1% loses are considered in the circuit. This subsystem includes, as well, three distillation columns with intermediate decanting steps to separate the acetic acid (at the bottom of the third column) at 97% purity (Kautto et al., 2013).

SS8. Furfural recovery. As a lateral extraction of the distillation columns used for ethanol recovery (SS2), a furfural stream is recovered. The side-draw from the distillation columns is further separated in a decanter, where the aqueous phase is recycled to SS2. Part of the recovered furfural is used as extraction solvent to recover LMW lignin in SS3; the rest of the recovered furfural can be commercialized (Kautto et al., 2013).

The background system consists of processes that indirectly influence the system and contribute to environmental impacts. The background systems include the chemical production of ethanol, sulfuric acid and ammonia as well as transport.

Alternative approaches were assessed parting from the system layout described above. Based on the general outline presented in this section, several hypothetical case studies have been considered (Table 3.1). The case studies differ in terms of the downstream options considered and the final products obtained.

The simplest considered scenario is a biorefinery with the function of producing the most basic chemicals feasible to be obtained with minimum downstream processing. Biorefinery 1.0 produces glucose, hemicellulose and lignin, with an arrangement similar to that studied by Laure et al (2014). The system boundaries are reduced to six subsystems presented in this scenario.

Biorefinery 2.0 was assessed including the production of bioethanol, furfural and lignin. This involves the inclusion of the processing steps in subsystems 6 and 7 for fermentation to ethanol and furfural recovery. Under the scope of Biorefinery 2.0, several distinct scenarios have been proposed for discussion.

i. Furfural recovery methods (scenarios 2.1-2.4). In Biorefinery 2.0, furfural was recovered through distillation (Kautto et al., 2013). However, the recovery of furfural exclusively by distillation is an energy consuming process.

Furfural is the precursor of multiple furan-based biochemicals and biofuels that could eventually lead to substitution of the petroleum-based counterparts. It is listed as one of the top 30 biomass derived platform compounds by the US. Department of Energy (Werpy and Petersen, 2004). Improving the efficiency of furfural recovery may be a significant aspect given its importance in the market. Nhien et al.(2017) have proposed an alternative configuration for the recovery of furfural obtained from lignocellulosic biomass.

Table 3.1 Studied scenarios and specification of boundaries.

Case study	Description	Products	Subsystems included
Biorefinery 1.0	Basic biorefinery	glucose, lignin, hemicellulose	SS0-SS5
Biorefinery 2.0	Advanced biorefinery	ethanol, furfural, lignin	SS0-SS6, SS8
Scenario 2.1	Distillation for furfural recovery	ethanol, furfural, lignin	SS0-SS6, SS8
Scenario 2.2	Hybrid extraction-distillation with benzene for furfural recovery	ethanol, furfural, lignin	SS0-SS6, SS8
Scenario 2.3	Hybrid extraction-distillation with toluene for furfural recovery	ethanol, furfural, lignin	SS0-SS6, SS8
Scenario 2.4	Hybrid extraction-distillation with butyl chloride for furfural recovery	ethanol, furfural, lignin	SS0-SS6, SS8
Scenario 2.5	Implementation of acetic acid co-production	ethanol, furfural, lignin, acetic acid	SS0-SS8

The process implements a two-step recovery system, combining extraction and distillation. Liquid-liquid extraction with three different solvents (toluene, benzene, and butyl chloride) results in two streams: an extract, containing most of the furfural in the feed stream, and a raffinate. The extract was then introduced into a distillation column to separate furfural and the solvent, which was recycled.

ii. Acetic acid co-production (scenario 2.5). Acetic acid is usually produced in bulk fermentation. The production of acetic acid has not been considered in the Biorefinery 2.0 case study, in view of the very low amount produced from such a common chemical. Therefore, an additional scenario has been considered to allow discussion about the adequacy of implementing acetic acid recovery onto the biorefinery route. The objective is to assess whether the co-production of acetic acid (in Biorefinery 2.5) provides advantageous results considering its revenues and environmental factors.

3.2.3. Life cycle inventory

In this study, basic process data, mass balances as well as the biochemical production route considered have been adapted from the simulation of an organosolv process for bioethanol production (Kautto et al., 2013). Foreground data consists therefore of peer-reviewed literature sources (secondary data). The background system components (transport, chemicals, water), have been detailed through the ecoinvent database (Wernet et al., 2016). A summary of data sources considered for inventory collection is presented in Table 3.2. Table A23 and Table A24 in Annex II display the inventories of the foreground systems considered throughout the LCA.

Table 3.2. Summary of data sources for each subsystem under the scope of the study

Subsystem	Reference
SS0. Feedstock	
SS0.1 Forest activities	(González-García et al., 2014)
SS0.2 Sawmill	(Werner et al., 2007)
SS0.3 Chipping	(Laschi et al., 2016)
SS1. Organosolv pulping	(Kautto et al., 2013)
SS2. Solvent recovery	(Kautto et al., 2013)
SS3. Hemicellulose conditioning	(Kautto et al., 2013)
SS4. Enzymatic hydrolysis	(Kautto et al., 2013)
Enzyme production	(Heinzle et al., 2006),(Dunn et al., 2012)
SS5. Cogeneration unit	(Kautto et al., 2013)
SS6. Fermentation to ethanol	(Kautto et al., 2013)
SS7. Acetic acid recovery	(Kautto et al., 2013)
SS8. Furfural recovery	(Kautto et al., 2013)

3.2.4. Allocation

According to the considered disposition of SS0, multiple products are obtained as output of the subsystem. However, not all wood products are used as input of the organosolv pulping subsystem (SS1). When assessing the environmental impacts of SS0, the resulting impacts are associated with all products leaving the subsystem and not just one. Subsystem 0 includes sawn timber, bark chips and woodchips as outputs. Since only woodchips are the product used as raw material in subsequent subsystems, it is only responsible for its corresponding fraction of the overall impacts. Therefore, allocation of impacts to residual woodchips has been applied.

Volumetric allocation could be considered as a viable option, allocating impacts to co-products in proportion to the produced volume of each product; volumetric allocation factors are 51% for sawn timber, 13% for bark chips and 36% for residual woodchips.

However, even if all products from SS0 are marketable, they do not have the same economic value. Considering the reference market prices of products from sawmills (Lundmark, 2006) the allocation factors are modified to 77% for sawn timber, 14% for bark and 9% for woodchips. Nowadays, residual wood is not as valuable for other applications, as can be seen through the calculated economic allocation factors. The second allocation method better reflects the purpose of finding a niche market for the residual fraction of a sawmill. It should be noted that the economic allocation has been considered for SS0.1 and SS0.2, but not for SS0.3, since this subsystem only treats residual wood to obtain woodchips.

3.2.5. Assumptions and limitations

The results presented in this study may show some uncertainty arising from assumptions made due to data gaps. The following are the hypotheses considered throughout the evaluation as the best possible approximation.

i. Transport of woodchips from SS0 to SS1 is the only transport process included. The transport distance has been considered as 100 km, and impacts derived from transport have been assigned to SS1. Lorry freight (16-32 metric tons) was the selected mode of transport. Transport losses of 5% have been considered, with a resulting ton-kilometre (tkm) value of 105.

ii. One of the distinctive characteristics of the considered system is the cogeneration unit (SS5). Cogeneration provides energy and steam to the entire system through the burning of natural gas and process residues in a dual boiler. When a subsystem consumes electricity or uses utilities, these are supplied entirely through the cogeneration subsystem. This means that the impacts assigned to SS5 can be divided between all subsystems that consume energy. This is relevant for the sake of result interpretation. The boiler produces energy for the plant. In turn, when any process unit uses the energy produced by the boiler, the impacts of energy consumption are the corresponding fraction of the environmental impacts derived from energy production (e.g., combustion emissions). If the energy produced in SS5 were to be accounted within the energy consumer subsystem, the impacts of that energy would be duplicated (counted once in SS5 and again in the consumer subsystem).

iii. The cogeneration unit of the plant supplies electricity to SS1, SS2, SS3, SS4 (except for on-site enzyme production), SS6, SS7, SS8. Among these subsystems, SS1 is the main electricity and steam consumer with a percentage of demand with respect to the total around 35%. Subsystem 0 includes off-site activities ranging from forestry to wood pre-treatment; electricity demands for SS0 are retrieved directly from the grid.

iv. No infrastructure process was considered in the assessment to assure uniformity of conditions across all subsystems, as no reliable data is available for all considered equipment. On the other hand, environmental impacts per process unit, from the installation, construction, decommissioning, infrastructure, machinery, etc. have been considered negligible during the lifetime of a biorefinery facility. This has been a common practice in other biorefinery LCA studies (González-García et al., 2011, 2009c; Jeswani et al., 2015; Karlsson et al., 2014; Lim and Lee, 2011).

3.2.6. Methods

The ReCiPe 1.12 hierarchist method (Goedkoop et al., 2009) was used for the calculation of impacts. Impact categories at midpoint level were studied. SimaPro 8.02 software was used for the computational implementation of the inventories.

Although all categories of the ReCiPe method were studied, environmental results are presented in terms of the following impact categories: global warming (GW), ozone depletion (OD), terrestrial acidification (TA), freshwater eutrophication (FE), marine eutrophication (ME), human toxicity (HT), photochemical oxidant formation (OF), freshwater ecotoxicity (FET), marine ecotoxicity (MET), land use (LU), water consumption (WC) and fossil scarcity (FS). The above-mentioned impact categories are the most representative for European bioprocessing systems (González-García et al., 2016, 2009c; Uihlein and Schebek, 2009).

3.3. RESULTS AND DISCUSSION

The relative contributions to the environmental burdens in each of the selected impact categories are presented below for each studied alternative. The contribution of each process subsystem to each category is shown, allowing to discern which are the critical points of the process.

3.3.1. Environmental performance of different biorefinery configurations

The characterization results of Biorefinery 1.0, Biorefinery 2.0 and Biorefinery 2.5 are shown in Figure 3.2. Analyzing the complete set of environmental results in Biorefinery 1.0, SS1 can be appointed as the most burdening subsystem; however, there was no major difference with respect to SS4 (enzymatic hydrolysis) or SS5 (cogeneration unit). Nevertheless, SS1 is the largest energy and steam consumer, therefore, it is indirectly responsible for a significant fraction of environmental impacts associated to SS5.

For Biorefinery 1.0, the feedstock subsystem (SS0) presented a considerably uniform distribution of environmental impacts across all categories, with contributions always below 23%. FE (23%), ME (19%) and GW (18%) were the groups most affected by wood preparation activities. SS0 contributions were mostly appointed to SS0.2 (sawmill activities). Sawmill activities require high electricity consumption due to the use of machinery; electricity for SS0 is directly retrieved from the grid and not from the cogeneration unit. Other burdens were derived from the use of lubricant oil for maintenance, plastics for packaging and chemicals for finishing operations.

OF was the most impacted category in the organosolv pulping subsystem with a share of 43%. This is mainly due to emissions of volatile organic compounds from road transport of woodchips to the site. The organosolv pulping subsystem (SS1) presented the largest contributions to OD, TA and HT, with values of 38, 27 and 34% respectively.

SS1 was the second major contributor to climate change with 22%. Factors from SS1 responsible of GW were mainly emissions from road transport of woodchips.

Solvent recovery and hemicellulose conditioning (SS2 and SS3) did not contribute significantly to the overall environmental impact of the system. Solvent recovery (SS2) caused contributions to impact categories ranging from 1 to 13%. Hemicellulose conditioning presented slightly higher values ranging from 5 to 16%. In general, the contributions to the environmental profile were not significant.

The environmental impacts of SS4 were the result of enzyme production. For this subsystem, eutrophication categories (FE and ME) were the most impacted, together with MET. Surprisingly, the contributions of this subsystem are very comparable to the organosolv pre-treatment. However, it should be noted that the cogeneration unit does not supply the heat and electricity demands, as the on-site cellulase production unit is not present in the plant originally considered. Enzyme production is the only input process into SS4.

For GW, FET and FS, SS5 was the most burdensome subsystem, with a maximum relative contribution of 40% allocated to FS. Although SS5 uses part of the residues from the process to burn, it also needs a fresh supply of natural gas to meet the energetic demand of the plant. On the other hand, fossil CO_2 emissions from the boiler also contribute to the overall results.

Results for Biorefinery 2.0 in Figure 3.2 show the impacts for the subsystems in the advanced biorefinery, producing bioethanol, furfural and lignin. Although the furfural recovery subsystem (SS8) was included in the analysis, it showed no environmental impacts. The only input of the furfural recovery subsystem is energy supplied by SS5. Although SS8 does not have direct environmental burdens to any category, one must assume that indirectly, part of the burdens assigned to SS5, were in fact due to energetic consumption in SS8. In general, the environmental profile of the plant, in relative terms, has not been greatly affected by the addition of more downstream processing units.

The feedstock subsystem (SS0) presented the same results as in Biorefinery 1.0 with very slight changes and contributions always below 22%. FE (22%), ME (17%) and GW (17%) were the most impacted groups.

For SS1 the profile was once again quite similar to Biorefinery 1.0. OF was the most impacted category in the organosolv pulping subsystem with a share of 39%. OD (37%) and HT (33%) categories contributed to SS1 total impacts with values close to OF. SS1 also contributed to emissions due to the use of chemicals (ethanol and sulfuric acid). Organosolv pulping was the greatest contributor among the subsystems in 4 out of 10 impact categories.

Solvent recovery and hemicellulose conditioning (SS2 and SS3) did not greatly contribute to the overall results. Solvent recovery made contributions to impact categories ranging from 2 to 12%. Hemicellulose conditioning presented slightly higher values ranging from 5 to 15%.

Enzymatic hydrolysis (SS4) contributed to overall impacts with significant values. The same reasoning as Biorefinery 1.0 can be used. Although the results are comparable to the organosolv pulping subsystem, organosolv does not include its impact contributions due to the consumption of electricity, heat and steam. Cellulase production is an energy-intensive fermentation process, which, together with the carbon source consumption contribute to the overall results in SS4. Both eutrophication categories presented relevant contributions to the total results (46% and 28% for FE and ME respectively) mainly due to the use of nutrients (nitrogen, phosphorous) in the fermentation process.

The largest contribution to FS was originated in the cogeneration unit (44%), specifically due to the use of natural gas as fuel. The cogeneration subsystem was also the main contributor to GW (33%).

Finally, the fermentation subsystem contributed slightly to the overall environmental results. Contributions to TA (17%) and marine eutrophication (13%) were the major impacts caused by SS6. Overall, the fermentation subsystem was not very significant to the total. The environmental profile of the plant, when analyzing the relative contributions from subsystems, was not significantly altered due to the ethanol fermentation subsystem.

No significant overall differences were found when analyzing Biorefinery 2.0 and Biorefinery 2.5 (with the co-production of acetic acid). The environmental profile of the overlapping subsystems was maintained, and the only difference was the incorporation of environmental impacts due to SS7. SS7 for acetic acid co-production presents the major contributions to ozone depletion (39%) followed by considerable impacts to fossil depletion (23%) and photochemical oxidant formation (15%). All contributions to every impact category from SS7 originate from the use of chemicals (TOPO and undecane).

The LU impact category displays the least differing results. All impacts in LU for the three Biorefinery configurations are attributed to SS0, with no differences in the impact intensity when widening the production scope of the biorefinery. This category displays the resource efficiency behavior, which is increased as the complexity of the biorefinery increases. While the input raw material to the system does not change —thus, the same land is occupied per functional unit for silviculture— the value added from the biorefinery does increase.

On the other hand, after LU, WC is the impact category with the least variability of impacts when comparing Biorefineries 1.0, 2.0 and 2.5. Most of the contributions to water consumption are originated in SS1, for the pulping of the wood, which are equal for the three configurations. The differences in WC arise from the increasing use of water in SS5, SS6 and SS7.

When benchmarking all scenarios comparatively, not talking in relative terms, the results unfold as expected for the most part. The increasing complexity of biorefineries showed a proportional increase of the net environmental impacts in each category. Biorefinery 2.0 with acetic acid co-production (scenario 2.5) displayed the greatest burdens for all impact categories. In contrast, the simplest scenario (Biorefinery 1.0) displayed the lowest environmental impacts overall. According to expectations, when the biorefinery increased its downstream steps, equipment for processing, inputs from technosphere, emissions, etc., the environmental impacts were greater. However, this comparative analysis alone is not sufficient to assess whether one scenario is more environmentally efficient than another. Since the production scope of every biorefinery changed for each scenario, the facilities were not considered comparable and therefore further analysis should be performed (Section 3.3.3).

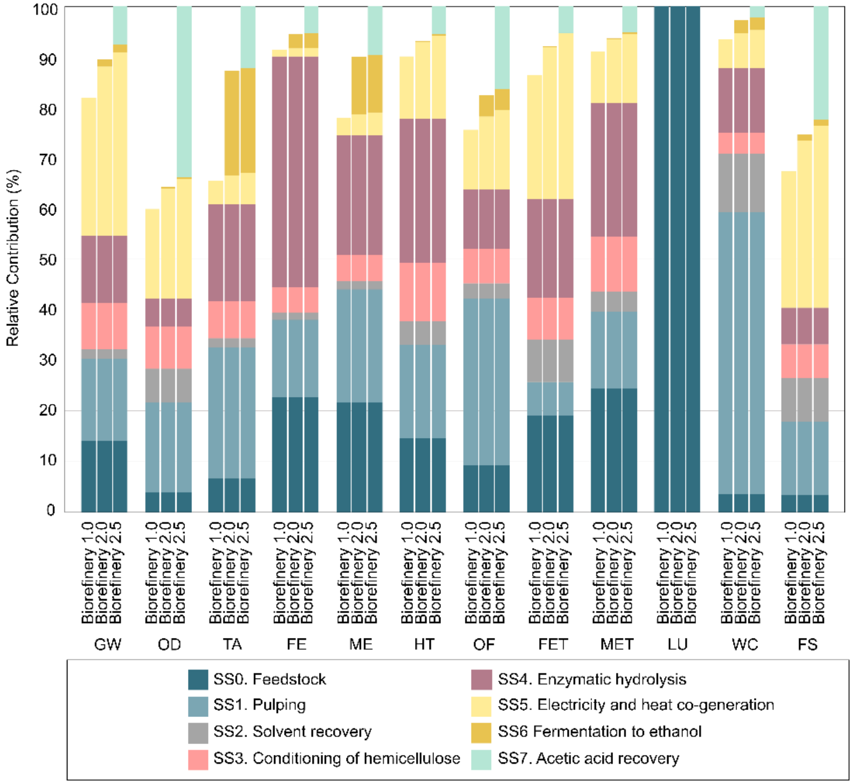

Figure 3.2 Comparative contributions (in %) per subsystem in the overall production process of the Biorefinery 1.0, Biorefinery 2.0 and Biorefinery 2.5 (with acetic acid co-production). Results were obtained per functional unit. Global warming (GW), ozone depletion (OD), terrestrial acidification (TA), freshwater eutrophication (FE), marine eutrophication (ME), human toxicity (HT), photochemical oxidant formation (OF), freshwater ecotoxicity (FET), marine ecotoxicity (MET), land use (LU), water consumption (WC) and fossil scarcity (FS)

3.3.2. Comparative assessment of furfural recovery methods

The comparative assessment for the recovery of furfural with four different alternatives (scenarios 2.1, 2.2, 2.3 and 2.4) is illustrated in Figure 3.3. Eight impact categories out of twelve, presented higher impacts when considering only distillation (base case scenario, Biorefinery 2.1). Only GW, OD and FS displayed the hybrid extraction process with toluene as the most unfavorable scenario. These categories (GW, OD and FS) were the most impacted because the hybrid alternative (Biorefinery 2.3) uses fossil-based extractants for separation.

The extraction-distillation hybrid (for all the solvents studied) presented a better environmental performance than the purification process through distillation, mainly because it consumes less energy. The results showed that the use of benzene for extraction in the hybrid process was the best-case scenario among the alternatives studied. In general, the hybrid separation is more efficient, technologically feasible and environmentally friendly.

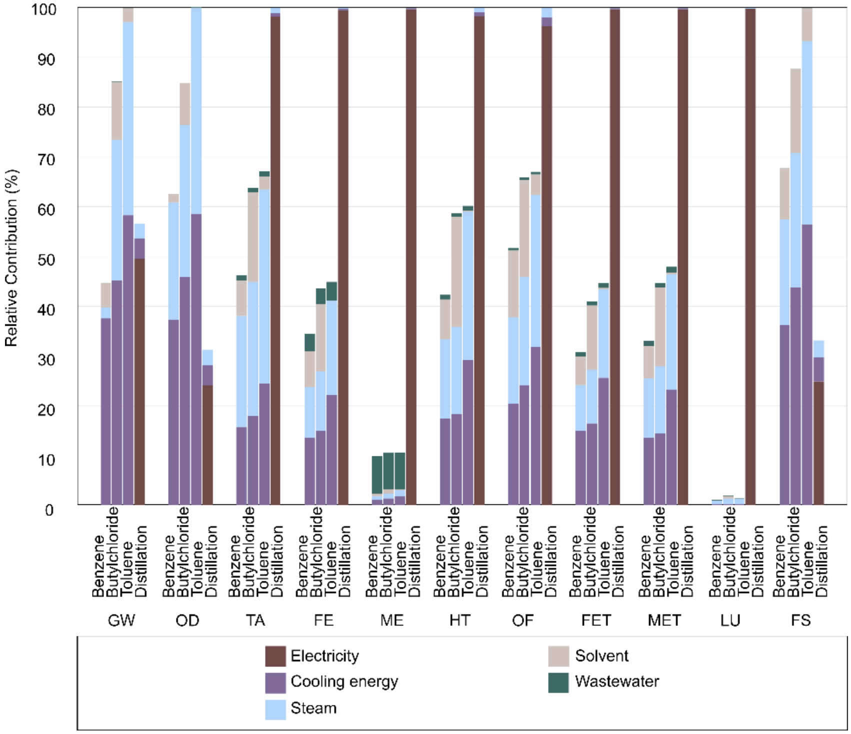

Figure 3.3 Comparative environmental profiles (in %) for furfural recovery methods: exclusive distillation and hybrid distillation-extraction with benzene, butyl chloride and toluene. Global warming (GW), ozone depletion (OD), terrestrial acidification (TA), freshwater eutrophication (FE), marine eutrophication (ME), human toxicity (HT), photochemical oxidant formation (OF), freshwater ecotoxicity (FET), marine ecotoxicity (MET), land use (LU), water consumption (WC) and fossil scarcity (FS)

3.3.3. Eco-efficiency assessment of the scenarios considered

As reported in Section 3.3.1, one would assume that the most environmentally sustainable LCB is Biorefinery 1.0. However, the research question is not fully answered through the concluding remarks on the section. The objective of this chapter was to perform the holistic sustainability assessment of a Biorefinery and to conclude whether a more complex biorefinery would be more sustainable than a simplistic one. In the case of this LCA study, it was found that comparing the three scenarios with only environmental impacts in mind did not meet the objective of determining the best-case scenario from the sustainability perspective. Generally speaking, if one scenario involves the use of more resources (chemicals, energy) than another, it is consistent that it results in more environmental impacts. However, the only quantification of environmental impacts does not take into account whether one scenario produces two bioproducts and another scenario produces three bioproducts, or the volume of production and potential value added. For the sake of simplification, it was decided that the determination of potential revenues from each scenario would better describe the latter concern.

Considering the monetary benefit of each LCB scenario in parallel to the environmental indicators, a comparative evaluation of environmental performance of integrated biorefineries is given. Other studies have concluded the imminent need to integrate issues related to environmental impacts and economic profitability in order to simultaneously evaluate processes and technologies. Quantitative evaluation of the different provisions across both perspectives is highly profitable for stakeholders and companies (Gavrilescu, 2014).

Environmental impact versus revenue was the selected indicator of sustainability since it allows to tackle the objectives of economic growth and environmental protection. The monetary benefit of each biorefinery according to product sales prices (Table 3.3) and environmental impact (GW, TA, OD, WC) were the selected indicators for the assessment of eco-efficiency. When the emission factor is presented per unitary benefit potentially achieved by the biorefinery, the outcome of the assessment is different. In fact, the eco-efficiency indicator is a reliable score to make comparable two systems which are not. Biorefinery 2.0 attains lower emissions per unitary benefit than Biorefinery 1.0. The eco-efficiency indicator (Table 3.4) for each impact category is lower for Biorefinery 2.0 in all cases except for ozone depletion and terrestrial acidification. Conversely, Biorefinery 2.5 (which includes acetic acid coproduction) does not follow the same trend and is less environmentally sustainable.

Table 3.3 Market selling prices of biorefinery products for the calculation of revenues.

Product	Average market selling price (€/t)	References
Glucose	355.0	(Heinzle et al., 2006; Klein-Marcuschamer et al., 2012)
Lignin	530.6	(Budzinski and Nitzsche, 2016; Hodásová et al., 2015; Nitzsche et al., 2016; Schwiderski and Kruse, 2016; Zhao et al., 2017)
Hemicellulose	105.4	(Li et al., 2013; Persson et al., 2007; Qureshi et al., 2014)
Bioethanol	830.5	(Bechara et al., 2016; Frankó et al., 2016; Joelsson et al., 2016; Macrelli et al., 2014; Rodrigues Gurgel da Silva et al., 2017)
Furfural	865.3	(Brentzel et al., 2017; Huang et al., 2017; Kaylen et al., 2000; Machado et al., 2016; Moncada et al., 2016; Win, 2005)
Acetic acid	834.2	(Himmelblau and Riggs, 2004; ICIS, 2018; Straathof and Bampouli, 2017; Zhu and Jones, 2009)

The objectives for optimizing the eco-efficiency in this biorefinery system are to minimize environmental impacts and maximize economic benefits. Figure 3.4 is the representation of the eco-efficiency indicator used in this study combining economic benefits with GW, TA, OD and WC impact categories. Within the set of studied biorefineries the best-case scenario is achieved when the solutions fall in the Q3 quarter of the graph (low environmental impact and high revenue). The virtual division of the eco-efficiency graph (Figure 3.4) into four quadrants allows to qualitatively categorize a biorefinery scenario according to the area of the graph in which it falls. The quadrant-divisions were located at the average value of each represented variable in the axis (environmental impact and revenue). Depending on its environmental impact and revenues, a scenario could be environmentally optimal (Q4, Q3), maximize the potential benefits of plant revenues (Q3, Q2), accomplish both objectives (Q3) or neither of them (Q1) to a greater or lesser extent. The aim is to have a visual comparison tool to quickly define how a scenario behaves in relation to both the values of environmental impact and revenue for representative environmental impact categories.

Table 3.4 Eco-efficiency indicator, calculated for every impact category considered in the study and for every biorefinery scenario.

Eco-efficiency indicator	Biorefinery 1.0	Biorefinery 2.0	Biorefinery 2.5
GW (kg CO$_2$ eq/€)	0.47	0.42	0.45
OD (kg CFC-11 eq/€)	$5.34\cdot10^{-8}$	$7.64\cdot10^{-8}$	$4.38\cdot10^{-8}$
TA (kg SO$_2$ eq/€)	$2.32\cdot10^{-3}$	$2.41\cdot10^{-3}$	$2.62\cdot10^{-3}$
FE (kg P eq/€)	$9.85\cdot10^{-5}$	$8.32\cdot10^{-5}$	$8.42\cdot10^{-5}$
ME (kg N eq/€)	$5.81\cdot10^{-5}$	$5.52\cdot10^{-5}$	$5.91\cdot10^{-5}$
HT (kg 1,4-DB eq/€)	$1.26\cdot10^{-3}$	$1.13\cdot10^{-3}$	0.097
OF (kg NMVOC/€)	$3.04\cdot10^{-3}$	$1.13\cdot10^{-3}$	$1.30\cdot10^{-3}$
FET (kg 1,4-DB eq/€)	$3.04\cdot10^{-3}$	$2.64\cdot10^{-3}$	$2.75\cdot10^{-3}$
MET (kg 1,4-DB eq/€)	$2.62\cdot10^{-3}$	$2.19\cdot10^{-3}$	$2.23\cdot10^{-3}$
LU (m^{2}a/€)	$1.21\cdot10^{-2}$	$9.89\cdot10^{-3}$	$9.47\cdot10^{-3}$
WC (m^3/€)	$3.56\cdot10^{-5}$	$3.03\cdot10^{-5}$	$2.98\cdot10^{-5}$
FS (kg oil eq/€)	0.24	0.22	0.28

From the carbon footprint perspective, when the expansion of the biorefinery is specifically performed for specialty bio-products, the biorefinery is more sustainable. However, the production of bulk chemicals such as acetic acid in this type of facility is not as environmentally sustainable, especially when the production volume is very small. Therefore, the suggestion resulting from the results of the study would be to broaden the multi-production spectrum of the biorefinery only when the production volume and the type of product are reasonable. From an environmental point of view, an integrated biorefinery is sustainable when the intensification of resource demand is not useless, for instance, if the yield for the different products is satisfactory or the final goods meet their specifications. This behavior is mimicked in other categories such as OF, HT, FE, MET or FS.

For TA, however, none of the studied scenarios fall within the optimal eco-efficient quadrant, being both Biorefineries 2.0 and 2.5 higher revenue achiever scenarios, with the consequential increase in environmental impact. In the OD impact category, however, the most eco-efficient configuration is that of Biorefinery 2.5, being the least ozone depleting one and the highest economically feasible configuration. Biorefinery 2.0 is the worst scenario when it comes to the OD impact category, being that the reason why it falls in Q2. Regarding WC, Biorefinery 2.0 has a shift of behavior similar to that of TA, in which it no longer falls in the most optimal quadrant (Q3). The results in Figure 3.4 show that to analyze the overall impact of a biorefinery system, the ideal situation would be to go beyond the analysis of a single indicator, but to analyze the environmental and economic effect in different systems that may affect the Earth's sustainability. However, when it comes to prioritizing the areas of improvement and environmental impact abatement, biorefineries are conceptualized mostly for decarbonization purposes and the reduction on the fossil fuel pressure. These results show that looking beyond that is key for a future sustainable bioeconomy.

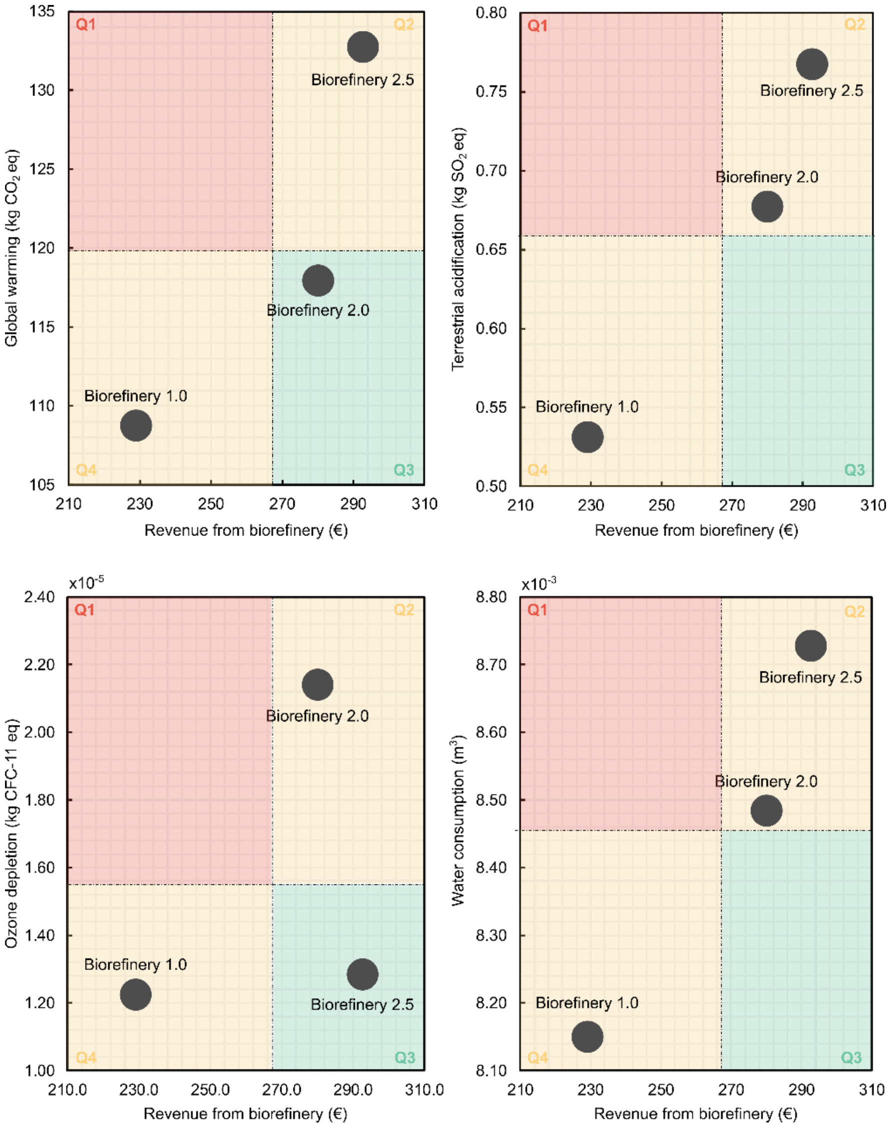

Figure 3.4 Eco-efficiency graphs displaying climate change, terrestrial acidification, ozone depletion and water depletion versus monetary benefit per functional unit (1 t dry wood /h) Quadrants are defined through the scenarios average of each variable.

Although social LCA is not the objective of the present study, and is beyond the scope, it would be indeed interesting to address the current views on the three pillars of sustainability as defined by the Brundtland Report (World Commission on Environment and Development, 1987). All three perceptions should be balanced to achieve the best possible production system in terms of sustainability. Social LCA and other assessments regarding social indicators are yet in their first steps towards the acquisition of a robust and reliable methodology commonly applied to case studies (Petti et al., 2018). The novelty of these type of studies makes it far more difficult to find reports of social analysis on lignocellulosic biorefineries, as they have not yet evolved into large scale facilities. Some studies have addressed social issues of interest to biorefineries, recognizing, in particular, the relevance of the selection of social indicators. Valente et al. (2018) have considered the implications of the use of some social indicators on bioethanol lignocellulosic biorefineries. Categories such as health and safety, community infrastructure, governance, human and labor rights, and decent work have been considered. Generally speaking, socio-economic indicators are more commonly used than exclusively social indicators to determine social sustainability in biorefineries, as presented by the work of Parada et al. (2017). Bearing these statements in mind, it can be argued that social conclusions may not have as many direct impacts on the design of biorefinery processes (a part from variables such as the location of the plant and sourcing alternatives), but have more repercussion, for instance, on the corporate values, vision and strategy of a company.

On the road to the selection of indicators for environmental assessment, there is a wide range of options. When social and economic issues are added, even more alternatives emerge. In any case, the selection of categories of indicators should be consistent with the objective of the evaluation. ISO 14045 establishes the combination indicator groups to be used to determine the eco-efficiency of a product or process. In general, the environmental impact and value of the system are the general concepts analyzed. Within the value of the system, different indicators can be considered, among others, the functional performance of products, monetary value of products, aesthetics, market studies, etc. (ISO 14045, 2012).

3.3.4. Acetic acid co-production

If the sustainability of a biorefinery is variable, then, what biorefinery products should be produced? In the case of acetic acid co-production, for instance, its recovery from the biorefinery route includes the use of TOPO and undecane, chemicals that, although recycled, have high environmental impacts. Therefore, the recovery of acetic acid is not sustainable. In fact, the average production of acetic acid in bulk is a process of fermentation (Dodds and Gross, 2007), that avoids the use of TOPO and undecane as well as petrochemical production options. The production of acetic acid through a LCB increases potential revenues as demonstrated in this assessment and in agreement to other studies (Zhang et al., 2007; Zhu and Jones, 2009). However, the negative environmental consequences shift the overall eco-efficiency indicator towards the Q2 quarter, where revenues are high, but so are the CO_2 equivalent emissions. Specialty products produced within a biorefinery support the overall environmental sustainability when there are not other business-as-usual routes with better overall performance.

3.3.5. Furfural recovery

This chapter shows the need not only to integrate the co-production of various bioproducts but to also optimize existing processes in the biorefinery route. An example would be the recovery of furfural. Recovery of furfural through less energy-intensive methods reduces global environmental impacts (Figure 3.3), which, in fact, improves the ecoefficiency indicator. For the same production volume of furfural, fewer overall impacts are obtained for the benzene extraction-distillation alternative. This is relevant in relation to fluctuations of furfural market prices (Brentzel et al., 2017). If the process is not fully optimized, a slight variation in the furfural price may change the eco-efficiency indicator towards the Q4 quarter (for GW) where overall benefits are not relevant. Selecting the most optimal separation alternative for furfural enables the biorefinery to achieve consistent eco-efficiency scores not highly dependent on the accounting method and assumptions taken.

3.3.6. Enzyme production

Unexpectedly, the enzymatic hydrolysis step considered in the system presents relevant impacts with respect to the biorefinery as a whole. The impacts of SS4 are derived from on-site enzyme production and furthermore, enzyme dosage for hydrolysis does not constitute a significant amount. However, environmental results are aligned with the cost of enzyme production. Other studies have demonstrated the implications that enzyme production has on total costs and emissions for the production of lignocellulosic ethanol (Olofsson et al., 2017). The further integration of enzyme production into the biorefinery is expected to result in a reduction of the total impacts. As in other studies (Singh et al., 2010), enzyme production technologies significantly affect environmental impacts and LCA results may be sensitive to changes in this subsystem. There seems to be an overall uncertainty in the literature when enzymes are included as inputs to systems. In many cases, the impact of enzymes has been overlooked or partially estimated, due to mainly, the lack of data, the scale of the production of enzymes (especially when these are very specific and function-driven enzymes) and the scarce presence in dedicated-LCA databases. The study of the environmental impact of enzymes (in particular, oxidative enzymes) for biobased systems will be addressed more in depth in Chapter 6.

3.4. CONCLUSIONS

Biorefining systems have been studied with the aim of reducing environmental burdens for some time: the topic on biorefineries is extensive and varied. Comparison of results with other studies is complex in the case of lignocellulosic systems, due to the limiting quantity of data available. Therefore, the introduction of eco-efficiency and exemplification through different biorefining scenarios is a steppingstone for the optimization of bioproduction building blocks that will be part of the future's bioeconomy. The evaluation of facilities with primary data should provide an interesting background on the best configurations towards the sustainability of biorefineries. On the other hand, if data availability is not a constraint, future research should focus on the assessment of a wider range of biorefinery scenarios. The system under study in this chapter, has shown that optimization of LCB hotspots should focus on further integration of enzyme production, optimization of technologies for the manufacture of high value added bioproducts and the optimization of the organosolv pretreatment process. It would be advantageous, as well, to study possibilities of further energy optimization to achieve full integration of the plant. All of these concepts will allow to reach systems that are more environmentally sustainable, while being able to compete with the current chemical production industry.

4

Lignocellulosic biorefinery beyond carbon neutrality

> *“The biggest challenge is avoiding messaging that makes it sounds like tree planting is an easy way out for climate change and environmental degradation”*
>
> Thomas Crowther

Chapter 4 Summary

As a natural transition from Chapter 3, this chapter focuses on the bioethanol as biofuel. The concept of Bioenergy with carbon capture and storage (BECCS), which is gaining broad interest as an effective strategy to go beyond carbon neutrality, is introduced here. So far, most of the work on BECCS focused on power systems, while its application to the transport sector has received much less attention. To contribute to filling this gap, this chapter investigates the potential of BECCS as a carbon-negative strategy in the transport sector by applying process modelling and life cycle assessment (LCA) to bioethanol production from lignocellulosic waste. The process was analyzed following a cradle-to-wheel approach, i.e., from biomass growth to the combustion of biofuel in the cars, assuming that the CO_2 emitted in the fermentation and cogeneration units is captured, compressed, and transported to be stored permanently in geological sites. Several scenarios differing in the bioethanol-gasoline blends (10–85% bioethanol) were considered for a functional unit of 1 km of distance travelled, comparing with fossil-based gasoline. The results show that blends above 85% (ethanol/gasoline) could have the potential to deliver a net-negative emissions balance of -2.74 kg CO_2 eq per 100 km travelled and up to -5.05 kg CO_2 eq per 100 km using a low carbon electricity source. The final amount of net CO_2 removal is highly dependent on the carbon intensity of the electricity and the heating utilities. Biofuels blends could, however, lead to burden-shifting in eutrophication, ozone depletion and formation, toxicity, land use, and water consumption. This chapter highlights the potential of BECCS in the transport sector, and the need to analyze impacts beyond climate change in future studies to avoid shifting burdens to other categories.

This chapter under the consent of the publisher was redrafted after: S. Bello, Á. Galán-Martín, G. Feijoo, M.T. Moreira, G. Guillén-Gosálbez, BECCS based on bioethanol from wood residues: Potential towards a carbon-negative transport and side-effects, Appl. Energy. 279 (2020). doi:10.1016/j.apenergy.2020.115884. More information about this publication can be found in Annex I.

This investigation was carried out during a research stay at the Institute for Chemical and Bioengineering, ETH Zürich.

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4.1. INTRODUCTION TO THE CONCEPT OF BECCS IN SECOND GENERATION BIOREFINERIES

The European goals and actions for climate neutrality will very likely have to be accompanied by carbon dioxide removal (CDR) strategies, which seem vital to meet the goals stated in the Paris Agreement (United Nations, 2015). The draft of the upcoming EU Climate Law explicitly mentions the necessity of CDR to achieve the EU 2050 climate-neutrality goal (European Commission, 2020), which could be delivered through carbon capture and storage (CCS). The portfolio of CDR options available includes afforestation and reforestation (AR), ocean alkalinity enhancement, biochar sequestration, mineralization of carbon dioxide, direct air capture and storage (DACCS) and bioenergy with carbon capture and storage (BECCS). Notably, CCS could be applied to a wide range of fossil-based industries. High emission sources include the cement industry, the iron and steel industry, and fossil refineries (Bains et al., 2017). CCS in the fossil-based industry is deemed necessary to reach the decarbonization goals, yet it cannot lead to a net negative carbon balance. On the other hand, BECCS and DACCS, regarded as promising CDR options, have the potential of achieving net negative emissions.

According to estimates, the CO_2 removal capacity for CDR options in 2050 will range from 0.5 to 3.6 $GtCO_2 \cdot yr^{-1}$ for afforestation and reforestation, 2.0 to 4.0 $GtCO_2 \cdot yr^{-1}$ for enhanced weathering, 0.5 to 2.0 $GtCO_2 \cdot yr^{-1}$ for biochar and reach 5.0 $GtCO_2 \cdot yr^{-1}$ for soil carbon sequestration. DACCS is assumed to be only limited by the geological storage capacity and the availability of energy resources. At the same time, the potential of BECCS varies significantly, between 0.5 and 5.0 $GtCO_2 \cdot yr^{-1}$, depending on the technical assumptions and land availability (i.e., degraded and marginal land and/or abandoned and unused agricultural land) (Chum et al., 2011; EU GeoCapacity, 2008; Fajardy et al., 2019; Fuss et al., 2018; Intergovernmental Panel on Climate Change, 2018; Smith et al., 2016).

Among all these CDR options, BECCS is receiving significant attention and already emerges as predominant in most of the climate change mitigation scenarios aligned with the 1.5ºC target. BECCS allows removing CO_2 while providing the clean and reliable energy needed to underpin economic growth and development, which makes it particularly appealing (Intergovernmental Panel on Climate Change, 2018; Moreira et al., 2016). Indeed, BECCS is already considered in some Integrated Assessment Models (IAMs), in which other CDR engineered options are rarely contemplated mainly due to lack of maturity (Fuss et al., 2018; Pozo et al., 2020; Realmonte et al., 2019). Hence, alongside with AR, the broad deployment of BECCS technologies will very likely play a pivotal role in meeting the climate goals as they represent a good compromise between the carbon removal potential and the associated removal costs (Fuss et al., 2018; Mendiara et al., 2018).

Primarily, the BECCS concept refers to technologies converting biomass resources into valuable products in tandem with CO_2 capture systems. The latter prevents the release of the CO_2, absorbed via photosynthesis during biomass growth, to the atmosphere. Then, the captured CO_2 is transported and injected into underground geological sites ensuring its long-term storage (Audoly et al., 2018). Compared with other CDR options, BECCS has the value-added of potentially providing a net negative balance of CO_2 with the atmosphere while delivering renewable energy-based products. The latter can, in turn, displace the use of their fossil-based counterparts, thereby avoiding their associated impacts (Calvo-Serrano et al., 2019).

The BECCS concept emerged in the last decade of the 20th century through conceptual studies addressing the production of biomass-based biofuels combined with CCS, as applied to the hydrogen fuel (Williams, 1998), and other bio-energy applications that could potentially deliver negative emissions (Herzog and Drake, 1996; Vergragt et al., 2011). The beginning of the 21st century brought formally the concept of BECCS (initially called biomass-energy with carbon removal and disposal) as a risk management strategy to maintain GHG emissions at a safe level even under conditions hard to predict (Obersteiner, 2001).

In this context, Möllersten et al. addressed the potential CO_2 reductions and associated costs in the chemical pulp and paper mill industry (2003b) and in sucrose fermentation to produce ethanol (2003a). In 2003, the term BECCS was first introduced as a technological solution to convert the energy system into a CO_2 remover (Kraxner et al., 2003). However, the kick-off for BECCS was the special report on CCS published in 2005 by the IPCC, which highlighted BECCS as a feasible large-scale option to provide net negative emissions (Intergovernmental Panel on Climate Change, 2005). Since then, due to the continued use of fossil fuels and the steady increase in the associated carbon emissions, BECCS has attracted increasing attention as a key option to meet the climate targets sought (Galik, 2020; Intergovernmental Panel on Climate Change, 2018).

Despite their expected pivotal role in climate change mitigation, the deployment of BECCS technologies would, however, face some obstacles. These challenges include constraints given by land availability and CO_2 storage capacity, socio-economic barriers, policy adequacy issues, logistical implementation difficulties, as well as other sustainability concerns (Azar et al., 2010; Fuss et al., 2014), all of them linked to the specific BECCS technology selected. There are a handful of BECCS technologies implementing several conversion routes and spanning different sectors. These include (among others) biomass feedstocks burned at power or heating plants with CCS (Bui et al., 2017), gas or liquid biofuels production at biorefineries with CCS (Carminati et al., 2019; de Freitas Dias Milão et al., 2019; Lu et al., 2019), and pulp and paper mills equipped with CCS (Kuparinen et al., 2019).

Several studies have delved into the BECCS technologies analyzing its cost-effectiveness, potentials and side-effects (Fuss et al., 2018; Galik, 2020; Kemper, 2015; Sanchez and Callaway, 2016; Schmidt et al., 2010). Other authors studied the negative emission potential of biomass co-fired with coal in a power plant coupled with CCS from a life cycle assessment (LCA) perspective (Yang et al., 2019). On the other hand, others focused on the BECCS supply chain optimization to deliver carbon-negative electricity (Akgul et al., 2014; Fajardy and Mac Dowell, 2017; Gabrielli et al., 2020a). Despite extensive research and the growing interest in BECCS at the industrial level (Bui et al., 2018), most of the efforts on BECCS have focused on biomass conversion to heat and power. In contrast, the BECCS concept applied to biorefineries that produce biofuels (Fajardy and Mac Dowell, 2017; Mendiara et al., 2018) remains mostly unexplored (Fajardy et al., 2019).

Carbon-negative biofuels could, however, become an appealing alternative to replace conventional fossil-based fuels in the transport sector. By 2050, a 60% reduction in GHG emissions from transport is expected compared to 1990 in order to comply with the recommendations (International Energy Agency, 2019). Accordingly, the use of alternative fuels in transport will need to grow by about 20% to meet the 2ºC scenario of decarbonization (Bauen et al., 2017). In this context, the use of carbon-negative biofuels could provide significant environmental benefits by reducing the dependence on fossil fuels and curbing the associated GHG emissions. Furthermore, they could also help to accomplish the more ambitious goal of achieving a carbon–neutral or even carbon-negative road transportation sector.

Previous works on carbon-negative biofuels focused only on quantifying the savings in global warming potential (GW) while disregarding the potential collateral damage on other environmental categories such as land use, acidification or toxicity. Some authors estimated the cradle-to-wheel GHG emissions of bioethanol (Guerrero and Muñoz, 2018; Pereira et al., 2019; Zucaro et al., 2018, 2016), while only a few considered CO_2 capture coupled with the biofuel production pathway (Bonijoly et al., 2009; Carminati et al., 2019; Fabbri et al., 2011; Laude et al., 2011; Visser et al., 2011). To the best of our knowledge, no single study carried out a full LCA of a bioethanol production system with CCS adopting a “cradle-to-wheel” scope and embracing impacts beyond the carbon footprint. This research gap is particularly critical, given the trade-offs between climate change and other environmental impacts inherent to some carbon mitigation strategies (Al-Qahtani et al., 2020; Algunaibet et al., 2019; Algunaibet and Guillén-Gosálbez, 2019; González-Garay et al., 2019; Heck et al., 2018). These trade-offs are exemplified in the case of first-generation biofuels, where carbon emissions are reduced at the expense of exacerbating impacts on land use and water consumption while posing the issue of competition for land with food crops (Realmonte et al., 2019; Tomei and Helliwell, 2016). Overlooking these trade-offs could lead to undesirable collateral damages, thereby potentially hampering sustainable development.

To contribute to filling this research gap, in this chapter, we investigate the production of bioethanol from residual woodchips covering a range of environmental categories beyond climate change. This analysis considers direct and indirect emissions throughout the whole supply chain, including biomass residues procurement, transportation, conversion, and the end-use of the biofuel in vehicles. Hence, acknowledging the potential role of BECCS as an effective strategy to go beyond carbon neutrality, LCA was applied to the production of wood-based bioethanol coupled with CCS as a potential negative emission biofuel for transport decarbonization. LCA allows conducting a negative emissions assessment by considering all the carbon emissions in the entire life cycle of the fuel while simultaneously evaluating other environmental categories. Hence, LCA allows to determine whether the system under study can deliver a net negative carbon balance and whether this may happen at the expense of worsening other categories. This holistic analysis is particularly relevant for BECCS technologies, as they have not yet been extensively deployed at large scale. The results from this chapter could help in the development of future policies aimed at promoting negative emissions technologies and practices, where holistic assessments are critical to ensure sustainable development

4.2. METHODS

A holistic evaluation of the value chain for bioethanol production was performed through the implementation of the LCA approach, as described in the ISO 14040 and 14044 standards (ISO 14040, 2006; ISO 14044, 2006). The goal and scope definition, life cycle inventory (LCI), life cycle impact assessment (LCIA), and the interpretation of the results stages were all completed, as discussed in detail in the ensuing sections.

4.2.1. Goal and scope

The goal of the study is to analyze the carbon footprint (CF), together with other environmental impacts, of the complete lignocellulosic bioethanol production and utilization value chain. To this end, this chapter follows a cradle-to-wheel scope that considers all the impacts from the growth and exploitation of lignocellulosic biomass to the end-use of the biofuel in a passenger vehicle. This scope, therefore, covers direct and indirect CO_2 emissions over the whole life cycle while avoiding double counting. The functional unit that best describes the main operational objectives of the system is 1 km travelled by the bio-fueled vehicle.

4.2.2. System boundaries

This section describes the system under study (Figure 4.1) based on a cradle-to-wheel scope. Five main subsystems (SS) have been defined: SS1 Feedstock; SS2 Biorefinery; SS3 CO_2 Capture and compression; SS4 CO_2 transport and injection; and SS5 Biofuel utilization.

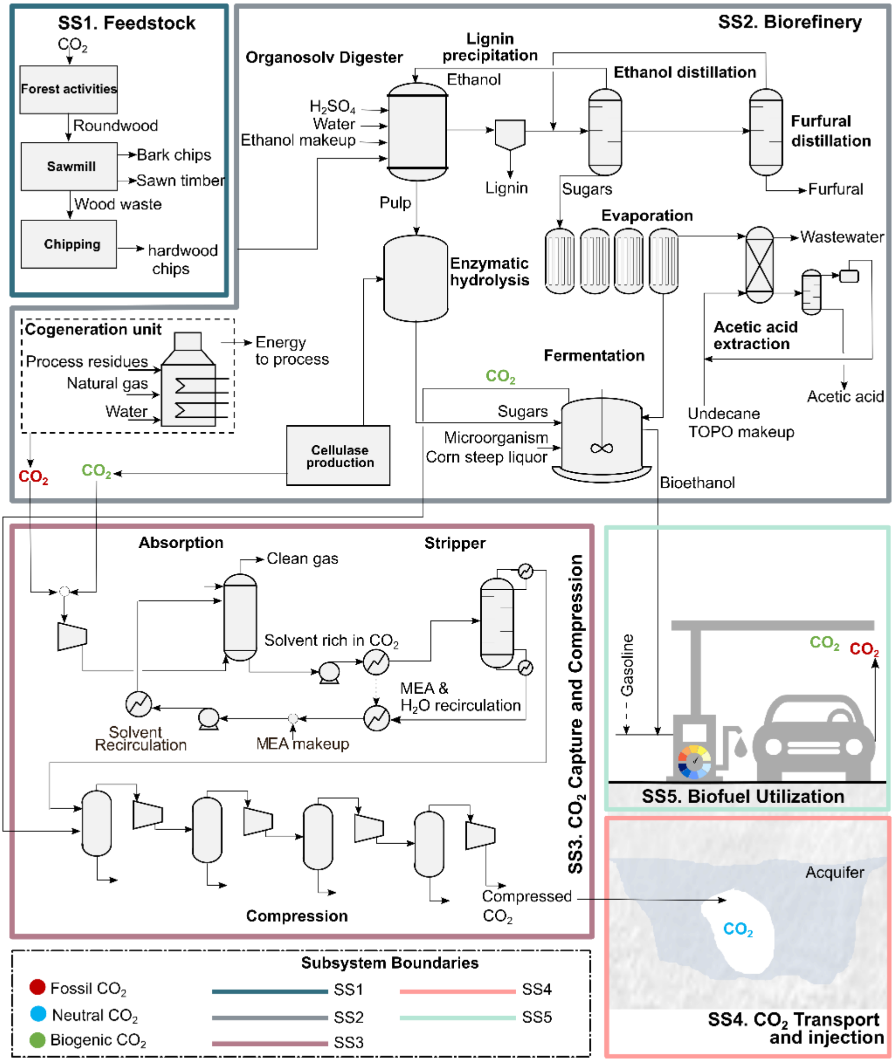

Figure 4.1 Cradle-to-wheel system boundaries for the use of bioethanol produced in a biorefinery with CCA (functional unit: 1 km travelled with bioethanol and/or a bioethanol blend with a gasoline-fueled vehicle)

SS1. Feedstock. The biomass feedstock consists of hardwood residues, specifically beechwood chips from a sawmill. This subsystem includes the silviculture activities, comprising the uptake of CO_2 associated with forest growth, soil preparation, and wood extraction activities. The extracted round wood is then further processed in sawmill facilities to obtain the three main products: bark, sawn timber and wood residues. The latter, corresponding to the waste fraction, is the target feedstock in this process and enters the biorefinery in the form of woodchips (González-García et al., 2014; Laschi et al., 2016).

SS2. Biorefinery. The biorefinery includes all the process units required for the transformation of the woodchips, which are transported from a sawmill. We assume a transportation distance of 100 km by lorry. Woodchips are first digested in an Organosolv reactor, using ethanol and sulfuric acid as the catalyst at 180ºC. Pulp and liquor fractions are recovered in this first unit. The pulp stream is rich in hydrolysable celluloses and hemicelluloses. These compounds are transformed into fermentable sugars in an enzymatic hydrolysis unit using cellulases. Lignin is precipitated from the liquor stream, which enters a distillation unit for the recovery of ethanol. A furfural stream is recovered via distillation as well. The sugars fraction is processed in an evaporator that removes water and acids. A liquid–liquid extraction unit separates then the acetic acid from a residual water flow. All lignocellulosic sugars are fed to the fermentation unit, where steep corn liquor and other micro-nutrients are added to produce bioethanol. Products other than ethanol are retrieved from the wood fractioning steps (furfural, lignin, acetic acid), yet this study focuses on bioethanol as the primary fermentation product. Process residues and natural gas are both combusted in the cogeneration unit in order to cover the energy requirements of the system (Kautto et al., 2013).

SS3. CO_2 capture and compression. The CO_2 flue emissions from the biorefinery are captured, purified and compressed in this subsystem. Three main emission streams are the target of this subsystem (see

, Table A25, and in Annex II). In the biorefinery (SS2), heating needs are supplied by combusting both process residues and fossil fuels. Therefore, the stream leaving the cogeneration unit contains a mix of biogenic and fossil CO_2, both of which are captured. On the other hand, the CO_2 emissions from the ethanol fermentation unit and the production of cellulases are entirely biogenic. The CO_2 streams from the cogeneration unit and the enzyme production process are fed to the capture system. In contrast, the biorefinery off-gas is fed just before the compression stage (due to its higher degree of purity), which reduces the energy and chemicals requirements of the system. Notably, the CO_2 flue gas and the off-gas from cellulase production are directed through a blower towards an absorption–desorption system with an aqueous monoethanolamine (MEA) solution (Adams II et al., 2014). MEA absorption was selected as CO_2 capture method due to its suitability for post-combustion capture. MEA is highly reactive in contact with CO_2 and is particularly recommended to treat gas streams with low concentrations of CO_2 (such as the one leaving the cogeneration system) (Bhave et al., 2017; Borhani and Wang, 2019). In the stripping section, the MEA is desorbed from the CO_2, resulting in a purified CO_2 stream that exits the top of the column at a purity of 13.9% wt., containing 86.1% wt. of residual water; this gaseous stream will later undergo a compression stage. The bottoms stream of the distillation column is recirculated to reuse the lean solvent back in the capture process. Before compression, the target CO_2 stream is directed through a flash unit, in which a fraction of the water is removed. The overall compression ratio of 110 requires four stages, with a constant inter-stage compression ratio of 3.2. Inter-stage cooling between compressors is applied to keep the temperature within the desired range (Luyben, 2011). The flash cooling allows delivering a purified CO_2 stream free of water, reaching the required quality specifications. The conditions of the stream leaving the compression stage should be fixed based on the pressure, temperature and purity conditions required for the transport and injection of CO_2.

SS4. CO_2 transport and injection. CO_2 exits the previous system at a pressure of 110 bar and 50ºC, that is, at a supercritical state that facilitates its transport, geological injection and long-term storage (e.g., in saline aquifers). Purity specifications are relevant to avoid pipeline corrosion, i.e., water limit of 400 ppm, and a concentration below 4% vol. of N_2 and H_2, the main compounds present in the treated streams. A concentration of CO_2 above 95.5% wt. is also recommended (in our case, 99.8% wt. in SS3) (de Visser et al., 2008). SS4 includes the pipeline for CO_2 transport, considering a distance of 200 km. Based on the physical conditions of the stream and the transport distance, we assume that no further recompression is needed. The LCA covers the drilling of the well and the CO_2 losses during pipeline transport, considering 0.026% of losses per 1,000 km (Wildbolz, 2007).

SS5. Biofuel utilization. The bioethanol produced in the biorefinery is used in internal combustion engine vehicles fueled with bioethanol-gasoline blends. Direct emissions in a vehicle travelling a distance of 1 km (functional unit) were considered. Eight scenarios were studied differing in the biofuel-gasoline blend percentages. Scenarios were also defined according to the heating source employed in the capture and compression system (SS3), i.e., either natural gas or sugar cane bagasse (Table 4.1) to provide a set of results ranging from fossil- to biobased resources. The latter resource is only available in specific geographic regions yet including it in the analysis sheds further light on the extent to which biofuels can deliver negative emissions. Moreover, biobased heating from sugar cane bagasse was selected following a conservative assumption, as it shows a poor GW performance among all the heating alternatives from biomass available in the ecoinvent v3.5 (Wernet et al., 2016) database (Figure A7 in Annex II). The fossil-based alternative is based on conventional gasoline since gasoline-fueled vehicles represent the largest share of the current fleet. This analysis excludes the vehicle infrastructure (i.e., manufacture, assembly, and end-of-life) since all the scenarios consider the same internal combustion engine vehicles.

Table 4.1 Scenarios considered based on the biofuel-gasoline blend percentages

Scenario acronym	**Heating source in the ethanol plant**	**Fuel blend**		**Vehicle**
		Bioethanol (%)	Gasoline (%)	
Gasoline	-	0	100	Gasoline compression ignition, internal combustion engine vehicle (GCI ICEV)
E10 SC	Sugar cane	10	90	Spark ignition, internal combustion engine vehicle (SI ICEV)
E10 NG	Natural gas			
E25 SC	Sugar cane	25	75	Spark ignition, internal combustion engine vehicle, high octane fuel (SI ICEV HOF)
E25 NG	Natural gas			
E40 SC	Sugar cane	40	60	Spark ignition, internal combustion engine vehicle, high octane fuel (SI ICEV HOF)
E40 NG	Natural gas			
E85 SC	Sugar cane	85	15	Spark ignition, internal combustion engine vehicle (SI ICEV dedicated)
E85 NG	Natural gas			

4.2.3. Assumptions and limitations

The transport of bioethanol to fueling stations was omitted. In contrast, we considered the transportation of woodchips from the sawmill to the biorefinery, assuming a distance of 100 km with 5% losses in a lorry freight. Electricity and chemical processes are based on a European average, when available, or a global average otherwise. The role of the carbon intensity of the electricity mix was analyzed by considering a wide range of mixes differing in their CFs (below and above the European average). Regarding the heat requirements of the CO_2 capture and compression system, we assumed that the cooling needs are covered using cooling water pumped in a closed circuit. Infrastructure was omitted (installation, construction and decommissioning), as it can be considered negligible over a typical lifetime of industrial installations of over 30 years (Jeswani et al., 2015). In SS1 —biomass feedstock acquisition— economic allocation was applied to split the total impact among the products and co-products. Impacts from forest activities and sawmill were economically allocated among co-products, while the impacts from chipping were allocated entirely to woodchips (Bello et al., 2018). All the impacts from the biorefinery subsystem were allocated to the bioethanol, which represents the most conservative approach. In this analysis, the impacts from the production, assembly and end-of-life stages of the vehicle itself were omitted. Note that all the scenarios consider the same conventional gasoline-fueled spark-ignition vehicle (ICEV), so they remain comparable. Direct combustion emissions from the use of bioethanol and gasoline were considered from the GREET 1.3 vehicle cycle model (Argonne National Laboratory, 2019), together with the indirect impacts from the production of each fuel.

4.2.4. Life cycle inventory

The LCA analysis relies on a compendium of different data sources, namely bibliographic-published data, simulation data, as well as databases. For the biomass silviculture (González-García et al., 2014; Laschi et al., 2016) and the biorefinery facility (Kautto et al., 2013), bibliographic data was used. Data for transport and injection of CO_2 were retrieved from literature sources (Wildbolz, 2007). The GREET 1.3 database was used for estimating the direct emissions of vehicles, including CO_2, CH_4 and NO_x emissions, by subtracting the well-to-pump emissions from the well-to-wheel emissions, both available in the database (Argonne National Laboratory, 2019). With regards to SS3, data are based on a process simulation of the CO_2 capture system following the work by Adams II et al. (2014). Further details regarding the process simulation for the capture and compression of CO_2 are presented in the Supplementary Material section. The inventory data for each subsystem are displayed in Table A28 to Table A32 in Annex II.

4.2.4.1. Life cycle impact assessment method

The attributional approach was followed to quantify a set of midpoint impact indicators. Characterization factors from the ReCiPe 1.1 Hierarchist method (Huijbregts et al., 2016) were applied using the SimaPro 9.0 software. The ecoinvent v3.5 database (Wernet et al., 2016) was used for the modelling of the background processes. This analysis covers the CF indicator derived from the GW category from ReCiPe

(Huijbregts et al., 2016), expressed in kg CO_2 eq, as well as a set of mid-level impact categories provided by the same impact assessment method. The latter include ozone depletion in kg CFC11 eq (OD), ozone formation in kg NO_x eq (OF), terrestrial acidification in kg SO_2 eq (TA), freshwater eutrophication in kg P eq (FE), marine eutrophication in kg N eq (ME), freshwater ecotoxicity in kg 1,4-DCB eq (FET), marine ecotoxicity in kg 1,4-DCB eq (MET), human toxicity in kg 1,4-DCB eq (HT), land use in m^2a crop eq (LU), fossil resources scarcity in kg oil eq (FS) and water consumption in m^3 (WC).

4.2.4.2. Carbon accounting within LCA: carbon footprint

Standard LCAs of systems involving biogenic inputs with a CO_2 uptake from the atmosphere, such as those involving forests, assume that this CO_2 uptake is released at the end of the product's life cycle. Accordingly, the biogenic CO_2 cycle is assumed to be mass balanced over the life cycle (van Zelm et al., 2015). In contrast, fossil CO_2 emissions (both direct and indirect) contribute to GW because they entail a net release of fossil carbon to the biosphere (atmosphere), which contributes to climate change. Accordingly, most standard LCA methods, such as ReCiPe or CML, assign a zero-characterization factor for GW to the biogenic CO_2 emissions (Guinée et al., 2002; Huijbregts et al., 2016).

In contrast, when assessing the CF in systems that capture CO_2 and store it permanently (CCS), it is critical to consider both the fossil and biogenic carbon flows adequately. A system either capturing fossil CO_2 or consuming biomass resources without CCS can lead, in the best case, to a zero-balance, i.e., carbon–neutral system (Figure 4.2). On the other hand, routes consuming biogenic carbon coupled with CCS systems could potentially achieve a net negative balance, provided the CO_2 is stored underground in the long-term (Gabrielli et al., 2020b; Tanzer and Ramírez, 2019). More precisely, a system can provide a net negative emissions balance if the biogenic CO_2 uptake exceeds the fossil and biogenic life cycle emissions (considering the capture system) embodied in the biofuel product (Figure 4.2). Therefore, to quantify the carbon emissions of CCS systems precisely, the biogenic CO_2 captured via photosynthesis during biomass growth (embodied in the biomass resource) is assigned a negative value to give credit to the CO_2 removed from the atmosphere. The carbon footprint accounting is then performed by considering all of the upstream and downstream activities and their corresponding direct and indirect (both biogenic and fossil) GHG emissions occurring throughout the fuel's value chain. The latter include, as well, the end-of-life direct emissions from burning the biofuel in the engine. Furthermore, to assess the real potential to deliver negative emissions (physical net removal of CO_2 from the atmosphere), we consider a cradle-to-wheel approach (also known as cradle-to-grave or well-to-wheel) (Tanzer and Ramírez, 2019). Hence, based on this tailored LCA accounting system, a fuel is deemed carbon-negative if it achieves a negative GHG emissions balance over its life cycle (Mathews, 2008; Mendiara et al., 2018). All data are included in Table A33 in Annex II.

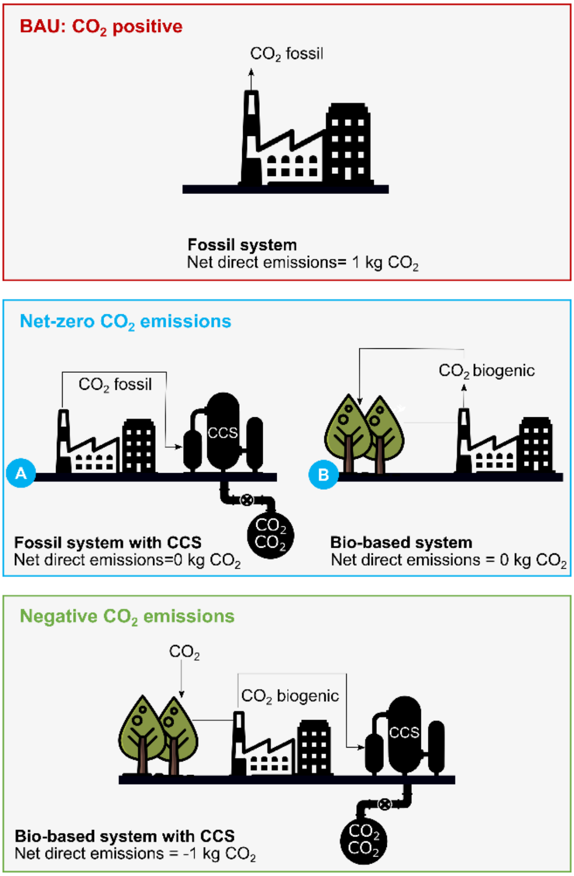

Figure 4.2 Carbon accounting of direct CO_2 emissions in fossil and biobased systems with and without CCS

4.3. RESULTS AND DISCUSSION

The results section presented below focus, firstly, on discussing the CF results, to then extend the analysis to other environmental indicators, investigating the potential occurrence of burden-shifting.

4.3.1. Carbon footprint assessment: negativity potential

The CF was analyzed following the methodology explained in Section 4.2. Several fuel blends as well as national electricity mixes and renewable technologies (i.e., solar photovoltaic and wind energy), which differ in their carbon intensity (i.e., kg CO_2eq·kWh $^{-1}$) were covered. The base-case corresponds to the European average electricity mix.

Recall that the electricity is consumed in the sawmill activities, the biorefinery section, and in the CO_2 capture and compression stage (Figure 4.1).

Figure 4.3 shows the CF results as a function of the carbon intensity of the electricity consumed by the process. Each scenario is depicted by a line whose slope depends on the specific composition of the blend. Similarly, the intercept of the line is given by the concentration of bioethanol in the blend and the heat source in the process. Higher slopes correspond to blends with a higher concentration of bioethanol, in which the contribution of electricity towards the total emissions is higher. For a carbon-free electricity source, it holds that a higher bioethanol content results in a lower CF. Furthermore, the efficiency of the engine increases with the bioethanol content (Turner et al., 2011) (e.g., the energy consumed per distance travelled for the E40 is 2,677.9 $J \cdot m^{-1}$, while for the E85 is 2,016.7 $J \cdot m^{-1}$) (Argonne National Laboratory, 2019). Therefore, increasing the bioethanol content in the blend provides environmental benefits directly related to the lower fuel requirements. In all the biobased heating scenarios (depicted in blue shades in Figure 4.3), it holds that increasing the bioethanol content decreases the CF for the whole range of carbon intensities considered. However, in the scenarios using natural gas as the heating source, some of the lines cross for high carbon intensities. Consequently, higher bioethanol contents can lead to larger CFs, e.g., E40 NG vs. E25 NG for a carbon intensity above 0.70 kg CO_2 eq· kWh^{-1}.

For the biobased heating scenarios, all bioethanol blends, except for E10 SC for carbon-intensities above 0.85 kg CO_2 eq· kWh^{-1}, perform better than the business as usual (BAU) scenario (i.e., conventional gasoline depicted with a horizontal pink line). However, for the scenarios based on natural gas as the heating source for SS3, only the E40 NG and the E85 NG scenarios would outperform the conventional benchmark gasoline for low carbon electricity sources. Notably, the only blend delivering negative emissions is E85 SC, which does so for carbon intensities below 0.91 kg CO_2 eq·kWh^{-1}. For the average electricity mix in Europe, E85 SC would deliver -2.74 kg CO_2 eq/100 km, while in Switzerland or France, the CF would be further reduced to -4.62 kg CO_2 eq/100 km and -4.87 kg CO_2 eq/100 km, respectively. Furthermore, wind power could reduce the CF of E85 SC to -5.05 kg CO_2 eq/100 km. In contrast, European countries such as Poland, which plans to maintain coal power plants to enhance its energy security (Herold et al., 2017), would be unable to produce biofuels leading to net negative emissions.

Considering that a regular passenger car may typically travel an average of 14,000 $km \cdot yr^{-1}$ (Genta and Morello, 2020), the potential for decarbonization of a E85 SC vehicle would be -382.98 kg CO_2 eq·$(car \cdot yr)^{-1}$ assuming an average European electricity mix. In comparison, the avoided emissions by gasoline replacement are 3,121 kg CO_2 eq·$(car \cdot yr)^{-1}$ (Argonne National Laboratory, 2019). Considering, for instance, the average carbon emissions in Spain, i.e., 5,030 kg CO_2 per capita for 2017

(Ristic et al., 2019), the implementation of the E85 SC fuel could reduce 52.98% current per capita emissions. Similarly, reductions of 37.51% in per capita emissions (relative to average values) could be achieved in Europe (Ristic et al., 2019).

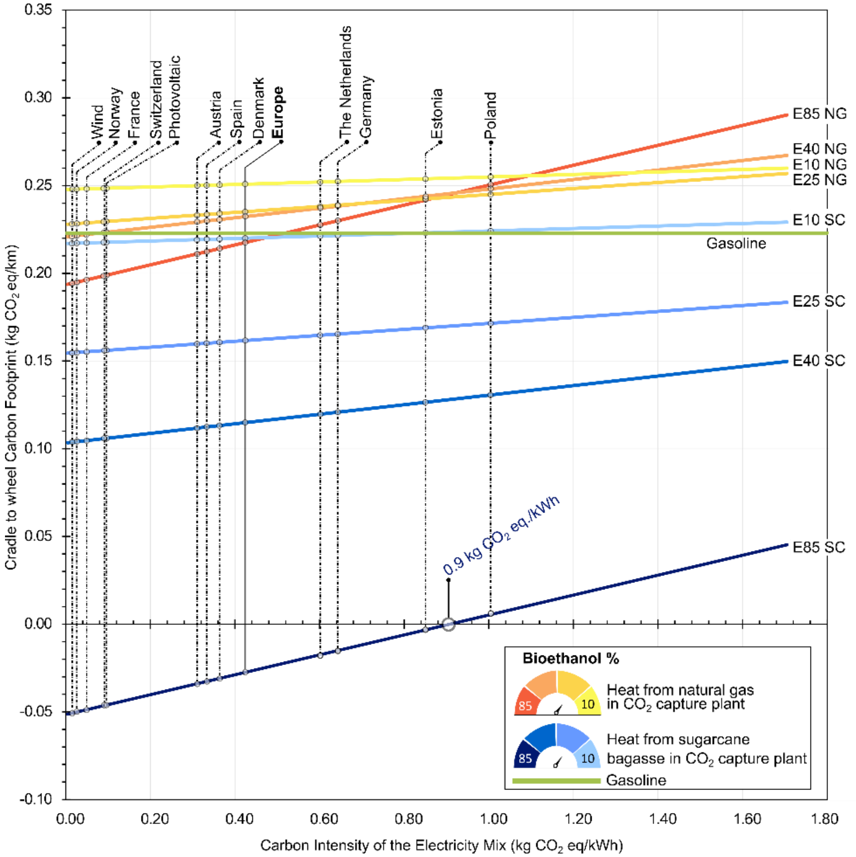

Figure 4.3 Cradle-to-wheel carbon footprint (kg CO_2 eq km $^{-1}$) for eight scenarios as a function of the carbon intensity of the electricity mix (kg CO_2 eq kWh $^{-1}$). Green scenarios use sugarcane bagasse as the heat source in SS3. Red scenarios use natural gas as the heat source in SS3. The darker the shade of the color, the higher the bioethanol content in the blend (E10, E25, E40, E85). Vertical dotted lines denote the carbon intensities of the electricity mixes of some EU countries and renewable electricity technologies. For comparison purposes, gasoline is depicted with a horizontal blue line.

Meeting the environmental goals of the European Commission will critically depend on our ability to change the European vehicle fleet. According to the IPCC, the global transport sector could reduce its emissions 4.7 $GtCO_2$ eq·yr^{-1} by 2030

(Intergovernmental Panel on Climate Change, 2018). The implementation of carbon-negative bioethanol fueled vehicles could help to offset emissions from hard-to-abate aviation or shipping transportation (Creutzig et al., 2015). Considering the total passenger-car fleet in 2015 in the European Union (Genta and Morello, 2020), replacing gasoline-fueled passenger vehicles by E85 SC vehicles could reduce 0.88 $GtCO_2$ eq yr^{-1}, which represents 18.79% (16.73% from the removal of gasoline cars and 2.06% from the negative emissions in E85 vehicles) of the global transportation sector reduction target for 2030 in the 1.5ºC scenario (4.7 Gt CO_2 eq·yr^{-1}). Note, however, that the final CDR potential required to meet the climate targets remains uncertain as it ultimately depends on the delay of the mitigation actions. Moreover, other BECCS technologies, such as biomass conversion to power and heat, as well as other negative technologies and practices in the portfolio of CDR options, could help to reduce the reliance on BECCS (Pozo et al., 2020). The large-scale deployment of BECCS will face many challenges, such as sustainability concerns (e.g., land-system change and loss of biodiversity) (Heck et al., 2018), governance problems, sociopolitical constraints and economic viability barriers (Bednar et al., 2019).

The pathways to avoid overshooting the 1.5ºC target by 2050 require removing globally around 8 Gt CO_2·yr^{-1} by BECCS (Intergovernmental Panel on Climate Change, 2018). Removing this amount of carbon using E85 SC vehicles would require producing 3,400 GL per year of lignocellulosic bioethanol (considering the full displacement of gasoline). The annual world production of bioethanol in 2018 was 110 GL, while only<1% of the global bioethanol production in Europe was second-generation fuel (Sharma et al., 2020). Hence, the commercialization of lignocellulosic bioethanol with CCS should be dramatically increased for this fuel to play a significant role in combatting climate change. Note, however, that the CDR that would be required to reach the climate goals is expected to be provided by BECCS applied also to the power and heating sector.

To provide a full picture of the CF balance, the breakdown of emissions by subsystem for the extreme cases, i.e., the E85 SC and E10 NG scenarios (waterfall plot in Figure 4.4, subplot A and subplot B, respectively) in the base case (i.e., European average electricity mix) are analyzed. The results for the remaining scenarios are presented in Annex II (Figure A8 through Figure A13).

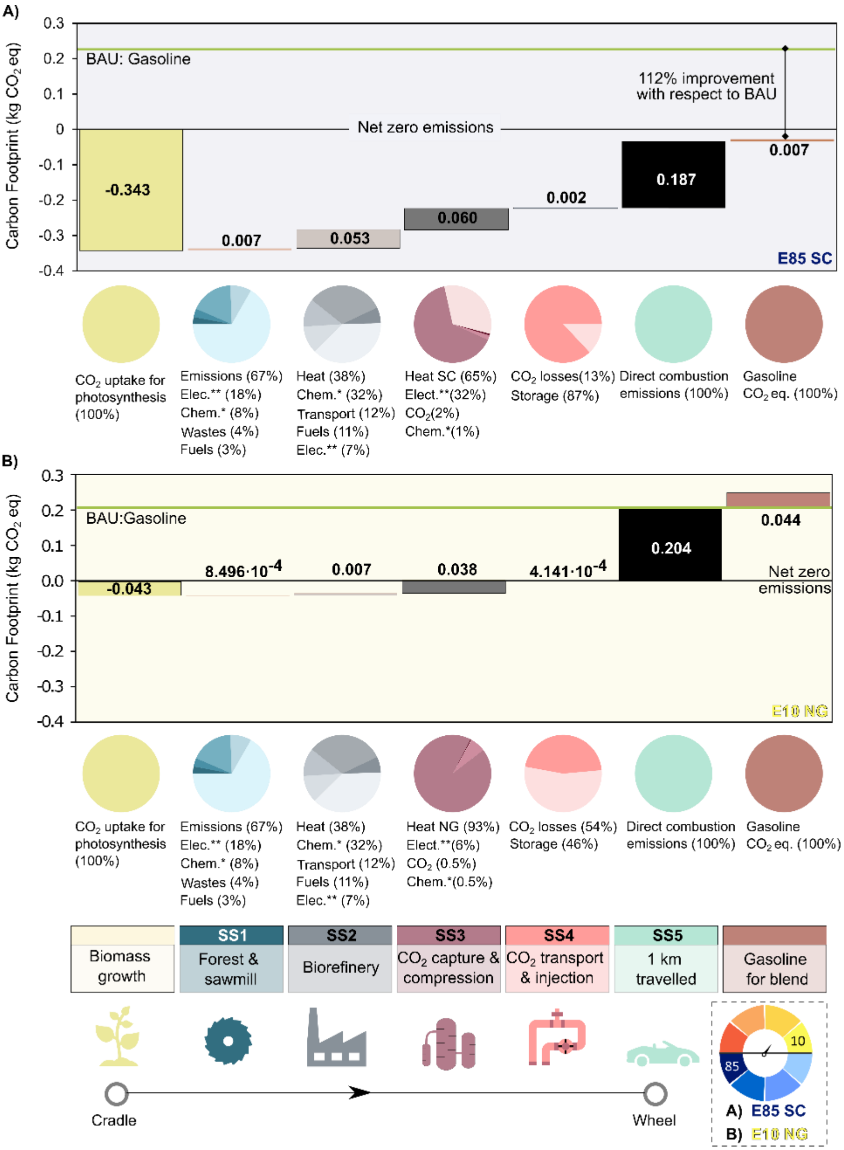

Figure 4.4 Breakdown of contributions of each subsystem to the CF for the E85 SC and E10 NG scenarios expressed per 1 km travelled. Subplot A corresponds to the E85 SC, i.e., the best-case scenario, while subplot B corresponds to E10 NG, i.e., the worse-case scenario. Pie charts show the relative CF contributions per activity for each subsystem.

For the E85 SC scenario (Figure 4.4 A), the negative emissions from the CO_2 uptake during biomass growth account for 52% of the total absolute value. The direct emissions in the vehicle engine are the most significant positive contributor to the total CF impact (28%), followed by the capture and compression plant (SS3), and then the production process in the biorefinery (SS2), which account for 9.1% and 8.1% of the total emissions, respectively. In contrast, the contributions of the silviculture and sawmill-related activities (SS1) and the CO_2 pipeline transportation and injection (SS4) are both marginal (1.03 and 0.26% relative contributions, respectively). Overall, the negative emissions exceed the positive ones, thereby resulting in a carbon-negative biofuel providing -0.027 kg CO_2 eq·km^{-1}.

The sensitivity of the CF results to the CO_2 transport distance to the geological site has been studied in the range of 1–400 km, considering that after the first 200 km, recompression of the CO_2 is needed (Wildbolz, 2007) (Figure A14 in Annex II). The CF of the scenarios varies very little with the CO_2 transportation distance, ranging from 0.11% to 8.40% of increase in CF for the E10 NG and the E85 SC scenarios, respectively. Note that the overall conclusions remain qualitatively the same, as the scenarios still lead to a negative balance (although the net carbon efficiency would be reduced). The transport distance from the BECCS plant to the geological site, together with the distance to the areas of larger lignocellulosic biomass availability, will determine the optimal geographical location of the plant. The low emissions of the CO_2 transport through pipelines and the low energy density of biomass make locations near the biomass source more appealing. However, the need of infrastructure for CO_2 transport could hinder a quick deployment of BECCS for biofuels, which might be essential to meet the decarbonization goals (Fajardy and Mac Dowell, 2017; Turner et al., 2018).

Regarding E10 NG (Figure 4.4, subplot B), its positive emissions exceed the negative ones linked to the uptake of CO_2 during the biomass growth, thereby making the fuel carbon-positive on a life cycle basis (+0.25 kg CO_2 eq·km^{-1}). Negative emissions from biomass growth represent 13% of the total emissions (-0.043 kg CO_2 eq·km^{-1}), and (in absolute value) lie slightly below the positive cradle-to-gate emissions embodied in the gasoline contained in the blend, 0.044 kg CO_2 eq·km^{-1} (i.e., 90% gasoline, 10% bioethanol). The emissions from the biomass pretreatment and biorefining activities are quite small (<2% of the total). In contrast, the CO_2 capture and compression stage accounts for 11% of the total emissions due to the large amount of energy required to regenerate the amine in the CCS system. Most of the positive emissions correspond to the biofuel combustion in the vehicle, around 60% of the total well-to-wheel emissions; meanwhile, the emissions of the silviculture and sawmill activities and the CO_2 transportation are, again, negligible (<0.5%).

The breakdown of the CO_2 emissions per activity of each subsystem (pie charts in Figure 4.4) allows identifying environmental hotspots where potential improvement efforts are most needed. The heat consumed to regenerate the MEA is a major source of CO_2 emissions in SS3. Hence, the CF performance of biofuels could be improved by using low-carbon heating sources or taking advantage of waste heat from industrial activities. Identifying new solvents or developing new catalytic processes to reduce energy consumption in the CCS system (SS3) could also help to reduce this contribution (Hepburn et al., 2019; Raynal et al., 2011). At present, this is the primary hotspot for this subsystem in both the natural gas scenarios (93% share within the subsystem) and the biobased heating scenarios (65% share within the subsystem). As for the biorefinery plant (SS2), the primary hotspot is given jointly by the consumption of chemicals and heat, with 32% and 38% shares of the total impact, respectively.

The feedstock (SS1) contributes with 1.03% in scenario E85 SC and 0.25% in scenario E10 NG. The impact of beech wood (given by the fertilizers, water use, machinery and associated yield) may vary in forestry residues of other species (e.g., birch, eucalyptus, spruce) (González-García et al., 2012). However, these changes might not be that significant unless second-generation biomass (i.e., wood or residues) is replaced by first-generation biomass (i.e., edible crops). The latter shows worse performance in all of the environmental categories (Figure A15) and also competes with food (Maga et al., 2019). Furthermore, the process would need to be adjusted to accommodate other feedstocks, e.g., the biomass pretreatment method might entail a lower environmental impact when dealing with first-generation feedstocks (Wang et al., 2012). Specifically, Organosolv or other pretreatment methods for delignification, such as steam explosion or liquid hot water, are generally more energy-intensive due to the recalcitrance of biomass (Prasad et al., 2016) as also depicted in Chapter 2 and 3.

Regardless of the fuel blend, the subsystem of capture and compression plant causes a significant impact (Figure 4.4 and Figure 4.5). With gasoline percentages above 75% in the blend, however, the hotspot shifts from the capture plant to the direct emissions from the gasoline combustion (Figure A8 through Figure A13). The development of new sorbents could help to reduce the substantial energy requirements (and costs) of the CO_2 separation, thereby decreasing its impact (Hepburn et al., 2019). Accordingly, Figure A16 in Annex II provides the results of a sensitivity analysis on the heating demand of the CCS plant for the different scenarios benchmarked against bibliographic heat demands for MEA absorption processes (Choi et al., 2019; Ferrara et al., 2017; Li et al., 2016; Mathisen et al., 2019; Sahraie et al., 2019; Singh et al., 2003). The CCS system in this chapter requires 7.5 MJ per kg CO_2 captured, an amount slightly above the values reported in the literature (5.5–3.5 $MJ \cdot kg^{-1}$ CO_2 captured). Note that, for lower heating needs, the E85 NG scenario would be able to achieve carbon-negativity, even when relying on natural gas as the heating source (Figure A16). These results indicate that the CF of biofuels could be further improved by reducing the heating needs for the solvent regeneration and by exploiting waste-heat recovery options and other synergies with other industries (Bui et al., 2017). Ultimately, the impact of the heating demand is dependent on its magnitude ($MJ \cdot kg^{-1}$ CO_2 captured) as well as the heating source. As presented in Figure A16, for biobased heating, lowering the energy consumption would not affect that much the impact, especially for values below 35 GJ·kg^{-1} bioethanol. On the contrary, heating via natural gas offers more room for improvement.

Very pure CO_2 streams from fermentation could be handled via direct dehydration and compression of the gas stream, thereby reducing the energy needs substantially (Smith et al., 2016). Flue gas with a lower CO_2 concentration would increase the energy and solvent requirements in CCS, and, consequently, the impact of SS3. Thus, the BECCS potential for net CO_2 removal would be lower in less concentrated streams and higher in more concentrated ones. The CO_2 source, therefore, impacts the net removal efficiency and, thus, needs to be considered in the selection of the capture method (Intergovernmental Panel on Climate Change, 2005). Either way, there is a clear need to cut down the energy needs, mostly through better solvents and, whenever possible, through the use of waste heat (or heat from waste biomass).

4.3.2. Other environmental implications and burden-shifting

Burden-shifting, that is, the collateral damage to some environmental areas of protection taking place when attempting to mitigate carbon emissions is the focus of this section. Accordingly, Figure 4.5 (as well as Table A34 and Table A35 in Annex II), shows the relative performance (compared to gasoline) of the two extreme scenarios (E85 SC and E10 NG) in the midpoint impacts of the ReCiPe 1.1.

Indeed, burden-shifting takes place in the E85 SC fuel, which displays a negative CF (Figure 4.3) and emerges as the best option in fossil resource scarcity but shows the worst performance in all the other impact categories (Yang et al., 2012). Similarly, E10 NG performs worse than gasoline in all the categories, except for fossil resource scarcity and terrestrial acidification. The latter impacts are strongly linked to fossil fuel combustion and the atmospheric deposition of acidifying compounds. Note that, due to the use of chemicals in SS2 (e.g., sulfuric acid), increasing the bioethanol content worsens the TA and OF categories.

The results show that burden-shifting is particularly critical in ME, LU and WC, i.e., E85 SC biofuel with 42.5, 82.9 and 23.6 times higher impact relative to gasoline, respectively (and 1.5, 1.5 and 2.3 times in each category, for the E10 NG benchmarked against gasoline). Furthermore, the E10 NG outperforms the E85 SC biofuel in all the categories except for CF and fossil resource scarcity, where it is inferior due to its higher content of fossil-based resources (gasoline in the blend and natural gas for heating). Therefore, it becomes clear that the potential collateral damage of biofuels should not be overlooked.

Delving into the drivers of burden-shifting, the breakdown of impacts in Figure 4.5 allows pinpointing the main hotspots in each impact category. The relative burdens and environmental profile change substantially attending to the scenario analyzed

(Figure 4.5), which can be further observed in Figure A8 through Figure A13 Annex II for the scenarios omitted here. Overall, for blends rich in bioethanol, the biorefinery (SS2) and the CO_2 capture and compression (SS3), are the main hotspots of the system in most of the impact categories.

Figure 4.5 Comparative evaluation of environmental profiles for the best-case scenario E85 SC, the worst-case scenario E10 NG and the BAU alternative, i.e., conventional gasoline. OD: ozone depletion, OF: ozone formation, TA: terrestrial acidification, FE: freshwater eutrophication, ME: marine eutrophication, FET: freshwater ecotoxicity, MET: marine ecotoxicity, HT: human toxicity, LU: land use, FS: fossil resource scarcity and WC: water consumption.

The ozone depletion category for the bioethanol blends worsens with respect to gasoline, mainly due to the high heating needs in the capture process (SS3) and the marginal increase in the unburned hydrocarbons and nitrogen oxide in the engines (Salvo and Geiger, 2014). Similarly, in the ozone formation and terrestrial acidification categories, the E85 SC performs worse than the E10 NG and gasoline alternatives due to the large impacts of the biorefinery and the capture activities. Note that the impact of the fuel utilization subsystem (SS5) is negligible in most non-climate change related impact categories, with the exception of ozone-related indicators (ozone depletion and ozone formation) where it represents around 18% of the total impact in both categories.

As seen in Figure 4.5, the E10 NG fuel performs slightly better than gasoline due to the reduction in the emissions of organic compounds (contributing to the ozone formation burdens), nitrogen oxides and ammonia (main drivers of the acidification category). These emissions are strongly linked to the refining and combustion of fossil fuels.

Freshwater eutrophication and marine eutrophication worsen substantially in the E85 SC and, to a lesser extent, in the E10 NG. The main drivers of these impacts are the use of nitrogen fertilizers (soil N_2O, ammonia and NOx emissions) and phosphorous fertilizers (phosphoric acid emissions, phosphates, phosphorous oxides). Both compounds are linked to the production of dedicated bioenergy crops (i.e., the sugar cane bagasse employed for heating in SS3). In the marine eutrophication category, 97% of the impacts of E85 SC are due to the capture and compression plant. This high impact might be linked to the nutrient accumulation in water bodies due to the loss of nitrogen and phosphorus fertilizers (associated with the heat source) and the use of monoethanolamine. The latter is an amine-compound that can act as a driver of nutrient oversupply in marine environments.

Ecotoxicity in the freshwater and marine compartments also worsens in both biofuels (Figure 4.5). Particularly, E85 SC increases the ecotoxicity impacts by 74% and 69%, respectively (and 30% and 26%, for the E10 NG). The trend in human toxicity is quite similar, where the best option is, again, gasoline followed by the E10 NG and, finally, the E85 SC fuel. For scenarios rich in bioethanol, the main contributors are the CO_2 capture and compression (SS3) and biorefinery sub-systems (SS2), while for the others, the primary hotspot is the gasoline. This might be due to the pesticides and fertilizers consumed during the biomass growth (e.g., sugarcane cultivation), which evaporate and runoff into freshwater and marine water bodies, and also to some compounds involved in the pretreatment and fermentation of the wood residues (Falano et al., 2014).

Regarding the land use and water consumption, the E85 SC fuel is by far the worst option, with the E10 NG alternative lying close to gasoline. The negative impact in these categories is mainly due to the contribution of the sugar cane burnt to provide heat in the CO_2 capture system (SS3). The land use impact is mostly linked to the transformation and occupation of land to grow the sugarcane feedstock. Furthermore, the increase in water consumption is due to the irrigation needs and the water required for pulp washing and lignin precipitation (SS2).

4.4. CONCLUSIONS

In this work, the concept of BECCS was investigated applied to a biorefinery coupled with CCS that converts wood waste material into bioethanol. It was concluded that blends with higher contents of bioethanol have the potential to deliver negative emissions. Moreover, in most of the scenarios, biofuels with CCS reduce the CF of conventional gasoline, more so when using low-carbon electricity and/or biomass as the heating source in the process. Particularly, with an E85 blend, a net balance of -2.74 kg CO_2 eq per 100 km travelled could be attained considering the European average electricity mix and heating for the capture and compression system supplied by biomass resources.

Furthermore, electricity mixes with higher shares of renewable energy (e.g., Switzerland, France or Norway) would double the final net negative emissions (e.g., -5.01 kg CO_2 eq/100 km in Norway). Hence, the geographical location of the BECCS facilities becomes a key aspect in the production of net negative biofuels. Ideally, the biorefinery with CCS should be placed near the low-carbon energy resources available (electricity and heat), the biomass resources and the CO_2 geological storage sites. In practice, finding a suitable site might be challenging because these resources tend to be geographically dispersed. Locations near the biomass source might be preferred, which will require pipeline infrastructure yet to be developed.

Policies aiming at the decarbonization of the electricity mix will help to curb the CO_2 emissions in the transport sector. Further improvements in bioethanol production with CCS should focus on minimizing the heating demand of the CCS technologies, opting for heating systems relying on biobased residues, and exploiting opportunities for waste heat from other industries. In this context, process integration concepts and tools could help to use energy more efficiently. This chapter shows that substantial environmental benefits may be attained in climate change and fossil depletion categories while simultaneously enhancing energy security, a primary focus of most environmental policies. However, biofuels can lead to burden-shifting, i.e., CF improves at the expense of worsening other categories, which highlights the need to enlarge the scope of current environmental assessments beyond climate change. Policies such as mandates on biofuels consumption solely focused on climate change mitigation may exacerbate impacts on eutrophication, ozone depletion and formation, toxicity, land use, and water consumption. Minimizing energy consumption in the CO_2 capture and compression stages, e.g., via heat integration and the use of biobased residues for heating, could reduce the collateral damage to other environmental areas. Nevertheless, trade-offs will arise in the deployment of biofuels, which should not be overlooked to avoid potential undesirable side-effects.

Overall, the BECCS concept applied to biorefineries offers excellent opportunities to reduce the carbon footprint of the passenger-vehicle fleet in the transition towards a carbon–neutral (or even carbon-negative) mobility system. In this context, the occurrence and severity of burden-shifting should be analyzed in-depth.

5

Production of chemical platforms for the bioplastic value chain

"It is essential to ensure that the Fourth Industrial Revolution is a sustainable one for people and planet."

Johan Rockström

Chapter 5 Summary

Within the framework of an economy excessively dependent on fossil resources, not only biofuels —Chapter 3 and 4— have the potential to improve the environmental status quo. Biorefineries are productors of chemicals from lignocellulosic biomass allowing to seize opportunities of decarbonization. Among the multiple basic chemicals that can be obtained from biomass (e.g., sugars— Chapter 2, furfural—Chapter 3), 2,5-furandicarboxylic acid (FDCA) and 5-hydroxymethylfurfural (HMF) are top biomass-based platform chemicals with promising potential and an essential part of the future of green chemistry. FDCA (produced from HMF) is the precursor of polyethylene furanoate (PEF) polymer, which is considered a feasible substitute for polyethylene terephthalate (PET). In this chapter, the environmental analysis of the process sections for the transformation of lignocelluloses to FDCA through HMF is presented. The hotspot analysis aims to study the effect of the separation sequence for FDCA comparing crystallization and distillation. The environmental performance of the production of novel chemicals from wood should be analyzed as a new development for environmental optimization. Therefore, the aim of this chapter is that of performance management for the implementation in the future industry of feasible bio-routes. Among other conclusions, this chapter displays that the use of solvents and energy should be targeted for further analysis in future studies

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5.1. INTRODUCTION TO HMF AND FDCA

According to the US Department of Energy, the biomass-based compound 2,5-furandicarboxylic acid (FDCA) is one of the 12 uppermost chemical building blocks. FDCA can be used to produce polymers and resins and is often referred to as "the sleeping giant". It can replace the fossil-based terephthalic acid (TPA) for manufacture of novel products (Wang et al. 2017). There is a growing interest to search different ways of producing FDCA from biomass, justified by its great potential to replace petroleum-based chemicals. This top platform chemical (Bozell and Petersen, 2010) will clearly undercut the use of non-renewable raw materials for the production of, for instance, plastic bottles, textiles or coatings (Huang et al., 2016). Polyethylene furanoate (PEF) is the polymer that can be obtained from FDCA, which is renewable and achieves better mechanical properties than its fossil counterpart polyethylene terephthalate (PET). The production of PEF compared to PET is expected to experience a marked reduction in the environmental impacts (E4tech et al., 2015; Huang et al., 2016). Considered to be the "biopolymer of the future", it can potentially reduce the non-renewable energy (NREU) need from 51% to 43%, and the greenhouse gas (GHG) emissions from 54% to 46% (Eerhart et al. 2012). Due to high costs, FDCA production is today at a niche level and only a few companies, mainly located in Europe, are involved in its manufacture. Currently, its production is dominated by the Dutch company Avantium (Sajid et al., 2018).

Most research efforts are directed towards FDCA production from 5-hydroxymethylfurfural (HMF). HMF is a furan derivative obtained from sugars (generally fructose) derived from cellulose hydrolysis (Van Putten et al., 2013). As it is formed by an aromatic ring and two functional groups (hydroxymethyl and aldehyde), HMF is an interesting option to be a starting material for chemical applications. Special attention has been paid to its oxidation, as it provides convenient synthetic pathways for the production of chemical building blocks for the polymer industry as the before mentioned FDCA (Torres et al. 2012). First-generation feedstock such as starch and cereal crops are the main source for HMF (Parshetti et al. 2015), but lignocellulosic biomass (second-generation feedstock) can also be a potentially reliable raw material.

To date, many studies have been conducted on the conversion of fructose to HMF (Lansalot-Matras and Moreau, 2003; Moreau et al., 1996) instead of using glucose as a starting point. The production of HMF from fructose has been shown to achieve higher yield and selectivity than from glucose, since the dehydration reaction proceeds more efficiently. For instance, a review of Xie et al. (2018) revealed a fructose-based HMF yield of 92%, while the study of Zhou et al. (2017) determined a maximum glucose-based HMF yield of about 54%. Aldohexoses (glucose) are only able to enolyze to a low degree and are therefore a limiting step in the production of HMF. However, the use of fructose implies a higher production cost than glucose. Fructose can be obtained by using enzymes or acid-catalyzed hydrolysis of sucrose and inulin or by isomerization of glucose to fructose. Industrially, the most common pathway for fructose production is glucose isomerization using immobilized glucose isomerase (Boisen et al., 2009).

From lignocellulosic glucose, HMF production is achieved by triple dehydration of hexoses in the presence of an acid catalyst (Boisen et al., 2009; Kougioumtzis et al., 2018). Regarding the solvent used (reaction media), many studies have carried out the reaction in aqueous medium; however, the rehydration process of fructose to levulinic acid restricts the process yield (Boisen et al., 2009). An alternative to water has been the use of dimethyl sulfoxide (DMSO), an aprotic solvent that prevents competitive reactions and acts simultaneously as a catalyst. The downside to this solvent is its high boiling point, which makes its separation and recycling very costly. The resulting solution has been the adoption of modified aqueous media and two-phase systems. Phase modifiers such as DMSO or acetone reduce the rehydration rate; the introduction of a second immiscible phase (organic phase) allows for the extraction of HMF, potentially reducing downstream costs. Although the results have not been excellent, another option, in terms of solvents, is the use of subcritical and supercritical solvents (e.g., subcritical water). Finally, ionic liquids represent a potential alternative, providing the ability of designing ions to function as solvent and reagent (Boisen et al., 2009).

One drawback of lignocellulosic HMF synthesis is the considerable amount of by and co-products formed, such as acetic, levulinic, formic acids, undesirable salts and insoluble polymers, e.g. humins (E4tech et al., 2015; Kougioumtzis et al., 2018), which substantially reduce the product yield. Some studies have assessed ways to valorize these side products with the aim of exploiting the biomass to its fullest extent or to reduce the production of residual streams. For instance, humins are complex organic compounds and their formation is difficult to understand; however, the study of Tsilomelekis et al. (2016) analyzed the molecular structure and morphology of humin with the aim of providing insights for further research to reduce humin production. Some studies have also tried to find ways to minimize, reuse, recycle and/or replace these input materials, such as the recycling of sulfuric acid (Havasi et al., 2017).

Research has highlighted the need to consider the sustainability of HMF production. Rout et al. (Rout et al., 2016) have emphasized the importance of process integration, design and development of more environmentally-friendly catalytic mechanisms to improve HMF sustainability and production performance. In addition, Albini and Protti (2016) addressed the issue of green solvents; particularly chromium-free alternatives for HMF synthesis. Some of the options for the synthesis of HMF are included in Figure 5.1.

On the other hand, the production of FDCA has been performed through the use of heterogeneous chemical catalysts —with noble or non-noble metals (Albonetti et al., 2015; Triebl et al., 2013). Homogeneous catalysis does not have great performance, having lower yields and formation of by-products (Sajid et al., 2018). Other alternatives for oxidation of HMF to FDCA include carbon catalysts, one pot synthesis, electrolytic transformation or whole cell biocatalysis. In recent years, there has also been a proliferation of studies attempting the enzymatic conversion of HMF to FDCA (Carro et al., 2018; Karich et al., 2018; Koopman et al., 2010).

The chemical steps for the synthesis of FDCA from HMF and potential technological routes of this process are shown in Figure 5.1. Considering the reaction mechanism depicted in the figure, yields are 90% for FDCA production from HMF, 2% for 2,5-diformylfuran (DFF) production, 0.5% for 5-formyl-2-furancarboxylic acid (FFCA) production, 10% for FDCA production from FFCA and 10% for FDCA production from DFF (Lilga et al., 2012).

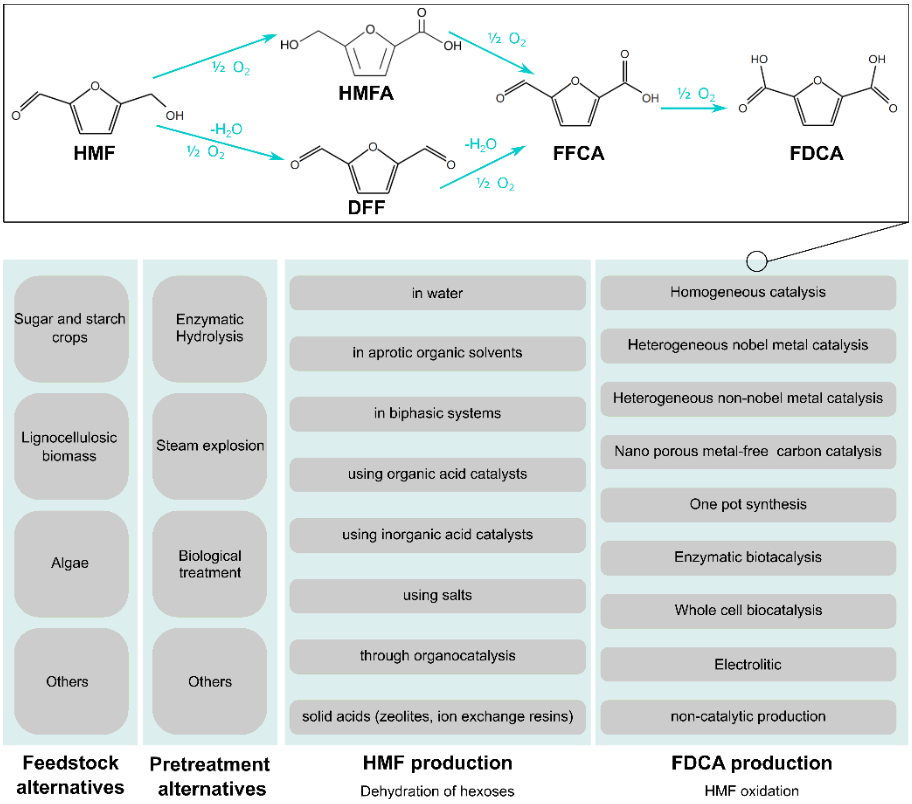

Figure 5.1 Mechanism of HMF oxidation to FDCA, adapted from Lolli et al. (2015) and below the technological alternatives for the production of HMF and oxidation to FDCA from different biomass feedstocks.

Regarding the application of Life Cycle Assessment (LCA) methodology in the production process of biobased building blocks via HMF intermediate, few studies were identified. Isola et al. (2017) assessed biopolymer production taking the FDCA route from fructose-based carbohydrates to evaluate the environmental impacts of each production stage from a cradle-to-grave perspective; Dros et al. (2015) investigated different ways of producing Hexamethylenediamine (HMDA) from starch-based biomass with the aim of comparing the environmental impact with their carbon counterparts; and Zhaojia Lin et al. (2015) used LCA to compare p-xylene from first and second generation biomass.

The aim of this chapter is to environmentally analyze the route of production of lignocelluloses-HMF-FDCA, to support the sustainable conceptual design from an early stage. In this chapter, HMF production is based on the publication of Kougioumtzis et al. (2018), which uses sulfuric acid for acid hydrolysis of lignocelluloses, DMSO for HMF synthesis, and dichloromethane (DCM) for HMF recovery. The HMF route towards FDCA is catalyzed by with a precious metal catalyst according to Triebl et al. (2013). It is also an objective, to comparatively assess the environmental implications of two different separation routes for FDCA. Separation processes are known to be economically demanding, not only in bioprocessing but also in conventional production routes. For the most part, this is due to their energy intensive characteristics, which is a challenge that is definitely tied to the environmental performance of any configuration. Furthermore, separation processes in biorefineries are challenging in many cases due to the dilution of the product in the streams, inhibitory effects or the need of separation in water-based streams (Kiss et al., 2016).

5.2. METHODS

Process simulation was required in this chapter to build the inventories for the HMF to FDCA production and separation route. This section of the process has been modeled through the Aspen Plus® V9 process simulator. Further details on the simulation model are available in Annex II Section A4.2. Data obtained from a simulation (together with literature data) were used for the environmental assessment of the production of lignocellulosic FDCA through the LCA methodology.

5.2.1. Goal and scope definition

In this work, the main objective is to ensure the sustainable production of the combined route: lignocellulosic biomass-HMF-FDCA. The functional unit of the LCA study is the production of 1 kg of FDCA/h at the factory gate. The scope is defined as a cradle-to-gate, taking into account the processes involved in the production of raw materials up to the final recovery of the purified FDCA. Due to the great versatility of the FDCA, sections of the value chain such as the use stage or final disposal were not considered.

5.2.2. System boundaries

The HMF production route in this assessment is a configuration involving triple dehydration of hydrolyzed glucose by catalytic synthesis. The production of FDCA is based on heterogeneous catalysis with precious metals. Two scenarios will be considered: Scenario 1 includes a flash separation process after the production of FDCA followed by crystallization and filtration. Scenario 2 combines two flash separation processes and a distillation column for the purification of FDCA.

Kougioumtzis et al. (2018) studied the experimental and simulated process production of HMF via glucose. Triebl et al. (2013) discussed the production of FDCA from HMF via process simulation work. The production scheme has been segmented into 7 subsystems (SS) as shown in Figure 5.2 based on the previously cited works and the simulation work included in Annex II, Section 0.

SS1. Hydrolysis. Hardwood chips, which are residues from forestry operations, undergo acid hydrolysis to obtain lignin, cellulose, and hemicellulose fractions of wood and hydrolyze cellulose into glucose. The wood chips are mixed with sulfuric acid (0.75% wt.) in aqueous solution at 175°C. After filtration for the elimination of residual solids (biotar), the stream is thermally treated to evaporate water and achieve a glucose concentration of 7.8% wt.

SS2. HMF synthesis. The glucose is converted to HMF in a catalytic reactor at 150°C and 8.2 bar. The catalyst is $Sn20\text{-}\gamma\text{-}Al_2O_3$, and DMSO/water (8/2) is used as solvent. The solution is filtered before the next processing steps.

SS3. HMF recovery. The final goal is a 96.5% HMF concentration. HMF is extracted from other reaction products with DCM/water (9/1) in a liquid-liquid extraction column. The DCM/water mixture is used in a quantity 10 times greater than the solution to be separated. For extraction, 3 flash separators are used with decreasing pressures (1, 0.8, and 0.1 bar). DCM is recirculated to the extraction column. The solution, which consists of by-products of the reaction, is treated in a distillation column to separate DMSO and recirculate it back to SS2.

SS4. FDCA synthesis. HMF (0.5%) enters the catalytic reactor together with an acetic acid solution (40%) at 100°C and 10 bar. The catalyst is Pt/ZrO_2. Oxygen is introduced in the reactor as excess air with a compressor.

SS5. FDCA flash separation. In Scenario 1, a single flash separator is used for the initial separation at 30°C and 1.5 bar. The output stream from the reactor is cooled in a heat exchanger in one step prior to the flash-drum. The main objective of the flash is the separation of air (mainly N_2 and O_2), which comes from the column top. The bottoms stream is pumped into a crystallization unit working at 25°C. Scenario 2 includes two flash separator steps. The first one works at 100°C and 1 bar. The vapor phase, at the top, is a stream containing mainly water, acetic acid and air (N_2 and O_2). This stream is led to the next flash separator, which separates as much air as possible from the stream, to facilitate the recirculation of water and acetic acid to the reactor feed. The second flash separator operates at 37.5°C and 1 bar.

SS6. FDCA purification. In Scenario 1, the bottom flow of the flash separator (SS5) is pumped to a crystallization unit operating at 25°C. The crystallized FDCA is separated in a rotary vacuum filter as a solid, and the remaining solution is recirculated to the reactor feed. In Scenario 2, the bottom flow of the first flash separator (SS5) is directed to a distillation column operating at 0.55 bar. The product —FDCA— leaves the column through the bottom with a concentration of 99.7%. The distillate contains mainly water and acetic acid is ready for reuse.

SS7. HMF boiler. The boiler provides energy exclusively to the HMF production subsystems (SS1, SS2, and SS3). It burns residual solids from the HMF production (biotar) and natural gas.

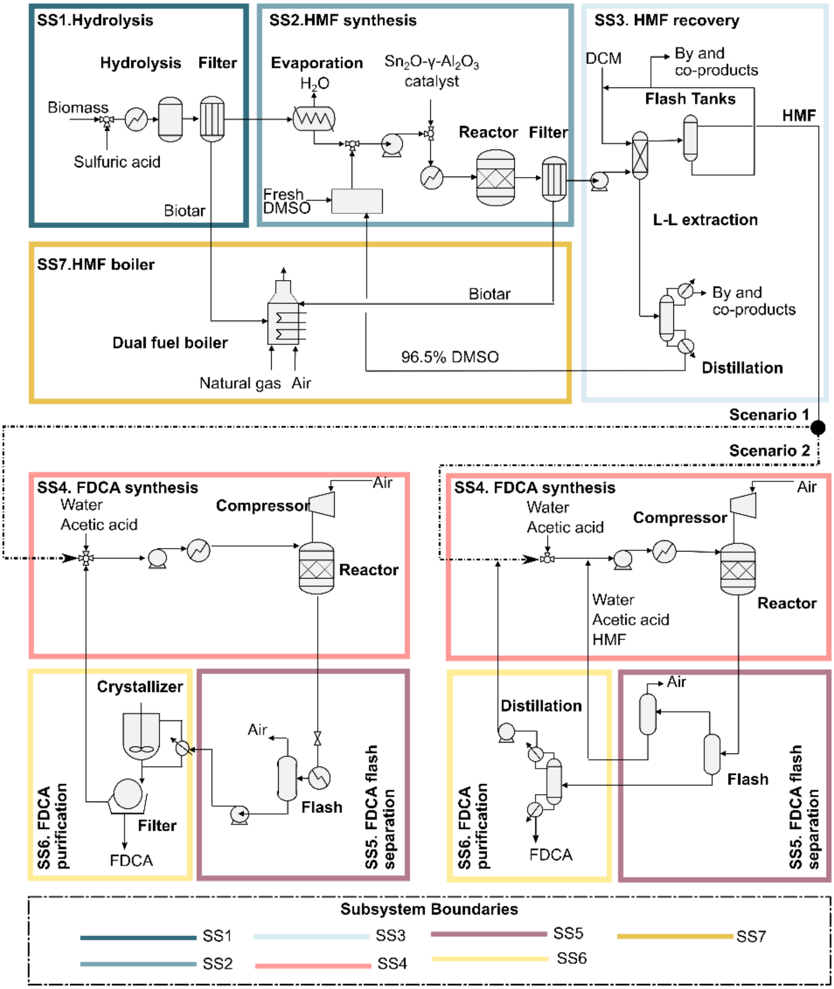

Figure 5.2 System boundaries for the system involving the production of FDCA from lignocellulosic HMF.

5.2.3. Assumptions and limitations

Economic allocation was considered for both scenarios in the subsystems related to the production of HMF (SS1-SS3 and SS7). The production of HMF is characterized by synthesising alongside other by-products and co-products that could be marketed. For economic allocation, selling prices of the main marketable products were considered Table 5.1. HMF was assumed to represent 16.4% of the total impacts of the affected subsystems.

Table 5.1 Economic allocation factors

Products	Value (€/h)	Allocation factor (%)	Source
HMF	110.31	16.4	(Mukherjee et al. 2015)
Acetic acid	17.25	2.6	(Himmelblau and Riggs 2004; ICIS 2018; Straathof and Bampoul 2017; Zhu and Jones 2009)
Formic acid	26.89	4.0	(ICIS 2018)
Fructose	0.84	0.1	(Mukherjee et al. 2015)
Lactic acid	53.17	7.9	(ICIS 2018)
Levulinic acid	14.93	2.2	(Mukherjee et al. 2015)
Mannitol	6.46	1.0	(ICIS 2018)
Hemicelluloses	1.07	0.2	(Li et al. 2013; Persson et al. 2007; Stoklosa, et al. 2014)
Propionic acid	1.24	0.2	(ICIS, 2018)
Lignin	422.22	63.0	(Budzinski and Nitzsche 2016; Hodásová et al. 2015; Nitzsche et al. 2016; Schwiderski and Kruse 2016; Zhao et al. 2017).
Glucose	16.30	2.4	(Heinzle et al. 2006; Klein-Marcuschamer et al. 2012)

The data considered for the environmental assessment is the data retrieved from the literature (Kougioumtzis et al., 2018) and the process simulation (Annex II Section 0) for the foreground processes. The inventories of most of the background activities were included through the ecoinvent 3.5 database processes (Wernet et al., 2016).

No transport activities were considered in the production of FDCA. In fact, it is considered that in a real site, HMF would be produced on site as part of the same value chain. Infrastructure, construction, installation or decommissioning processes were not considered, since for this type of industrial facilities, due to their expected lifetime, their impact is generally considered negligible (Jeswani et al., 2015; Lim and Lee, 2011). The hypothetical plant was considered to operate continuously 330 days a year.

Concerning the catalyst —$Sn20\text{-}\gamma\text{-}Al_2O_3$— for the production of HMF, a lifetime of 5 years was assumed. A lifetime of 10 years was considered for the metal catalyst used in the FDCA synthesis, and the quantity needed was calculated using the flow and the residence time of the reactor. The unavailability of the catalyst in the used database was overcome through the use of literature data, considering the use of platinum and zirconium oxide (Lilga et al., 2012). A catalyst bed density of 1300 kg/m^3 was assumed (Aboudheir et al., 2006) along with the values of energy consumption during its production (Frazier et al., 2015). The Spanish electric mix was considered when dealing with electricity consumptions throughout the FDCA production system. The use of utilities was modeled environmentally by considering heating and cooling resources available in the ecoinvent 3.5 database. A generic cooling energy source was selected from the ecoinvent 3.5 database, which consists of the recovery of the cooling utility of a cogeneration unit that uses natural gas with an absorption chiller. On the other hand, the heating source considered was heat obtained from steam in the chemical industry. The wastewater produced within the process was considered to be treated in a generic wastewater treatment plant selected from the ecoinvent 3.5 database. The components of emissions to air, such as the intermediates of the route HMF to FDCA (FFCA or DFF) were considered negligible in quantity and were not considered.

5.2.4. Life cycle inventory

Input and output inventories based on mass and energy balances of the bioproduction route are presented in Table 5.2 (Scenario 1) and Table 5.3 (Scenario 2). The inventories for the production of HMF have been adapted from the work of Kougioumtzis et al. (2018). The data for the production of FDCA from HMF were evaluated by means of the simulation software in Aspen Plus^{TM} based on an adaptation of the work of Triebl et al. (2013). In the case of HMF-related subsystems (SS1, SS2, SS3, SS7), inventory data are included considering the economic allocation of products.

Table 5.2 Inventory for the production of 1 kg/h of FDCA from HMF through the processing steps of Scenario 1 (purification through crystallization).

SS1 Hydrolysis			**SS2 HMF synthesis**		
Inputs			Inputs		
Biomass feedstock	3.06	kg	DMSO	0.58	kg
Water	27.57	kg	Sn20-γ-Al_2O_3	$1.35 \cdot 10^{-5}$	kg
H_2SO_4	0.21	kg	Electricity	0.87	kWh
Energy	$7.76 \cdot 10^{-3}$	kWh	Heating	3.9	kWh
			Outputs to technosphere		
			Wastewater	0.025	m^3
SS3 HMF recovery			**SS4 FDCA synthesis**		
Inputs			Inputs		
DCM	6.79	kg	Acetic acid	3.67	kg
Water	3.39	kg	Water	5.50	kg
Energy	$4.8 \cdot 10^{-3}$	kW	HMF	0.82	kg
HMF (96.5%) to SS4	65.85	kg	$PtZrO_2$ catalyst	0.037	g
Outputs to technosphere			Electricity	15.83	kWh
Wastewater	22.10	m^3	Heating	14.08	kWh
			Cooling	1.40	kWh
SS5 Flash separation			**SS6 FDCA purification**		
Inputs			Inputs		
Cooling	11.97	kWh	Cooling	3.69	kWh
Electricity	0.017	kWh	Outputs to technosphere		
Outputs (emissions to air)			Wastewater	0.0088	m^3
Water	0.32	kg			
Acetic acid	0.23	kg			
Nitrogen	16.62	kg			
Oxygen	4.64	kg			
SS7 HMF boiler					
Inputs			Outputs		
Natural gas	0.63	kg	CO_2 fossil	0.53	kg
Electricity	1.46	kW	CO_2 biogenic	1.73	kg
Water	$1.93 \cdot 10^{3}$	kg			
Refrigerant R134a	Closed Circuit				

Table 5.3 Inventory for the production of 1 kg/h of FDCA from HMF through the processing steps of Scenario 2 (purification through distillation).

SS1 Hydrolysis			**SS2 HMF synthesis**		
Inputs			Inputs		
Biomass feedstock	3.06	kg	DMSO	0.58	kg
Water	27.57	kg	Sn20-γ-Al_2O_3	$1.35 \cdot 10^{-5}$	kg
H_2SO_4	0.21	kg	Electricity	0.87	kWh
Energy	$7.76 \cdot 10^{-3}$	kWh	Heating	3.9	kWh
			Outputs to technosphere		
			Wastewater	0.025	m^3
SS3 HMF recovery			**SS4 FDCA synthesis**		
Inputs			Inputs		
DCM	6.79	kg	Acetic acid	3.92	kg
Water	3.39	kg	Water	5.88	kg
Energy	$4.8 \cdot 10^{-3}$	kW	HMF	0.82	kg
HMF (96.5%) to SS4	65.85	kg	Pt-ZrO_2	0.039	g
Outputs to technosphere			Electricity	10.87	kWh
Wastewater	22.10	m^3	Heating	8.92	kWh
			Cooling	1.98	kWh
SS5 Flash separation			**SS6 FDCA purification**		
Inputs			Inputs		
Cooling	65.26	kWh	Cooling	8.42	kWh
Electricity	74.47	kWh	Heating	8.24	kWh
Outputs to technosphere			Electricity	$1.14 \cdot 10^{-3}$	kWh
Emissions to air			Outputs to technosphere		
Water	0.81	kg	Emissions to air		
Acetic acid	0.33	kg	Water	0.012	kg
Nitrogen	17.57	kg	Acetic acid	0.0083	kg
Oxygen	5.02	kg	Nitrogen	$8.86 \cdot 10^{-4}$	Kg
Wastewater	$7.99 \cdot 10^{-3}$	m^3	Oxygen	$2.79 \cdot 10^{-4}$	kg
			Wastewater	0.0088	m^3
SS7 HMF boiler					
Inputs			Outputs		
Natural gas	0.63	kg	CO_2 fossil	0.53	kg
Electricity	1.46	kW	CO_2 biogenic	1.73	kg
Water	$1.93 \cdot 10^{3}$	kg			
Refrigerant R134a	Closed Circuit				

5.2.5. Methods

The environmental evaluation was based on the attributional LCA approach. The ReCiPe 1.1 hierarchist method (Huijbregts et al., 2016) was implemented at the mid-point level through the SimaPro 9.0 software. The environmental impacts of the system under study were analyzed through the following impact categories: global warming expressed in kg CO_2 eq (GW), ozone depletion in kg CFC11 eq (OD), ozone formation in kg NO_x eq (OF), terrestrial acidification in kg SO_2 eq (TA), freshwater eutrophication in kg P eq (FE), marine eutrophication in kg N eq (ME), freshwater ecotoxicity in kg 1,4-DCB eq (FET), marine ecotoxicity in kg 1,4-DCB eq (MET), human toxicity in kg 1,4-DCB eq (HT), land use in in m^2a crop eq (LU), water consumption in m^3 (WC) and fossil scarcity in kg oil eq (FS). These categories are considered to represent in a comprehensive way a range of potential environmental issues derived from the processes under study. Many biorefinery-related peer reviewed articles have assessed their systems considering indicators related with climate change, eutrophication, acidification, toxicity and ozone depletion/formation (González-García et al., 2016; Isola et al., 2017; Lin et al., 2015).

5.3. RESULTS AND DISCUSSION

5.3.1. Environmental assessment

Figure 5.3 depicts the environmental impacts for scenarios 1 (crystallization) and 2 (distillation) per subsystem. Overall, scenario 2 has greater impacts when compared to scenario 1 for all categories studied. Scenario 1 displays 40% less environmental impacts in GW, 1% in OD, 24% in OF, 21% in TA, 18% in FE, 15% in ME, 28% in FET, 30% in MET, 24% in HT, 8% in LU, 8% in WC and 50% in FS.

Scenario 1 illustrates that HMF recovery (SS3) and FDCA flash separation (SS5) are its major contributors to the global impact of the process. In all, SS3 and SS5 are the largest contributor to impacts in 5 of the 12 impact categories in both cases.

Particularly, in GW, SS3 and SS5 show 47.1 and 32.6% contribution to the total impact in scenario 1. The rest of subsystems depict lower contributions. For instance, FDCA crystallization (SS6) has a contribution of 8.5% and FDCA synthesis (SS4) shows a 5.4% share in global warming. The pretreatment of biomass and its conversion to HMF (SS1 and SS2) have a comparatively lower contribution to the GW impact of the system. In scenario 2, SS3 has a 28.2% share in GW, while SS6 presents 49.8% and SS5 10.6%. The rest of subsystems (SS1, SS2, SS4 and SS7) present lower shares (0.13, 2.1, 3.3 and 5.9% respectively). GW represents one of the most sensitive categories to the variation marked by scenario 1 and scenario 2 differences. Together with FS which is expected to be somewhat in line with the trend displayed in GW, they both present an increase of impacts for scenario 2 due to SS6.

In scenario 2 the distribution of impact contributions between subsystems tends to change slightly with some redistribution. HMF recovery (SS3) continues to be a relevant contributor to all impact categories in the range of 1.5% (LU) to 99.3% (OD). The FDCA purification and separation subsystem (SS6) in scenario 2 is a significant contributor to all subsystems (unlike in scenario 1), being even more relevant than SS3. In 7 of the 12 impact categories, SS6 represents the largest impacts with relative contributions of 50% GW, 48% FE, 41% HT, 42% OF, 46% FET, 47% MET, and 52%

FS. SS5, which is one of the most relevant contributors to environmental burdens in scenario 1, is displaced by SS6 in scenario 2 due to its high energy demand. In scenario 2, the separation train includes a vacuum distillation column as well as flash separators.

In OD, SS3 (HMF recovery) is the subsystem that basically contributes the most to both scenarios. The synthesis of FDCA (SS4) can be highlighted in WC, for both scenarios, with 82.3 and 75.9% contributions to the total of the category.

For agricultural land occupation (LU), as expected, 70.8% and 65.1% of the impacts in scenario 1 and scenario 2 respectively, are due to hydrolysis (SS1), which includes aspects of land use related to forestry activities for the production of hardwood chips. LU is an important factor to be considered, particularly from the point of view of long-term application. An inappropriate land management may have very negative side effects, which are difficult to quantify, for example, concerning soil fertility, carbon loss and biodiversity loss, etc.

The bulk of impacts in SS5 are due to the flash separations carried out in the subsystem. The flash separation operates at 1.5 bar because cooling is required in the output flow of the FDCA synthesis reactor. The exit flow of the reactor for the synthesis of FDCA (SS4) is at 10 bar and 100°C, making the separation step (SS5) prior to crystallization quite energy consuming.

Due to its energy-intensive nature, the FDCA flash separation subsystem (SS5) has a major impact on scenario 1. However, the reconfiguration of the purification scheme substantially reduced this impact, converting the FDCA purification and separation subsystem (SS6) into the largest contributor among all impact categories in scenario 2, again due to the high energy demand. The comparative environmental assessment depicts that scenario 1 is more sustainable than scenario 2.

In all, if the scenarios studied were to be optimized in order to reduce their environmental impacts, the focus of the improvement work would have to be on different subsystems. In scenario 1, the revision would have to focus on SS3 and SS5, while in scenario 2 a reduction of impacts on SS3 and SS7 would be desirable.

To further delve into the process evaluation for each scenario, their environmental profile is provided per main substance or component in a disaggregated way. The results can be found in Figure 5.4. When analyzing the detailed results for scenario 1, it becomes clear that the greatest hotspot of the system is the production of HMF. Despite being produced from lignocellulosic biomass, its production process involves the use of organic solvents such as DCM or DMSO, which are of high environmental concern. To a greater extent, the production of HMF from lignocellulosic biomass is not yet mastered to obtain high conversion yields (Kougioumtzis et al., 2018). This is, most probably, the reason why the environmental impacts derived from a biobased chemical show relevant contributions to the environmental profile of the system, with shares higher than 20%, reaching in multiple categories values over 60% (GW, OD, OF, TA, ME, HT and FS).

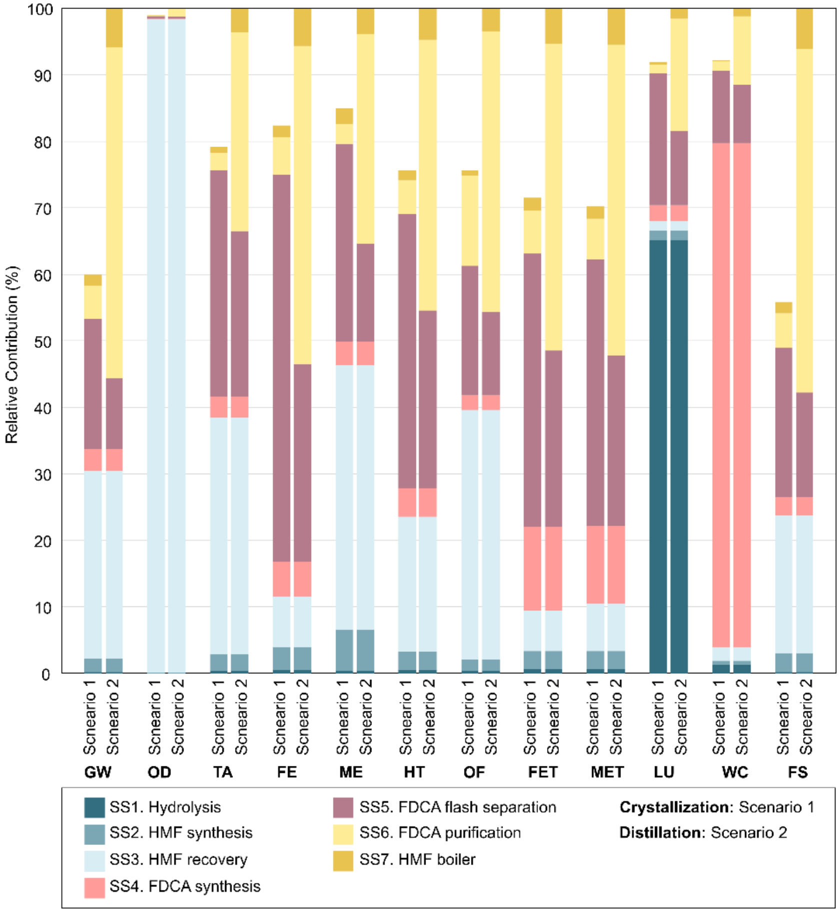

Figure 5.3 Comparative evaluation of environmental profiles for scenario 1 (crystallization) and scenario 2 (distillation) per subsystem considering a functional unit of 1 kg/h FDCA produced. GW: global warming, OD: ozone depletion, OF: ozone formation, TA: terrestrial acidification, FE: freshwater eutrophication, ME: marine eutrophication, FET: freshwater ecotoxicity, MET: marine ecotoxicity, HT: human toxicity, LU: land use, FS: fossil resource scarcity and WC: water consumption

In scenario 1, DCM in the production of HMF is primarily responsible for the 98% contribution to the OD category, due to its chlorinated nature and being a volatile organic compound, and its potential ability to impact the balance of the chemical reactions occurring in the atmosphere (Feng et al., 2018). DCM is widely used in industry as a solvent, is also a carcinogenic chemical (Guo et al., 2004). This implies that stratospheric ozone depletion is not sensitive to modifications in the downstream separation process for FDCA. In short, this stems from the fact that OD is a category mainly influenced by the use of DCM in this system, which is an ozone-depleting gas utilized in the upstream section of the process, for the production of HMF. There are studies concerning the use of green solvents for HMF production instead of DCM (Yu et al. 2018). An option is the efficient γ-valerolactone (Alonso et al. 2013), which can be derived from biomass and has a potential to improve environmental sustainability (Fegyverneki et al. 2010; Yan et al. 2015).

The use of the metal catalyst for FDCA synthesis becomes apparent mainly in four categories: TA, FE, FET and MET, with impact contributions of 21, 14, 29 and 28% respectively. The impact of acetic acid is also important, although significantly lower than the impact contributions of HMF. Acetic acid has contributions above 10% most times, reaching values of 29% in some categories (FE), with the exception of OD, where a contribution of 1% is observed. The use of the cooling utility in the system has a resulting effect on most categories, also with the exception of OD. The greatest impacts of cooling energy are found in GW, FET, MET and FS. The lowest impacts on the system studied are the use of electricity, heat, wastewater treatment process and the emissions to air, which are slightly relevant in the OF category only (7%).

In the profile shown in Figure 5.4 for scenario 2, a rearrangement of the relative contributions can be observed again. In this case, the profile reveals that the use of cooling energy utility was the process that led to increased environmental impacts in SS5 for this scenario. There is also a smaller but relevant increase in the impacts derived from the use of heat. In general, the deduction that can be drawn suggests that the substitution of the crystallization unit with a distillation column has an effect on the energy consumption of the process. Energy consumption increased by modifying the operation downstream of the process, and it was found that this increase resulted in a subsequent increase in the environmental impacts of the system. This response shows that while the energy consumption profile was not an issue in scenario 1, it became significant in scenario 2 as the requirements increased. For instance, the cooling energy has a 35% contribution to the GW impact category. Cooling energy also contributes with a 38% share to the impacts in FE and with a slightly lower value to the ME category (26%). The toxicity categories analyzed have 48 and 49% contributions in FET and MET respectively deriving from the cooling utility. The contribution of this process to FS is relevant as well, representing 38% of contributions to the category. There is an apparent trend showing how the use of the cooling energy system affects the impact categories dealing with anthropogenic emissions, toxic effects on the environment and depletion of fossil resources. All these environmental effects are related to the use of a non-renewable energy source. In this study, a generic cooling energy source was selected from the ecoinvent 3.5 database, which consists of the recovery of the cooling utility of a cogeneration unit that uses natural gas with an absorption chiller. The effect of an electricity mix and cooling energy with a higher renewable percent would positively influence the environmental optimization of the processing routes.

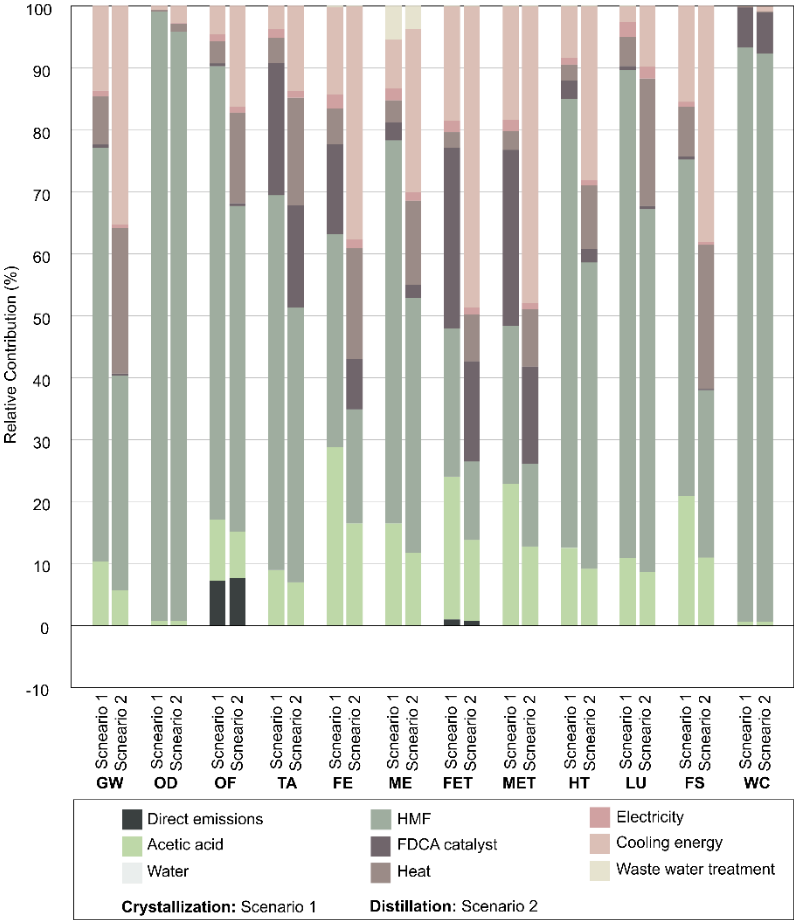

Figure 5.4 Comparative evaluation of environmental profiles for scenario 1 (crystallization) and scenario 2 (distillation) per main contributors to impact considering a functional unit of 1 kg/h FDCA produced. GW: global warming, OD: ozone depletion, OF: ozone formation, TA: terrestrial acidification, FE: freshwater eutrophication, ME: marine eutrophication, FET: freshwater ecotoxicity, MET: marine ecotoxicity, HT: human toxicity, LU: land use, FS: fossil resource scarcity and WC: water consumption

5.3.2. Process design-guided sensitivity assessment

Supplementary Annex II, Section A4.3 presents the results from a sensitivity assessment performed in the downstream section of the Aspen Plus® simulations. The objective of the environmental sensitivity assessment is to analyze how the results of the simulation affect the environmental indicators. In this case, not only were isolated process units analyzed, but all the simulation results of each sensitivity case study were considered in order to recalculate the environmental impacts of the system. The Aspen Plus simulation was computed for 3 case studies and the base case scenario for the three variables deemed potentially influential in the sensitivity assessment described in Annex A.4 (operation pressure in units F-1 for scenarios 1 and 2 and operation pressure of unit D-1 in scenario B). The LCA for every sensitivity case was conducted using the same method presented in previous sections of this chapter. The results are presented in Figure 5.5. Figures 5.5B and 5.5C only represent the two impact categories with the most and the least variability of their due to the narrow range of variation among categories.

In Figure 5.5A, the objective was to analyze environmentally how the decrease in the energy requirements of the involved units and the consequent decrease in the product yield would affect the environmental results of the system. It can be observed that, as the pressure increases, the OF category experiences a quite remarkable decrease. The increase of pressure provides, as shown in Figure A19 subplot A, a decrease in the energy needed for P-2 and E-2. The increase of pressure also results in lower emissions to air and slightly lower demand for fresh acetic acid and water. These are the parameters that influence the overall increase in OF. The category among the studied that experienced the least reduction in impact was OD. In this case, the operating range in which environmental impacts would be minimized is 1.2-1.5 bar. These findings show that the environmental assessment is quite sensitive to the change in pressure of the F-1 unit for scenario 1.

Figure 5.5B shows the results of the sensitivity analysis of the same unit in scenario 2. In this case, the variability of the environmental impact as a function of the pressure of the flash unit is almost negligible. The impact category that experienced the largest change was OF, with a 2% improvement with increasing pressure. MET shows the lowest improvements with only a 1.5% impact reduction. In a general analysis of the scenario, the concluding observation is that the operating pressure of F-1 does not influence the overall results of the plant when analyzed from an environmental perspective.

Finally, Figure 5.5C displays the results of the sensitivity assessment to the distillation unit in scenario 2. The greatest improvement in the environmental impacts was observed in FS (0.35%), while the lowest variability was that of OD (0.14%). Once again, for scenario 2, the variation in the simulated pressure for D-1 did not affect the results of the environmental assessment.

The conclusion drawn from the results is that in scenario 1 (crystallization), the effect decreasing the pressure reduced energy consumption, also having an effect in the FDCA production yield. This led to a relatively relevant sensitivity in the environmental impact. However, in scenario 2 (distillation), the increase in energy consumed was directly proportional to the yield of FDCA in the system, which led to a less relevant effect in environmental impacts.

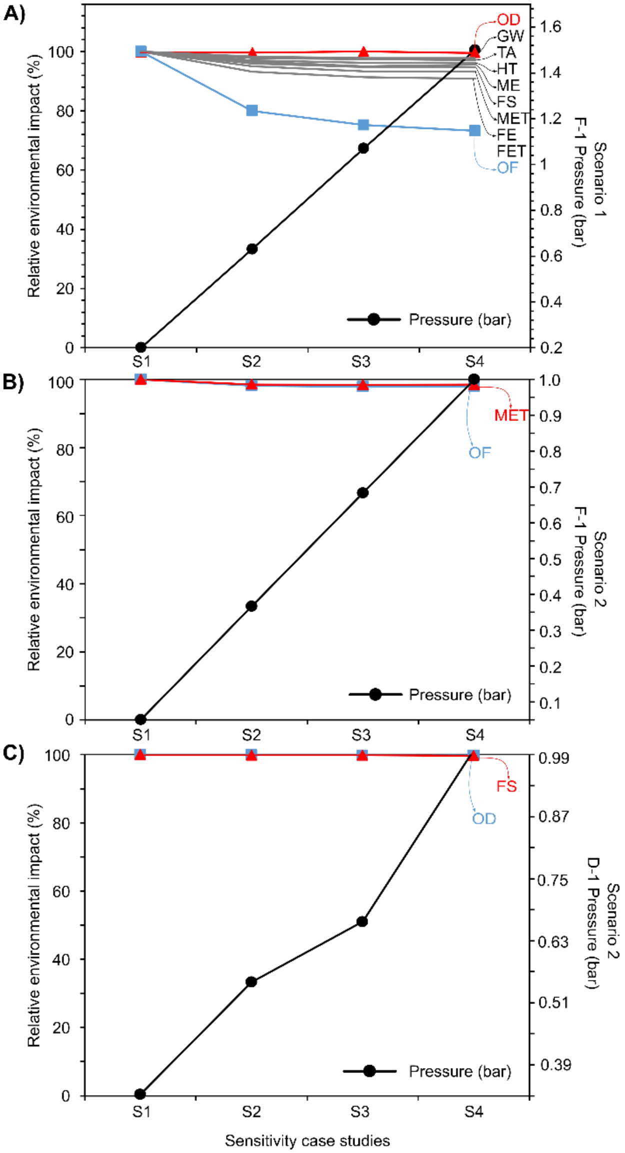

Figure 5.5 A). Environmental results presented for ozone depletion (OD), global warming (GW), terrestrial acidification (TA), human toxicity (HT), marine eutrophication (ME), fossil scarcity (FS), marine ecotoxicity (MET), freshwater eutrophication (FE) and freshwater ecotoxicity (FET). Sensitivity study performed in the pressure of unit F-1, scenario 1. Sensitivity scenarios: S1 (0.2 bar), S2 (0.63 bar), S3 (1.07 bar) and S4 (1.5 bar). B). Environmental results presented for ozone formation (OF) and marine

ecotoxicity (MET) impact categories for the sensitivity study performed in the pressure of unit F-1, scenario 2. Sensitivity scenarios: S1 (0.05 bar), S2 (0.37 bar), S3 (0.68 bar) and S4 (1 bar). C). Environmental results presented for ozone depletion (OD) and fossil scarcity (FS) impact categories for the sensitivity study performed in the pressure of unit D-1, scenario B. Sensitivity scenarios: S1 (0.33 bar), S2 (0.55 bar), S3 (0.67 bar) and S4 (0.99 bar).

5.3.3. Benchmarking of LCA results to produce FDCA through lignocellulosic HMF

It is quite difficult to compare the results of this study with other work on the environmental assessment of the FDCA, as there are very few studies dealing with the topic. Furthermore, in studies that would somehow be under the same scope, comparability of results is very limited due to differences in the definition of the functional unit, system boundaries, method, cut-off criteria, etc.

Take, for example, the work done by Eerhart et al. (2012). Their work is based on an environmental assessment of PEF production for its comparison with PET. Their system boundaries extend up to the polymerization of FDCA. The authors analyzed the environmental impact based on two indicators: GHG emissions and NREU. Its main raw material is fructose, which is used for the manufacture of HFM, unlike our study, which based the process on the use of HMF based on lignocellulose. Data relating to the production of FDCA by oxidation of HMF were assumed to be similar to those for the production of PTA and PET. Their system resulted in emissions of 0.59 and 0.97 kg CO_2/ (kg FDCA/h) for the best- and worst-case scenarios respectively. The NREU of their study resulted in a range of 10.4-16.8 MJ/ (kg FDCA/h). In our study, the GW category presented 61.5 kg CO_2 eq./ (kg FDCA/h) for scenario 1 and 118.4 kg CO_2 eq./ (kg FDCA/h) for scenario 2. Although our results differ largely from the reported impacts in the study by Eerhart et al. (2012), it is an expected behavior. Firstly, due to the differences between the boundaries of the system and the data sources of both, for example, it was mentioned above that the production of HMF was a hotspot of the system due to the immaturity of the production process. It has been reported that the production of HMF from fructose results in higher conversions (Sarwono et al., 2017).

On the other hand, although the authors do not mention it directly, when the GHG and NREU indicators are used, GHGs usually represent direct emissions to the environment rather than indirect emissions due to process activities. Thus, the energy use of the process could have been accounted for within the NREU indicator, drastically reducing GHG emissions. Earhart et al.(2012) also modelled a system in which a CHP unit was used to produce energy from residual fractions of process biomass. Considering that energy seems to be an important hotspot, at least on scenario 2, this can be a feasible improvement of the process to minimize overall environmental impacts.

In a more recent study (Isola et al., 2017), the authors analyzed the LCA results for the production of a polymeric material derived from FDCA. Again, their system boundaries covered the polymerization phase. HMF was considered to be obtained from fructose once again, and their inventory data was mostly retrieved from laboratory scale experiments. This implies a very different downstream separation sequence for FDCA in comparison to either scenario 1 or scenario 2. Their system for the FDCA synthesis from HMF included the use of chemicals such as NaOH and $KMnO_4$. As far as separation goes, the product was filtered through a celite bed, cooled with ice and acidified with HCl. The precipitate was then vacuum pumped in a process that is the laboratory-scale variant of scenario 1, with lower yields achieved (64%).

The authors analyzed the environmental impacts as a function of GW, ecotoxicity, HT, FE, FS, TA and agricultural land occupation impact categories. Adding up the impacts of stages I, II and II of the study (corresponding to the production of fructose, HMF and FDCA), it was found that the impact for the GW category was approximately 5000 kg CO_2/kg FDCA. Their environmental impacts result in higher impacts than the results of this study. However, the comparison of results should be considered with caution, as the authors worked with assumptions different from those in the present study (e.g., transport activities were considered). In addition, the evaluation of laboratory processes through LCA has been shown to yield broader results, which are optimized as the scale of production increases (Piccinno et al., 2016).

Finally, in 2018, García-Gonzalez et al. (2018) proposed the environmental evaluation of polyester binders containing FDCA. They studied the NREU from the Cumulative Energy Demand method (Frischknecht et al., 2007) and the GHG through the Greenhouse Gas Protocol (IPPC Intergovernmental Panel on Climate, 2007). In this case, again GHG constituted the contributions of direct emissions into the atmosphere from fossil and biogenic sources, as well as the emissions from land use change. Total GHG emissions from FDCA production from sugar beet resulted in 1.18 kg CO_2 eq/kg FDCA, while for NREU 16 MJ/kg FDCA were reported. The results of this study are more similar to those of Eerhart et al. (2012), probably due to the similarity in the accounting of emissions and selected indicators.

For both Isola et al. (2017) and García-González et al. (2018) neither inventories nor functional unit were time bound data, as it may be expected from any laboratory experimentation. Therefore, the functional units (kg FDCA rather than kg FDCA/h) make their results not 100% comparable to this chapter. However, it is the best possible approximation.

The high variability of the results shows the need to develop more research on the topic, working on production routes that lead to stable and high FDCA yields and through LCA studies that present in detail their approach to evaluation for comparability reasons.

5.4. CONCLUSIONS

The transformation of biomass into chemicals or biofuels has been studied, depending on the process, mainly in the laboratory or on a pilot scale, being optimization and scaling up to industrial scale still in their infancy. In the present study the potential production route for FDCA was assessed to fill the gap in terms of environmental feasibility of such processes towards their scale-up. Simulation through Aspen Plus and LCA allowed to study how relevant separation parameters in the simulation affect the performance of the process. In scenario 1, FDCA separation is achieved through product crystallization and filtration while in scenario 2 a distillation column is used instead. When comparing crystallization and distillation for the separation, crystallization presented a significantly lower environmental footprint. HMF and FDCA production still needs conventional solvents such as DCM, which harm health and the environment. Therefore, the research on FDCA production should be extended to the use of more environmentally friendly substances. Lowering the energy requirements should also be considered, especially in line with European decarbonization objectives in which renewability should be favored. Based on the results obtained from this study, it would be interesting to analyze, in future research, a scenario in which most of the fossil energy sources would be replaced by renewable energy sources. For example, this could be done through the implementation of a CHP unit burning biomass residues from the process and producing energy for self-use. Biomass-based chemicals do not contribute necessarily to environmental sustainability. Further assessment of the FDCA route would need to focus on the environmental viability of enzymatic transformations, which would potentially deliver better results than the catalytic routes of production.


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6

Early-stage sustainability assessment of enzyme production

> *"You never change things by fighting the existing reality. To change something, build a new model that makes the existing model obsolete."*
>
> R. Buckminster Fuller

Chapter 6 Summary

As it was mentioned in Chapter 5, there are chemicals that could potentially, not only be produced from biobased resources, but also have processing routes based on bio catalysis (e.g., enzymes). These kinds of synergies could be the base to the future potential decarbonization of the chemical industry. The use and integration of enzymatic processes for the biotransformation of biomass within the biorefinery framework creates the need to confirm whether these novel production systems are in the route to environmental sustainability. In this chapter, the environmental profiles of the production of two oxidative enzymes, hydroxymethylfurfural oxidase (HMFO) from *Methylovorus* and unspecific peroxygenase (UPO) from *Chaetomium globosum* (*Cgl*UPO) for the enzymatic production of furandicarboxylic acid as precursor of bioplastics were analyzed. Laboratory-scale experiments allowed the identification of the consumption of energy, with over 80% share in every impact category for HMFO and chemicals and energy in *Cgl*UPO as primary hotspots of the systems. The results are transposed for HMFO when laboratory inventories were extrapolated to full scale processing, showing that impacts are attributed not only to energy demand but also to the use of chemicals required for the formulation of the culture medium. In terms of process units, the fermenter, where enzyme production takes place, corresponds to the stage that contributes the most to the environmental impacts, followed by the downstream separation scheme. Extrapolation of laboratory data to full-scale also represented a change in the relative difference of the impact per functional unit of 45% for *Cgl*UPO. The endpoint damage categories showed a significant reduction in their full-scale impacts to about half the burden. This study shows that, although being biobased catalysts, the production of enzymes involves several steps which may incur in a relevant environmental impact. From this chapter, it is recommended that enzymes are carefully included within the system boundaries of bioprocesses for their evaluation, since they could be the major hotspot in the biorefinery value chain. De-fossilization of the chemical and plastic industries will be possible with thoroughly optimized bio-transformations, with carbon-based media from residual resources, minimized use of chemicals and the implementation of energy integration measures.

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6.1. INTRODUCTION TO OXIDATIVE ENZYMES AND ENVIRONMENTAL ASSESSMENT STATUS

Several studies have been developed to gear research towards the production of specific enzymes for the biotransformation of lignocelluloses. Commonly used enzymes in lignocellulosic biorefineries include cellulases, hemicellulases, monooxygenases, ligninases, amylases, pectinases, lipases and proteases (Choudhury, 2020) that are typically used in biomass pre-treatment, enzymatic hydrolysis, saccharification and fermentation processes (Álvarez et al., 2016; Maclean and Spatari, 2009).

Referencing back to Chapter 5, most of the methods described in the literature for the oxidation of hydroxymethyl furfural (HMF) into furandicarboxylic acid (FDCA) are usually based in the use of metal catalysts such as carbon or alumina-supported platinum or platinum supported lead (Tong et al., 2010). However, although some of them are promising, all of these methods are typically performed at elevated temperatures and pressures and with low selectivity, rendering the process expensive and polluting.

Because of this, there is an increasing interest in shifting away from heterogeneous and chemically based catalysis processes, analyzing the production pathways of FDCA from the enzymatic perspective. To this end, several oxidative enzymes have been reported as promising alternatives with high potential to achieve such transformation (Sajid et al., 2018). Through these oxidative enzymes and their potential scalability for FDCA production, the biocatalytic routes could potentially reduce to a maximum the environmental and economic impact of producing biochemicals. Enzymatic catalysis shifts the oxidation process to milder conditions, higher selectivity to the production of furan-based compounds and the use of less harsh chemicals (Domínguez de María and Guajardo, 2017; Yuan et al., 2020).

Hydroxymethylfurfural oxidase (HMFO) is able to produce FDCA from HMF (Dijkman and Fraaije, 2014). Unspecific peroxygenase (UPO) catalyzes the limiting-step for FDCA production for most oxidases (Serrano et al., 2019): the oxidation of formylfurancarboxylic acid (FFCA) into FDCA with hydrogen peroxide as co-substrate; its use in combination with oxidases such as aryl alcohol oxidase or galactose oxidase lead to FDCA production (Carro et al., 2018, 2015; Karich et al., 2018). This chapter aims to answer several research questions in the field of oxidative enzymes for the bioproduction of FDCA, using HMFO from Methylovorus expressed in E. coli (Viñambres et al., 2020) and *Cgl*UPO expressed in Chaetomium globosum (Kiebist et al., 2017) as model enzymes for this process.

Nonetheless, despite the boost in formulating a variety of enzymes targeted to participate in quite specific processes, there are challenges that must be addressed when it comes to the application of enzymes in full-scale processes. The overall efficiency of the process in technical and economic terms must be confirmed, considering the requirements of the enzymes and the environmental assessment of the enzymatic process.

However, there is little to no knowledge on how the production of enzymes may affect the environmental performance of enzymatic transformations, as most of the life cycle assessment (LCA) studies found in the literature include the usage of enzymes as an anecdotal part of the whole assessment (Raman and Henning, 2013). In most cases, inventorying a complete list of flows involved in the production of enzymes, is a time-consuming process. Data unavailability results in a very superficial focus on the value chain of enzyme production when environmentally analyzing enzymatic processes in biorefining routes.

Olofsson et al. (2017) present the environmental study of ethanol production with a focus on the differences found when considering an on-site versus off-site production of cellulase enzymes. While they are able to provide detailed inventories for their simulated production of on-site enzymes, their ability to gather inventories for the externalized production was very limited due to the scarce availability of data in literature and the aggregated nature of the information. The study provides the environmental results by means of greenhouse gas emissions, concluding that off-site enzyme production achieved significantly higher impacts, considering that reported data regarding enzyme dosage as well as their production present great uncertainty. These gaps in the evaluation of enzyme production processes may lead to incur in errors in the environmental evaluation of enzymatic bio-transformations (e.g., biofuel production).

Likewise, Hong et al. (2013) provide the environmental impact of biofuel production in which cellulases are accounted for by means of the global warming indicator. When calculating and projecting the impacts of enzymes the main highlighted challenges are the proprietary or non-disclosable character of the majority of available data with regards to enzymes, the wide variety of available enzymes, enzyme cocktails and production methods, and the experimental scale of many of the existing production processes. These challenges should be addressed in further research, to which this study aims to contribute (Nielsen et al., 2007).

As other scientific studies state, gaps in the literature were found with, for example, the transparency in inventories of LCA studies, which fail to include the enzyme production process. In some cases, they do not explore whether available datasets in databases are applicable to the specific characteristics of the study. In some instances, they even fail to include them in the inventory, pleading that they are used in a very small quantity and cut-off rules apply. These gaps make the environmentally-good nature of enzymes and their use in bio-transformations debatable (Maclean and Spatari, 2009). Enzymes have been known to have very high production costs (Klein-Marcuschamer et al., 2012), which may lead to believe that their environmental contributions to processing systems are not negligible, and furthermore they could be very relevant. Considering the possibility of recycling and reusing enzymes to reduce their high cost and environmental impact may be key in many cases (Cheng et al., 2019b). However, whether reuse is applicable or not depends on the specific type of enzymes under assessment, and their utilization objective. In all, this implies that including them within the boundaries of LCA studies as part of the foreground processes, rather than background processes should shed light into the missing gaps and provide an in-depth analysis considering all sensitive factors to their production and utilization (i.e., externalization of their production, reuse and recycle, scalability, production yield).

Cellulase is one of the most studied enzymes in the biorefinery framework, and yet, the available LCAs in literature do not focus on detailing the value chain of its production with disaggregated inventories or evaluating a range of impact categories relevant to the study besides global warming potential (also depicted as greenhouse gas emissions, climate change, etc.). Moreover, very few studies assess endpoint impact categories or uncertainty of the dataset. As laboratory scale production processes are not usually under the scope of LCA application, this work will serve as basis for further research on the upscale and deployment of oxidative enzymes, as it aims to provide the environmental weaknesses and advantages of the production of said enzymes (i.e., HMFO and UPO) and their areas of improvement. The specific objectives are:

1) To evaluate the robustness and reliability of laboratory-scale process evaluation using LCA and the effect of scale on the enzyme production process. To do so, the laboratory inventory data of enzyme production will be analyzed through LCA providing an estimated full-scale environmental outlook as well.

2) To analyze which are the environmental hotspots of enzyme production, considering both midpoint and endpoint indicators, in order to study the direct consequences to the environment and the damage produced to the three main areas of protection (human, ecosystems and resources). This will serve as basis to depict what are the optimization steps needed to improve the sustainability of these processes.

3) As the ecoinvent database (Wernet et al., 2016), one of the most important datasets in the field of LCA practitioners, does not yet provide detailed inventories for the production of enzymes, this work is intended to represent an ex-ante LCA contributing to the early stages of enzyme database compilation and evaluation of environmental results.

6.2. METHODS

The evaluation of the environmental burdens for enzyme production was performed by implementing the methodology of attributional LCA, described through the ISO 14040 and ISO 14044 standards (ISO 14040, 2006; ISO 14044, 2006).

6.2.1. Goal and scope

The production of two enzymes, HMFO and *Cgl*UPO was assessed by means of LCA with the objective of determining the main hotspots of their production process. The enzymes under study are used in oxidative reactions for the conversion of HMF to FDCA and of FFCA to FDCA. The functional unit of the study was defined as the enzyme activity (measured with vanillyl alcohol for HMFO and veratryl alcohol for *Cgl*UPO) achieved at the gate of the process, expressed in units (1 unit). The results of this analysis introduce a starting point for the evaluation and optimization of enzyme production processes, evaluated from an early-stage perspective with primary data at laboratory scale. The environmental assessment was performed under a holistic perspective, including the inventory, midpoint results and an analysis of the damage categories. A streamlined upscale, in which energy was considered the key factor, was included to analyze the preliminary robustness of the environmental assessment of laboratory processes through LCA.

6.2.2. Production system and system boundaries

The production process for HMFO and CgIUPO follows a standard biotechnological process sequence, which includes the pre-inoculum, inoculum, fermentation and downstream stages. The generic boundary of the system is presented in Figure 6.1.

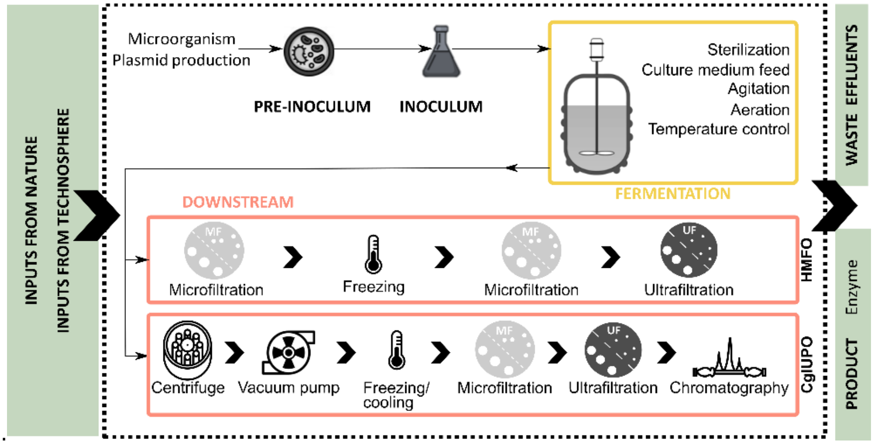


Figure 6.1 Generic cradle-to-gate system boundaries for the production of HMFO and *Cgl*UPO enzymes at laboratory scale

6.2.2.1. HMFO production

The pre-inoculum phase consists of the growth of the cell culture in a Petri dish with Luria-Bertani (LB) medium with bacteriological agar and antibiotics. This was transferred to a flask in which the inoculum is grown, again with LB medium and antibiotics. The inoculum was then transferred to the bioreactor with a volume of 25 L, where the production of the enzyme occurs in two phases: cell growth and induction of protein expression. The bioreactor and its contents were sterilized with an autoclave. The fermentation was aerated and agitated during the whole reaction time, at 37°C during the growth phase and at 16°C for the induction phase. The overall batch time of the production process is 120 h. The downstream scheme includes two microfiltration units with an intermediate freezing stage, as well as an ultrafiltration with an output of 7000 units.

*6.2.2.2. CgI*UPO *production*

The inoculum for *CglUPO* production was fed with a medium containing sodium chloride, malt extract and agar-agar. The seed fermentation was transferred to a fermenter with an operating volume of 6 L for 672 h with a culture medium composed of glucose, peptone and yeast extract. The fermenter and its contents were sterilized with an autoclave. The fermenter was agitated, aerated and kept at 24°C. The downstream processing includes a vacuum pump, centrifugation, microfiltration, ultrafiltration, freezing, cooling and a chromatography unit. Each batch yields 1200 units.

6.2.3. Life cycle inventory

Input and output inventories were provided as primary data flows from the laboratory experiments. The energy consumption of the equipment was calculated based on the operating time and the maximum power consumption of each piece of equipment. The results from the LCI phase are presented in Table 6.1 for HMFO and Table 6.2 for *Cgl*UPO. The inventory data is specified per batch of production, which will be normalized to the functional unit in the life cycle impact assessment stage of the study.

As an approach to validate and analyze the LCA results obtained from laboratory experiments, a simplified scale-up approach has been adopted in which the electricity consumption was the main concern. The production was scaled to 100 m^3 by extrapolation of the inputs and outputs. The target volume was considered a feasible production volume in biotechnology operations and fermentations involving enzyme production. Regarding electricity consumption, several simulation case studies for bioprocesses have been analyzed, retrieving typical energy consumption values for common unit operations: agitation in a fermenter, steam demand for heating, cooling water demand, aeration, microfiltration, ultrafiltration, centrifugation and vacuum filtration.

Table 6.1 Inventory for the production of HMFO enzyme at laboratory scale per batch (25 L)

Stage 1: Pre-inoculum and inoculum		
Cells BL21 (DE3)pLys	1	g
Plasmid pET23b	1	g
Tryptone (LB media)	8.54	g
Yeast extract (LB media)	4.27	g
NaCl (LB media)	4.27	g
Bacteriological agar	0.81	g
Antibiotics	0.114	g
Distilled water	1,854	g
Filters (PET)	6.86	g
Filters (polyether sulfone)	2.94	g
Autoclave water consumption	1,000	g
Autoclave electricity consumption	3.46	kWh
Incubator electricity consumption	14.67	kWh
Polyether sulfone (urban solid residue)	9.8	g
Stage 2: Bioreactor		
Tryptone (LB media)	250	g
Yeast extract (LB media)	125	g
NaCl (LB media)	125	g
Antibiotics	3.35	g
Distilled water	27,000	g
Tap water	20,000	g
Isopropyl β-D-1-thiogalactopyranoside (IPTG)	0.596	g
Bioreactor sterilization electricity	3.52	kWh
Bioreactor agitation electricity (induction)	13.14	kWh
Temperature maintenance bioreactor electricity	5.92	kWh
Bioreactor agitation electricity (growth)	0.72	kWh
Air compressor electricity	2.26	kWh
Air dehumidifier electricity	14.25	kWh
Electricity consumption (recirculator)	144	kWh
Stage 3: Downstream		
Tris(hydroxymethyl)aminomethane	12.1	g
HCl	5	g
NaOH	48	g
Distilled water	120	kg
Bleach	700	g
Peristaltic pump electricity	1.15	kWh
Agitator electricity	73.34	kWh
Freezer electricity consumption	6	kWh
Wastewater to treatment	29	L
Output		
HMFO	1.16	g/batch
	7,000	units/batch

Table 6.2 Inventory for the production of CglUPO enzyme at laboratory scale per batch (6 L)

Stage 1: Inoculum		
Item	Amount	Units
Inoculum (out of boundaries)	0.28	L
Malt extract	6.60	g
NaCl	0.30	g
Agar agar	6.60	g
Stage 2: Fermentation		
Item	Amount	Units
Glucose	235.20	g
Peptone	100.80	g
Yeast extract	25.20	g
Water for sterilization	5.00	L
Water	5.60	L
Sterilization	1.50	kWh
Agitation	1.66	kWh
Stage 3: Downstream		
Item	Amount	Units
Ammonium sulfate	663.00	g
Phenyl sepharose	25.00	g
Bis-Tris	37.00	g
Vacuum pump for filtration	0.028	kWh
Centrifugation	0.168	kWh
Ultrafiltration	0.13	kWh
Microfiltration	0.01	kWh
Freezing	18.00	kg day
Cooling	12.00	kg day
Chromatography	12.00	kWh
Output		
Peroxygenase (*Cgl*UPO)	1.82	g/batch
	1,200	units/batch

The updated data and process descriptors for the two analyzed processes are presented in Table 6.3 for HMFO and Table 6.4 for *Cgl*UPO. The mass conversion factor allows extrapolating the laboratory scale inventories to the hypothetical production volume of 100 m^3. Although it cannot be predicted, it was considered that the enzyme activity produced in a large-scale process would increase in direct proportion to the production volume.

Table 6.3 Inventory data for the scale-up production of HMFO

Upscaled HMFO		
Volume	100	m^3
Batch Time	120	h
Fermentation time	76	h
Units	$28\cdot10^6$	U
Mass conversion factor	4,000	
Energy consumption estimation		
Steam for sterilization	982.52	kg/batch
Agitation	16,875.32	kWh/batch
Cooling water	3,540.39	kg/h
Aeration	290.97	kW/batch
Microfiltration 1	9.87	kWh/batch
Microfiltration 2	0.06	kWh/batch
Ultrafiltration	294.94	kW
Cooling chamber	125.00	kg day
Freezing chamber	20.00	kg day
Total energy consumption	17,471.16	kWh
Quantity of enzyme	4.67	kg
Units of enzyme/batch	28,000,000	U

Table 6.4. Scale up of inventory data for the production of CglUPO

Upscaled CglUPO		
Volume	100	m^3
Batch Time	672	h
Fermentation time	672	h
Units	$20\cdot10^6$	U
Mass conversion factor	16,666.7	
Energy consumption estimation		
Steam for sterilization	2,678.90	kg/batch
Agitation	149,213.37	kWh/batch
Cooling water	3,540.39	kg/h
Aeration	308.11	kW/batch
Vacuum filtration	531.02	kWh/batch
Centrifugation	173.40	kWh/batch
Ultrafiltration	3,560.07	kWh/batch
Microfiltration	9.72	kWh/batch
Freezing chamber	18	kg day
Cooling chamber	12	kg day
Total energy consumption	153,487.58	kWh
Quantity of enzyme/batch	30.30	kg
Units of enzyme/batch	20,000,000	U

6.2.4. Assumptions and limitations

The main assumptions of the study were related to limitations in data availability. The plasmid, cells and biotin used in the pre-inoculum, were considered to have a negligible impact on the system under study. For the chemicals that were not available in the ecoinvent 3.5 database, either other chemicals with equivalent characteristics were considered or bibliographic inventories were implemented in the software. Tryptone and peptone were replaced by soybean meal, available in ecoinvent 3.5 (Delgove et al., 2019). Yeast extract and malt extract were substituted by protein feed and polyether sulfone was included in the LCA as polycarbonate. The inventory for bacteriological agar was retrieved from the production of carrageenan (Ghosh et al., 2015). The inventory for the production of antibiotics (ampicillin, chloramphenicol, zeocin) was considered as that for the production of Penicillin V (Harding, 2008). For IPTG (Carlsson et al., 1991) and tris(hydroxymethyl) aminomethane (Bourguignon et al., 1980), it was considered that the best approach was to build inventories based on stoichiometric ratios, which means that energy consumption was not included.

For this study, the country in which each enzyme was produced was the selected location from which the electricity was retrieved for each of the production processes. The German electric mix from the ecoinvent database was selected for the energy consumption of *Cgl*UPO production process, while for HMFO production the electricity was sourced from the Spanish electric mix. No transport processes were considered for the foreground or background systems.

Off-gas emissions (i.e., CO_2) were excluded from the inventories of the system since they are of biogenic origin. This entails that they are derived from the biomass-based carbon introduced in the system (e. g. in the form of nutrients for the fermentation medium). Biomass-derived carbon emissions are assumed to be neutral since it is considered that the carbon intake, at the end of its life cycle will be released back to the atmosphere and absorbed for plant growth. Neutrality in the emissions is depicted as a zero-characterization factor in the carbon footprint computation (Penman et al., 2006).

6.2.5. Methods

The environmental evaluation was based on the attributional approach, analyzing the processes under study with midpoint and endpoint impact categories. Midpoint categories are the environmental mechanisms linking the causes to the final effects (endpoint categories) in the cause-effect chain of environmental consequences (Goedkoop et al., 2009).

The ReCiPe 1.1 (Huijbregts et al., 2016) hierarchist method was applied and implemented through the SimaPro 9.0 software. The ecoinvent 3.5 database was used for the implementation and transformation of inventories for background processes in the system. The mid-level impact categories analyzed were global warming expressed in kg CO_2 eq (GW), ozone depletion in kg CFC11 eq (OD), ozone formation in kg NOx eq (OF), terrestrial acidification in kg SO_2 eq (TA), freshwater eutrophication in kg P eq (FE), marine eutrophication in kg N eq (ME), freshwater ecotoxicity in kg 1,4-DCB eq (FET), marine ecotoxicity in kg 1,4-DCB eq (MET), human toxicity in kg 1,4-DCB eq (HT), land use in m^2a crop eq (LU) and fossil scarcity in kg oil eq (FS). These are categories that can describe, overall, the environmental profile of biorefinery and enzymatic systems. Burden shifting of impacts when implementing biobased scenarios may happen when de-fossilization is the main objective. Thus, a representative range of indicators, describing relevant factors such as land use, eutrophication, acidification of soils, ozone-related categories and toxicity (due to the use of chemicals) should be addressed (Katakojwala and Mohan, 2021; Parajuli et al., 2015).

The three endpoint categories were studied to have a generic view of the main damage areas: human health (Disability-Adjusted Life Years, DALY), ecosystems quality (species·year) and resource depletion (USD, 2013). All midpoint impact categories were contributors to the endpoint results, including, together with the midpoint categories specified above and ionizing radiation in kBq Co-60 eq. (IR), particulate matter formation in kg PM2.5 eq. (PMF), terrestrial ecotoxicity in kg 1,4-DCB (TET) mineral resource scarcity in kg Cu eq. (MS) and water consumption in m3 (WC). An uncertainty analysis of the endpoint results was conducted through the Monte Carlo simulation module in the SimaPro software. The input parameters were considered as the available data uncertainties for the implemented activities (ecoinvent 3.5 flows), which considered a default lognormal distribution. The Monte Carlo analysis was performed by setting the number of iterations to 2000 at a 95% significance level.

6.3. RESULTS AND DISCUSSION

6.3.1. Environmental study of enzyme production through the midpoint perspective

The produced enzymes, at laboratory scale achieved 1.16 g/batch (7000 units per 25 L batch) for HMFO and 1.82 g/batch (1200 units per 6 L batch) for *Cgl*UPO. Some authors have presented the production of HMFO at experimental scale (1 L batch) in which an activity of 120 units was achieved (Viñambres et al., 2020). If these results were to be extrapolated to a 25 L production volume, 3000 units would be obtained. Thus, the fermenter in this study doubles the production of HMFO at 25 L. In this study, it was assumed that through scale-up, the energy input to the system would be reduced, however, these results allow to argue that the productivity could be potentially increased through the use of a fermenter at larger scale —as indicated here— reducing the environmental impact per functional unit. In this way, the results presented here can be viewed as a conservative approach in terms of productivity.

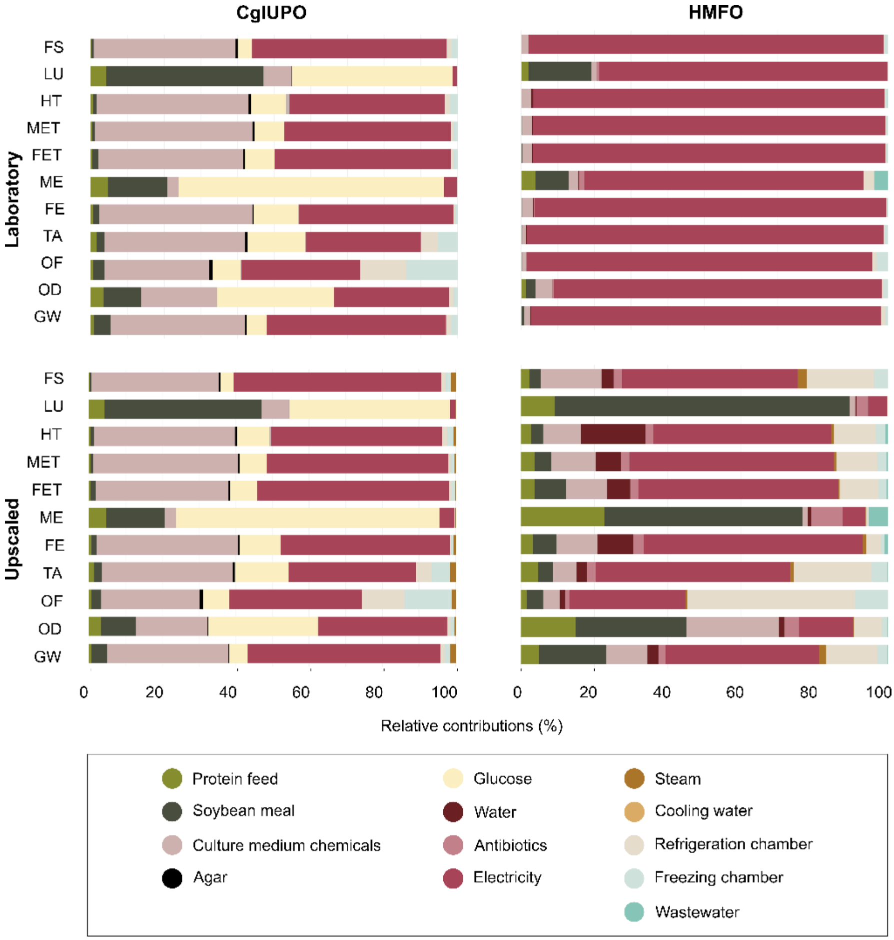


Figure 6.2 Environmental profiles displaying relative contributions (%) of characterization results for *Cgl*UPO and HMFO enzymes for laboratory experiments and the estimated upscaled production per functional unit (1 Unit of enzyme). FS: fossil scarcity, LU: land use, HT: human toxicity, MET: marine ecotoxicity, FET: freshwater ecotoxicity, ME: marine eutrophication, FE: freshwater eutrophication, TA: terrestrial acidification, OF: ozone formation, OD: ozone depletion, GW: global warming.

The relative contributions of the main activities in the production process of the two enzymes are presented in Figure 6.2, both for laboratory scale and up-scaled inventories. For the laboratory experiments, during the production of HMFO, the largest contributor to the environmental impacts for all categories is electricity consumption. Electricity impacts are above 76% in all impact categories, while the use of chemicals for the culture medium or the consumption of soybean meal have minor contributions in LU and ME impact categories. This is a trend that is interconnected with the lack of energy optimization in laboratory experiments. Laboratory-scale processes are characterized by the focus on the design of a process or a product in an experimental environment, rather than on optimizing the use of resources.

To the contrary, the environmental profile of the *Cgl*UPO produced in the laboratory does not show one single hotspot. In this case, electricity consumption, chemical requirements (principally sodium chloride, tris(hydroxymethyl)aminomethane and ammonium sulfate) are presented as the most relevant activities. This trend is similar in all impact categories, except for ME, where the hotspot is glucose (72% contribution). In LU the impacts are, again, originated in processes related with cropping activities for the production of sugar feedstock and nutrients (glucose and soybean meal) which require vast extensions of land. Glucose from the ecoinvent database is produced from maize grain, where cropping activities include the use of several nitrogen-based fertilizers, with nitrogen being the main contributor to the ME impacts. Glucose has minor impacts, in the range of 4-30% in the other categories. Ozone formation displays higher impacts for freezing (13%) and refrigeration (14%), which is not observed for other categories.

When processes were upscaled, as expected in the case of HMFO the fluctuation of the relative contributions is in the direction of reducing the environmental contribution of electricity. This results in increased contributions from other activities such as chemical consumptions, energy for refrigeration or nutrients for the formulation of the fermentation broth such as yeast paste. The scale-up in the HMFO production resulted in electricity remaining the largest contributor to the impact in eight out of ten categories, its relative contribution being, however, lower than in the laboratory-scale scenario, with values ranging from 6 to 60% for ME and FE, respectively. Tryptone, simulated as soybean meal, contributes with 54% of the burdens to ME. The refrigeration activity contributes with 46% to the impacts in the OF category. For HMFO the relative contribution of each activity and its distribution underwent a significant difference when comparing the laboratory scale and the scaled-up inventories, shifting the area of environmental interest. In this case, the conclusions that can be drawn from the environmental relative contributions at the laboratory scale are the need to optimize the use of electricity at every stage of production, from stirring and temperature maintenance to downstream unit operations to make the process feasibly scalable.

In the case of *Cgl*UPO, the upscaling of the electricity consumption implied a proportionally lower value with a linear reduction. The relative contributions of the process remain almost unchanged to those of laboratory-scale production. While most relative impacts remain unchanged, the contribution from steam is incorporated. Steam is typically used in fermentation processes at larger scale, for activities such as sterilization.

The TA indicator is impacted by acidifying substances contributing to the change in pH of the soil. Main acidifying pollutants are ammonia, nitrates, nitrogen and sulfur oxides and sulfuric acid. In the production network of the *Cgl*UPO enzymes, TA has its root cause in glucose, ammonium sulfate and electricity. In the case of glucose, the production of starch from maize grain carries impacts related to the use of nitrogen fertilizers (ammonium nitrate) and the diffuse emissions from applying such fertilizers. For HMFO, the tree of contributions is mostly marked by electricity production by coal, to which the fuel in transoceanic ship transport was the most relevant background process in the chain.

In toxicity categories (FET and MET), HMFO displays, apart from electricity, which is the main contributor, protein feed, soybean meal and antibiotics as relevant contributors, which have background processes leading back to different chemicals, that raise the toxicity potential of the system. The same trend is seen in *Cgl*UPO, in which the chemicals from the background of nutrient production for the medium are the root cause for toxicity. In these enzymes, protein feed, (mostly affected by sulfuric acid in its background), tris(hydroxymethyl) aminomethane (with the effect of methanol in its value chain) and ammonium sulfate are the most polluting chemicals.

The use of electricity has the most prominent effect in the GW results in this study, being the main hotspot for all the evaluated enzymes. The attributed shares to the impacts are 49% and 95% for laboratory production of *Cgl*UPO and HMFO and 52% and 42% for the upscaled scenarios. In this study, German and Spanish electricity mixes were selected, yielding a high impact in the carbon footprint category, derived from the coal dependability in the overall generation of electricity, which is the form of electricity production with most carbon intensity (Tranberg et al., 2019). The use of electricity mixes with a higher share of renewables (i.e., Norway) would provide potential to diminish the impacts in this category, especially in cases in which the use of electricity is under optimized (i.e., laboratory production of HMFO). However, the geographic location of the production site for enzymes will most probably be located within the facility employing the produced enzymes. Energy optimization and integration should be the first step sought in order to reduce the carbon dependability of the system, which should lean into the use of energy produced within system boundaries, for instance through cogeneration systems exploiting biomass-based residues as a carbon abatement option (which would emit non-fossil carbon emissions).

Heat production in the chemical industry was another major hotspot —specifically in the case of *Cgl*UPO— contributing to GW. Although chemicals are used in lower quantities, their impact is characterized by the energetic demand (heating systems) of their production. For such results, again, depending in nutrients for the culture medium such as agro-industrial residues (Pandey et al., 2000), can potentially curb the impact of chemicals from the petrochemical industry. Although having small deviations, the

FS impact category parallels almost perfectly the behavior of the GW category. The root cause is the dependency on fossil fuels of the energy and chemicals selected in the system, which directly affects the carbon emissions of the system.

The presentation of the relative contribution of each of the activities contributing to the production of the enzymes is interesting in the sense of analyzing the areas of improvement of each production route. However, the enzymes are produced with the sole purpose of contributing to the overall reduction of the impacts of bioprocessing routes. For this, in this study, the GW results were put into context for different potential enzyme loads in a hypothetical bioprocessing route. The enzyme loads were analyzed in a range of 1-333,000 activity units (Figure 6.3).

Figure 6.3 allows discerning whether the impact of the production of enzymes is low, high or very high in relation to the impact of the process using such enzymes. For instance, for HMFO results at laboratory scale, the environmental feasibility of the use of the enzyme as a catalyst for biotransformation, in terms of kg of CO_2 eq, will be determined by the overall impact of the production process (e.g., oxidation of HMF to FDCA with the use of HMFO or oxidation of FFCA to FDCA by *Cgl*UPO) and the enzyme load needed for such transformation.

For the impact values in the enzymatic conversion process equal or higher than the GW impact for each enzyme load, the impact contribution of HMFO production would be very significant and the enzymatic transformation would be considered highly disadvantageous. When the enzyme contribution to the process is in the range of 40-100%, the production of enzyme would be a relevant hotspot in the transformation, having to perform a substantial optimization of the consumables affecting the environmental results. For relative impacts below 40%, the use of enzymes may be considered feasible, always at the expense of performing a direct comparison with the conventional or non-enzymatic production process.

Figure 6.3 also illustrates the main differences in the net value of GW impacts for laboratory inventories compared to their upscaled counterpart per functional unit. According to the results, the laboratory scale processes always present a higher GW than their upscaled counterparts. In the case of HMFO, the relative difference per functional unit displays a 97% decrease in the GW category when the process is upscaled for the studied unit loading range. However, the relative difference per functional unit is 45% for *Cgl*UPO. It can be concluded that it is not reliable to evaluate the potential environmental impacts of enzyme production processes that are intended to be upscaled with data of experiments at smaller volumes. This is especially true, in this study, for HMFO enzyme, while *Cgl*UPO may experience lower errors if this procedure is followed.

Since electricity was the main contributor to impact in laboratory scale processes, its potential optimization towards scalability of the processes, will indeed reduce substantially the impacts associated with the production of enzymes. Disclosing energy use as one of the most important aspects in upscale, for the reduction of impacts, is common in a wide range of biobased systems (Carvalho et al., 2019).

Other studies have revealed the limitations of laboratory scale LCA results and the relevant differences when benchmarked with scaled-up results. This is a trend in the sectors of emerging technologies and products, which are still developed at low Technology Readiness Levels, for which primary data is not readily available and the processes are not considered mature. For instance, Gavankar et al. (2014) have analyzed the effect of the scale-up in the production of nanotubes, obtaining reduction values of 84-94% in a cradle-to-gate LCA and have detected, similarly to this study, the intensity of energy demand in smaller production volumes. Piccinno et al. (2018) analyzed the environmental results by means of LCA of the nanocellulose production process through the estimation of inventories at industrial scale, reporting the reductions per functional unit of the upscaled results when compared to laboratory production.

Figure 6.4 shows the comparative evaluation for the two enzymes analyzed in this study in the two scenarios (laboratory and upscaled production). In the case of GW, the results were presented in Figure 6.3. Regarding the rest of the impact categories evaluated, the comparative distribution maintains a similar trend to GW. The upscaled HMFO is the scenario with the lowest impacts in most of the considered categories, followed by the upscaled production of *Cgl*UPO, laboratory *Cgl*UPO and laboratory HMFO. This trend is not followed in ME, for which *Cgl*UPO at laboratory scale has the greatest impacts. The laboratory scale of HMFO presents a reduction of 23% of the impacts with respect to *Cgl*UPO production at the same scale. In the case of the upscale production, the enzymes differ in 74% of impacts, being HMFO the worse scenario.

The overall results of these enzymes, that can be potentially utilized for the same purpose (i.e., oxidation of HMF or FFCA to FDCA), and that present a wide range of differing impacts, show that including the production process of enzymes within the boundaries and scope of bioprocess environmental studies is recommended when possible.

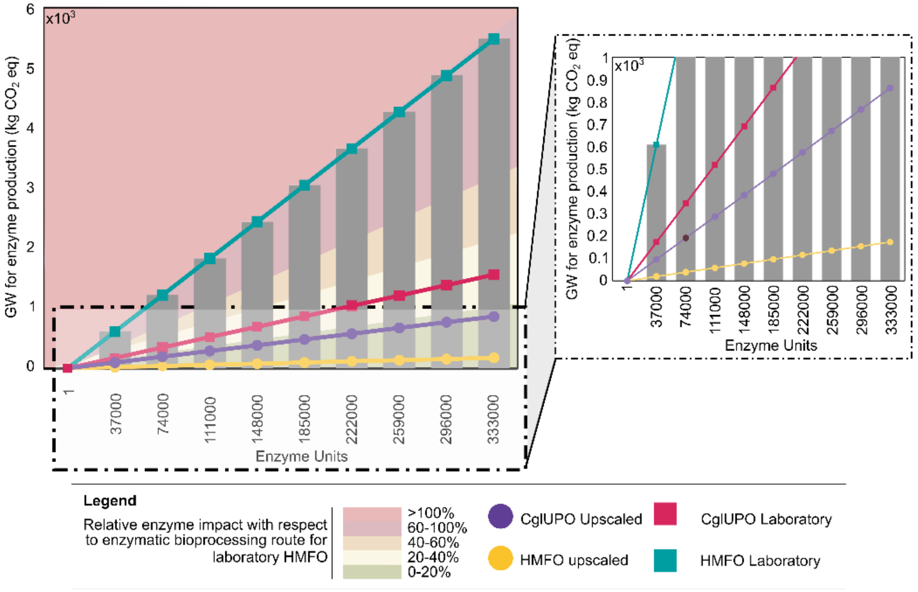


Figure 6.3 Variability of the GW impact category characterization results (kg CO_2 eq.) per functional unit as a function of enzyme loading units. Results appear displayed for the two enzymes analyzed (HMFO, *Cgl*UPO) for both laboratory and upscaled inventories. The bars in grey display the maximum GW impact value among the included cases corresponding to laboratory HMFO.

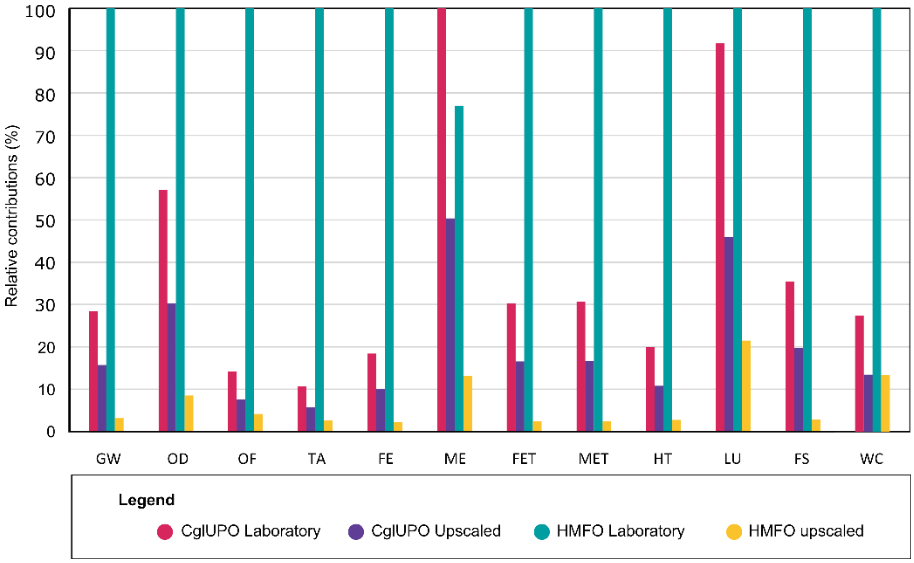


Figure 6.4 Comparative evaluation of *Cgl*UPO and HMFO at laboratory and large-scale per functional unit (1 unit). FS: fossil scarcity, LU: land use, HT: human toxicity, MET: marine ecotoxicity, FET: freshwater ecotoxicity, ME: marine eutrophication, FE: freshwater eutrophication, TA: terrestrial acidification, OF: ozone formation, OD: ozone depletion, GW: global warming.

6.3.2. Environmental impact assessment through the endpoint perspective

Figure 6.5 presents a perspective in which the damage pathways are analyzed through endpoint categories implementing the method previously described. The graph displays the endpoint results for three impact categories: human health, ecosystems quality and resource depletion for all the enzyme scenarios presented (laboratory and up-scaled inventories). The bar-graph additionally includes the relevance of each midpoint indicator within each endpoint category. The plots to the right side of the figure include the results of the Monte Carlo analysis uncertainty displayed through boxplots which show the median, first and third quartiles and the minimum and maximum values. The reason for presenting the Monte Carlo results for endpoint indicators is to consider the aggregation of uncertainties when introducing additional considerations and assumptions into the calculations with the implementation of endpoint characterization factors. It is also relevant to understand the effect of uncertainty related to the inventories and how this uncertainty is changed by the effect of scale. The midpoint categories present cause-related indicators, while the endpoint results are more oriented towards the effect of the activities on the three main areas of environmental protection.

The human health impact category presented in Disability-Adjusted Life Years (DALY) represents the years of life lost or the years of disability due to diseases or accidents caused by the environmental consequences derived from the system under study (Huijbregts et al., 2016). In this study, as expected, the production of enzymes at lab scale presents, per functional unit, higher contributions to the human health indicator, while these values are reduced for the upscaled scenario. Continuing with the trend observed in the midpoint analysis, *Cgl*UPO experiences the least reductions in impact when upscaled. This is due to the lower contributions from the energy consumption activity in the process compared to HMFO enzyme.

The human health impact category for the enzyme production system manifests relevant contributions mainly from the midpoint categories of GW, PMF and HT. In the case of HT, the enzyme HMFO is the scenario with the least impacts for both scales analyzed. For *Cgl*UPO, the percentage contributions are 50%, 36% and 13% for GW, PMF and HT. For HMFO the contributions from the three main midpoint indicators have values of 35%, 55% and 8% for GW, PMF and HT. The greatest difference in the upscaled scenario occurs for HMFO, where the main contribution to human health is derived from GW with an 81% share. While the relative contributions of the midpoint categories do not experience a significant shift, it is notable that, in a direct comparison per functional unit, a potential energy optimization of the biotransformation (e.g., through upscale of the production volume) would decrease the effect in the category of human health. The impacts are reduced by a factor of 2 for *Cgl*UPO and 7 for HMFO.

Regarding the uncertainty of the values, the Monte Carlo simulation presents a way to perform a data validation analysis, in which the deviations in each scenario can be compared with their upscaled counterpart. The HMFO production at laboratory scale shows a major dispersion of the calculated endpoint impact, but also the greatest reductions in the uncertainty for human health. The dispersion of the results, characterized through the standard deviation, is reduced by 98.6% for HMFO, which depicts a great unreliability of the laboratory endpoint results for human health estimated for the enzyme, which can be addressed with upscaling procedures. The most significant results per functional unit for the human health impact category are those of the production of upscaled HMFO, presenting a standard deviation of $1.27\cdot10^{-9} \pm 1.37\cdot10^{-9}$ DALY which is the result with the least dataset dispersion. In the case of *Cgl*UPO, the upscaled results present higher scattering than their laboratory counterparts in relative terms. The reductions of data dispersion in the upscaled scenario are not as relevant when one of the hotspots is the consumption of chemicals rather than electricity consumption. This is probably due to the higher contribution that chemicals have in the human health impact category, which is a trend that can be observed for this enzyme. Also, higher reductions in the consumption of electricity, present higher reductions in the human health impact category. While HMFO presents contributions to human health that reach more than 95% in electricity use, *Cgl*UPO presents a more distributed profile, with half of the impacts on human health coming from electricity consumption, about 25% from ammonium sulfate, 12% from tris(hydroxymethyl)-aminomethane, 5% from soybean meal and 5% from glucose.

The second endpoint category represented in Figure 6.5, ecosystems quality, as opposed to human health, presents different trends when comparing laboratory and upscaled results. In the laboratory results, HMFO is the enzyme that has the greatest impacts in the category, reaching values of almost $9\cdot10^{-11}$ species·year; however, this is transposed in the upscaled scenario, *CgI*UPO being the enzyme that contributes most to the ecosystems quality damage category. The midpoint impact categories with most relevance to the endpoint category are, for all the analyzed scenarios, GW, TA and LU. In laboratory HMFO production, for instance, GW contributes with a 53% share, TA with 24% and LU with 8%. Other midpoint categories such as OF and FE also present a relevant contribution to the overall impact of laboratory HMFO (9 and 4%). For this endpoint category, the upscaled HMFO is the best-case scenario, with the lowest impact. When directly comparing the laboratory and their upscaled counterparts, *CgI*UPO experiences a 46% reduction per functional unit and HMFO a 95% reduction.

With reference to the Monte Carlo uncertainty, the least data dispersion can be observed in the upscaled HMFO scenario ($4.03\cdot10^{-12} \pm 2.51\cdot10^{-12}$ species·year), following the same trend as in the previously discussed impact category. Data dispersion is quite relevant in this impact category, with quite large deviations from the mean. While HMFO shows less data dispersion when upscaled, this is not the case for *CgI*UPO. Hereby, it can be concluded that the inventories for chemicals present larger uncertainties than that of the electricity mix. In the case of ecosystems quality, the greatest reductions in uncertainty are achieved when electricity consumption values are reduced through upscaling.

Regarding the last set of graphs in Figure 6.5, fossil scarcity (FS) is the midpoint category primarily responsible for most impacts on the resource depletion endpoint indicator. Contrarily, metal scarcity (MS) does not present practically any contribution. This trend is accurate for every enzyme studied in the assessment of both production volumes. In this case, the most unfavorable production system is that of HMFO in laboratory scale. However, the results fluctuate for the upscaled systems, where *CgI*UPO becomes the worst case with the highest contribution to the resource depletion category. In relative terms, when upscaled, *CgI*UPO and HMFO experience a decrease of 44% and 97%, being HMFO the enzyme with the greatest improvement.

In terms of uncertainty, resource depletion is the endpoint impact category with the least data dispersion, resulting in the lowest standard deviation relatively. This effect may be due to the fact that resource depletion is affected by only two midpoint categories, FS and MS, while the other endpoint indicators have implications derived in a wider range of midpoint categories. The list of substances that globally contribute to the impact in these two categories will therefore be smaller than that of the other two endpoint categories. This means that more elementary flows will be involved in the final results, which will derive the aggregation of the effect of the uncertainties considered in the analyzed inventories. The standard deviations are within or below the order of magnitude of the mean values displaying the most representative endpoint category. The uncertainty of the samples is decreased in all cases for the upscaled scenarios compared to the laboratory experiments. The dataset with the least uncertainty is that of HMFO for the upscaled scenario of production with standard deviation value of $4.13 \cdot 10^{-5} \pm 3.97 \cdot 10^{-6}$ USD while *Cgl*UPO achieves $1.98 \cdot 10^{-6} \pm 1.80 \cdot 10^{-7}$ USD. The uncertainty in the resource depletion category is mainly affected by activities such as electricity consumption (fossil-based energy production). The significance of uncertainty datasets may be increased if real data on several trials were used for the Monte Carlo Assessment. However, since the objective of this study is to compare the scenarios analyzed, the results achieved are considered valuable for this purpose solely.

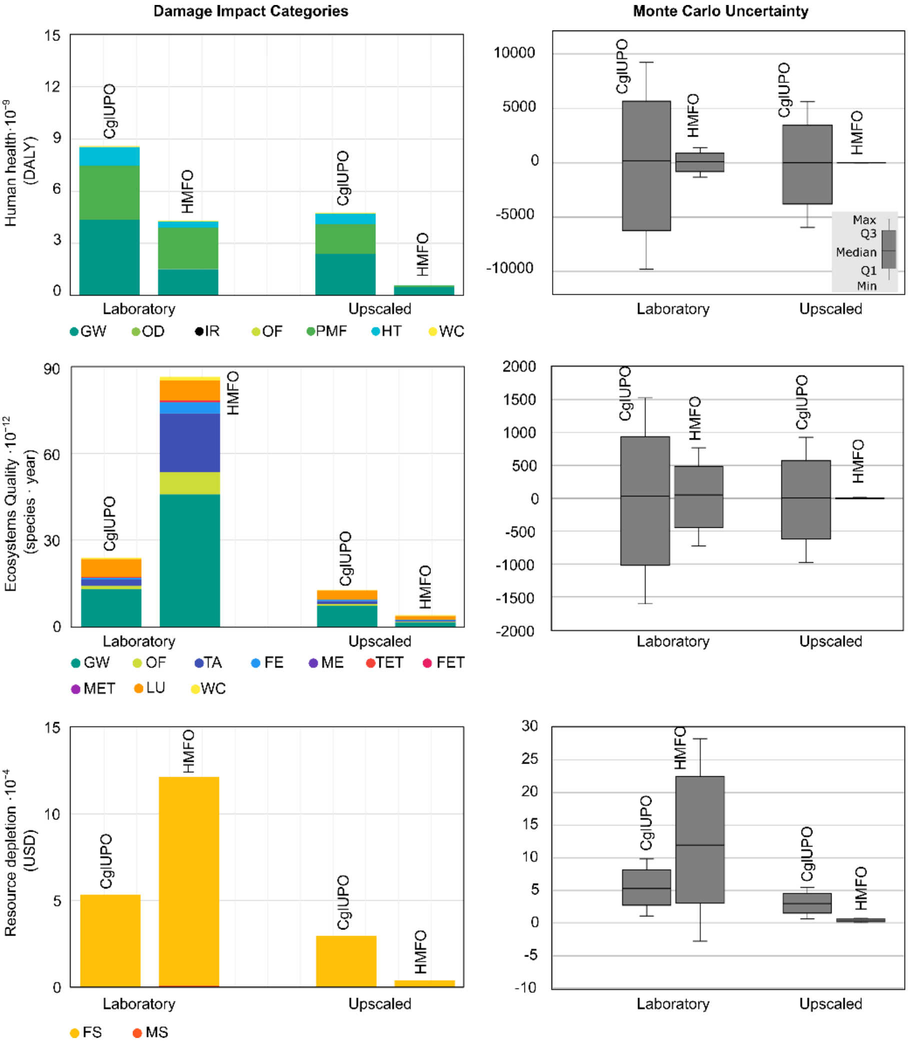


Figure 6.5 Combined assessment of endpoint impact categories (human health, ecosystems quality and resource depletion) and the corresponding Monte Carlo uncertainty values for *Cgl*UPO and HMFO per functional unit.

6.3.3. HMFO evaluation and benchmark

In general, the greatest difference in impacts occurs in the case of HMFO, from lab to upscaled scenarios. For the production of this enzyme, in which the primary dataset inventory is fairly complete, it is interesting to analyze which stage contributes most to impacts when analyzing a generic bioprocessing flowsheet. Figure 6.6 displays the impacts for three relevant midpoint indicators in the assessment. GW is one of the most relevant indicators nowadays to describe a system environmentally. OD and ME were selected because they display the categories in which the upscale results in the lowest reductions, which, in turn, are still quite meaningful. In the upscaled results, the inventories were implemented slightly different, considering electricity and heating demands as separate activities contributing to each stage (shaded grey area in the graphs). In the laboratory scale scenarios, electricity consumption is considered within each stage. The figure presents in the same column, the impacts of both laboratory and upscaled scenario, which allows to see their differences in value. It also represents the impacts per stage of production: pre-inoculum, inoculum, bioreactor, microfiltration, and ultrafiltration.

For the three studied categories, the most relevant stage, regardless of the impact category, is the bioreactor stage with 57%, 58% and 60% contributions for GW, OD and ME. The pre-inoculum and inoculum stages are the stages with the least environmental impact, reaching a maximum of 3% contribution to the overall impact for the evaluated categories. Apart from the stage dealing with the main fermenter, the downstream processing as a whole is a major contributing step, mainly due to the electricity consumption required for separation. The downstream stage, for the production of HMFO involves two subsequent microfiltration units, and an ultrafiltration step. While separately they present contributions about 10-14% each, if combined, the downstream is responsible for 34 and 37% of the overall environmental burden. The greatest contributor to the impacts in the laboratory scenario is electricity consumption, which is reduced in the upscaled version, where all the impact represented in each of the stages is due to other activities, mainly chemicals, nutrients and water.

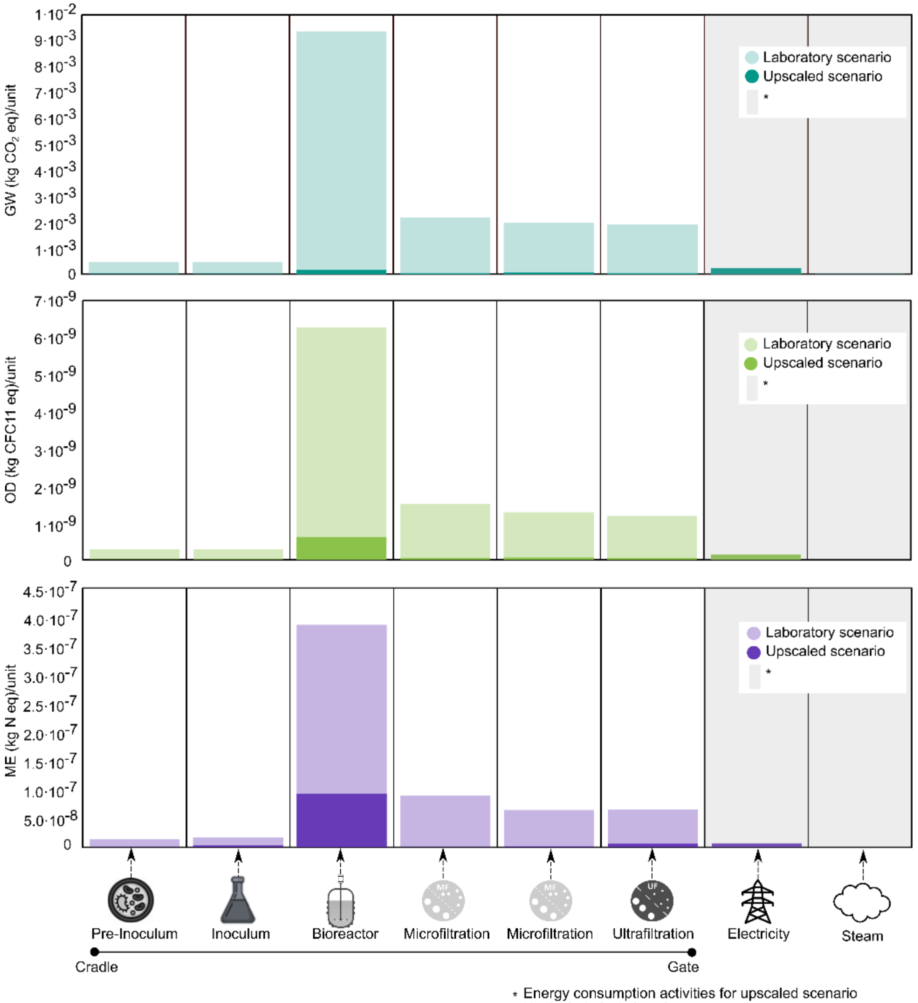
While most studies present the results of the impact of enzymes with a functional unit based on mass-based values (1 kg enzyme), in this case it makes sense to analyze it as a function of units which will be useful in the sense of allowing future further implementation of LCA results within studies with extended system boundaries (e.g., enzymatic oxidation of HMF into FDCA). Whereas there are some published studies evaluating the environmental impact of certain enzymes, there are no studies specifically geared towards the assessment of enzymes directed to the enzymatic production of platform chemicals such as FDCA from lignocellulosic feedstock. There is no reported data involving an endpoint and uncertainty assessment.

The study of the environmental assessment of enzyme production is considered very relevant. Works have usually analyzed the significance of the environmental impacts of enzymes within a production route and not as a standalone process. For instance, Gilpin et al. (2017) present the attributional assessment of cellulase enzyme required for bioethanol production. In this case they analyze different case studies for the production of cellulase per kg of enzyme produced, concluding that the highest impact achieved is 10.6 kg CO_2 eq/kg enzyme. The great variation of results in the literature regarding the production of cellulases is attributed to the lack of a common framework for enzyme evaluation and the absence of adequate inventories. The GW result for HMFO production 98,729.13 kg CO_2/ kg enzyme, is much higher, however, is not comparable to the results obtained in cellulase studies. Firstly, the objective or function of the enzymes is far from being the same, while the assumptions and scale of evaluations are completely different. The enzyme loads and activities are not depicted when mass-based systems are studied, which does not allow a fair comparison.

Although Delgove et al. (2019) present an LCA study of an enzymatic production process of functionalized lactones, using monooxygenases, they do not focus on the inventories and results obtained for the enzymes, but rather on the comparative assessment of enzymatic versus chemical routes of oxidation. However, some of the main conclusions reached in their study are similar to those attained in this assessment. The authors expressed the relevance of the electricity consumption and electricity mix within laboratory scale processes. The GW impact of the enzymes represents a 16% contribution to the process, with a value of 0.26 kg CO_2 eq./g product. In this chapter, considering the use of 4000 units for the production of 15 g of FDCA, the GW impact for the HMFO enzyme produced in laboratory scale is 4.39 kg CO_2 eq. /g FDCA, while if the upscaled experiment is considered, the impact is 0.14 kg CO_2/g FDCA. Regarding endpoint results, Delgove et al. (2019) report human health values of $1.64 \cdot 10^{-7}$ DALY/g product, while for HMFO with the assumed conditions for FDCA production the results would be $1.15 \cdot 10^{-5}$ DALY/g FDCA for the laboratory scenario and $4.32 \cdot 10^{-7}$ DALY/g FDCA for the upscaled scenario, attaining similar results to the baseline study. The authors also concluded that the Monte Carlo uncertainties acquired high values, and more for laboratory experiments than for industrial scale systems.

The results in this assessment indicate that the transformation of laboratory processes to upscale production is a requisite for the reduction of environmental impacts. Not only energy should be optimized, but also common laboratory procedures should be updated to more industrial-like processes. For instance, the optimization of the fermentation mode of operation (e.g., continuous, fed batch) and medium composition could potentially increase the productivity of the enzymes, thus reducing the impacts per functional unit. On the other hand, implementing sterilization processes in continuous mode, using steam, or optimizing the downstream separation sequence will potentially reduce, as well, the energy footprint of the system and maximize the final product yield. For example, cell disruption to release the enzymes has been performed through freezing, which increases the energetic consumption of the system. Other methods using chemicals could reduce the overall impact of the utilization of refrigeration chambers.

Other foreseeable improvements, at a broader scale, are in the way the utilization of enzymes is targeted. If enzymes were to be recovered and reutilized, their impacts would be reduced significantly. For instance, an option would be to recover them from the fermentation broth through the use of filtration membranes (Saha et al., 2017), the immobilization with hetero functional epoxy supports (Nath et al., 2014) or the immobilization and recovery through magnetic nanoparticles (Moldes-Diz et al., 2018). These options provide a way to potentially diminish the impact of enzyme utilization significantly. For instance, applying a hypothetical activity recovery after two cycles in the range of 31-100% (Saha et al., 2017), the reduction of the environmental impact of the use of enzymes could reach 15.5-50%. The immobilization in epoxy-amino beads has shown the possibility of reutilizing β-Galactosidase without any loss in activity (Torres et al., 2003), which would suppose a 50% reduction in impacts if the enzymes were to be reused for two cycles, and greater improvements (i.e. environmental impact/number of cycles without activity loss) if more reuse cycles were achieved. Similarly, the use of immobilized laccase in silica magnetic nanoparticles for dye decolorization was implemented for 6 cycles, maintaining most of the activity of enzymes, which would mean a reduction of the environmental impact of about 6 times (Moldes-Diz et al., 2018).



* Energy consumption activities for upscaled scenario
Not included within subsystems

Figure 6.6 Midpoint impact results displayed per processing subsystem and functional unit for the production of HMFO at laboratory scale and the upscaled scenario. GW: global warming, OD: ozone depletion and ME: marine eutrophication.

6.4. CONCLUSIONS

This study was focused on filling the gap in issues related to environmental evaluation of the production of oxidative enzymes (HMFO and UPO) as support for the enzymatic transformation to obtain bioplastics. It was found that enzyme production through non-optimized, highly specialized low-volume production processes reveals electricity consumption as a major environmental hotspot. This hotspot shifts, in most cases, to the use of chemicals for the formulation of the culture medium when scale-up is performed. This study has confirmed that evaluating the environmental impacts of industrial enzymatic processes (large volumes of production) through data from laboratory scale experiments would incur in significant errors. Appropriate scale-up procedures are needed if environmental results for large production volumes are to be estimated from laboratory data. Laboratory-based LCA results may be valid as a predictive benchmark to set optimization objectives. According to the results, the laboratory scale processes always present a higher GW than their upscaled counterparts: 97 and 45% decrease for HMFO and *Cgl*UPO, due to the overestimated energy consumptions. The differences found in LCA results for enzymes with the same function, shows the need to include these and other biocatalysts within the scope and boundaries of environmental assessments of biobased production systems. Further research should be focused on the development of databases with primary data on the production of various enzymes at different scales. The purpose is to be able to widen the knowledge on the real environmental effect of substituting chemical production routes with bioprocessing enzymatic routes, aiming at a feasible increase in environmental sustainability of the obtained products.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7

Renewable carbon opportunities in the production of succinic acid

> *"We cannot have infinite growth in a finite planet."*
> Paul Polman

Chapter 7 Summary

Succinic acid (SA) is a top biobased chemical with numerous opportunities in the field of circular economy for climate neutrality. The objective of this chapter is to environmentally analyze the bio-production of SA from residual sugar-based streams from the pulp and paper industry (spent sulfite liquors, SSL). First, an attributional life cycle assessment (A-LCA) was completed, analyzing the effect of mass versus economic allocation. However, the main objective of this chapter was to investigate consequential life cycle assessment (C-LCA) with the objective of analyzing the potential net reductions of carbon emissions in the chemical industry. Understanding that chemical or biochemical processes are not standalone systems and evaluating the effect of novel decisions into their value chain and beyond, will become increasingly relevant in the context of an increasingly growing decarbonization regulatory framework. The results present an analysis of the environmental effects of producing SA with two operation modes: fed-batch and continuous fermentation as well as the influence of assuming different geographical locations of the bio-SA production plant through the assessment of the effect of the electricity mix. On the other hand, utilizing the facultative anaerobic and capnophilic bacterium *Basfia succiniciproducens* in the fermentation and thus being CO_2 an input, brings up the opportunity of assessing the carbon capture and utilization potential of the bio-SA value chain. An assessment of the upstream section and origin of CO_2 was performed by studying the effect of capturing CO_2 from industrial static point sources (cement industry and bioethanol production from fermentation). The carbon footprint attributional results suggest that SA from SSL provides a reasonable substitution for the SA fossil alternative although not reaching the same results when comparing against first generation SA produced from sorghum, which is 62% better. From the consequential perspective, substituting the current market of SA (fossil and 1st generation SA) by SA from SSL will provide improvements of up to 1465% by 2060.

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7.1. INTRODUCTION TO RENEWABLE CARBON OPPORTUNITIES FOR SUCCINIC ACID

The “Top ten biobased building blocks” list reported by the US Department of Energy includes the biobased production of succinic acid (SA). This biochemical excels in having a growing niche market and in its potential as platform to produce petrochemicals such as 1,4-butanediol, tetrahydrofuran, γ-butyrolactone, and polymers such as Polybutylene succinate (PBS) (Bozell and Petersen, 2010). On the other hand, its feasibility to replace the petrochemical business as usual (BAU) production process from maleic anhydride presents the potential of achieving reductions in the life cycle environmental impacts, making SA more attractive than other fossil-based precursors. There is wide interest in producing biochemicals such as SA because of their application in many areas such as food, feed, pharmaceuticals, surfactants and detergents, plastics, fibers, solvents, etc. (Morales et al., 2016).

The market of SA has experienced exponential growth over the past two decades and a turnover in which biobased SA has become the primary form of production and petrochemical SA has mostly plateaued (Pinazo et al., 2015). The world’s consolidated commercial volume of production of bio- SA reached an annual 65 kt in the year 2019 (Vertès, 2020) and is expected to grow up to 245 kt produced annually (Bozell and Petersen, 2010), with some degree of uncertainty due to a recent decline in production. The limited market growth of end products and high failed investment of the company BioAmber, which experienced bankruptcy, contribute to this uncertainty (Rosales-Calderon and Arantes, 2019). SA is a product with high selling price, in the range of 2.2 €/kg to 2.6 €/kg. In the case of the biobased production, the production costs and market price tend to be in the upper range (Pateraki et al., 2016b). Thus, lowering the cost of production of biobased SA is one of the areas of improvement expected for full deployment of biobased routes. Its full deployment is also closely related to the price evolution of glucose or the sugar source in fermentation (Morales et al., 2016; Pinazo et al., 2015).

The production of bio-SA from diverse nutrient sources has been extensively studied in literature. Research mainly focuses on first generation feedstocks or wastes from food (Becker et al., 2015; Du et al., 2008; Huang et al., 2019; Klein et al., 2017; Leung et al., 2012; Zhao et al., 2016). Implementing the utilization of a residual biomass-based stream rather than crops could be a potential way to decrease production costs as well as environmental effects in direct and indirect land utilization changes (Patel et al., 2018). Alternative renewable resources used as feedstocks for the fermentation, such as sugar-rich residual streams from the pulp and paper industry, may put in place measures for sustainable production of bio-SA at lower cost nearing the predicted 0.9–1 €/kg (Ladakis et al., 2018). The pulp and paper industry (specifically sulfite pulping) is a large producer of spent sulfite liquor (SSL), which is a residual lignocellulosic-based stream containing sugars fit for SA fermentation. This sector processes one of the largest amounts of forest biomass, producing around 400 million metric tons of paper annually in around 5000 paper mill facilities worldwide for 2015 (Branco et al., 2019; Vaez and Zilouei, 2020). SSL has been traditionally incinerated for energy recovery when possible or used for the production of vanillin (Hocking, 1997) or bioethanol (Modahl et al., 2015; Xavier et al., 2010). Diverting the SSL stream to a bio-factory producing SA presents potential for sustainability improvement.

The production of SA through microbial fermentation presents another great sideline opportunity for further decarbonization of the chemical industry. It arises from the conditions of the fermentation, in which the capnophilic microorganism *B. succiniciproducens* requires CO_2 fixation for SA production (Ladakis et al., 2018; Salvachúa et al., 2016). Thus, CO_2 is fed as a raw material into the bioreactor and fixed into the bio-SA produced. This CO_2 fixation introduces to the value chain of SA the concept of Carbon capture and utilization (CCU) (Zhang et al., 2017). CCU together with Carbon capture and storage (CCS) have been acknowledged as feasible routes for sustainable industrialization and decarbonization by the Intergovernmental Panel for Climate Change (IPCC) (Intergovernmental Panel on Climate Change, 2018). The embodiment of carbon in the bioproduct allows a delay in the global warming emissions to the atmosphere, which do not account as net credits to climate change but aid in the overall climate change mitigation efforts. Efforts directed towards implementation of technologies that are able to capture CO_2 emissions from industrial sources, and either store them or utilize them, have at stake the objective of limiting the global temperature rise predicted for the next decades (Cuéllar-Franca and Azapagic, 2015). While some studies have mentioned this as an advantage, to our knowledge the assessment of the potential origin of CO_2 and its environmental implications in the production of bio-SA has not been analyzed yet with detail (Bataille et al., 2018).

In this chapter, we investigate the environmental implications of the production of bio-SA using SSL from the pulp and paper industry. There are multiple studies addressing the LCA of bio-SA (Gnansounou and Kenthorai Raman, 2016; González-García et al., 2018; Morales et al., 2016; Moussa et al., 2016; Tecchio et al., 2016), however, to the best of our knowledge, none have analyzed the effect of carbon accounting within the life cycle of the bio-SA product due to CCU implementation. Furthermore, when including CCU into the modelled system, the evaluation through consequential LCA (C-LCA), in combination with attributional LCA (A-LCA) becomes key to analyze the broad environmental consequences within the chemical industry.

The focus of this chapter is not on the experimental feasibility of SA production involving the use of CO_2 —there are many studies that thoroughly analyze and optimize its manufacture (Amulya and Mohan, 2021; Salma et al., 2021; Xu et al., 2021). This chapter aims to verify whether such production would actually be aligned with the environmental targets set by policy-making bodies. This is even more critical when analyzing the rising trends in the number of studies on bio-SA production. The quantification of environmental impacts along the value chain of production allows to analyze whether there is a quid pro quo when producing bio-SA and implementing

CCU. It also allows to determine whether these kinds of systems are truly sustainable and aligned with decarbonization strategies. In any novel biotechnological process, there is a balancing act between the potential carbon reductions achieved, and the potential increase in impacts in other areas of protection affecting other natural systems and cycles. The specific novelties sought through this chapter are described below.

1) In the manufacture of bioproducts there is a knowledge gap on the environmental impacts of novel systems framed within the circular economy trend (e.g., utilization of SSL). The results of this assessment aim to shed light on their environmental particularities and complexities and to draw science-based conclusions valuable for stakeholders.

2) While some studies analyze the economic implications and cost effectiveness of substituting fossil alternatives, in this study we carry out a tailor-made LCA implementing the consequential perspective, going beyond standard LCAs. This is especially critical in products involving interconnected systems or value chains, which will have a change in their environmental impacts as a consequence of a change in the foreground system. Covering the consequential perspective introduces the possibility of assessing future scenarios, through different timelines, by looking at the potential behavior of the SA market share. While this is not intended to predict the future, it gives valuable insight to the interested parties on whether potential actions are aligned with environmental objectives. C-LCA provides the study with a context that attributional studies may lack.

3) CCU and carbon accounting have been included in the system, extending the inventory to the upstream value chain, exploiting the opportunity to obtain CO_2 from a point emission source. Experts state that any reduction in the production of fossil-based products, principles of collaboration and integration should apply, making the possibility that these kinds of systems give with regards to CCU very attractive. The objective is to be able to draw conclusions of the weaknesses and opportunities that these kinds of synergies bring to the chemical industry.

7.2. METHODS

The environmental assessment for the production of bio-SA was addressed through the LCA methodology (ISO 14040, 2006; ISO 14044, 2006). The LCA was performed through two modelling perspectives: attributional and consequential, each of which is further detailed in Annex II, Section A5.1. The concept of the true cost of biobased succinic acid production through life cycle monetization will also be introduced to obtain the environmental costs of the system. The environmental costs are the virtual costs that would be required for the compensation mechanisms needed to counter act the negative environmental consequences derived from the system under study. Thus, the true cost of a product can be estimated as the final price of the product plus the addition of the environmental cost as externalities (Pizzol et al., 2015). Accounting for the impact along the value chain of a product through a practical metric such as money allows to intuitively help decision makers gear policies and strategic approaches into the needed decarbonization measures for climate protection (Ahlroth, 2014).

7.2.1. Goal and scope definition

The goal of this study is to determine whether biobased SA produced from SSL is environmentally competitive when compared to the petrochemical production of SA. The second objective lies in analyzing which are the hot spots, pitfalls, and strengths of SA production through fermentation when SSL is the main carbon source. On the other hand, to analyze whether the mode of operation in fermentation (i.e., continuous fermentation or fed-batch fermentation) and other variables influence in a great deal the overall impact of the system under study.

The common methodological assumptions in LCA for the determination of the carbon footprint (CF) of the product will be closely addressed and examined. Different modelling choices when complex systems —forestry growth, CCU and temporary storage of CO_2— are included in the life cycle of biobased products, will be assessed. The environmental consequences (C-LCA) of the implementation of bio- SA production from SSL will be addressed through system expansion and an analysis of the marginal products within the system boundaries considered. The objective for C-LCA is to further analyze the effect of multifunctionality without incurring in the uncertainty of the somewhat arbitrary allocation procedures implemented. The functional unit of the study is 1 kg of bio-SA produced from SSL as main nutrient of fermentation and using CO_2 from an industrial point source.

Finally, another goal was to analyze the external environmental costs in which the process for production of SA from SSL would incur and assess which variables would yield better results environmentally.

7.2.2. System boundary definition

The LCA methodology was implemented in a cradle-to-gate perspective, considering, thus, environmental impacts associated to the production of bio-SA from the production of raw materials to the gate of the bio-SA production plant. This includes an assessment of the silviculture activities involved in eucalyptus wood production, the sulfite pulping process, the origin of CO_2 used to guarantee strongly anaerobic conditions in the fermentation, as well as the fermentation and downstream of bio-SA.

The scope of the analysis was not extended to grave because bio-SA is a direct substitute of fossil SA, thus, the use and end of life phases are likely to be the same, resulting, in a comparative assessment, in the same relative differences.

The system (Figure 7.1) was divided into several processing subsections: SS1. Eucalyptus woodchips, SS2. Pulp and paper industry, SS3. Pretreatment, SS4. Sterilization, SS5. Fermentation (including carbon capture) and SS6. Downstream. The fossil-based production of SA from maleic anhydride was considered for comparative purposes as the BAU fossil scenario. The production of SA from sorghum was considered as the BAU biobased scenario (Pinazo et al., 2015).

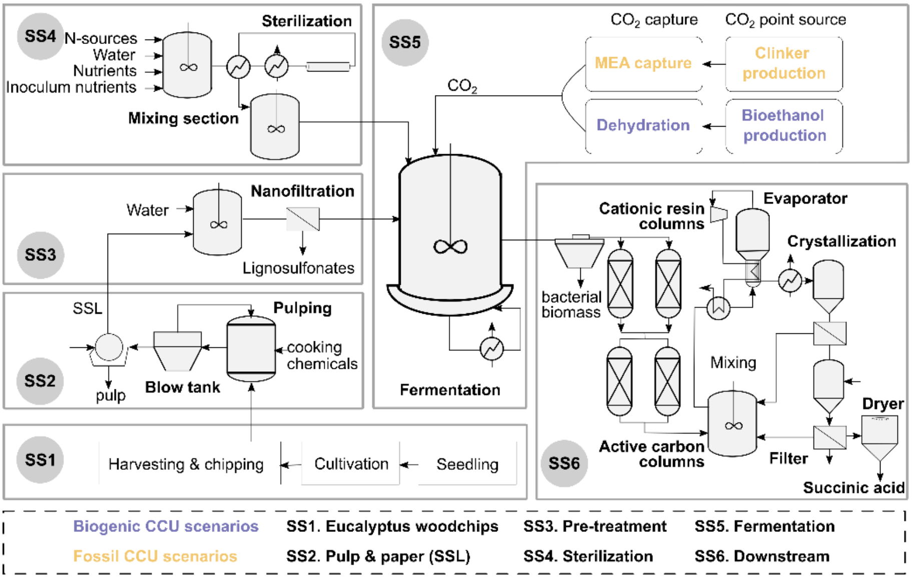

Figure 7.1 Cradle-to-gate system boundaries for production of biobased SA from SSL with CCU (functional unit: 1 kg bio-SA)

SS1. Eucalyptus woodchips. Short rotation *Eucalyptus globulus* wood is the raw material processed in the paper pulping facility. This subsystem includes seedling activities, planting, weed control and fertilizing, felling, forwarding, harvesting and wood chipping. The production yield was considered as 10.1 m^3/ (year ha) in the region of Galicia (Spain) (González-García et al., 2012; Morales et al., 2015a) and a carbon content of 31.7% (Phyllis2 ECN, 1998).

SS2. Pulp and paper industry. In this subsystem, eucalyptus chips were transported over 100 km from the wood production site through road transportation (lorry). Bisulfite pulping was the processing technology considered for pulp production, yielding the SSL stream used as sugar nutrient source in subsequent subsystems. Calcium bisulfite ($Ca(HSO_3)_2$) is the main the cooking chemical utilized for the digestion of wood. It is produced on site, with liquid sulfur, burned to obtain SO_2 and put in contact in an absorption column with an aqueous calcium carbonate solution. The digester, which is operated at 145°C for 4 hours requires 4 metric tons of liquor per ton of wood chips. The contents of the digester are transferred to a blow tank, in which vapors —mainly SO_2— are recovered and recycled. The pulped wood is washed in countercurrent with water. Two main streams are obtained after the washing cycle. First, the pulp which is further processed and bleached to obtain paper (out of the scope of this work). Second, the liquor or SSL, which is a stream containing dissolved sugars and lignosulfonates (Chen et al., 2016). Emissions to water and air from the pulping section of the paper producing facility were considered (Modahl et al., 2015).

SS3. Pretreatment. The SSL stream from SS2 —the pulp and paper facility— contains solubilized lignin in the form of lignosulfonates and sugars (mostly xylose, galactose and glucose). Thus, pretreatment is required prior to the fermentation section in order to remove the lignosulfonates (which act inhibitory to microbial growth) and to obtain a lignin-free stream rich in sugars. SSL is diluted with water in a 1:3.5 ratio. Successively, lignosulfonates are separated through nanofiltration (800 Da) with a 97% removal efficiency (Pateraki et al., 2016a). Nanofiltration also served as sterilization procedure for the SSL stream prior to fermentation.

SS4. Sterilization. This subsystem includes the mixing of nitrogen sources and minerals (NaH_2PO_4, Na_2HPO_4, NaCl, $MgCl_2$, $CaCl_2$) that are necessary for the fermentation, and inoculum preparation. The nutrients are sterilized via continuous sterilization at 140°C using low pressure stream at 160°C.

SS5. Fermentation. The fermenter was operated in fed-batch and continuous mode, with the bacterial strain *Basfia succiniciproducens* for an annual succinic acid production capacity of 30 kt. The fermentation was conducted at 37°C with agitation and maintaining pH at 6.7 with NaOH. For the fed-batch mode, the final SA concentration was 33.8 g/L with a productivity of 0.56 g/(L·h) and yield 0.58 $g_{SA}/g_{SSL\ Sugar}$ (Pateraki et al., 2016a). The respective values for continuous fermentations were 19.6 g/L, 0.79 g/(L·h) and 0.49 $g_{SA}/g_{SSL\ Sugar}$ at a dilution rate of 0.04 h^{-1} (Ladakis et al., 2018).

CO_2 was supplied continuously to the bioreactor. The origin of the CO_2 was considered as a relevant factor to the system. Therefore, rather than cutting off the system's boundary, the sourcing and conditioning of the stream was assessed. Including CO_2 within the model is in agreement with the "At the point of substitution, APOS'' modelling approach (Steubing et al., 2016) depicted in the ecoinvent 3 database (Wernet et al., 2016). This modelling option assumes that CO_2 is allocated with some impacts from the producer process, rather than considering zero impact highlighting the transformation from emission to technical flow (Zimmermann et al., 2018). CO_2 was considered to be captured at source and used locally, therefore the transport (through pipelines, up to 200 km without recompression) was not included in the subsystem (Wildbolz, 2007). Furthermore, some authors have analyzed the environmental contribution of the pipeline distribution in CO_2 capture, being negligible in most cases (Pehnt and Henkel, 2009).

Two scenarios for the carbon capture and utilization section were considered, assuming a 90% capture rate (McKinsey Climate Change Initiative, 2008). In the first scenario, CO_2 was obtained from a high volume of emission fossil point source: the production of clinker for the cement industry. A post combustion plant with monoethanolamine was included in the system boundaries for the fossil CO_2 capture and purification (García-Gusano et al., 2015). In the second scenario, biogenic CO_2 was sourced from bioethanol production industries. Although many studies present that fermentation processes using CO_2 do not require further purification or processing, we considered the most unfavorable scenario, to obtain conservative results, in which CO_2 is dehydrated (Carminati et al., 2019). Both scenarios allow to study under which circumstances succinic acid from SSL has the potential to be a temporal carbon fixation system. They represent two opposite cases, referencing the potential use of different CO_2 sources in industry. For the near term it is projected that CO_2 will be used from systems in which it exits at higher purity (e.g. fermentation off-gas), while in the long term it is expected that the increase in demand will introduce less pure, post combustion sources for which capture infrastructure must be set in place (e.g. cement industry emissions) (Thonemann and Pizzol, 2019).

SS6. Downstream. bio-SA was recovered from the fermentation broth in a series of steps in the downstream section. First the bacterial biomass was separated and discarded through a centrifuge. The active carbon columns allow the decolorization and removal of impurities from the solution. Cationic resins were used for the acidification of organic acid salts (e.g., acetate, formate, lactate) into their corresponding acid forms. The rich-in-organic-acids stream was concentrated in an evaporator system where part of the volatile organic acids are removed (formic acid 89% and acetic acid 76%). The concentrated liquid was driven to a crystallizer where the succinic acid was separated in the form of crystals. The SA crystals are removed and dried through rotary filter and spray drier units, respectively.

BAU scenarios. The fossil production of SA considered for benchmark was the production of SA from maleic anhydrite hydrogenation in liquid phase and metallic catalysts. The process includes SA hydration, crystallization, filtration, and drying steps (Pinazo et al., 2015). The BAU biobased alternative was the production of SA from sorghum saccharification and fermentation by anaerobic bacteria. In this process ammonium sulfate is produced as co-product (Moussa et al., 2016).

7.2.3. LCI assumptions and limitations

The LCI data, provided in the Supplementary information for Chapter 7, Table A37 through Table A50, were implemented under the following assumptions, for the most part opting for the most conservative decision. Eucalyptus globulus short rotation plantations were considered for the eucalyptus silviculture subsystem (Morales et al., 2015a), considered to be extensible to European locations (González-García et al., 2012; Morales et al., 2015a). A distance of 100 km was considered from the wood site to the pulp and paper industry for pre-processing, with 5% losses during transportation (Höglmeier et al., 2015; Pettersson et al., 2015). Data for calcium bisulfite pulping was considered for SS2 (Chen et al., 2016). This available data for spruce pulping (softwood), was considered to be adaptable to eucalyptus (hardwood) since it was estimated that the energy consumption did not show significant differences (Mafe et al., 2015). Two main products exit SS2, the pulp and the sugar-rich liquor. Pretreatment in SS3 allows to separate lignosulfonates as a valuable coproduct to the cement industry, utilized in many instances as additives.

The SA plant was considered to be located nearby the point source of CO_2 emissions for both alternatives (biobased and fossil CO_2). Data of mass and energy balances for the bio-SA production, including SSL pretreatment, fermentation and downstream (SS3–SS6) stages was based on process simulation results from UniSim process design and simulator software. The inputs for the simulation of the process were derived from the experimental results of bio-SA production (Ladakis et al., 2018; Pateraki et al., 2016a).

Disodium hydrogen phosphate in the culture medium was modelled through sodium phosphate as proxy. Carnallite was used as proxy for magnesium chloride. Wastewater (with low salt concentrations) from the system, exiting in SS6 was treated with in a generic wastewater plant. Bacterial biomass (including condensate water from evaporation with trace amounts of organic acids) was considered as biowaste treated through incineration. The use of ion exchange columns implies the result of spent activated carbon and ion exchange resin, which were treated as waste. For evaporation in the downstream section of the continuous operation, steam was only needed in a negligible amount for start-up, and the operation could be maintained with electricity.

Capture and conditioning of CO_2 from clinker production and bioethanol fermentation was considered from bibliographic published data assuming that 90% of the emissions were captured (McKinsey Climate Change Initiative, 2008). Data on the actual clinker and bioethanol processes was considered as an adapted background process from the ecoinvent database (Wernet et al., 2016).

7.2.4. Methodology

7.2.4.1. Modelling approach and scenario definition

This assessment was approached from two LCA perspectives, attributional and consequential (Figure 7.2) implemented with the ReCiPe 1.1 hierarchist method in the SimaPro 9.0 software. The ecoinvent 3.5 database (Wernet et al., 2016) was used for the modelling of the background processes. For the attributional approach, the “at the point of substitution” database set was used while for the consequential assessment the database was modified accordingly (Steubing et al., 2016).

A-LCA is a modelling approach in which there is an exclusive accounting of the share of impacts assigned to our system, per functional unit, from the overall anthropogenic activity. In the boundaries in which the system is interconnected with external systems, system expansion or allocation can be performed, to partition impacts. For the attributional perspective, allocation is the recommended choice to deal with multifunctionality in diverse subsystems along the life cycle of SA (Figure 7.2). Due to the controversy among physical or causal relationships between products both mass and economic allocation (MA and EA respectively) have been studied (Ekvall, 2019). For the biobased BAU alternative, ammonium sulphate was a relevant co-product, and for the purpose of comparability, MA and EA were applied as well.

The scenarios (8 in total) considered in the implementation of the attributional approach are a combination of the following variables: continuous and fed batch operation, CO_2 from biobased point source and CO_2 from fossil point source, MA and EA. Mass and economic allocation factors as well as prices considered for EA are presented in Table A51 and Table A52 in the Supplementary Information. A sensitivity assessment of the electricity mix was performed considering two boundaries of action that give a range of possible results. For the improvement scenario, Norway was used as electricity of foreground processes. As far as the worsening scenario, Poland was considered to represent the most carbon-based mix among European Union (EU) countries (Ang and Su, 2016). Results for any other EU country mix were considered to fall within this range of plausible operation.

In C-LCA a causal relationship between our system and limiting external systems is studied. In this sense, the action of producing 1 kg of SA (functional unit) has a positive or negative effect in delimiting systems. In this modelling approach, these consequences are quantitatively accounted (Muñoz, 2020). In C-LCA multifunctionality is approached differently, through system boundary expansion (Figure 7.2). While C-LCA starts also with the definition of the functional unit (1 kg bio-SA) and the scope of system boundaries (cradle-to-gate), the latter includes those activities that change as a response of a change derived from the functional unit. The objective is to determine what unit processes are affected by a change introduced through the functional unit and their causal relationships, assuming an elastic supply-demand relationship —not large price variations should be expected as a result of demand variations (Plevin et al., 2013).

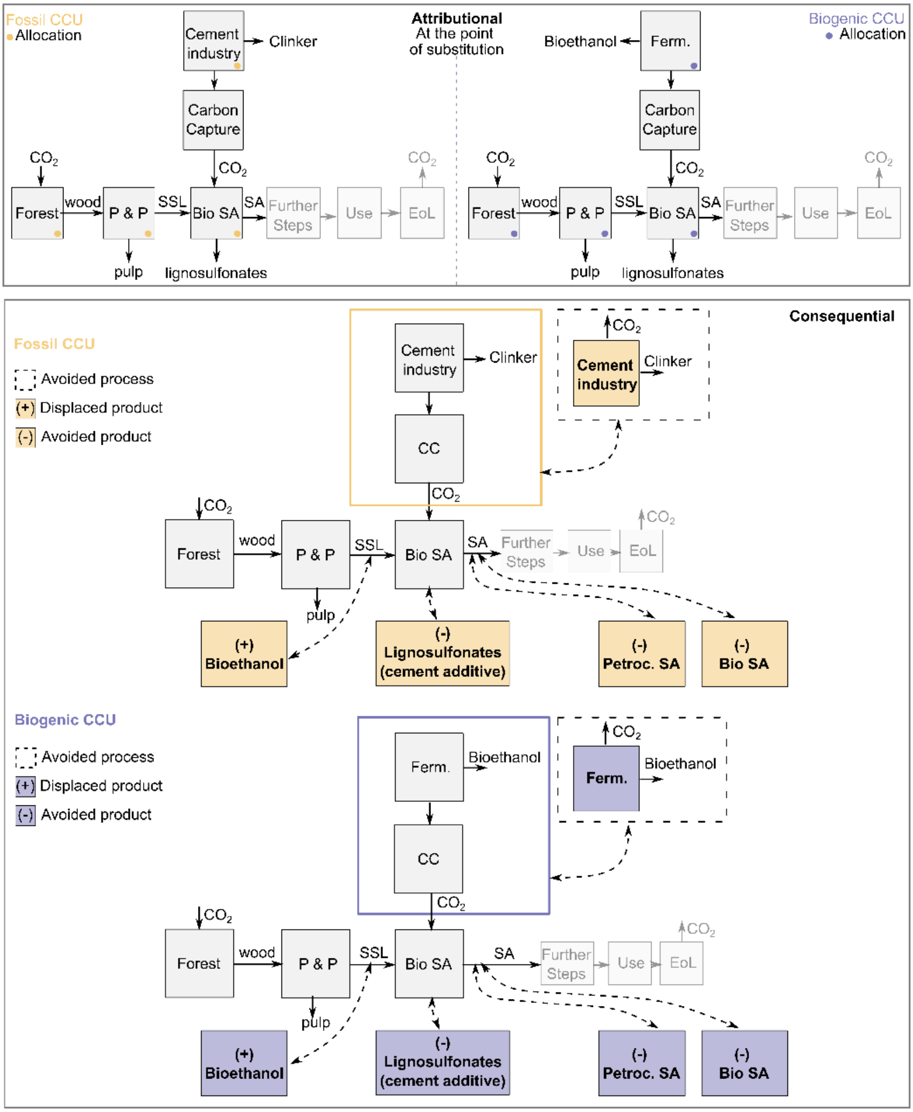

Figure 7.2 Methodological and system boundary framework for SA production system under attributional and consequential perspectives. In attributional systems boxes with a purple or turquoise circle have undergone allocation. In consequential systems boxes with a discontinued line display avoided systems. Boxes with (+) display products that have been displaced by the production of 1 kg of bio-SA. Boxes with (-) display products in which their production has been avoided by the production of 1 kg of bio-SA.

Determining which are the reference products of the system, the constrained markets and marginal suppliers through the 5-step procedure developed by Weidema et al. (1999), are key steps of the C-LCA approach depicted with further detail in Section A5.3 in Annex II. In summary the cause-effect events analyzed through C-LCA are: i. System boundaries are expanded to include the co-product (lignosulfonates) which is considered as an avoided burden of another market (i.e., plasticizer additive in the cement industry) (Schmidt, 2014) ii) Bioethanol is the main product derived from SSL —stream rich in sugars apt for any fermentation. The shift of producing SA from SSL rather than the state-of-the-art production of bioethanol results in the need to compensate the bioethanol produced by SSL. iii) Obtaining CO_2 from point sources, to produce bio-SA from SSL would lead to an intrinsic change of the clinker and bioethanol industries. iv) The production of SA with SLL as carbon source will lead to displacing the BAU production methods in the current market. The affected suppliers in this study are part of the selection of a marginal supply mix obtained by extrapolating available market trends.

Depending on the possible SA market behaviors in the future, the forecasted market displacements are studied through different scenarios. The premise is that trends of production are considered to favor bioproduction in the mid to long term, having a transition that works towards decarbonization goals and a reduction of the dependence in fossil fuels. In the short term the displacement of the SA market would be that of a mix of biobased SA produced from sorghum (1st generation) and the fossil production (from maleic anhydride) (Pinazo et al., 2015). The market that is more fit to absorb a diminution in the production in the short term (next 20 years) is a mix of both technologies. Two divergent scenarios have been considered for the short term. In the first hypothetic timeline (TL1), the SA market is expected to go in a direction of growth in which fossil is not completely substituted by biobased production considering a mix of 50.9% fossil SA and 49.1% SA from sorghum. For the second hypothetical short-term timeline, the growth of biobased SA is considered to upkeep nowadays market and moves away from the fossil alternative (17.2% fossil, 82.8% biobased from sorghum). For long term effects (next 40 years), the future scenario is based on a biobased generalized economy, in which the SA will completely be produced through biogenic sources (SA from sorghum). Thus, the long-term introduction of SA from SSL in the market is expected to substitute 100% BAU biobased SA production for both timelines. The estimations related to the market growth of SA and calculations of market mixes are included in the Supplementary Information Annex (Table A53 and Marginal mix estimation for short-term scenarios in timeline 1 (LT1 scenarios)Table A55–Table A57303) according to recommendations in methodology (Consequential LCA, 2020; Muñoz, 2020). The inventories considered for C-LCA are available as well in the Supplementary Information Table A58 through Table A61 in Annex II. A summary of the scenarios considered for C-LCA is provided in Table 7.1.

Table 7.1 Selection of C-LCA scenarios attending to the marginal SA mix, the timeline of application and the source of CO_2 (biogenic or fossil). These scenarios were applied to both the continuous and fed-batch modes of operation

Scenario	**Timeframe**	**Year**	**CO_2 source**	**Substituted SA mix (%)**	
				Fossil SA	Sorghum SA
Current	present	2020	-	-	
B-ST-TL1	short-term, timeline 1	2040	biogenic	50.9	49.1
F-ST-TL1	short-term, timeline 1	2040	fossil	50.9	49.1
B-ST-TL2	short-term, timeline 2	2040	biogenic	17.2	82.8
F-ST-TL2	short-term, timeline 2	2040	fossil	17.2	82.8
B-LT	long-term	2060	biogenic	0	100
F-LT	long-term	2060	fossil	0	100

7.2.4.2. Carbon accounting and selection of impact categories

The evaluation of the CF in biogenic systems has been assessed through the consideration of carbon uptake during the growth phase of the trees, adapting the global warming potential impact category in ReCiPe (Rabl et al., 2007).

On the other hand, in this study, the production of SA acts as a carbon fixation process due to the use of CO_2 as feedstock in fermentation. Carbon storage in biobased systems through CCU allows for a delay in the emissions to the atmosphere. In this study we consider the delay of emissions embodied in SA through the temporal closure of the carbon cycle, which leads to the accounting of the carbon uptake by forest growth as negative emissions. This is feasible since the carbon is chemically stored in SA and because this will be a comparative study in which differences in scenarios can be analyzed in relative terms (Zucaro et al., 2017). Furthermore, the further processing and end-of-life of the compared systems (i.e., SA in this study and BAU SA) are considered to be identical (von der Assen et al., 2014; Zimmermann et al., 2018). Although the delay of emissions is not discounted over time in our assessment, the time delay of a pulse emission of CO_2 in the framework of emissions with a time horizon of 100 years could be considered to absorb radiation only for the remaining time after the delay. This concept would introduce the time-dependent correction of the Global Warming (GW) emissions over time, which has been proposed by von der Assen et al. (von der Assen et al., 2013).

Other depicted impact categories in the assessment were ozone depletion, OD in kg CFC11 eq., ozone formation, OF in kg NOx eq., terrestrial acidification, TA in kg SO_2 eq., freshwater eutrophication, FE in kg P eq., marine eutrophication, ME in kg N eq., freshwater ecotoxicity, FET in kg 1,4-DCB eq., marine ecotoxicity, MET in kg 1,4-DCB eq., human toxicity, HT in kg 1,4-DCB eq., land use, LU in m^2a crop eq., fossil scarcity, FS in kg oil eq. and water consumption, WC in m^3.

7.2.4.3. Environmental prices methodology

The environmental prices evaluation was based on the attributional approach of LCA. In the first step impacts are calculated through characterization factors (ReCiPe midpoint indicators) to then implement weighting through the Environmental Prices methodology (de Bruyn et al., 2018). The Environmental Prices reports conversion prices for the European Union average (EU28) in 2015 and ReCiPe 2008 (Goedkoop et al., 2009). The ecoinvent 3.5 database was used for the characterization of background processes and systems in the succinic acid value chain (Steubing et al., 2016).

For the midpoint environmental externalities, the categories accounted for are global warming (GW), ozone depletion (OD), terrestrial acidification (TA), freshwater eutrophication (FE), marine eutrophication (ME), human toxicity (HT), photochemical oxidant formation (OF), particulate matter formation (PMF), terrestrial ecotoxicity (TET), freshwater ecotoxicity (FET), ionizing radiation (IR), agricultural land occupation (ALO) and urban land occupation (ULO). Note that, according to the methodology, resource scarcity categories are not included in the assessment of midpoint external costs, as it was assumed that they did not incur in technical externalities. The willingness to pay to prevent a direct impact to environmental themes or reduce direct emissions is presented through midpoint externalities. Environmental prices are expressed as a lower, central, and upper value to reflect the uncertainties in the appointment of prices to impacts. In this assessment the central value was adopted according to recommendations. The scenarios analyzed under the Environmental prices methodology are presented in Table 7.2.

Table 7.2 Scenarios under study for the monetization of environmental impacts through LCA

Scenario	Process mode	CO_2 source	Electricity mix	Carbon source
A	Continuous	Biogenic	Europe	SSL
B	Continuous	Fossil	Europe	SSL
C	Fed-batch	Biogenic	Europe	SSL
D	Fed-batch	Fossil	Europe	SSL
E	Continuous	Biogenic	Norway	SSL
F	Continuous	Fossil	Norway	SSL
G	Fed-batch	Biogenic	Norway	SSL
H	Fed-batch	Fossil	Norway	SSL
I	Continuous	Biogenic	Europe	Glucose (no carbon uptake)
J	Fed-batch	Biogenic	Europe	Glucose (no carbon uptake)
K	Continuous	No impact	Europe	SSL (no carbon uptake)
L	Fossil prod.	-	Europe	-

7.3. RESULTS AND DISCUSSION

The results are presented in three main sections, first dealing with the A-LCA, and then delving into C-LCA conclusions, where an analysis of the implications of the environmental assessment approach is included. Finally, the external costs of the systems are discussed. Nowadays, the need to make improvements based on science-based targets, makes the quantification of impacts key in the development of technologies based in environmental awareness and abatement of impacts. Thus, providing insight through three perspectives is expected to enrich the conclusions from the study.

7.3.1. A-LCA perspective for SA production and sensitivity to parameters

Figure 7.3 shows the comparative profile for the most relevant impact categories studied against the BAU fossil SA and the BAU biobased SA with EA and MA. The CF category (Figure 7.3-A) displays low dispersion of results among scenarios for SA produced from SSL. The best case regarding the CF is the continuous production, utilizing fossil CO_2 considering MA (1.92 kg CO_2 eq.). This scenario improves the BAU fossil alternative by 40.84%, however, it does not present better results when compared to the BAU biobased alternative which is 3.78 times better (1.62 times better when considering EA). The worst alternative is the fed-batch fermentation utilizing fossil CO_2 and considering EA (3.47 kg CO_2 eq.). While being very close to the 3.24 kg CO_2 eq. of the fossil BAU, this scenario shows significantly worse results when compared to the biobased BAU, being 2.92 times higher (EA).

Regarding the carbon intensity of the electricity used within foreground processes, the range of CF variation is significant, showing the relevance of the location of the processing plant, when energy is supplied with the country's electricity mix and the importance of favoring renewable energy. While the European average presents reductions of the CF for all scenarios, a different picture is shown if the Polish electricity mix is analyzed. All scenarios experience an increase of their CF overreaching the fossil production of SA when electricity is very carbon driven. An increase in the equivalent CO_2 emissions in the range of 56.91 to 107.75% is expected for the analyzed scenarios, presenting no improvement with respect to any of the BAU options. However, when a less carbon intensive mix (i.e., Norwegian electricity) substitutes the European average, the drops in the CF are observable for all scenarios in a range of 39.24 to 74.30%. The MA alternatives with Norwegian electricity experience a decrease that results in making an improvement with respect to the biobased SA with EA alternative. Although fed-batch operation presents slightly differing results to continuous operation, it is safe to say that the environmental results for the studied categories are not sensitive to the mode of operation. The differences among MA and EA, however, are more pronounced.

When the OD impact category is analyzed (Figure 7.3-B), the worse scenario among the BAU alternatives is the biobased production of SA with EA. None of the SA scenarios from SSL result in higher impacts than the benchmark. It becomes apparent that OD is not affected as much as CF (Figure 7.3-A) by the electricity of the system varying only in the short range of 7.27 to 10.23% when comparing the percent change from Poland-to- Norway sensitivity scenarios. Regarding the scenarios studied in this work, the best alternative for OD is the fed-batch production with fossil CO_2 and EA, while the worse scenario becomes the opposite combination (continuous operation, biobased CO_2, and MA). In OD, the differences among scenarios with MA due to the origin of the CO_2 utilized are more pronounced. MA produces an effect in which the assigned impacts to the CO_2 (as technosphere flow) from its value chain are increased. Here, the involvement of nitrogenous emissions in the plantation of biomass for bioethanol production makes contributions to the OD category that are slightly more pronounced than those for fossil CO_2. The mentioned differences suppose a decrease of 13 and 16% (for continuous and fed-batch fermentation respectively), not reaching further improvement with respect to the best BAU alternatives.

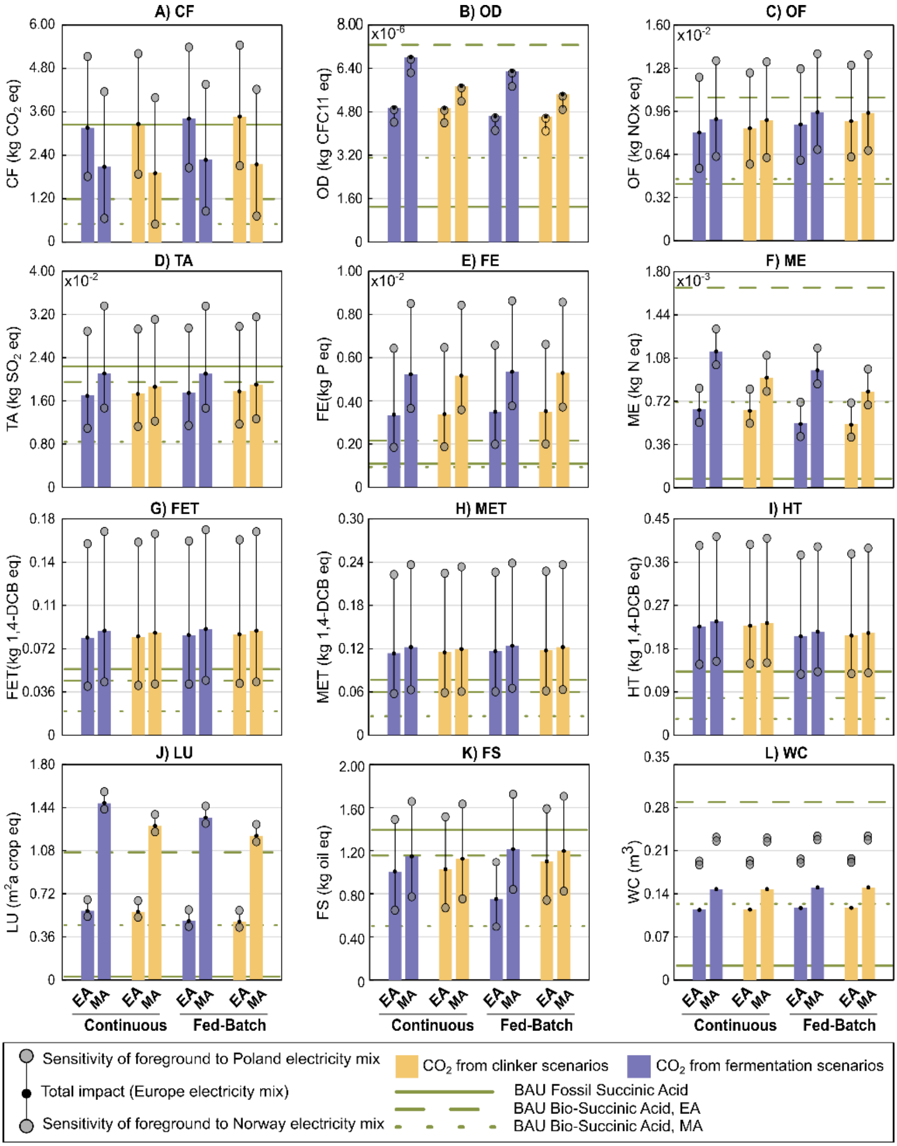

Figure 7.3 Comparative evaluation of environmental profiles through A-LCA for SA production scenarios from SSL per functional unit (1 kg SA). A) Carbon footprint B) Ozone depletion C) Ozone formation D) Terrestrial acidification E) Freshwater eutrophication F) Marine eutrophication G) Freshwater ecotoxicity H) Marine ecotoxicity I) Human toxicity J) Land use K) Fossil scarcity L) Water consumption. EA: energy allocation, MA: mass allocation.

In OF (Figure 7.3-C), the different scenarios present quite uniform results, with small variations present in the change from EA to MA —around 1.1 times higher results when allocating with the mass criterion. Although with a smaller range than that of CF, the effect of the electricity mix is remarkable in this impact category. However, even with the greatest reductions achieved through the Norwegian electricity scenarios, none of the alternatives experience further improvement than that of the base case (European electricity), which is better than biobased BAU SA (considering EA) exclusively.

Biobased transformations are penalized in TA (Figure 7.3-D) which is more affected by CO_2 utilized in SA production that originates in fermentation. In this case, the processing of biomass (additionally to SSL from wood) results in slight increases in the impacts of TA similarly to OF (Figure 7.3-C). However, in all, the scenarios are quite stable. The greatest difference is found in scenarios concerning continuous operation and biobased CO_2 ranging from $1.70 \cdot 10^{-2}$ kg SO_2 eq (EA) to $2.10 \cdot 10^{-2}$ kg SO_2 eq. (MA). All scenarios are better than the fossil BAU alternative and the economic-allocated-biobased BAU.

All scenarios, in the FE category, are worse than any of the BAU alternatives (Figure 7.3-E). The results are anywhere from 67.60 to 79.68% worse than the fossil BAU alternative. They are only slightly improved with the low carbon intensive electricity mix reaching a maximum 16.70% improvement when comparing the biobased BAU (with EA) and the scenario with continuous fermentation, utilization of biobased CO_2 and EA. The ME indicator (Figure 7.3-F) presented lower dependability on the electricity mix than FE, reaching a low margin of improvement (10.02–20.46%) through the less carbon intensive electricity supply.

Toxicity categories (FET, MET, HT) results (Figure 7.3-G, -H, -I) are mostly constant throughout scenarios when observing each of the analyzed parameters (allocation, CO_2 origin and mode of operation). In these categories, most of the contributions have their origin in the use of harsh chemicals, toxic to water bodies as well as to the human health. These chemicals are mostly utilized during fermentation and are not affected by allocation procedures (as otherwise are CO_2 or SSL inputs). They also remain mostly constant when it comes to changes in the system related to the mode of operation. For the three studied indicators, the present study displays worse contributions than the fossil and biobased BAU alternatives. FET and MET (Figure 7.3-G, -H) could reach better results than the fossil BAU option only with improvements regarding the electric mix, with 49.15 and 48.52% improvement margin on average for FET and MET, respectively.

LU is the impact category most affected by allocation (Figure 7.3-J). When MA is the principle applied, results worsen in the range of 126.23 to 175.24% with respect to EA. LU is very sensitive to allocation because SSL bears impacts directly related to forestry activities. Land occupation of forest systems is being allocated quite differently with respect to the pulp in the cases where mass or economic criteria are selected —56.10

versus 15.65% allocation factor respectively— which goes to prove the volatility of allocation criteria in multifunctional systems.

Although FS (Figure 7.3-K) behaves usually in a trend like that of CF, in this case there are slight differences due to the accounting of negative emissions related to the growth of biomass and uptake of CO_2 in CF. While the sensitivity to the electricity mix varies in similar ranges, the differences in results among scenarios, especially when modifying the source of CO_2 in fermentation, are mostly unobservable. The FS category improves the BAU fossil alternative by a range of 1.15 to 1.40 times, being the fed-batch production of SA (EA) with biobased CO_2 the best alternative.

In WC, as expected, the electricity does not have a direct effect in the results (Figure 7.3-L). The allocation method changes the results up to 22.78%. The production of SA from SSL consumes more water than the fossil BAU and the biobased BAU (MA), penalization that happens at the expense of reducing the overall CF.

In all, the results show a marked dispersion among categories and parameters. This suggests that, as expected, it is not straight forward to conclude whether fossil SA production or biobased production should be recommended from the environmental perspective. The production of SA from SSL presents results in the same order of magnitude as the benchmarked studies (Moussa et al., 2016; Pinazo et al., 2015). While there is an improvement in the CF category with respect to the fossil production of SA (Pinazo et al., 2015), this improvement comes at the expense of burden shifting. Other categories of protection appear to worsen when compared to the fossil alternative, especially OD, eutrophication of waters, WC and LU. First generation biomass —sorghum— provides good expectations with respect to the CF of SA along with some other indicators such as FE, and toxicity categories (Moussa et al., 2016). However, first generation feedstocks compete with food and feed in land and resource utilization (Tomei and Helliwell, 2016). Utilizing the residual SSL fraction along with CO_2 emissions from point sources provides good potential for the circularity of the process. Circular economy processes allow for the full exploitation of resources, limiting the exacerbation of bioavailability. Accordingly, it is expected that European policies recommend a reduction of consumption, the adoption of circular design standards and the creation of relationships within industrial sites (Hartley et al., 2020) to foster sustainable growth.

Some authors have analyzed the attributional results from different systems producing SA. Foulet et al. (2018) evaluate biobased SA synthesized from municipal solid waste, observing an improvement of the climate change indicator with respect to SA produced from sorghum or sugar beet. However, burden shifting also occurs in their study: ecotoxicity (water and terrestrial) and OD categories experience worsening with respect to the BAU. They highlight the need of awareness towards the methodology and assumptions selected in LCA which be carefully considered and reported. Other studies have also evaluated the climate change impact and non-renewable energy use, showing improvements with respect to the petrochemical production of SA (Cok et al., 2013; Moussa et al., 2016). However, the disparity of results is again highlighted by the authors, when addressing the influence that the allocation approach has to the system.

In all, a marked dispersion is found in literature, which confirms the need of going one step beyond A-LCA in complex systems involving circularity of residues, capture and use of CO_2 and carbon accounting. This will be addressed in the next section of the manuscript, through C-LCA analysis.

The impact breakdown for the CF in Figure 7.4 allows to analyze the impact contributions from input flows and emissions in the system, going beyond the net environmental results shown in Figure 7.3. The contribution analysis in the production of SA is interesting in order to pinpoint which areas of the system contribute the most to the overall CF of 1 kg of SA. Figure 7.4-A, shows that, in the production of SA with biogenic CO_2, the main contributor to impact is SS5, fermentation (53.8%) followed by the downstream operations in SS6 (28.23%). In the case of both subsystems, electricity is responsible for most of the impacts, being also the greatest input flow contribution to all subsystems. From this substantial share of impacts stems the variability found when analyzing the effect of the carbon intensity in the grid. Other hotspot of the system, and the main contributor to SS5 is the utilization of sodium hydroxide, having an effect very comparable to that of the electricity. Sulfuric acid is relevant to SS6, accounting for 36.80% of the CF in the subsystem.

The burdens from the value chain of CO_2 from a biogenic source are accounted for, however, in this case (Figure 7.4-A), the contributions are not substantially relevant in CF. This is also due to the consideration of EA, which gives more weight to the added value of bioethanol rather than to CO_2 with a 97.30% allocation factor. In EA, also the purchase value of SSL is lower than that of the paper pulp, leading to contributions from the fixation of CO_2 during plant growth of -14.35%.

Better CF is reached in the fed-batch production mode (Figure 7.4-B) totaling 2.15 kg CO_2 eq. Differences arise in the CO_2 uptake contribution, -33.98%, which accounts for one of the greatest shares in this scenario due to the MA calculations. This goes to show the importance of the methodological approaches in LCA. In this scenario SS5 and SS6 are, again, the greatest burdening subsystems. The fed-batch production depicts a slightly greater impact contribution from steam, being used in SS2, SS4 and SS6, and a relative reduction in the contributions from electricity and sodium hydroxide which originates in changes on the allocation procedure mainly. Along the same lines, the use of CO_2 from cement shows no relevant shares to the total CF.

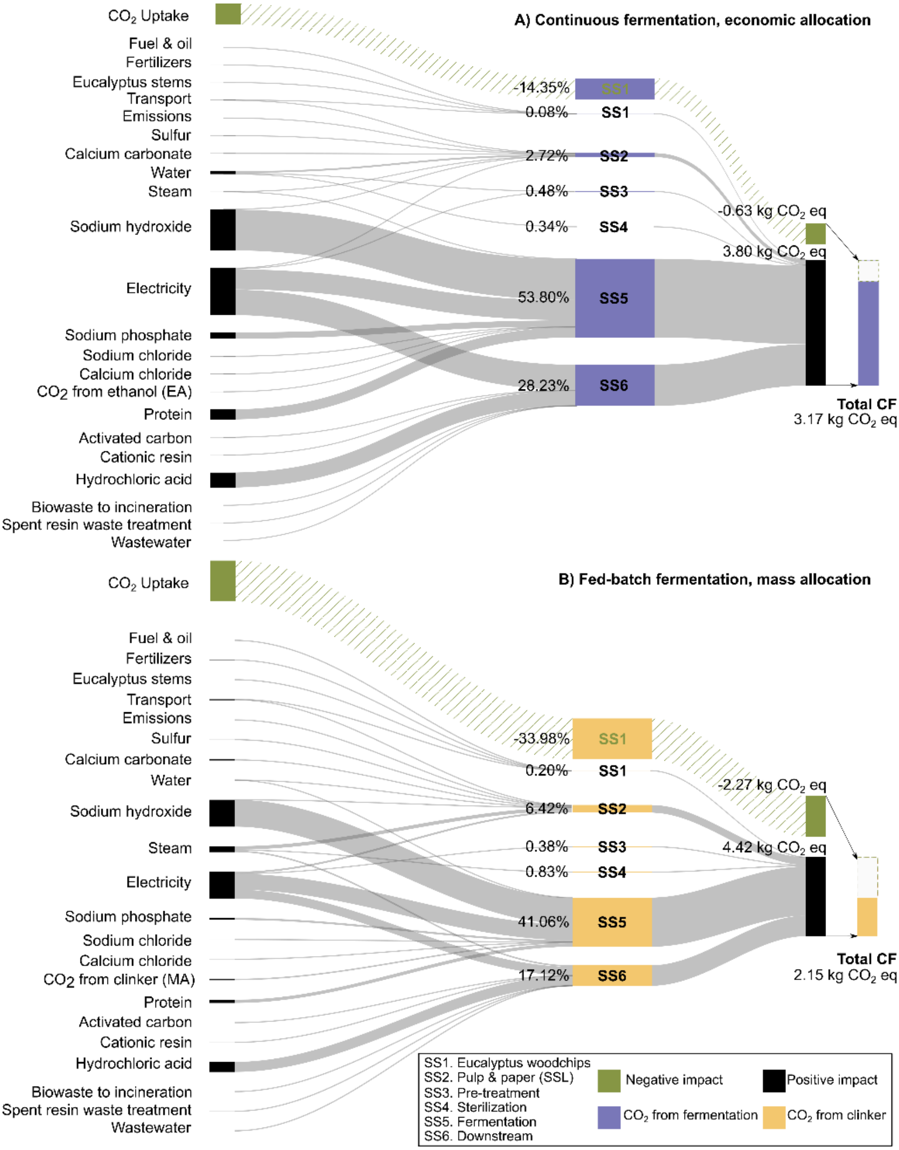

Figure 7.4 Sankey diagrams depicting the CF breakdown calculated through A-LCA for A) continuous fermentation considering economic allocation and biobased CO_2 and B) fed-batch fermentation considering MA and fossil CO_2. Each breakdown presents the activity contribution to each subsystem as well as the subsystem contribution to the total CF. Note that A) and B) are scaled differently and should not be directly compared.

Other studies have shown contribution assessments in the production of SA from apple pomace, with hotspots found in the downstream section, being very electricity and chemical intensive (González-García et al., 2018). In González-García et al. (2018), results of 5.30 kg CO_2 eq were reported, showing a benchmark above other results found in the literature which were presented in our study as BAU alternatives. Any of the scenarios in our study present promising results in CF showing 59% improvement with respect to the aforementioned production from apple pomace.

7.3.2. Abatement cost of SA production

As an additional dimension to the study, the environmental cost of producing SA was included in this chapter. The overall view of the environmental profile as a function of environmental prices of bio-SA production is presented in Figure 7.5. In the figure, midpoint externalities are displayed, as well as the total cost (or true cost) of bio-SA. Midpoint externalities (subplot A) present the cost to produce 1 kg of SA in the different proposed scenarios (A through L). Considering the total midpoint externality value, it can be observed that the fossil production of SA is the best alternative. However, one must contemplate, first, the completeness of inventories, which, for fossil SA was retrieved in all totality from the literature. The differences in cost between biobased and fossil alternatives, in the range of 0.3-0.8 €/kg SA, stem from, as expected, land use and marine eutrophication categories (agricultural land occupation and use of nitrogen base fertilizers in agricultural activities related to eucalyptus). For most scenarios, the most relevant impacts contributing to the environmental price are CC, TA, HT, PMF and ALO.

It was found that the mode of operation in the fermenter did not greatly influence the overall environmental costs. The differences in costs among continuous and fed-batch —A versus C or B versus D— are 5 and 7 cents respectively, being the fed-batch option the costlier mode of operation. The most sensitive variables were the electricity mix and the source of CO_2 for fermentation. In the case of carbon capture for utilization of CO_2 scenarios, the use of point sources that emit more CO_2 (per kg of product) is more expensive than when CO_2 from fossil origin is used. In all, this is due to the mass allocation considered since environmental charges from the emitting process (production of clinker and ethanol) are assigned proportionally. Decarbonization of the electricity mix would reduce the abatement costs of the process up to a 27% for fossil CO_2 and 25% for biogenic CO_2. The best biobased scenarios are F and H (1.02 €/kg SA), both involving the use of CO_2 from a fossil source as the cement industry and a low-carbon electricity mix in foreground processes.

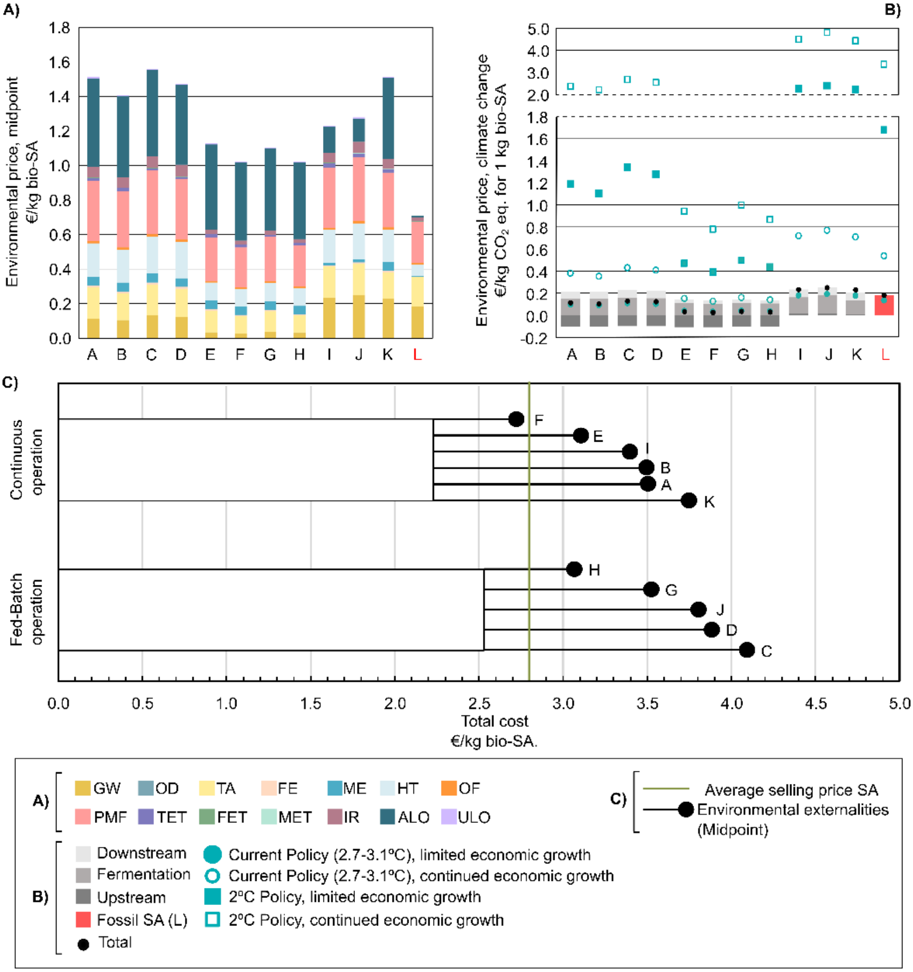

Figure 7.5 Monetization of impact assessment results through the Environmental Prices methodology (production of 1 kg bio-SA). A) Monetization of the midpoint impacts and benchmark against SA fossil production (scenario L). B) Disaggregation of the climate change environmental costs and sensitivity assessment of different policy scenarios for global warming projections, the current policy, projecting a rise of 2.7 to 3.1°C and the 2°C policy (Paris agreement) C) True cost of biobased succinic acid production (minimum selling price and midpoint externalities.

In scenario K, with the implementation of the cut-off procedure for CO_2 (no contribution of impacts from its value chain and no impacts from its capture considered), and with CO_2 uptake from biomass, there is negligible increase in the overall cost when compared to scenarios A-D. Thus, the impacts in which the processes incur due to the capture and utilization of CO_2 are counter-acted by the negative CO_2 from biomass growth in scenarios A-D. There is a redistribution of the profile of contributions —an increase of the GW contribution to the environmental costs is observed— while the rest of midpoint impacts remain mostly uniform.

When analyzing the sensitivity of the results regarding the carbon source (i.e., SSL or glucose), there is a reduction of the impacts originated in the ME but mostly ALO midpoint categories (comparing scenarios I and K, for the consistency of assumptions). Thus, the land use value implemented in the production of glucose from maize in the ecoinvent database is significantly lower than that needed for the silviculture of eucalyptus, per kg of sugar retrieved from the biomass. This stems from the lower sugar availability per kg of wood (SSL is the residual stream obtained after the pulping of wood) than per kg of maize.

In fossil SA, 26.5 % contribution to the cost is assigned to the abatement of damages due to GW. However, for the rest of alternatives, ALO is the most contributing category, in the range of 31.5-44.0% for scenarios utilizing SSL as carbon source. Thus, the abatement of impacts is cheaper in scenario L (fossil SA), than in the biobased scenarios. However, decarbonizing the chemical industry is a current priority in the European Projections for climate protection (United Nations, 2015), making the biobased scenarios a plausible option for substitution of the carbon-based fossil alternative.

Regarding the subplot B of the figure, the contributions per process section to the midpoint environmental cost of climate change are presented for every scenario. The costs are displayed disaggregated between upstream (including silviculture, wood pretreatment, SSL pretreatment and sterilization), fermentation, and downstream (including all steps in the separation sequence). In this graph, the negative emissions in the upstream process section are displayed.

For all scenarios, the greatest contribution to impact is in the fermentation phase, which includes the use of several chemicals for supplementation of the culture medium, electricity for agitation and cooling and CO_2. Furthermore, in this figure, a top-down approach has been included analyzing the potential needs of abatement per kg of SA if the recommended climate policies for decarbonization were to be followed. The Environmental Prices methodology derives the midpoint weighting factors for climate change as a combination of damage and abatement costs (de Bruyn et al., 2018). In Figure 7.5-B, each scenario presents 4 further dispersion points representing the abatement costs from possible climate policies and growth projections in 2050. The projection which is closer to the result from the Environmental prices methodology is that of the current policies with a limited economic growth. This value is situated, for all scenarios either on or below the total environmental cost of climate change for SA. However, this comes at the expense of an increase of the temperature of 2.7-3.1°C not reaching the target set by the Paris Agreement, and unrealistic economic and population growth expectations (Climate Analytics and New Climate Institute, 2020). When the economic growth is expected to continue with current trends of globalization, the cost of climate change increases from the low economic growth scenario 0.09 (scenario F) to 0.58 € (scenario J) every kg of SA produced. The 2°C scenarios correspond to the optimistic targets with net zero carbon emissions. This optimistic scenario, together with a sustained growth would signify the need to pay for abatement costs in the higher range of 0.78-4.80 € per functional unit. Limiting growth would mean reducing these costs by 50%.

In conclusion, for both current projections and optimistic scenarios, the implementation in the chemical industry of production processes with carbon uptake due to forest land extensions and the utilization of fossil CO_2 (scenarios F, E, H) would allow for a continued economic growth with a more controlled increase in the abatement costs needed for climate change than for scenarios with carbon intensive mix and the fossil alternative (scenarios J, K, L).

Finally, subplot C shows the total cost of SA, also referred to as true cost of SA, which includes the minimum selling price of SA and the addition of midpoint environmental costs as externalities. In this figure, the plausible ranges in the cost of commercialization of SA considering environmental damage abatement are presented. From the presented scenarios, only alternative F stays below the average selling price of SA in literature (Biddy et al., 2016). The highest total cost (4.1 €/kg SA) is obtained for scenario C, in which the fed-batch operation together with the retrieved electricity from the European mix were penalized. For those scenarios in which electricity carbon intensities are below that of the European mix, it could be expected that the cost of SA should stay closer to the reported average. It would be interesting to assess how the increase of price due the use of alternative, non-residual carbon sources (i.e., glucose) would affect the final cost. Taking into consideration the cost of glucose would potentially shift the ranking of scenarios presented in the figure regarding scenarios I, J and K.

7.3.3. Analyzing the consequences of SA production in the prospect of a future bioeconomy

The consequential modelling alternative allows not only to account for decarbonization synergies in multifunctional systems, and renewable carbon but also to study potential future projections in the implementation of bioeconomic routes of production. Figure 7.6 shows the encouraging potential that SA production from renewable carbon and circular value chains has. The CF over the next 40 years is depicted for a projected exponential increase of the SA market production (Figure 7.6-B). It is also depicted as percent improvement per functional unit with respect to the current mix of SA production (12% fossil SA, 88% biobased SA) in Figure 7.6-A. The implications of these results sustain the capabilities of CCU and biomass utilization (i.e., renewable carbon) in the decarbonization of the chemical industry, to the contrary of what was expected when analyzing the attributional model.

The current mix of SA production is expected to experience very little increase of CF even considering that its production will exponentially grow. This is due to the main contribution from non-carbon-intensive production methods (SA from sorghum), with respect to the declining market of fossil SA production. However, these results are still unparalleled by the potential of producing SA from SSL and implementing CCU. The CF for the next 40 years is expected not only to break through the carbon neutral barrier, but to deliver a negative CF in the cradle to gate approach. One could expect improvements of to up to 1465% with respect to the current market per functional unit for SA with fossil-based CO_2. Improvements of up to 1022% could be expected for the biogenic CO_2 SA scenario.

In these results, the effect of using renewable carbon in the form of CO_2 is far clearer than in the attributional approach. There is an actual measurable effect for the introduction of carbon capture technologies in the studied sectors. Consequential modelling allows to measure how much the change in the emissions profile of SA and its ancillary sectors (cement industry, bioethanol industry) can be expected to vary, and in which direction. Also, differences between using biobased and fossil CO_2 from each industry are visible here. It is more beneficial, when analyzing the CF, to produce SA with captured fossil CO_2 than with biogenic CO_2. For an increase in production, fossil CO_2 could potentially provide a 1.5 times greater sink of carbon emissions than the production with CO_2 from fermentation in the next 40 years.

Here, we not only analyze the potential effects of reducing CO_2 emissions to the atmosphere by coupling the SA production system with emitting industries, but we have also included the effect of multiproduction (production of ammonium sulfate as co-product) in the BAU options, making both alternatives comparable. The results suggest that increasing the resource potential of biomass through the production of multiple products (Moussa et al., 2016) is not as beneficial as reducing carbon emissions from other industries, especially when those are fossil CO_2 emissions. Due to the complexity of the intertwined systems and data acquisition in the analysis of these industrial synergies, there is no comparable study to the one presented here. The enlightening results suggest that finding areas of improvement by means of finding synergistic approaches to biochemical production is by far the route with most potential to stay within temperature warming scenarios below 2°C (Intergovernmental Panel on Climate Change, 2018).

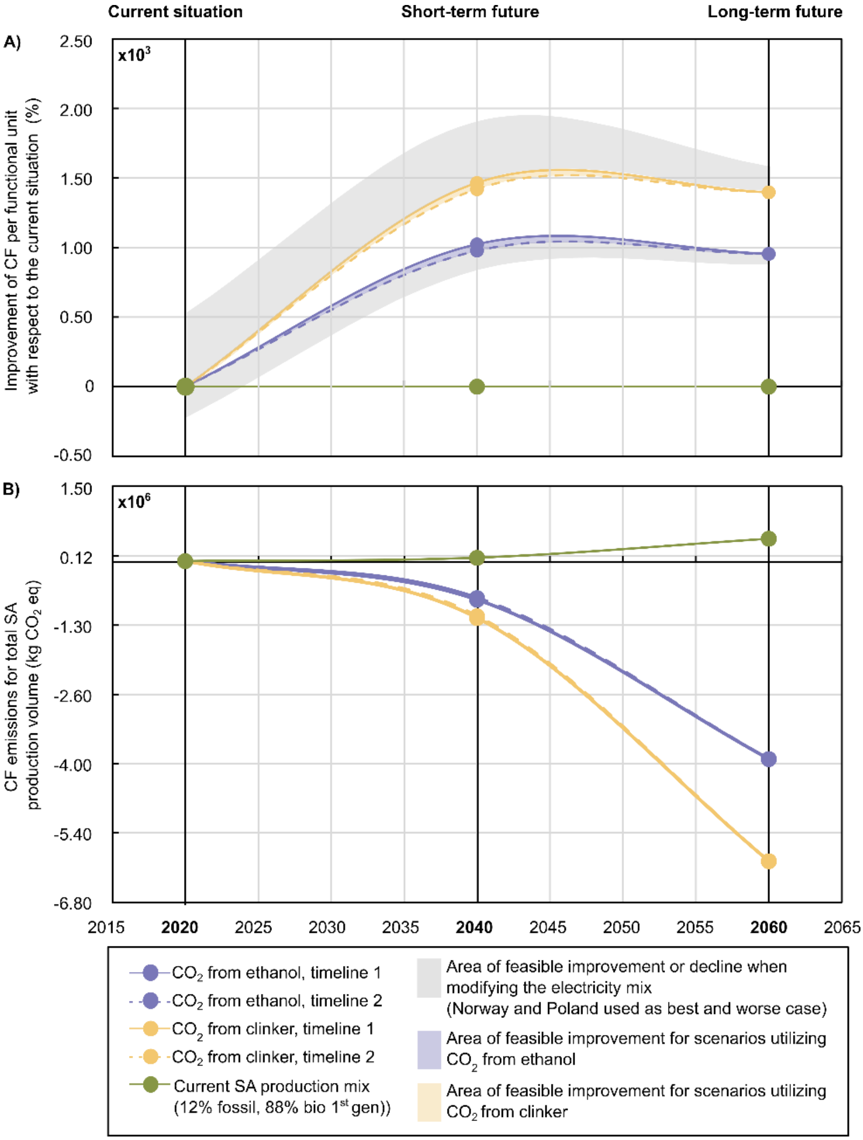

Figure 7.6 Projection of C-LCA impacts in CF to 20 and 40 years from the current situation. SA is produced in continuous operation. A) Displays the percent improvement of the CF with respect to the current SA scenario per functional unit B) Displays the total CF of SA market considering a growth in the SA production volume.

The effect of the carbon intensity of the electricity is well depicted in Figure 7.6-A. The good potential for improvement is illustrated in the figure, following the conclusions drawn from the attributional model. The CF of the fossil CO_2 alternative could be improved 1.3 times additionally in the Norwegian grid, while the effect of a very carbon intensive mix could suppose a 0.8 times decay with respect to the biogenic CO_2 scenario.

Regarding the two temporal approaches taken —TL1 and TL2— their effect is not very pronounced in the results. In terms of market substitutions by the SA proposed in this study, it is not as important whether the decarbonization of the SA feedstock happens at a higher or lower rate, considering that in the long run a complete biobased market is predicted. As expected, the CF prediction is slightly better for the substitution of a SA mix of production that is more fossil-based (TL1) than biobased (TL2). Improvements in the CF will be greater if the starting point includes higher shares of fossil markets.

When expanding the indicator portfolio to other environmental impact categories (Figure 7.7) the results show that, although being a great decarbonization system, the production of SA still presents burden shifting to other natural systems. In CF, the substitution of clinker production and bioethanol production systems with systems involving CCU, as well as the accounting of lignosulfonates as avoided product, provide credits to the system (Figure 7.7-A). In the current scenario, the inclusion of ammonium sulfate as credits to the system has the same impact. However, as mentioned earlier, the first is a better contribution to decarbonization strategies than the latter.

In the same way, all scenarios present better results than the current alternative of production in impact categories such as TA (Figure 7.7-C), OF (Figure 7.7-D), ME (Figure 7.7-E), FS (Figure 7.7-K), and WC (Figure 7.7-L). In these impact categories, the improvements are mainly due to the avoided burdens that arise in the substitution of the current market of SA by our SA from SSL. In the attributional perspective it was harder to depict which scenario was best in categories other than CF (Figure 7.7-A). On few occasions, the allocation scenarios and methodological implications did not help in providing a clear answer as to which alternative was better. Going back to Figure 7.7, for OD (Figure 7.7-B), FE (Figure 7.7-F), MET (Figure 7.7-G), FET (Figure 7.7-H), HT (Figure 7.7-J), and LU (Figure 7.7-I) the proposed scenarios of SA production from SSL are worse than the current mix of production. For these categories, the substitution of SA markets has an inverse effect, affecting mostly toxicity-related impact categories. A similar behavior is encountered for the fed-batch operation mode, which is presented in Figure A21 and Figure A22 in Annex II.

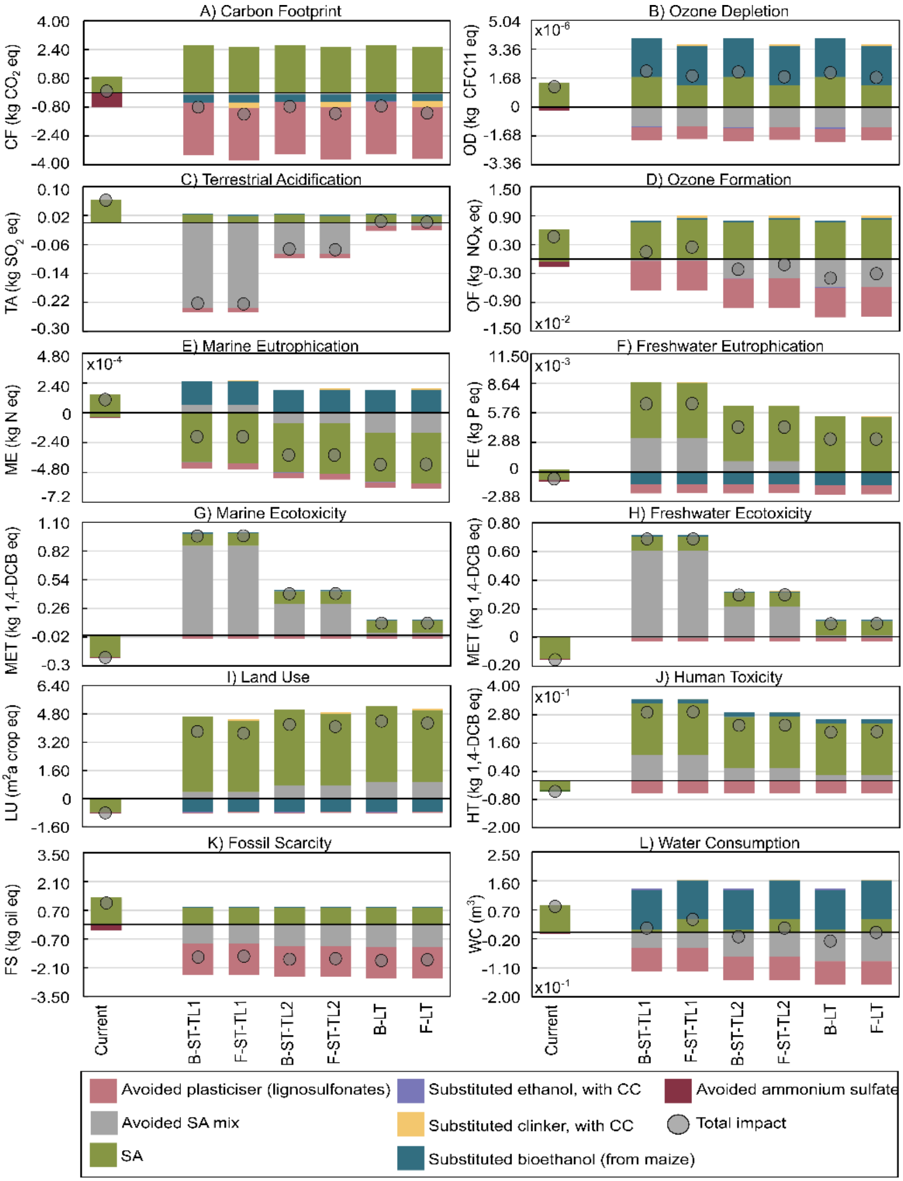

Figure 7.7 Comparative evaluation and breakdown of environmental profiles through C-LCA for SA produced in continuous operation. A) Carbon footprint B) Ozone depletion C) Terrestrial acidification D) Ozone formation E) Marine eutrophication F) Freshwater eutrophication G) Marine ecotoxicity H) Freshwater ecotoxicity I) Land use J) Human toxicity K) Fossil scarcity L) Water consumption.

The decision of the modelling approach comes early in LCA, and the attributional approach is usually selected, especially for the comparison of scenarios (Plevin et al., 2013). However, the results in this study suggest that for systems clearly involving effects outside the foreground boundaries, further assessment of the modelling choice should be made. In this category should fall bioenergy systems, land use change for bioproduction, carbon utilization strategies and circular economy processes. Future research should be focused on analyzing from a holistic perspective —be it C-LCA modelling, or other methodologies— the real effects of implementing novel bioeconomy-based routes of chemical production.

This does not take away from the fact that more complex mathematical and modelling approaches come with higher uncertainty, especially when data is not readily available (Yang and Heijungs, 2018). The effect of sensitivity to free parameters in the consequential model should be addressed and studied. For example, in this assessment, we have evaluated different timelines, SA market mixes and different CO_2 point sources to account for uncertainty. Standardization bodies such as the ISO standard (ISO 14044, 2006) recommend performing sensitivity, consistency, and/or completeness checks within the compulsory interpretation phase. The World Business Council for Sustainable Development (WBSD) also recommends sensitivity checks when analyzing systems involving delayed emissions and carbon storage (WBCSD chemicals, 2014). The GHG protocol standard also highlights the need to perform a sensitivity check, to analyze in qualitative and quantitative terms which parameters of the study are most sensitive to changes in assumptions (Greenhouse gas Protocol, 2014). In general, the recommendations show that performing analysis of sensitivity of different variables that may affect the results of the model is highly encouraged.

The intrinsic advantage of temporary storage is to delay emissions (buying time) so that other mitigation and fossil resource reduction strategies can be developed. In general, all efforts are made towards eluding the tipping points in the global warming trends that would make the climate situation irreversible. Looking over the next 100 or 150 years, a sustained delay in the emissions to the atmosphere may prove valuable, as the peaks in radiation resulting in the consequential warming of the atmosphere would be substantially reduced. This, in turn reduces the high probability of overreaching the Earth’s biocapacity, and further destabilization of the natural carbon cycles. The urgency of meeting reduction targets in the next 10 years makes a delay in the emissions in periods of high atmospheric concentration of GHG emissions overall valuable (Intergovernmental Panel on Climate Change, 2018). Of course, there is still controversy about carbon accounting and how this delay in emissions should be considered, especially depending on the time horizon. Also, controversy lies in the actual benefit of temporary storage, in which opposers argue that the reversibility of temporary carbon storage would result in increased emissions to the atmosphere in the future (Levasseur et al., 2012).

7.4. CONCLUSIONS

A-LCA results, especially of complex systems present a great dispersion leading to troublesome decision making. Many times, the need of assumptions hinders the study, leaving LCA practitioners and stakeholders even more so undecided in the selection of the best processing alternative or best available technique environmentally. When carbon capture —for storage or utilization— comes into play, the complexity of emission and technical flow accounting adds to the uncertainty and dispersion of the conclusions drawn from any study. Biomass adds to this, driving the need of more complex and detailed evaluations such as C-LCA. Although not fit for all systems, in this case, the proposed C-LCA has shed light to the study of alternatives in SA production. In all, relying on fossil chemicals (SA from maleic anhydride) is not an option to encompass the objectives of decarbonization set in the Paris agreement. Beyond the status quo, the utilization of CO_2 emissions as valuable carbon (i.e., renewable carbon) presents promising results for the reduction of the CF when analyzing the system through a synergistic approach. The attributional approach depicts results that appear to fit within the state of the art in the literature, showing improvements 41% in the CF of the product when compared against the fossil alternative. However, SA from SSL and CCU does not show improvements with respect to the biobased BAU alternative, which presents 62% better results in CF, when the market value of the co-product ammonium sulfate is considered through EA. However, in decision-based consequential approach, the projections to the next 20 and 40 years of the SA market, show the great carbon sinking potential of SA produced from SSL and CCU. The production of SA has a cascade of effects, starting from the reduction of the CO_2 emissions in high volume emitting industries such as that of cement or bioethanol. The use the SSL residual stream also presents great potential to decarbonize the future bio-chemical industry. Substitutions of the current market mix of SA by SA from SSL depict up to 1465% improvement with respect to the current market. However, this great potential in CF comes at the expense of degrading other impact categories, such as toxicity-related indicators or LU which are worsened with respect to BAU alternatives.

8

General findings and conclusions

8.1. GENERAL CONCLUSIONS

The hypothesis driving this thesis was that biorefineries and biobased systems involving negative emission technologies are essential for the decarbonization and defossilization of the chemical industry. The objective was to prove, through the LCA methodology the alleged reduction in carbon emissions. Although biobased processes are leading systems in the bioeconomy framework, they may also be drivers of negative effects of some environmental protection areas. As it was mentioned in the introduction section, 'bio' is not always synonym of sustainable. The aim was to analyze in depth which kind of systems would provide good results with respect to the status quo and propose areas of research and industrial interest for further evaluation.

The complexities of biobased systems, and in particular of second-generation biorefineries, make the methodological backdrop of LCA critical. Some of the particularities of biorefining systems are the novelty of most of the production routes (specially for second generation biomass), their multifunctional nature, the biogenic carbon uptake in the upstream of feedstocks and the potential burden shifting to other categories of impact. These systems are, for the most part, not deployed at industrial scale, hindering the availability of primary data. There is also an impending need to consider streamlined LCA models such as consequential-LCA. The general conclusions of this thesis are summarized below.

Chapter 1 provided the framework of the current climate situation, trends of global heating and the chain effects, that, if are not curbed soon, will continue to cause irreversible harm. Some systems affected are water (toxicity, eutrophication), thinning of the ozone layer, toxicity effects to humans, biodiversity of different ecosystems, land use changes, deforestation etc.

In **Chapter 2** first- and second-generation biomass systems for the production of sugars were analyzed, concluding that:

- Future production systems should tend to exploit residual fractions from agriculture and forestry to substitute fossil fuels with the potential to provide sustainable value-added products.
- First-generation systems for the production of sugars, overall present better results than those of second-generation, especially in global warming, fossil scarcity and human toxicity impact categories.
- While first-generation sugar production systems involve more mature technology, cultivation practices with fertilizer production and use still have a significant impact on categories such as marine and freshwater eutrophication and terrestrial acidification.
- This is not the case for the second-generation systems which present burdens related to mostly the processing of wood for delignification, which usually translate into chemically or energetically intensive processes and lower to no-use of

fertilizers. The upstream section of the value chain of biorefineries is relevant, because of the pretreatment processes involved and even more so for lignocellulosic biomass.
- Environmental results suggest that further optimization of enzymatic hydrolysis processes is needed to curb the overall energy consumption of these lignocellulosic processing operations. Some specific wood systems for the production of sugars are environmentally comparable and even less burdensome than the production of sugars from crops such as wheat.
- It can be expected that, in the future, the conventional sugar industry will be become part of the biorefinery multipurpose concept, producing high value-added products along with the primary product.
- The supplementation of the sugar market with lignocellulosic raw materials should not be viewed with an interest to completely substitute the traditional sugar production from crops. In fact, such production for food-grade sugars should be maintained according to the results in this study.
- The production of sugars from sugar crops should be prioritized as suppose to the use of starch crops. Lignocelluloses provide good opportunities for fuel or chemical-grade sugars if the technologies and pretreatments evolve.
- The conclusions in this chapter and the ability to provide clear recommendations for the use of first- or second-generation biomass should be confirmed when primary data is available.

In **Chapter 3**, a lignocellulosic biorefinery system has been studied from cradle-to-gate, finding that:

- In general terms, the environmental hotspots of the lignocellulosic biorefinery were found to be the feedstock and pulping sections as well as the production of energy. These hotspots are dependent on the impact category analyzed.
- The comparison of results among different systems and studies is complex in the case of lignocellulosic systems, due to the limiting quantity of data available and assumptions. Therefore, the introduction of eco-efficiency and exemplification through different biorefining scenarios is key for the optimization of the process.
- Biorefinery configurations that have better eco-efficiency scores are those with better integration and better exploitation of the feedstock into a multiple range of valuable products.
- The optimization of the biorefinery system studied should focus on further integration of enzyme production, optimization of technologies for the manufacture of high value added bioproducts and the optimization of the organosolv pretreatment process.
- It would be advantageous to study possibilities of further energy optimization to achieve full integration of the plant.

In **Chapter 4** the biorefinery outlook has been analyzed in a cradle-to-wheel approach, including the coupling with carbon capture and storage concluding that:

- Biofuels with CCS reduce the carbon footprint of conventional gasoline, more so when using low-carbon electricity and/or biomass as the heating source in the process.
- Blends with higher contents of bioethanol have the potential to deliver negative emissions. Particularly, with an E85 blend, a net balance of -2.74 kg CO_2 eq per 100 km travelled could be attained considering the European average electricity mix and heating for the capture and compression system supplied by biomass resources.
- Electricity mixes with higher shares of renewable energy (e.g., Switzerland, France or Norway) would double the final net negative emissions achieved (-5.01 kg CO_2 eq/100 km in Norway).
- The geographical location of the BECCS facilities becomes a key aspect in the production of net negative biofuels. Ideally, the biorefinery with CCS should be placed near the low-carbon energy resources available (electricity and heat), the biomass resources and the CO_2 geological storage sites.
- In practice, finding a suitable site might be challenging because these resources tend to be geographically dispersed. Locations near the biomass source might be preferred, which will require pipeline infrastructure yet to be developed.
- Further improvements in bioethanol production with CCS should focus on minimizing the heating demand of the CCS technologies, opting for heating systems relying on biobased residues, and exploiting opportunities for waste heat from other industries.
- As in previous chapters, substantial environmental benefits may be attained in climate change and fossil depletion. However, these systems also lead to burden-shifting worsening other categories.
- Minimizing energy consumption in the CO_2 capture and compression stages, e.g., via heat integration and the use of biobased residues for heating, could reduce the collateral damage to other environmental areas. Nevertheless, trade-offs will arise in the deployment of biofuels, which should not be overlooked to avoid potential undesirable side-effects.
- Overall, the BECCS concept applied to biorefineries offers excellent opportunities to reduce the carbon footprint of the passenger-vehicle fleet in the transition towards a carbon–neutral (or even carbon-negative) mobility system. The occurrence and severity of burden-shifting should be analyzed in-depth.

In **Chapter 5** the potential production route for FDCA was assessed concluding that:

- Simulation through Aspen Plus and LCA allowed to compare crystallization and filtration to distillation column as downstream processes in the production of FDCA. Crystallization presented a significantly lower environmental footprint.

- HMF and FDCA production still needs conventional solvents such as DCM, which harm health and the environment. Therefore, the research on FDCA production should be extended to the use of more environmentally friendly solvents and catalysts.
- Lowering the energy requirements should also be considered, especially in line with European decarbonization objectives in which renewable mixes should be favored.
- This study shows that biomass-based chemicals do not contribute necessarily to environmental sustainability. The way production routes for biomass are developed is far more important to deliver sustainable processes than the use of biomass.
- Further assessment of the FDCA route would need to focus on the environmental viability of enzymatic transformations, which would potentially deliver better results than the catalytic routes of production.
- The development of routes for the production of biobased intermediates for the production of bioplastics has the potential of becoming environmentally competent when comparing to fossil plastics. However, this is dependent on the continuous deployment of LCAs throughout the development and scale-up process.

Chapter 6 has assessed the production of oxidative enzymes (HMFO and UPO) as support for the enzymatic transformation to obtain bioplastics. It was found that:

- Enzyme production through non-optimized, highly specialized low-volume production processes reveals electricity consumption as a major environmental hotspot.
- The use of chemicals for the formulation of the culture medium are the major environmental hotspot when scale-up is performed.
- This study has confirmed that evaluating the environmental impacts of industrial enzymatic processes (large volumes of production) through data from laboratory scale experiments would incur in significant errors. Appropriate scale-up procedures are needed if environmental results for large production volumes are to be estimated from laboratory data.
- Laboratory-based LCA results may be valid as a predictive benchmark to set optimization objectives.
- According to the results, the laboratory scale processes always present a higher GW than their upscaled counterparts: 97 and 45% decrease for HMFO and *Cgl*UPO, due to the overestimated energy consumptions.
- The differences found in LCA results for enzymes with the same function, shows the need to include these and other biocatalysts within the scope and boundaries of environmental assessments of biobased production systems.
- Further research should be focused on the development of databases with primary data on the production of various enzymes at different scales.

In **Chapter 7**, the production of biobased succinic acid from sulfite spent liquors and carbon capture and utilization led to understanding that:

- Attributional LCA results, especially of complex systems, present a great dispersion leading to troublesome decision making. Many times, the need of assumptions hinders the study, leaving LCA practitioners and stakeholders undecided in the selection of the best processing alternative or best available technique, environmentally.
- When carbon capture —for storage or utilization— is considered, the complexity of emission and technical flow accounting adds to the uncertainty and dispersion of the conclusions drawn from any study.
- Biomass accounting adds to this, driving the need of more complex and detailed evaluations such as consequential LCA. Although not fit for all systems, in this case, the proposed consequential LCA has shed light to analysis of succinic acid production alternatives.
- The attributional approach depicts results that appear to fit within the state of the art in the literature, showing improvements 41% in the carbon footprint of the product when compared against the fossil alternative.
- However, succinic acid from SSL and CCU does not show improvements with respect to the biobased BAU alternative, which presents 62% better results in CF, when the market value of the co-product ammonium sulfate is considered through EA.
- The utilization of CO_2 emissions as valuable carbon (i.e., renewable carbon) presents promising results for the reduction of the carbon footprint when analyzing the system through a synergistic approach (C-LCA).
- In the consequential approach, the projections to the next 20 and 40 years of the SA market, show the great carbon sinking potential of SA produced from SSL and CCU.
- The production of succinic acid has a cascade of effects, starting from the potential reduction of the CO_2 emissions in high volume emitting industries such as that of cement or bioethanol.
- The use the SSL residual stream also presents great potential to decarbonize the future bio-chemical industry.
- Substitutions of the current market mix of succinic acid by succinic acid from SSL depict up to 1465% improvement with respect to the current market.
- In all, relying on fossil chemicals (succinic acid from maleic anhydride) is not an option to encompass the objectives of decarbonization set in the Paris agreement.
- This great carbon footprint improvement comes at the expense of worsening other impact categories, such as toxicity-related indicators or land use.

8.2. RECOMMENDATIONS AND FUTURE WORK

As evidenced in this thesis, decarbonization of the chemical industry will be possible with biobased systems that involve the use of second-generation biomass. This decarbonization will be more feasible if carbon capture and storage or utilization systems are deployed as well. However, the burden shift to other areas of protection has also been a common denominator in the biorefinery systems evaluated. Thus, the recommendations derived from this thesis are that, not only climate impacts should be considered in the drafting of policies, guidelines, standards, binding regulations, environmental product declarations, etc. These guidelines and standards should clearly reflect the need to evaluate other impact categories such as the ones analyzed throughout this thesis. Environmental product declarations, third-party reviewed LCAs, reported corporate carbon footprints, etc. should also be required to include an analysis of other relevant impact categories such as eutrophication, ozone depletion, toxicity, land use, water consumption, etc.

These same recommendations, regulations, standards and best practices are, at the moment, not providing a uniformized approach in terms of clear methodological recommendations for LCAs. These standards should regulate which assumptions should be favored in specific scenarios, and how to methodologically report uniformized results when carrying an LCA. This will allow to consistently be able to compare LCA results and conclusions from different studies without the need to continuously remark the need to be cautious when drawing conclusions upon comparisons with external studies. In all, regulatory systems need to be aware of the need for uniformity, clear and knowledge-based methodological recommendations and the need to provide these according to the studied system. Biorefinery systems are a good example of this, since they would need a framework of their own.

The evaluation of facilities with primary data should provide an interesting background on the best configurations towards sustainability of biorefineries. If data availability is not a constraint, future research should focus on the assessment of a wider range of biorefinery scenarios. It was found that the evaluation of laboratory scale processes should only be used for high level estimates and to find ground for process improvement. However, better data, based on the realistic large-scale production approach should be favored in subsequent revisions of the LCAs.

Also, in the theme of data, more systematic approaches in the gathering of data for LCAs should be favored. To do so, there should be a movement in the LCA practitioner’s world, towards the generation open data sources, and safe sharing of data cross-industrially (suppliers to producers and producers to consumers). This would ensure the feasibility to account global warming potentials and other impacts throughout the supply chain to propose global improvement measures.

In many cases, it was found that the analyzed systems would potentially benefit from the utilization of electricity mixes with a higher share of renewables. This should be done across all regions, through the implementation of more measures to systematically promote renewable energy in electricity mixes and industrial energy sources. This would allow to avoid the shifting of production to less-demanding countries in terms of emission legislation and carbon emission measures related to the Paris agreement.

Future studies should also embrace the evaluation of biomass availability regionally and the environmental effect to the system. Regionality should also be considered for certain processes studied throughout the thesis like the storage of CO_2, the areas with point source carbon emissions for carbon capture and utilization and others like the electricity mix available and the potential to achieve integrations within industrial parcs. This would affect, for example, the potential to optimize transport routes between feedstock locations, the biorefinery factory site, CO_2 point sources and geological underground storage sites. This allows to analyze whether it would be more environmentally feasible for a biorefinery facility to be near the biomass source, the site for underground storage of CO_2 or other highly emitting industrial factories.

This thesis has shown the need to consider alternative ways of implementing the LCA methodology. More concretely, modelling LCA through the consequential perspective should give a more holistic perspective to biorefinery systems involving both release and uptake of CO_2. Consequential LCA is also relevant for the evaluation of the market uptake of a new product, and whether this product would substitute or the BAU market or suppose a marginal change. Consequential LCA is very relevant to analyze the environmental consequences of the implementation of novel products and processing routes in the current production scene. Especially when these are bound to have significant effects in the availability of biomass, in land use changes, effects to current industrial infrastructure, transport networks, suppliers, etc. These alternative models should need to be considered as a complement to attributional studies, sensitivity assessments and other methodological considerations.

In the implementation of novel production lines and biorefinery systems, studies should also implement the evaluation of future scenarios through prospective assessments. The current electricity production system, transport network, chemical industry, is in the process of evolving to be less carbon-based, meaning that the near future systems would substantially differ from the data available nowadays through, for example, databases. The dynamic nature of processes should be considered in LCAs, especially when the changing factors are considered to be relevant to the system under study. This dynamic nature should also be considered in the methods used to calculate environmental impacts. When systems dealing with temporary or permanent storage of carbon emissions are considered, the temporal effect of the global warming indicator increases drastically in importance.

Finally, it would also be recommended to consider other methods for the quantification of impacts through the LCA methodology. Specifically absolute environmental sustainability methods would allow to assess systems with respect to the current environmental situation and the Earth’s biocapacity, for different categories. Each category of impact in this method represents the operating space margin for the Earth. The processes are analyzed with respect to this margin of operation, being able to quantitatively understand whether they are sustainable to keep within the margin in which humanity can continue to develop and thrive for generations to come without harm.

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Annex I

List of publications

PUBLICATIONS IN THIS THESIS

Comparative evaluation of lignocellulosic biorefinery scenarios under a life-cycle assessment approach

Authors: S. Bello[1], C. Ríos[1], G. Feijoo[1], M.T. Moreira[1]

[1] Department of Chemical Engineering, CRETUS Institute. Universidade de Santiago de Compostela, 15782 Santiago de Compostela, Spain

Journal: Biofuels, Bioproducts and Biorefining. 12 (2018) 1047–1064, ed. Society of Chemical Industry and John Wiley & Sons, Ltd, ISSN 1932-1031, doi:10.1002/bbb.1921.

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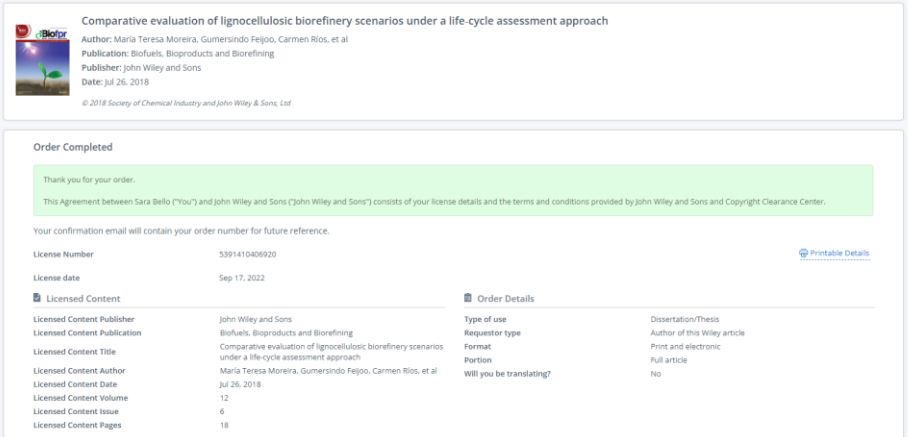

Comparative evaluation of lignocellulosic biorefinery scenarios under a life-cycle assessment approach

Author: María Teresa Moreira, Gumersindo Feijoo, Carmen Ríos, et al
Publication: Biofuels, Bioproducts and Biorefining
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Date: Jul 26, 2018

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Environmental sustainability assessment of HMF and FDCA production from lignocellulosic biomass through life cycle assessment (LCA)

Authors: S. Bello[1], I. Salim[1], P. Méndez-Trelles[1], E. Rodil[1], G. Feijoo[1], M.T. Moreira[1]

[1] Department of Chemical Engineering, CRETUS Institute. Universidade de Santiago de Compostela, 15782 Santiago de Compostela, Spain

Journal: Holzforschung 73 (2018) 105–115, ed. De Gruyter, ISSN 1437-434X, doi:10.1515/hf-2018-0100.

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Towards improving the sustainability of bioplastics: Process modelling and life cycle assessment of two separation routes for 2,5-furandicarboxylic acid

Authors: S. Bello[1], P. Méndez-Trelles[1], E. Rodil[1], G. Feijoo[1], M.T. Moreira[1]

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Journal: Separation and Purification Technology 233 (2020) 116056, ed. Elsevier, ISSN 1383-5866, doi:10.1016/j.seppur.2019.116056

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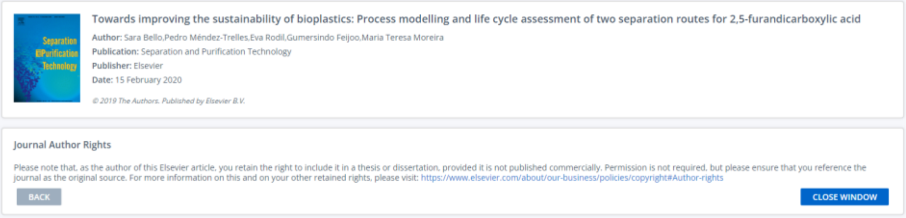

Towards improving the sustainability of bioplastics: Process modelling and life cycle assessment of two separation routes for 2,5-furandicarboxylic acid

Author: Sara Bello,Pedro Méndez-Trelles,Eva Rodil,Gumersindo Feijoo,Maria Teresa Moreira

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BECCS based on bioethanol from wood residues: Potential towards a carbon-negative transport and side-effects

Authors: S. Bello[1], Á. Galán-Martín[2], G. Feijoo[1], M.T. Moreira[1], G. Guillén-Gosálbez[2]

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Journal: Applied Energy 279 (2020) 115884, ed. Elsevier, ISSN 0306-2619, doi:10.1016/j.apenergy.2020.115884.

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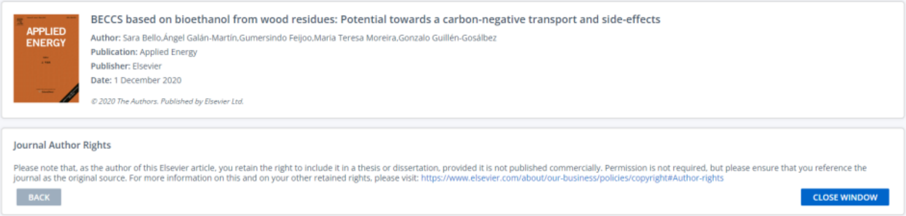

BECCS based on bioethanol from wood residues: Potential towards a carbon-negative transport and side-effects

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Author contribution: Formal analysis, Investigation, Methodology, Writing - original draft, Writing - review & editing, Visualization.

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Inventory review and environmental evaluation of first- and second-generation sugars through life cycle assessment

Authors: S. Bello[1], I. Salim[1], G. Feijoo[1], M.T. Moreira[1]

[1] Department of Chemical Engineering, CRETUS Institute. Universidade de Santiago de Compostela, 15782 Santiago de Compostela, Spain

Journal : Environmental Science and Pollution Research 28 (2021) 27345–27361, ed. Springer Nature, ISNN 1614-7499, doi:10.1007/s11356-021-12405-y.

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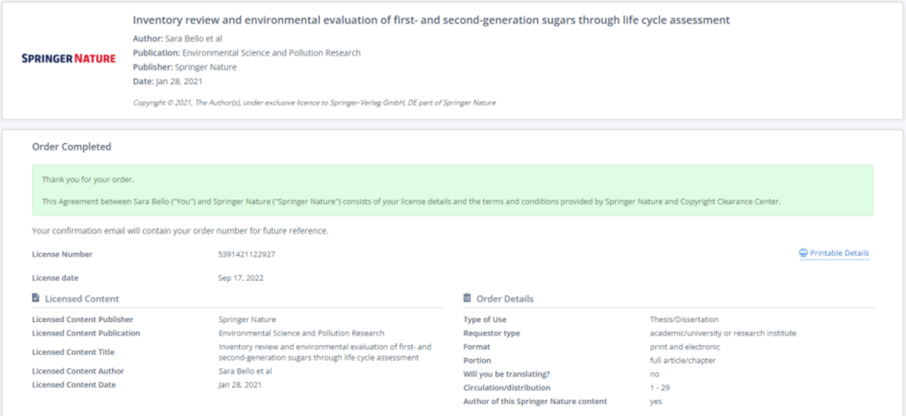

Inventory review and environmental evaluation of first- and second-generation sugars through life cycle assessment

Author: Sara Bello et al
Publication: Environmental Science and Pollution Research
Publisher: Springer Nature
Date: Jan 28, 2021

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Early-stage sustainability assessment of enzyme production in the framework of lignocellulosic biorefinery

Authors: S. Bello[1], N. Pérez[1], J. Kiebist[2], K. Scheibner[2], M.I. Sánchez Ruiz[3], A. Serrano[3], Á.T. Martínez[3], G. Feijoo[1], M.T. Moreira[1]

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Author: Sara Bello,Noelia Pérez,Jan Kiebist,Katrin Scheibner,Maria Isabel Sánchez Ruiz,Ana Serrano,Ángel T. Martínez,Gumersindo Feijoo,Maria Teresa Moreira

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Author contribution: Investigation, writing-original draft, writing-review and editing, visualization, formal analysis, conceptualization

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Renewable carbon opportunities in the production of succinic acid applying attributional and consequential modelling

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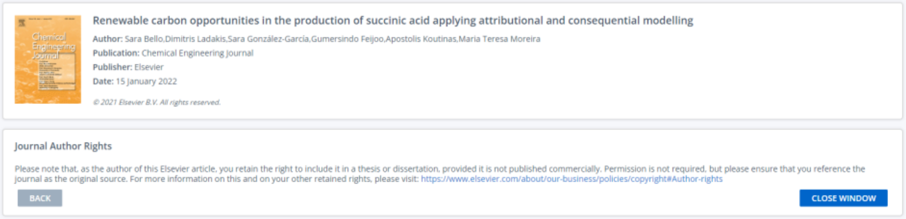

Renewable carbon opportunities in the production of succinic acid applying attributional and consequential modelling

Author: Sara Bello,Dimitris Ladakis,Sara González-García,Gumersindo Feijoo,Apostolis Koutinas,Maria Teresa Moreira

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BOOK CHAPTERS

S. Bello, G. Feijoo, M.T. Moreira, Energy Footprint of Biorefinery Schemes, in: S.S. Muthu (Ed.), Energy Footprints Bio-Refinery, Hotel Build. Sect. Environ. Footprints Eco-Design Prod. Process., Springer, Singapore, 2019: pp. 1–45. doi:10.1007/978-981-13-2466-6_1.

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M. T. Moreira, S. Bello, G. Feijoo. ‘Embedding the production of HMF into the biorefinery route’. Oral presentation. 7th International Conference on Engineering for Waste and Biomass Valorisation (WasteEng), July 2nd- 5th, 2018, Prague.

S. Bello, P. Méndez-Trelles, E. Rodil, G. Feijoo, M. T. Moreira. ‘Toward the improved sustainability of bioplastics: process modelling and life cycle assessment of an FDCA production route’. Oral presentation. 13th International Chemical and Biological Engineering Conference, October 2nd- 4th 2018, Aveiro.

S. Bello, I. Salim, G. Feijoo, M. T. Moreira. ‘Heterogeneous acid-catalysis for the production of furan-derived compounds from renewable carbohydrates: a life cycle approach’. Oral presentation. 4th Iberoamerican Congress on Biorefineries, October 24th- 26th 2018, Jaén.

S. Bello, I.Salim, P. Méndez-Trelles, G. Feijoo, M. T. Moreira. ‘Process modelling and life cycle assessment of furandicarboxylic acid as a precursor for bioplastics’. Oral presentation. 4th Iberoamerican Congress on Biorefineries, October 24th- 26th 2018, Jaén.

M. T. Moreira, S. Bello, L. Lijó, G. Feijoo. ‘Putting Responsible Research and Innovation (RRI) in practice: the case of the iFermenter project’. Oral presentation. 14th Conference on sustainable development of energy, water and environment systems (SDEWES), October 1st- 6th 2019, Dubrovnik.

S. Bello, I. Salim, G. Feijoo, M. T. Moreira. ‘Environmental evaluation of first- and second-generation sugars through Life Cycle Assessment methodology’. Oral presentation and archival paper. 14th Conference on sustainable development of energy, water and environment systems (SDEWES), October 1st- 6th 2019, Dubrovnik.

I. Salim, S. Bello, G. Feijoo, M. T. Moreira. ‘Identifying new sugar sources and their environmental impacts’. Oral presentation. 2nd International Conference ADAPTtoCLIMATE, June 24th- 25th 2019, Crete.

S. Bello, S. González, G. Feijoo, M. T. Moreira. ‘Putting Responsible Research and Innovation (RRI) in practice: the case of the WooBAdh project’. Oral presentation. International Conference on Innovation and Circular Economy, March 26th- 27th 2020, Santiago de Compostela.

Á. Galán-Martín, S. Bello, G. Feijoo, M. T. Moreira, G. Guillén-Gosálvez. ‘Bioethanol Production with Carbon, Capture and Storage: Potential as a Carbon-Negative Biofuel and Environmental Implications’. Oral presentation. AIChE Annual Meeting, November 15th- 20th 202

Annex II

Supplementary Information

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A1. Supplementary information Chapter 2

This section includes additional results for the assessment presented in Chapter 2 including sugar cane in Australia as an additional first-generation scenario. This scenario was not included in the main document due to the geographical scope of the system, which extended the scope to outside Europe, possibly increasing uncertainty. For sugarcane, milling allows the extraction of cane juice, which is subsequently clarified. The main co-product is energy in the form of steam, obtained from the incineration of bagasse in a cogeneration unit (Renouf et al., 2008). This section first presents the inventories for each scenario included in the environmental assessment to then include extra figures depicting further results.

A1.1 LIFE CYCLE INVENTORY: INVENTORY DATA

First generation scenarios

Table A1 Inventory for the cultivation of wheat grain (Achten and Acker, 2015)

	Wheat Germany	**Wheat Switzerland**	
Scenario	**A**	**D**	
Inputs	**Value**	**Value**	**Unit**
Occupation	1.4	1.7	m^2·year
Diesel	17	17	g
Seed	29	27	g
Fertilizer (as N)	27	22	g
Fertilizer (as P_2O_5)	8.5	8.5	g
Fertilizer (as K_2O)	20	2	g
Limestone	50	-	g
Pesticides	-	0.5	g
Outputs			
Wheat grain	1	1	kg

Table A2 Life cycle inventory for the production of glucose from wheat

Scenarios A, D					
(Mustafa et al., 2007; Renouf et al., 2008)					
Inputs	**Value**	**Unit**	**Outputs**	**Value**	**Unit**
Wheat	1.51	t	**Products**		
Cooling water	4.27	m^3	Glucose	1	t
Water	5.92	t	Wheat bran	0.26	t
Enzyme (mix)	3	kg	Vital gluten	0.14	t
Sodium hydroxide	10	kg	Gluten feed	0.11	t
Steam	0.32	t	**Emissions**		
Sulfuric acid	3	kg	BOD_5 (to water)	0.2	g
Electricity	946.93	MJ	Wastewater	4.5	m^3
Heat	2181	MJ			

Table A3 Inventory for the cultivation of maize

	Maize Italy	**Maize Belgium**	
Scenario	**B**	**E**	
	(Noya et al., 2015)	(Boone et al., 2016)	
Inputs	**Value**	**Value**	**Unit**
Occupation	0.67	1.0	m^2·year
Diesel	10.47	7.6	g
Seed	1.64	2.7	g
Urea (as N)	4	-	g
Nitrogen (as N)	-	3.5	g
Fertilizer (as P_2O_5)	-	1.7	g
Fertilizer (as K_2O)	-	8.7	g
Solid manure	5.7	-	kg
Pesticides	0.4	0.15	g
Outputs			
Maize grain	1	1	kg

Table A4. Life cycle inventory for the production of glucose from maize

Scenarios B, E					
(Mustafa et al., 2007; Noya et al., 2015; Renouf et al., 2008)					
Inputs	**Value**	**Unit**	**Outputs**	**Value**	**Unit**
Maize grain	1.51	t	**Products**		
Cooling water	4.27	m^3	Glucose	1	t
Lime	0.3	kg	Maize oil	27	kg
Sulphur dioxide	3.06	kg	Gluten feed	268	kg
Sodium hydroxide	282	g	Gluten meal	80	kg
Sodium chloride	65	g	**Emissions**		
Sulfuric acid	0.45	kg	Particulates (to air)	0.7	g
Urea-formaldehyde resin	208	g	BOD_5 (to water)	0.2	g
Cyclohexane	55	g	Chloride (to water)	118.8	g
Chlorine	12	g	Sulphate (to water)	0.2	g
Heat	2181	MJ	SS (to water)	0.7	g
Electricity	934	MJ	Wastewater	4.1	m^3

Table A5. Inventory for the cultivation of sugar beet

	Sugar beet UK	**Sugar beet France**	
Scenario	**C**	**F**	
	(Renouf et al. 2008)	(Muñoz et al. 2013)	
Inputs	**Value**	**Value**	**Unit**
Occupation	0.2	0.12	m^2·year
Diesel	3.8	1.57	g
Seed	0.02	0.02	g
Fertilizer (as N)	2.25	1.21	g
Fertilizer (as P_2O_5)	0.83	0.80	g
Fertilizer (as K_2O)	1.23	1.72	g
Magnesium	0.76	-	g
Sodium	1.81	-	g
Limestone	22	$1.18 \cdot 10^{-3}$	g
Pesticides	0.17	0.03	g
Outputs			
Sugar beet	1	1	kg

Table A6 Life cycle inventory for the production of sugar from sugar beet (Renouf et al., 2008)

Scenarios C, F					
Inputs	**Value**	**Unit**	**Outputs**	**Value**	**Unit**
Sugar beet	6.5	t	Products		
Limestone	150.5	kg	Sucrose	1	t
Sulfuric acid	1.1	kg	Beet pulp	651	kg
Gypsum	6.9	kg	Calcium carbonate	295	kg
Hydrochloric acid	0.16	kg	Residual fraction	1.11	kg
Sulphur dioxide	0.85	kg	**Emissions**		
Soda ash	327	g	BOD_5 (to water)	0.2	g
Formaldehyde	982	g			
Electricity	740	MJ			
Heat	2181	MJ			
Coke	334	MJ			

Table A7 Inventory for the cultivation of wheat grain (Renouf et al., 2008)

Scenario G		
Item	**Amount**	**Units**
Mass inputs from technosphere		
Agricultural land occupation	1.013	ha
Nitrogen fertilizer	166.00	kg
Phosphorous fertilizer	19	kg
Potassium fertilizer	65.00	kg
Sulfur	12.00	kg
Lime	669.00	kg
Pesticide	3.00	kg
Irrigation water	5200	m^3
Diesel in farming	7925.00	MJ
Electricity	6586	MJ
Outputs to technosphere		
Sugarcane	85000.00	kg
Emissions to air		
N_2O	170.20	kg
NO_x	39.00	kg
NH_3	4.50	kg
CH_4	2.90	kg
SOx	1.30	kg
NMVOC	6.50	kg
Emissions to water		
NO_3	46.8	kg
Phosphorous	2.40	kg
Pesticide	37.80	g

Table A8 Life cycle inventory for the production of sugar from sugar cane (Renouf et al., 2008)

Scenario G		
Item	**Amount**	**Units**
Mass inputs from technosphere		
Sugar cane	7000	kg
Coal	70	MJ
Lime (CaO)	3.50	kg
Phosphoric acid	0.28	kg
Flocculant	0.8	g
Outputs to technosphere		
Sucrose	1000.00	kg
LP steam	4200.00	kg
Waste to treatment		
Mud and ash	416	kg
Emissions to air		
N_2O	77.00	g
NO_x	1487.00	g
PM10	827.00	g
CH_4	174.00	g
SOx	621.00	g
NMVOC	1.70	g
Emissions to water		
BOD_5	1.2	g
suspended matter	1.80	g

Second generation scenarios

Table A9 Life Cycle Inventory for the production of glucose from beech wood (Bello et al., 2018; Kautto et al., 2013)

Scenario H					
Inputs	**Value**	**Unit**	**Outputs**	**Value**	**Unit**
Wood	1	t	Lignin	155.3	kg
Water	9.98	t	Glucose	388.5	kg
H_2SO_4	$1.01 \cdot 10^{-2}$	t	Hemicellulose	83.2	kg
Ethanol	3.74	t	CO_2	6.84	kg
Furfural	$1.92 \cdot 10^{-3}$	t			
Ammonia	$6.24 \cdot 10^{-3}$	t			
Cellulase	7.8	kg			
Steam	3.4	GJ			
Electricity	158.4	kWh			

Table A10 Inventory for the silviculture of spruce (González-García et al., 2009a, 2009b)

Scenario I		
Item	***Amount***	***Units***
Inputs from technosphere		
Land use	0.115	ha a
Nitrogen fertilizer	0.215	kg
Energy use in machinery (silvicultural, logging, hauling operations)	187.2	MJ
Chipping	0.0198	h/m3
Outputs to technosphere		
Spruce wood	1	m^3
	400	kg
Emissions to air		
NO_x	1.25	g
N_2O	12.48	g
CH_4	6.72	g
N_2	89.87	g
NH_3	10.09	g
Wood dust	8473.12	g

Table A11 Inventory for the production of glucose from spruce (Moncada et al., 2018)

Scenarios I, L					
Inputs	**Value**	**Unit**	**Outputs**	**Value**	**Unit**
Wood	138.88	t	CO_2	0.13	kg
Water	528.88	t	Wastewater	373.63	m^3
Cooling water	2495	t	Glucose	45.328	t
Sulfuric acid	0.75	t	Furfural	1.51	t
Ethanol	1.25	kg	Lignin	24.12	t
Cellulase	1.25	t	Hemicelluloses	119.95	t
Electricity	1625	MJ	Non-converted solids	108.21	t
Steam	83.47	t			

Table A12 Inventory for the silviculture of eucalyptus (González-García et al., 2012; Morales et al., 2015b)

Scenarios J, K		
Item	**Amount**	**Units**
Mass inputs from technosphere		
Land use	0.0909	ha a
E. globulus stems	22	stems
Diesel	0.68	kg
Petrol	7.78	g
Lubricants	30	g
Herbicide (glyphosate)	87	g
Ternary fertilizer (16%N 8%P_2O_5 12%K_2O)	0.14	kg
Diammonium phosphate (18%N 46%P_2O_5)	1.33	kg
Outputs to technosphere		
Wood chips	1	m^3
	652	kg
Emissions to air		
SO_2	7.26	g
NO_x	40	g
CO_2	2.38	kg
CO	9.17	g
VOC	5.4	g
N_2O	24	g
Pentane	0.24	g
NMVOC	24	mg
CH_4	97	mg
Particulates	0.89	g
N_2	70	g
NH_3	59	g
Emissions to water		
NO_3^-	1.51	kg
PO_4^-	12	g

Table A13 Inventory for the production of sugars from eucalyptus through dilute acid pretreatment (Kuo and Yu, 2020)

Scenario J		
Item	***Amount***	***Units***
Mass inputs from technosphere		
Ammonia	5.65	kg
Eucalyptus wood (dry basis)	1	kg
Enzyme	3.15	kg
Sulfuric acid	12.24	kg
Water	1318.88	kg
Transport, lorry	100	km
Energy inputs from technosphere		
Electricity	5.10	kWh
Steam	1746.01	kg
Cooling water	15443.57	kg
Outputs to technosphere		
C5+C6 mixed solution	416.10	kg
Waste to treatment		
Bio- solid waste (as municipal solid waste)	188.76	kg

Table A14 Inventory for the production of sugars from eucalyptus through dilute acid pretreatment (Kuo and Yu, 2020)

Scenario K		
Item	***Amount***	***Units***
Mass inputs from technosphere		
Eucalyptus wood (dry basis)	1	kg
enzyme	3.15	kg
Sulfuric acid	12.24	kg
Water	2300.96	kg
Ca $(OH)_2$	9.306	kg
Energy inputs from technosphere		
Electricity	5.64	kWh
Steam	2877.44	kg
Cooling water	6578.58	kg
Outputs to technosphere		
C6	328.5	kg
C5	52.56	kg
Waste to treatment		
Bio- solid waste (as municipal solid waste)	188.76	kg
Emissions to water		
Sugar losses	24.966	kg

Table A15 Inventory for silviculture of birch wood (Kuka et al., 2020)

Scenario M		
Item	***Amount***	***Units***
Inputs from technosphere (materials)		
Land use	1761.0	m^2a
Gasoline use in machinery	0.449	kg
Lubricant use in machinery	0.088	kg
Diesel use in machinery	2.008	kg
Outputs to technosphere		
Birch wood	1	m^3
	470	kg
Emissions to air		
CO_2 (biogenic)	190	kg
BC	0.26	g
CH_4	2.007	g
CO	83.1	g
CO_2	6.75	kg
N_2O	0.2811	g
NH_3	0.0164	g
NMVOC	27.5	g
NO_x	6.91	g
PM_{10}	0.796	g
$PM_{2.5}$	0.796	g
TSP	0.80	g
SO_2	857	mg
Lead	0.0328	g
Cadmium	0.0212	mg
Copper	3.6	mg
Chromium	0.106	mg
Nickel	0.148	mg
Selenium	0.0212	mg
Zinc	2.12	mg
Benz(a)anthracene	169	µg
Benzo(a)pyrene	64.5	µg
Chrysene	418	µg
Wood dust	8473.12	g
Emissions to soil		
Lubricant	0.067	kg

Table A16 Production of sugars from birch through organosolv-steam explosion hybrid pretreatment (Mesfun et al., 2019)

	Scenario M	
Item	***Amount***	***Units***
Mass inputs from technosphere		
Birch wood	$4.42\cdot10^{8}$	kg
Ethanol makeup	$2.00\cdot10^{6}$	kg
Sulfuric acid	$4.00\cdot10^{6}$	kg
Enzymes	$1.90\cdot10^{7}$	kg
Water	$6.73\cdot10^{8}$	kg
Nutrients	$1.00\cdot10^{6}$	kg
Yeast	$5.00\cdot10^{5}$	kg
Outputs to technosphere		
Hemicellulose syrup	$2.80\cdot10^{7}$	kg
Lignin	$8.10\cdot10^{7}$	kg
Ethanol	$6.10\cdot10^{7}$	kg
Waste to treatment		
Wastewater	$1.74\cdot10^{9}$	kg
Emissions to air		
CO_2	$5.20\cdot10^{7}$	kg

Table A17 Inventory for silviculture of pine wood (Kuka et al., 2019)

Scenario N		
Item	**Amount**	**Units**
Inputs from technosphere (materials)		
Land use	2427.00	m^2a
Gasoline use in machinery	0.037	kg
Lubricant use in machinery	0.067	kg
Diesel use in machinery	1.99	kg
Outputs to technosphere		
Birch wood	1	m^3
	380	kg
Emissions to air		
CO_2 (biogenic)	119	kg
BC	0.41	g
CH_4	0.83	g
CO	40.3	g
CO_2	6.46	kg
N_2O	0.28	g
NH_3	0.016	g
NMVOC	12.2	g
NO_x	7.35	g
PM_{10}	0.89	g
$PM_{2.5}$	0.89	g
TSP	0.89	g
SO_2	1494	mg
Lead	0.025	g
Cadmium	0.020	mg
Copper	3.45	mg
Chromium	0.10	mg
Nickel	0.14	mg
Selenium	0.020	mg
Zinc	2.03	mg
Benz(a)anthracene	162	µg
Benz(o)fluoranthene	101	µg
Dibenzo(a,h)anthracene	20.3	µg
Benzo(a)pyrene	61.2	µg
Chrysene	404	µg
Fluoranthene	913	µg
Phenanthrene	5023	µg
Emissions to soil		
Lubricant	0.054	kg

Table A18 Inventory for the production of sugars from pine through reductive catalytic fractionation (Liao et al., 2020; Snowden-Swan et al., 2016; Tschulkow et al., 2020)

Scenario N		
Item	**Amount**	**Units**
Mass inputs from technosphere		
Pine wood	18750	kg
methanol	1092.85	kg
hydrogen	181.32	kg
nitrogen	11.25	kg
Ru/C-Catalyst	0.17	kg
Dichloromethane	225.27	kg
n-hexane	18.11	kg
water	0.14	kg
HP steam	1021.9	kWh
MP steam	1351.59	kWh
Heating	1353.1	kWh
cooling	3428.74	kWh
Outputs to technosphere		
Oligomers	1771.91	kg
Monomers	1081.24	kg
Sugar pulp	13797.28	kg
Waste to treatment		
wastewater (with organics)	3332.15	kg
Emissions to air		
H_2	1584.97	kg
CH_4	8.1	kg
C_2H_4	0.28	kg
C_3H_6	0.12	kg

Table A19 Inventory for silviculture of poplar wood (González-García et al., 2010)

Scenario O		
Item	**Amount**	**Units**
Inputs from technosphere (materials)		
Land use	$6.94\cdot10^{-5}$	ha a
Fertilizer (9N/18P/27K)	$5.79\cdot10^{-6}$	kg
Ammonium nitrate 33%	$2.41\cdot10^{-6}$	kg
Glyphosate	$1.93\cdot10^{-8}$	L
Methyl pirimiphos (insecticide)	$4.82\cdot10^{-9}$	L
Propineb (fungicide)	$2.41\cdot10^{-9}$	L
Machinery (operating rate)	$9.54\cdot10^{-8}$	h
Diesel use in machinery	$1.67\cdot10^{-6}$	kg
Chipping	$4.4\cdot10^{-5}$	h
Outputs to technosphere		
Poplar wood	$2.2\cdot10^{-3}$	m^3
	1	kg
Emissions to air		
N_2O	$1.44\cdot10^{-8}$	g
NH_3	$4.80\cdot10^{-8}$	kg
NO_x	$4.80\cdot10^{-8}$	g
Wood dust	18.62	g

Table A20 Inventory for the production of sugars from poplar through ionic liquids (Baral and Shah, 2012; Righi et al., 2011)

Scenario O		
Item	**Amount**	**Units**
Mass inputs from technosphere		
Poplar wood	$4.47\cdot10^{4}$	kg
Ionic liquid	$2.29\cdot10^{4}$	kg
Enzyme (cellulase)	360.48	kg
Tripotassium phosphate (40%)	16118.0913	kg
Water	92820.4726	kg
Net external energy	$7.62\cdot10^{3}$	kwh
Electricity	$2.59\cdot10^{3}$	kwh
Heating energy/cooling energy	$5.02\cdot10^{3}$	kwh
Outputs to technosphere		
Hemicellulose solution	$9.44\cdot10^{4}$	kg
Glucose and xylose (main product)	$2.29\cdot10^{4}$	kg
Waste to treatment		
Wastewater	$5.96\cdot10^{4}$	kg

Table A21 Range of sugar costs and references

Scenario	Production cost (€/ton)		Reference
	Minimum	Maximum	
A	121	500	(Entwistle et al., 1998; Salim et al., 2019)
B	186	280	(Cheng et al., 2019a)
C	178	331	(Cheng et al., 2019a)
D	121	500	(Salim et al., 2019)
E	186	280	(Cheng et al., 2019a)
F	178	331	(Cheng et al., 2019a)
G	339	390	(Cheng et al., 2019a)
H_1	218	257	(Laure et al., 2014)
H_2	200	1500	(Laure et al., 2014; Mountraki et al., 2017)
I_1	300	567.8	(Cheng et al., 2019a; Moncada et al., 2018)
I_2	200	1500	(Laure et al., 2014; Mountraki et al., 2017)
J	262.7	288.1	(Kuo and Yu, 2020)
K_1	322.03	347.46	(Kuo and Yu, 2020)
K_2	200	1000	(Kuo and Yu, 2020)
L	200	1000	(Laure et al., 2014; Mesfun et al., 2019)
M	200	1000	(Laure et al., 2014; Mesfun et al., 2019)
N	218	404	(Laure et al., 2014; Liao et al., 2020)
O_1	389.8	8000	(Baral and Shah, 2012)
O_2	242	4605	(Laure et al., 2014; Mesfun et al., 2019)

Table A22 Mass and economic allocation factors for scenario G, sugar production from sugar cane in Australia

Scenario	Products	Quantity	Mass allocation	Price	Revenue	Economic allocation
		(kg)	(%)	(€/kg)	(€)	(%)
G	Sucrose	1000	19%	0.36	364.41	94%
Sugar cane	Steam	4200	81%	0.0056	23.53	6%

A1.2 LIFE CYCLE ASSESSMENT: ENVIRONMENTAL RESULTS

The attributional results from remaining impact categories in the midpoint ReCiPe methodology are presented in subsequent Figure A1 and Figure A2. Due to the relevance of sugar cane in the sugars industry, results including a sugar cane scenario are included in the figures in this document.

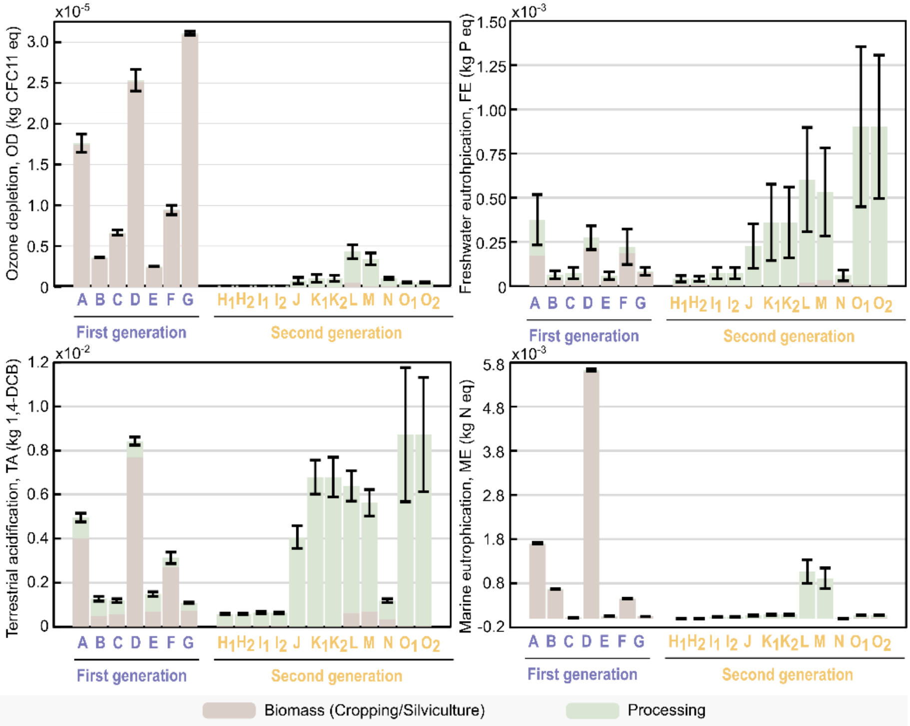

Figure A1 Environmental impact in ozone depletion (OD), terrestrial acidification (TA), freshwater eutrophication (FE) and marine eutrophication (ME) impact categories per kg of sugar produced at the gate of the system and standard deviations obtained through Monte Carlo simulation of the inventoried data for each scenario assessed. Scenarios A-G include first generation biomass processing and scenarios H_1-O_2 include second generation biomass processing.

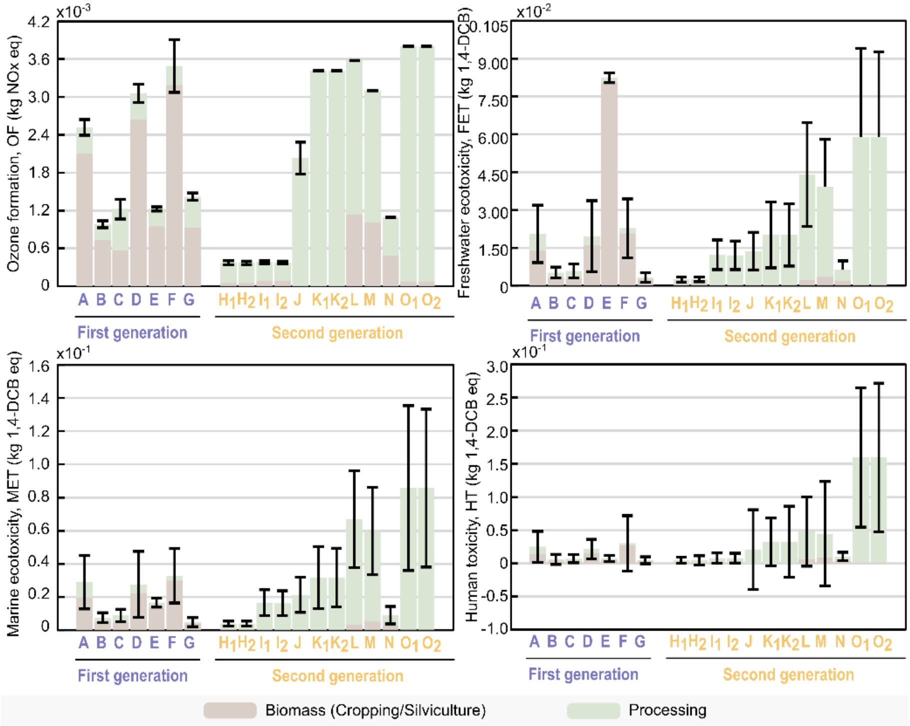

Figure A2 Environmental impact in ozone formation (OF), freshwater ecotoxicity (FET), marine ecotoxicity (MET) and human toxicity (HT) impact categories per kg of sugar produced at the gate of the system and standard deviations obtained through Monte Carlo simulation of the inventoried data for each scenario assessed. Scenarios A-G include first generation biomass processing and scenarios H_1-O_2 include second generation biomass processing.

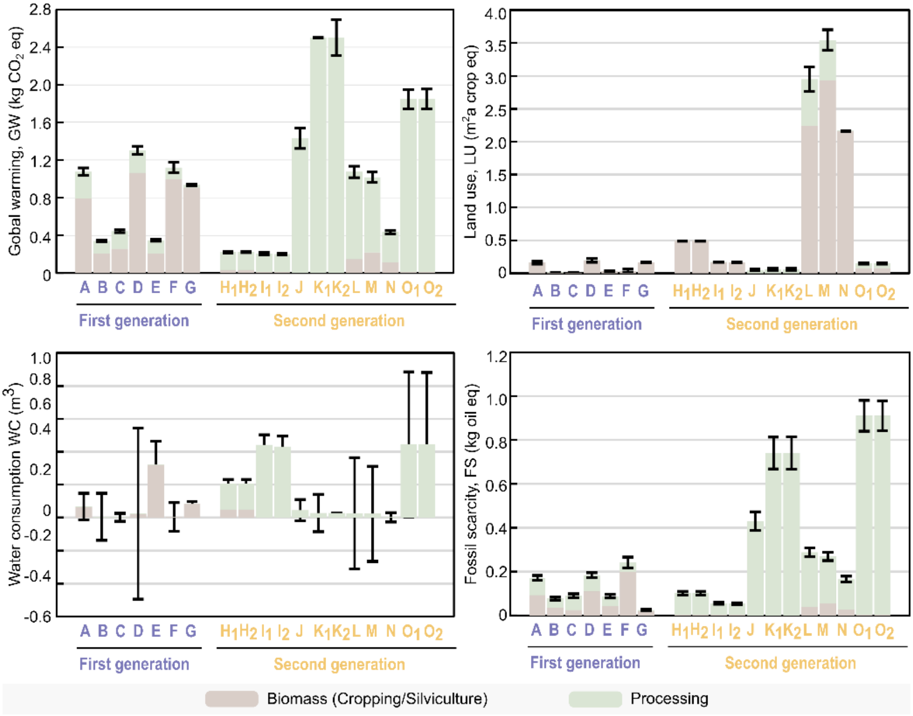

Figure A3 Environmental impact in global warming (GW), water consumption (WC), land use (LU) and fossil scarcity (FS) impact categories per kg of sugar produced (including sugar cane) at the gate of the system and standard deviations obtained through Monte Carlo simulation of the inventoried data for each scenario assessed. Scenarios A-G include first generation biomass processing and scenarios H_1-O_2 include second generation biomass processing**.**

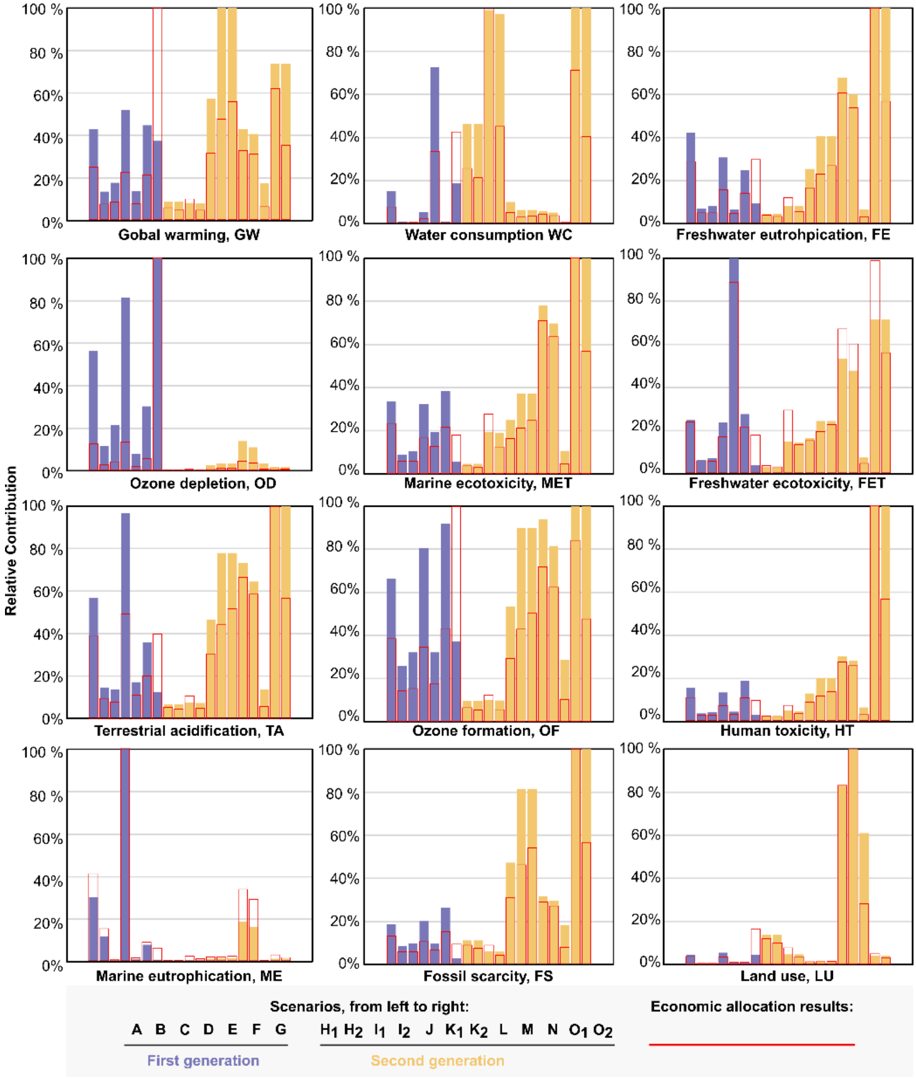

Figure A4 Comparative environmental profiles (in %) per kg of sugars produced from first (scenarios A-G) and second generation (scenarios H1-O2) biomass considering mass allocation and economic allocation (outlined results in red) for global warming (GW), water consumption (WC), freshwater eutrophication (FE), ozone depletion (OD), marine ecotoxicity (MET), freshwater ecotoxicity (FET), terrestrial acidification (TA), ozone formation (OF), human toxicity (HT), marine eutrophication (ME), fossil scarcity (FS) and land use (LU).

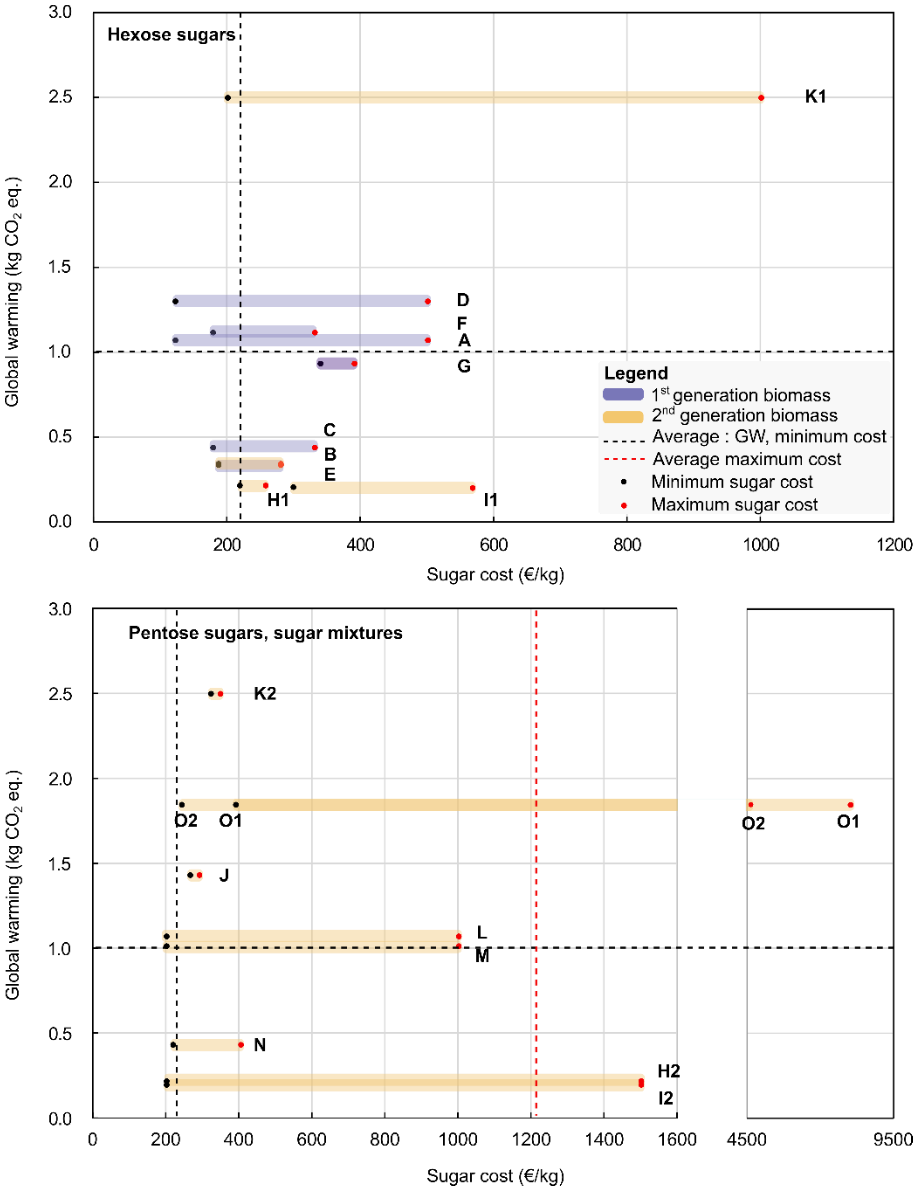

Figure A5 Ecoefficiency indicator as function of global warming (GW) for the environmental performance and range of sugar costs (€/kg) for first generation (A-G) and second generation (H1-O2) scenarios.

A2. Supplementary information Chapter 3

A2.1 LIFE CYCLE INVENTORIES

The inventories utilized for the modelling of the system analyzed in Chapter 3 are provided in this section.

Table A23 Inventory for feedstock related activities. Inventory is presented with economic allocation to SS0.1 and SS0.2

SS0.1 Forest activities		
Inputs from technosphere		
Diesel	1.03	kg
N-mineral fertilizer	0.15	kg
Outputs to environment		
N_2	13.54	g
NH_3	1.85	g
NO_x	2.50	g
SS0.2 Sawmill		
Inputs from process		
Roundwood from SS0.1	0.71	m^3
Inputs from technosphere		
Water	244.38	kg
Lubricating oil	0.09	kg
Steel (packaging)	0.11	kg
Polyethylene (HDPE)	0.16	kg
Inorganic chemicals (pretreatment)	22.11	g
Organic chemicals (solvent)	0.66	g
Electricity	19.18	kwh
Outputs to environment		
Heat	422.63	MJ
CO_2	30.76	kg
CO	15.67	g
NO_x	34.79	g
Particulates	14.98	g
SO_2	0.82	g
Municipal solid waste	1.50	kg
Outputs to technosphere		
Bark chips	0.10	m^3
Sawn timber	0.41	m^3
SS0.3 Chipping		
Inputs from process		
Residual wood from SS0.1	1.28	m^3
Inputs from technosphere		
Electricity	2.30	kwh
Outputs to SS1		
Residual wood chips	1.25	m^3

Table A24 (Part I) Global inventory for the lignocellulosic biorefinery considering all possible subsystems for the functional unit (1 t/h dry wood chips)

SS1 Pulping		
Inputs from technosphere		
Water (pulping)	3.72	t
Water (washing)	4.56	t
Sulfuric acid	$1.01\cdot10^{-2}$	t
Ethanol (pulping)	3.74	t
Transport, freight, lorry (16-32 metric ton)	105	tkm
High pressure steam	1.97	GJ
Electricity (pulping)	$7.80\cdot10^{-2}$	MWh
SS2 Solvent recovery		
Inputs from technosphere		
Water (dilution)	1.02	t
Natural gas	$5.40\cdot10^{-3}$	t
Low pressure steam	0.77	GJ
Electricity	$6.00\cdot10^{-2}$	MWh
Outputs to technosphere		
Lignin	0.16	t
SS3 Hemicellulose conditioning		
Inputs from technosphere		
Furfural (makeup)	$1.92\cdot10^{-3}$	t
Ammonia	$6.24\cdot10^{-3}$	t
Low pressure steam	0.36	t
High pressure steam	0.21	GJ
SS4 Enzymatic hydrolysis		
Inputs from technosphere		
Enzyme (cellulase)	$7.80\cdot10^{-3}$	t
Electricity	$2.04\cdot10^{-2}$	MWh
Low pressure steam	$9.12\cdot10^{-2}$	GJ
Cellulase production (7.8 kg)		
Inputs from technosphere		
Corn steep liquor	4.53	kg
Ammonia	0.61	kg
Water	577.74	kg
Nutrients	2.48	kg
Heat	37.90	MJ
Electricity	81.84	MJ
Outputs to environment		
N_2	$2.16\cdot10^{3}$	kg
O_2	$6.56\cdot10^{3}$	kg
CO_2	$1.10\cdot10^{3}$	kg

(Part II) Global inventory for the lignocellulosic biorefinery considering all possible subsystems for the functional unit (1 t/h dry wood chips)

SS5. Cogeneration unit		
Inputs from technosphere		
Water	0.68	t
Sludge (from WWT)	$5.78\cdot10^{-2}$	t
Biogas (from WWT)	$4.27\cdot10^{-2}$	t
Natural gas	$2.26\cdot10^{-2}$	t
Outputs to environment		
CO_2	6.84	kg
Water (vapor)	108.84	kg
SS6. Fermentation to bioethanol		
Inputs from technosphere		
Water	0.21	t
Diammonium phosphate	$1.68\cdot10^{-3}$	t
Corn steep liquor	$1.27\cdot10^{-2}$	t
Low pressure steam	1.74	GJ
Electricity	$8.40\cdot10^{-3}$	MWh
Outputs to technosphere		
Bioethanol	0.24	t
Water	0.37	t
Outputs to environment		
CO_2	218.77	kg
O_2	1.44	kg
Wastewater	0.0034	m^3
SS7. Acetic acid recovery		
Inputs from technosphere		
Low pressure steam	0.39	GJ
Electricity	$3.48\cdot10^{-2}$	MWh
TOPO	3.32	kg
Undecane	11.93	kg
Outputs to technosphere		
Acetic acid	$1.56\cdot10^{-2}$	t
Outputs to environment		
TOPO	3.32	kg
Undecane	11.93	kg
SS8. Furfural recovery		
Inputs from technosphere		
Low pressure steam	$2.40\cdot10^{-3}$	GJ
Electricity	$2.40\cdot10^{-2}$	MWh
Outputs to technosphere		
Furfural	$5.28\cdot10^{-3}$	t

A3. Supplementary information Chapter 4

This section includes supplementary information regarding the simulation model of the CO_2 capture process (SS3). Then, the LCA inventory used is provided as well as additional results from Chapter 4.

A3.1 CAPTURE AND COMPRESSION SYSTEM: ASPEN PLUS® FLOWSHEET

The flowsheet of the CCS plant is depicted in Figure S1. The process model was implemented in Aspen Plus® V10 (Aspen Technology Inc., 2017). The thermodynamic package selected for the simulation was Electrolyte NRTL, as recommended by Adams II et al., 2014 (Adams II et al., 2014). The CO_2 flue gas and off-gas from cellulase production are fed to the B-1 blower (polytropic type implementing the ASME method) with a discharge pressure of 1 bar and operating at 61°C. The composition of stream 2 to the absorber is 12% wt. CO_2, 9% wt. H_2O, 12% wt. O_2 and 67% wt. N_2.

The absorption column (A-1) was modelled with a *Radfrac* block with azeotropic convergence and 10 stages. The model for the column is thermodynamic-based (rather than rate-based), as recommended in the literature (Øi, 2012). The feed streams are fed in stage 1 (fresh makeup water and recirculated monoethanolamine, MEA), and stage 10 for the flue gas stream. The clean gas, rich in O_2 and N_2, exits through the first stage of the column (top of the column), at a flow rate of 5559 kg/h.

The solvent, rich in CO_2, is pumped through the heat exchanger HX1A to reach an output temperature of 80°C. The flow is circulated to the stripping section of the plant, in which S-1 allows to separate the MEA solvent from the CO_2. The lean MEA solvent is recirculated to the absorber A-1 through the heat exchangers HX1B and HX2. In the stripping section, S-1 was simulated with a *Radfrac* block, with a (partial) condenser and a kettle reboiler. The column, consisting of 11 stages and implementing a reflux ratio of 0.5, allows separating the CO_2 and water fractions from N_2 and O_2.

Stream 14 continues to the compression section of the flowsheet. In this section, the stream is compressed according to the specifications for pipeline transport and injection (110 bar and 50°C). Block F-1 is a flash operating at 30°C and 1 bar. The liquid stream from the bottom of the column is mostly pure water, while the vapor stream from the top of the flash contains CO_2 stream (stream 15) with a purity of 98.2% wt.

The first compressor in the sequence, C-1, reaches a discharge pressure of 3.24 bar, raising the temperature to 135.3°C. In the flash F-2, the operating conditions are 3.24 bar and 30°C, which favor water separation. In stream 18, the water content is reduced to 0.56% wt. The second compressor, C-2 increases the pressure to 10.5 bar and 137.6°C. The subsequent flash unit, F-3, which reduces the temperature back to 30°C, decreases the water content in the CO_2 stream to 0.19% wt. The third compression stage reaches 34 bar, while the flash F-4 decreases the temperature to 139.1°C at the compressor outlet. The water content in stream 24 was reduced to 0.08% wt. The final compression stage allows reaching 110 bar and a temperature of 143.4°C. The stream is cooled in the heat exchanger HX-3 to the required 50°C (supercritical conditions for CO_2). For all compressors, an isentropic efficiency of 80% was considered.

Regarding the energy requirements of the flowsheet, the main utilities are low pressure steam and cooling water. Cooling water is pumped in a closed circuit and passed through a cooling tower for its regeneration (pressure difference).

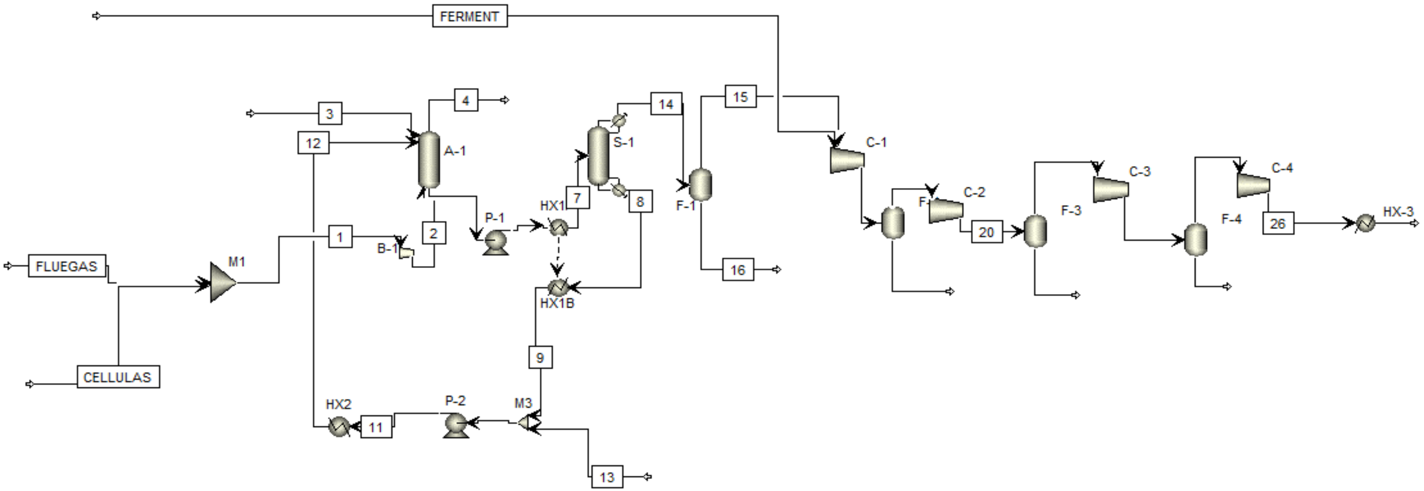

Figure A6. CO$_2$ capture and compression system flowsheet

Table A25 Mass balance results and stream conditions for SS3 CO_2 capture and compression (Part I)

Stream	**1**	**2**	**3**	**4**	**5**	**6**	**7**	**8**	**9**	**10**
From	**M1**	**B-1**		**A-1**	**A-1**	**P-1**	**HX1A**	**S-1**	**HX1B**	**M3**
To	**B-1**	**A-1**	**A-1**		**P-1**	**HX1A**	**S-1**	**HX1B**	**M3**	**P-2**
Temperature (°C)	55.1	61.2	37.0	38.1	69.2	69.2	80.0	106.4	92.5	92.5
Pressure (bar)	1.0	1.1	1.1	1.0	1.1	1.1	1.1	1.1	1.1	1.0
Mass Enthalpy (kcal/kg)	-524.9	-523.3	-3779.9	-117.4	-2930.8	-2930.8	-2922.1	-2689.5	-2701.1	-2701.1
Mass Density (kg/m^3)	1.0	1.1	993.4	1.1	945.9	945.9	937.2	925.0	937.7	937.7
Mass flow (kg/h)	6733.7	6733.7	4579.0	5559.0	23678.2	23678.2	23678.2	17923.3	17923.3	17924.5
CO_2	798.1	798.1	0.0	0.3	1405.2	1405.2	1405.2	607.5	607.5	607.5
H_2O	586.0	586.0	4579.0	208.6	15704.0	15704.0	15704.0	10747.5	10747.5	10747.5
O_2	840.7	840.7	0.0	840.7	0.0	0.0	0.0	0.0	0.0	0.0
N_2	4508.9	4508.9	0.0	4508.8	0.1	0.1	0.1	0.0	0.0	0.0
MEA	0.0	0.0	0.0	0.5	6568.9	6568.9	6568.9	6568.3	6568.3	6569.5
Mass Fractions										
CO_2	0.12	0.12	0.00	0.00	0.06	0.06	0.06	0.03	0.03	0.03
H_2O	0.09	0.09	1.00	0.04	0.66	0.66	0.66	0.60	0.60	0.60
O_2	0.12	0.12	0.00	0.15	0.00	0.00	0.00	0.00	0.00	0.00
N_2	0.67	0.67	0.00	0.81	0.00	0.00	0.00	0.00	0.00	0.00
MEA	0.00	0.00	0.00	0.00	0.28	0.28	0.28	0.37	0.37	0.37

Table A26 Mass balance results and stream conditions for SS3 CO_2 capture and compression (Part II)

Stream	**11**	**12**	**13**	**14**	**15**	**16**	**17**	**18**	**19**	**20**
From	**P-2**	**HX2**		**S-1**	**F-1**	**F-1**	**C-1**	**F-2**	**F-2**	**C-2**
To	**HX2**	**A-1**	**M3**	**F-1**	**C-1**		**F-2**	**C-2**		**F-3**
Temperature (°C)	92.4	37.0	37.0	98.0	30.0	30.0	135.3	30.0	30.0	137.6
Pressure (bar)	1.1	1.1	1.0	1.0	1.0	1.0	3.2	3.2	3.2	10.5
Mass Enthalpy (kcal/kg)	-2701.1	-2745.8	-1054.8	-3029.9	-2155.3	-3784.4	-2128.4	-2139.4	-3780.4	-2116.7
Mass Density (kg/m^3)	937.7	980.1	1010.1	0.6	1.7	995.0	4.1	5.7	993.4	13.7
Mass flow (kg/h)	17924.5	17924.5	0.5	5754.9	805.7	4949.2	1028.9	1017.0	11.9	1017.0
CO_2	607.5	607.5	0.0	797.7	791.0	6.7	1009.8	1009.7	0.0	1009.7
H_2O	10747.5	10747.5	0.0	4956.4	14.6	4941.9	17.6	5.7	11.9	5.7
O_2	0.0	0.0	0.0	0.0	0.0	0.0	1.5	1.5	0.0	1.5
N_2	0.0	0.0	0.0	0.1	0.1	0.0	0.1	0.1	0.0	0.1
MEA	6569.5	6569.5	0.5	0.7	0.0	0.7	0.0	0.0	0.0	0.0
Mass Fractions										
CO_2	0.03	0.03	0.00	0.14	0.98	0.00	0.98	0.99	0.00	0.99
H_2O	0.60	0.60	0.00	0.86	0.02	1.00	0.02	0.01	1.00	0.01
O_2	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
N_2	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
MEA	0.37	0.37	1.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00

Table A27 Mass balance results and stream conditions for SS3 CO_2 capture and compression (Part III)

Stream	**21**	**22**	**23**	**24**	**25**	**26**	**27**	**cellulas**	**ferment**	**fluegas**
From	**F-3**	**F-3**	**C-3**	**F-4**	**F-4**	**C-4**	**HX-3**			
To	**C-3**		**F-4**	**C-4**		**HX-3**		**M1**	**C-1**	**M1**
Temperature (°C)	30.0	30.0	139.1	30.0	30.0	143.4	50.0	32.0	24.0	70.0
Pressure (bar)	10.5	10.5	34.0	34.0	34.0	110.0	110.0	1.0	1.0	1.0
Mass Enthalpy (kcal/kg)	-2136.8	-3767.0	-2115.1	-2140.9	-3733.5	-2122.3	-2166.3	-11.0	-2138.5	-896.7
Mass Density (kg/m^3)	19.3	988.7	46.4	72.2	977.5	172.2	478.6	1.1	1.8	1.0
Mass flow (kg/h)	1013.1	3.9	1013.1	1012.0	1.1	1012.0	1012.0	2826.8	223.2	3907.0
CO_2	1009.7	0.0	1009.7	1009.6	0.0	1009.6	1009.6	16.7	218.8	781.4
H_2O	1.9	3.8	1.9	0.8	1.1	0.8	0.8	0.0	3.0	586.0
O_2	1.5	0.0	1.5	1.5	0.0	1.5	1.5	723.5	1.4	117.2
N_2	0.1	0.0	0.1	0.1	0.0	0.1	0.1	2086.5	0.0	2422.3
MEA	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
Mass Fractions										
CO_2	1.00	0.01	1.00	1.00	0.03	1.00	1.00	0.01	0.98	0.20
H_2O	0.00	0.99	0.00	0.00	0.97	0.00	0.00	0.00	0.01	0.15
O_2	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.26	0.01	0.03
N_2	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.74	0.00	0.62
MEA	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00

A3.2 SELECTION OF HEATING SOURCE

Heat from natural gas was selected as a generic heating source used in industry. It was selected to provide a range of results going from a heating source that was fossil-based (a plausible worse-case scenario) to a biobased heating source, which was were heating from sugar cane bagasse came into place. Sugar cane bagasse was selected because -considering the availability of data in the used database, ecoinvent- the heating from SG was the most restrictive scenario (i.e., higher impacts in the global warming category when compared to heating from sorghum or heating with wood chips as shown in Figure A7).

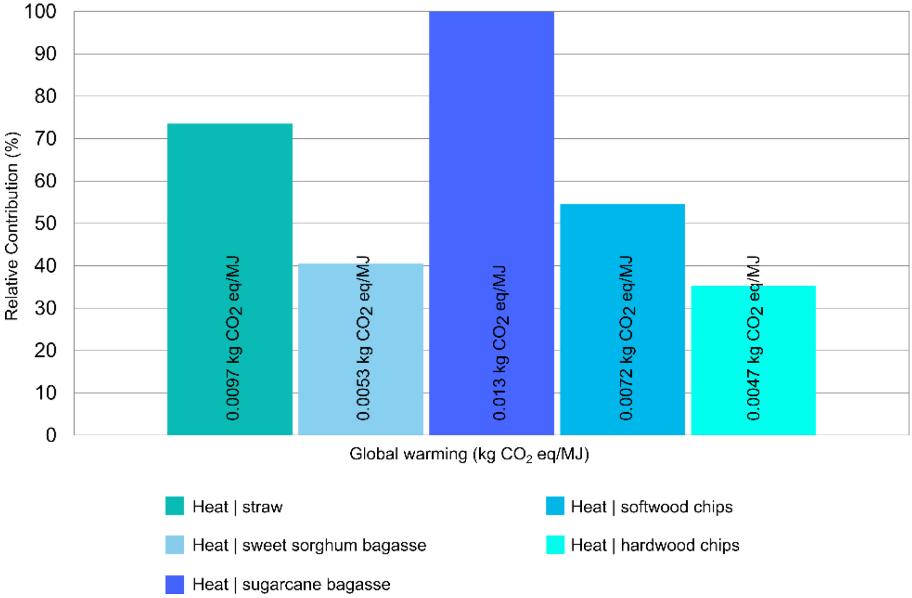

Figure A7 Global warming impact with ReCiPe 1.1 and ecoinvent 3.5 database processes comparing heat (1 MJ) from straw, sweet sorghum bagasse, sugarcane bagasse, softwood chips and hardwood chips

A3.3 ADDITIONAL DATA FOR THE LCA

Table A28 through Table A32 display the life cycle inventories for the subsystems in our study used for the environmental evaluation. Table A33 presents the carbon balance of the system.

Table A28 Inventory for silviculture and sawmilling activities per kilogram of bioethanol produced in the biorefinery. An economic allocation was considered for this inventory (González-García et al., 2014; Laschi et al., 2016)

SS1. Feedstock		
Input	Quantity	Unit
Diesel	$4.39\cdot10^{-3}$	kg
N fertilizer	$6.48\cdot10^{-4}$	kg
Tap water	$4.26\cdot10^{-1}$	kg
Lubricating oil	$1.55\cdot10^{-4}$	kg
Steel	$1.90\cdot10^{-4}$	kg
Polyethylene	$2.86\cdot10^{-4}$	kg
Sheet rolling	$1.90\cdot10^{-4}$	kg
Inorganic chemicals (pretreatment)	$3.85\cdot10^{-2}$	g
Organic chemicals (solvent)	$1.15\cdot10^{-3}$	g
Electricity	$3.34\cdot10^{-2}$	kWh
Output	Quantity	Unit
Emissions to air		
N_2	$5.75\cdot10^{-2}$	g
NH_3	$7.89\cdot10^{-3}$	g
NO_x	$7.12\cdot10^{-2}$	g
CO_2	$5.37\cdot10^{-2}$	kg
CO	$2.73\cdot10^{-2}$	g
Particulates	$2.61\cdot10^{-2}$	g
SO_2	$1.42\cdot10^{-3}$	g
Heat	$7.37\cdot10^{-1}$	MJ
Waste to treatment		
Municipal solid waste	$2.60\cdot10^{-3}$	kg

Table A29 Inventory for Organosolv-based biorefinery per kilogram of bioethanol produced (Kautto et al., 2013)

SS2. Biorefinery		
Input	Quantity	Unit
Sulfuric acid	$4.30 \cdot 10^{-2}$	kg
Ethanol	$2.15 \cdot 10^{-2}$	kg
Tap water	$2.76 \cdot 10^{-2}$	ton
Transport lorry	$4.48 \cdot 10^{-1}$	tkm
Natural gas	$1.81 \cdot 10^{-1}$	m^3
Ammonia	$2.66 \cdot 10^{-2}$	kg
Cellulase	$3.32 \cdot 10^{-2}$	kg
Digester sludge	$2.47 \cdot 10^{-1}$	kg
Biogas	$2.77 \cdot 10^{-1}$	m^3
Corn steep liquor	$5.42 \cdot 10^{-2}$	kg
Diammonium phosphate	$7.16 \cdot 10^{-3}$	kg
Kerosene	$5.09 \cdot 10^{-2}$	kg
Organic chemical	$1.42 \cdot 10^{-2}$	kg
Output	Quantity	Unit
Ethanol	1	kg
Lignin	$6.61 \cdot 10^{-1}$	kg
Furfural	$1.43 \cdot 10^{-2}$	kg
Acetic acid	$6.44 \cdot 10^{-2}$	kg
Emissions to air		
Water	0.46	kg
O_2	0.01	kg
Waste to treatment		
Wastewater	$1.45 \cdot 10^{-5}$	m^3
Emissions to water		
Organic compounds	$1.41 \cdot 10^{-2}$	kg
Hydrocarbons	$5.09 \cdot 10^{-2}$	kg

Table A30 Inventory for the CO_2 capture and compression plant per kg of ethanol produced (Adams II et al., 2014)

SS3. Capture and compression		
Input	Quantity	Unit
MEA	$1.43 \cdot 10^{-3}$	kg
H_2O	2.71	kg
Pumping electricity	0.15	kWh
Compression electricity	0.40	kWh
Heating	32.58	MJ
Output	Quantity	Unit
Captured CO_2	4.33	kg
Emissions to air		
CO_2	$1.40 \cdot 10^{-2}$	kg
H_2O	5.22	kg
O_2	3.58	kg
N_2	19.22	kg
MEA	$5.06 \cdot 10^{-4}$	kg

Table A31 Inventory for CO_2 transport and injection per km of pipeline and per kg of CO_2 (Wildbolz, 2007)

SS4 Transport and injection: 1 km pipeline		
Input	Quantity	Unit
Occupation, construction site	$3.33\cdot10^{3}$	m^{2}a
Transformation, from forest	$2.00\cdot10^{3}$	m^{2}
Transformation, to heterogeneous, agricultural	$2.00\cdot10^{3}$	m^{2}
Water, unspecified natural origin	$1.87\cdot10^{2}$	m^{3}
Sand, at mine	$4.40\cdot10^{6}$	kg
Diesel, burned in building machine	$3.31\cdot10^{6}$	MJ
Steel, low-alloyed, at plant	$2.70\cdot10^{5}$	kg
Drawing of pipes, steel	$2.70\cdot10^{5}$	kg
Rock wool, packed, at plant	$5.12\cdot10^{3}$	kg
Transport, helicopter	$2.60\cdot10^{1}$	h
Transport, helicopter, LTO cycle	$1.04\cdot10^{1}$	p
Transport, lorry 32t	$3.15\cdot10^{5}$	tkm
Transport, freight, rail	$5.51\cdot10^{4}$	tkm
Output	Quantity	Unit
Waste to treatment		
Disposal, inert waste, 5% water, to inert material landfill	$4.40\cdot10^{6}$	kg
Disposal, steel, 0% water, to inert material landfill	$1.35\cdot10^{5}$	kg
Disposal, mineral wool, to final disposal	$5.12\cdot10^{3}$	kg
SS4 Transport and injection: aquifer unit		
Occupation, industrial area	$9.00\cdot10^{2}$	m^{2}a
Occupation, industrial area, vegetation	$8.10\cdot10^{3}$	m^{2}a
Transformation, from pasture and meadow	$6.00\cdot10^{2}$	m^{2}
Transformation, to industrial area	$6.00\cdot10^{1}$	m^{2}
Transformation to industrial area, vegetation	$5.40\cdot10^{2}$	m^{2}
Drilling, deep borehole for HDR	$3.36\cdot10^{3}$	m
Cement, unspecified, at plant	$1.26\cdot10^{5}$	kg
Gravel, unspecified, at mine	$1.32\cdot10^{6}$	kg
Transport, lorry 28t	$2.89\cdot10^{4}$	tkm
Transport, freight, rail	$1.26\cdot10^{4}$	tkm

Table A32 Inventory for bioethanol use per km travelled in each scenario differing in the fuel blend (Argonne National Laboratory, 2019)

Scenario	**E10**	**E25**	**E40**	**E85**	
Input	Quantity				Units
CO_2 uptake	0.08	0.19	0.31	0.64	kg
Bioethanol	$1.06\cdot10^{-2}$	$2.51\cdot10^{-2}$	$4.03\cdot10^{-2}$	$8.40\cdot10^{-2}$	kg
Gasoline	$5.85\cdot10^{-2}$	$4.59\cdot10^{-2}$	$3.72\cdot10^{-2}$	$9.12\cdot10^{-3}$	kg
Pipeline fraction	$1.16\cdot10^{-12}$	$2.77\cdot10^{-12}$	$4.43\cdot10^{-12}$	$9.24\cdot10^{-12}$	km
Aquifer fraction	$5.80\cdot10^{-11}$	$1.38\cdot10^{-10}$	$2.21\cdot10^{-10}$	$4.61\cdot10^{-10}$	p
Emissions to air					
VOC	$8.36\cdot10^{-2}$	$8.36\cdot10^{-2}$	$8.36\cdot10^{-2}$	$8.36\cdot10^{-2}$	g
CO	$1.7\cdot10^{-3}$	$1.7\cdot10^{-3}$	$1.7\cdot10^{-3}$	$1.7\cdot10^{-3}$	kg
NOx	$7.46\cdot10^{-2}$	$7.46\cdot10^{-2}$	$7.46\cdot10^{-2}$	$7.46\cdot10^{-2}$	g
PM10	$3.4\cdot10^{-3}$	$3.4\cdot10^{-3}$	$3.4\cdot10^{-3}$	$3.4\cdot10^{-3}$	g
PM2.5	$3\cdot10^{-3}$	$3\cdot10^{-3}$	$3\cdot10^{-3}$	$3\cdot10^{-3}$	g
SO_x	$1.23\cdot10^{-3}$	$1\cdot10^{-3}$	0.90	0.37	mg
CH_4	$5.4\cdot10^{-3}$	$5.4\cdot10^{-3}$	$5.4\cdot10^{-3}$	$5.4\cdot10^{-3}$	g
CO_2 biogenic	1.34	$3.35\cdot10^{-2}$	$5.68\cdot10^{-2}$	0.14	kg
CO_2 fossil	0.20	0.19	0.19	0.19	kg
N_2O	$4.7\cdot10^{-3}$	$4.7\cdot10^{-3}$	$4.7\cdot10^{-3}$	$4.7\cdot10^{-3}$	g

Table A33 Carbon balance of the system under study

Inputs		**C Quantity (%)**	**Molecular weight (kg/mol)**	**C (kg)**
C content in beech wood		48.8	$1.20\cdot10^{-2}$	-2.08
Outputs	**Formula**	**Quantity (kg)**	**Molecular weight (kg/mol)**	**C (kg)**
CO_2 ethanol fermentation	CO_2	0.933	$4.40\cdot10^{-2}$	0.25
CO_2 cogeneration	CO_2	3.363	$4.40\cdot10^{-2}$	0.92
Biogenic (Residues)	CO_2	3.099	$4.40\cdot10^{-2}$	0.85
Fossil (Natural gas)	CO_2	0.264	$4.40\cdot10^{-2}$	0.07
CO_2 cellulase	CO_2	0.047	$4.40\cdot10^{-2}$	0.01
Acetic acid	CH_3COOH	0.064	$6.01\cdot10^{-2}$	0.03
Lignin	$C_{11}H_{14}O_4$	0.662	0.21	0.34
Furfural	$C_5H_4O_2$	0.014	$9.61\cdot10^{-2}$	0.01
Bioethanol	C_2H_5OH	1.000	$4.61\cdot10^{-2}$	0.52
Car emissions	CO_2	1.898	$4.40\cdot10^{-2}$	0.52

A3.4 SUPPLEMENTARY RESULTS

Here additional results that were omitted from the main manuscript due to space limitations are provided. These include the breakdown of contributions to the Carbon

Footprint as well as the characterization results as relative contributions per subsystem for scenarios E40 SC, E25 SC, E10 SC, E85 NG, E40 NG, E25 NG (Figure A8-Figure A13). A sensitivity assessment of the pipeline transport distance is included, analyzing the change in the CF impact category (Figure A14). The relative contribution of different first and second-generation biomass feedstocks from the ecoinvent 3.5 database (Wernet et al., 2016) has been included (Figure A15). A sensitivity analysis on the carbon footprint (kg CO_2 eq/km) and benchmark of the heat requirement values using different bibliographic sources is also presented (Figure A16). The impact categories presented in the figures are CF: carbon footprint, OD: ozone depletion, OF: ozone formation, TA: terrestrial acidification, FE: freshwater eutrophication, ME: marine eutrophication, FET: freshwater ecotoxicity, MET: marine ecotoxicity, HT: human toxicity, FS: fossil resource scarcity.

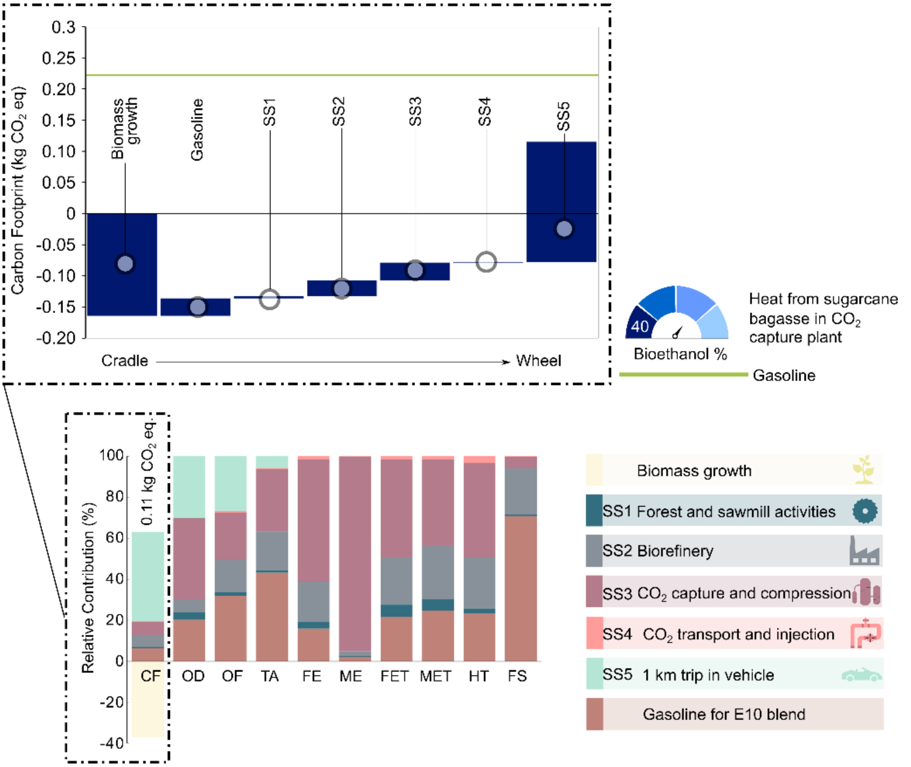

Figure A8 Breakdown of contributions to the Carbon Footprint for scenario E40 SC and environmental profiles (bar-graph plots) displaying characterization results for 1 km travelled in an E40 ethanol (40%) and gasoline (60%)-fueled vehicles in which heat from sugarcane bagasse is used in the CO_2 capture plant.

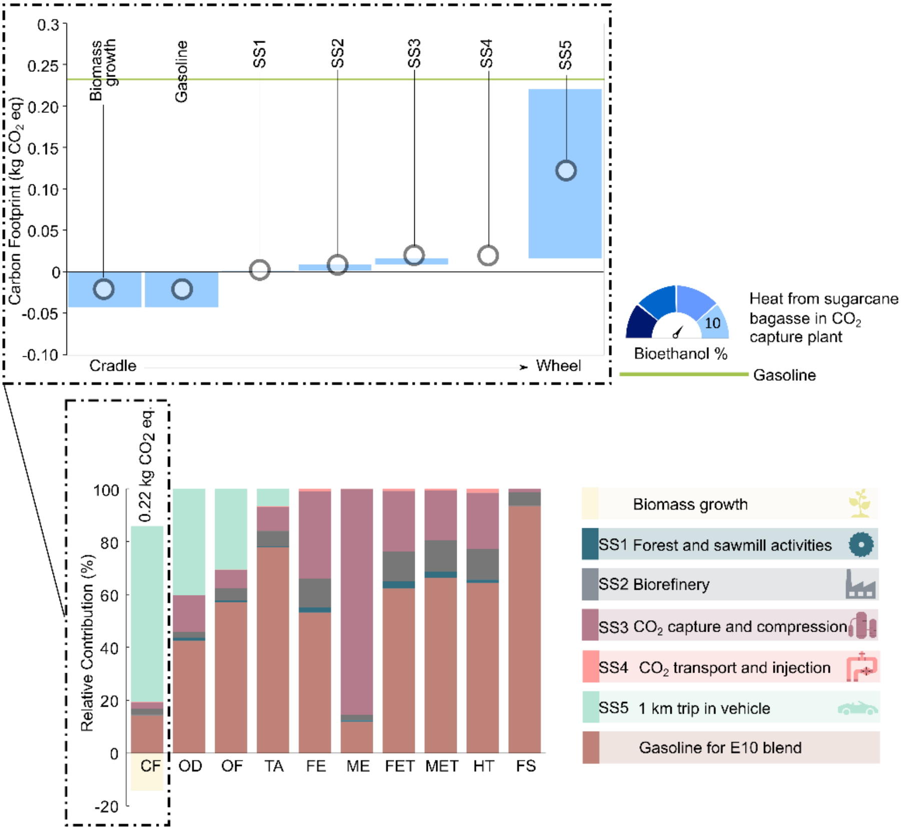

Figure A9 Breakdown of contributions to the Carbon Footprint for scenario E10 SC and environmental profiles (bar-graph plots) displaying characterization results for 1 km travelled in an E10 ethanol (10%) and gasoline (90%)-fueled vehicles in which heat from sugarcane bagasse is used in the CO$_2$ capture plant.

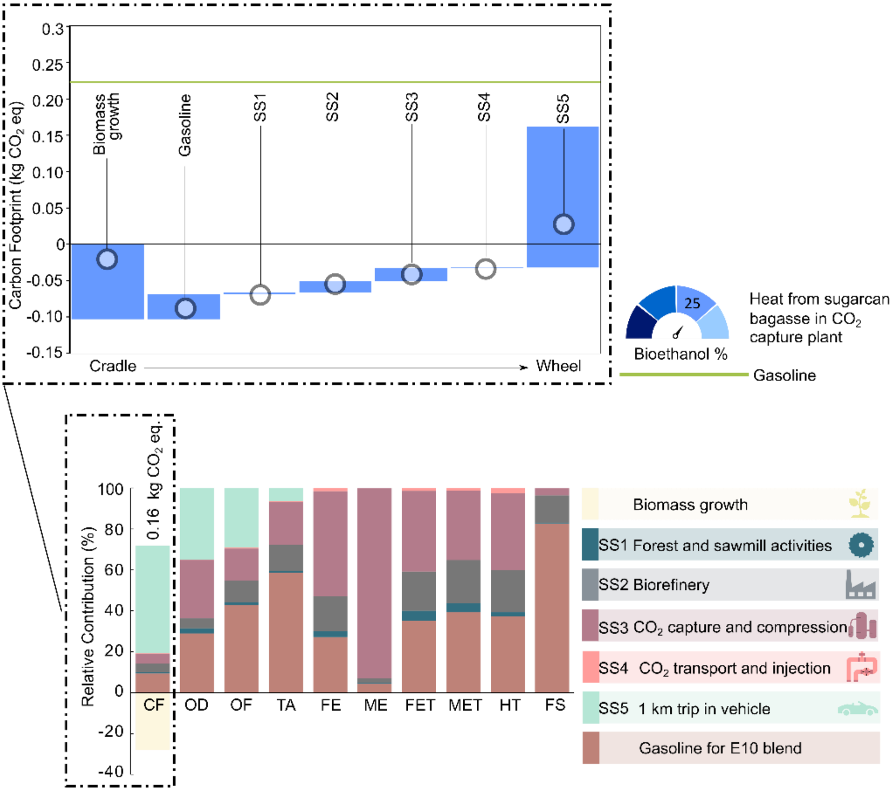

Figure A10 Breakdown of contributions to the Carbon Footprint for scenario E25 SC and environmental profiles (bar-graph plots) displaying characterization results for 1 km travelled in an E25 ethanol (25%) and gasoline (75%)-fueled vehicles in which heat from sugarcane bagasse is used in the CO_2 capture plant.

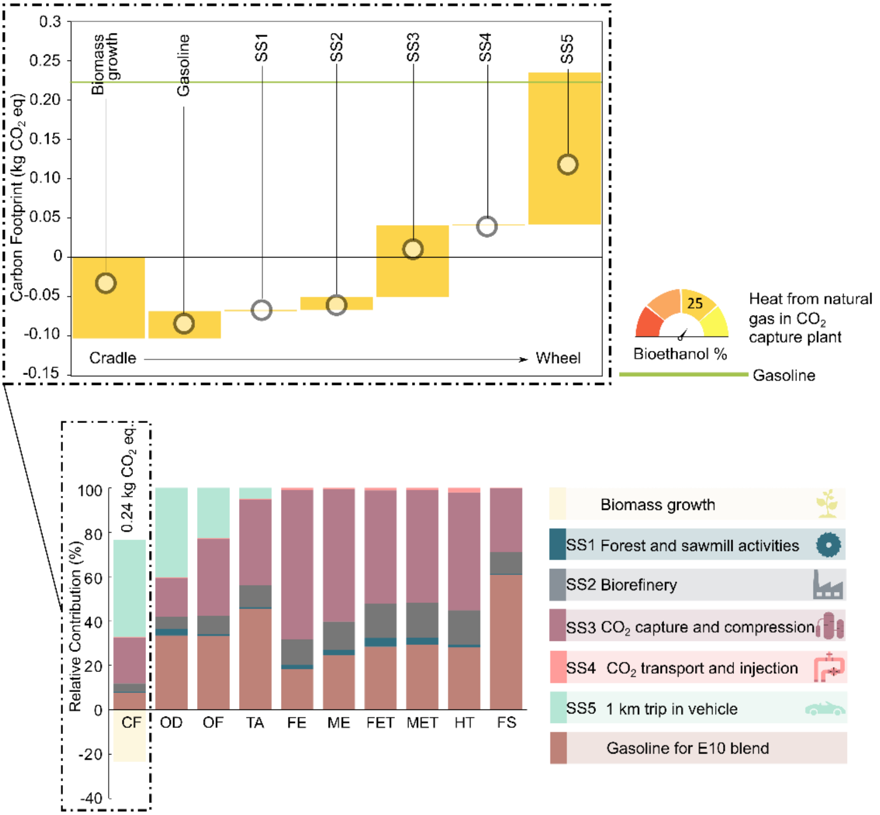

Figure A11 Breakdown of contributions to the Carbon Footprint for scenario E25 NG and environmental profiles (bar-graph plots) displaying characterization results for 1 km travelled in an E25 ethanol (25%) and gasoline (75%)-fueled vehicles in which heat from natural gas is used in the CO$_2$ capture plant.

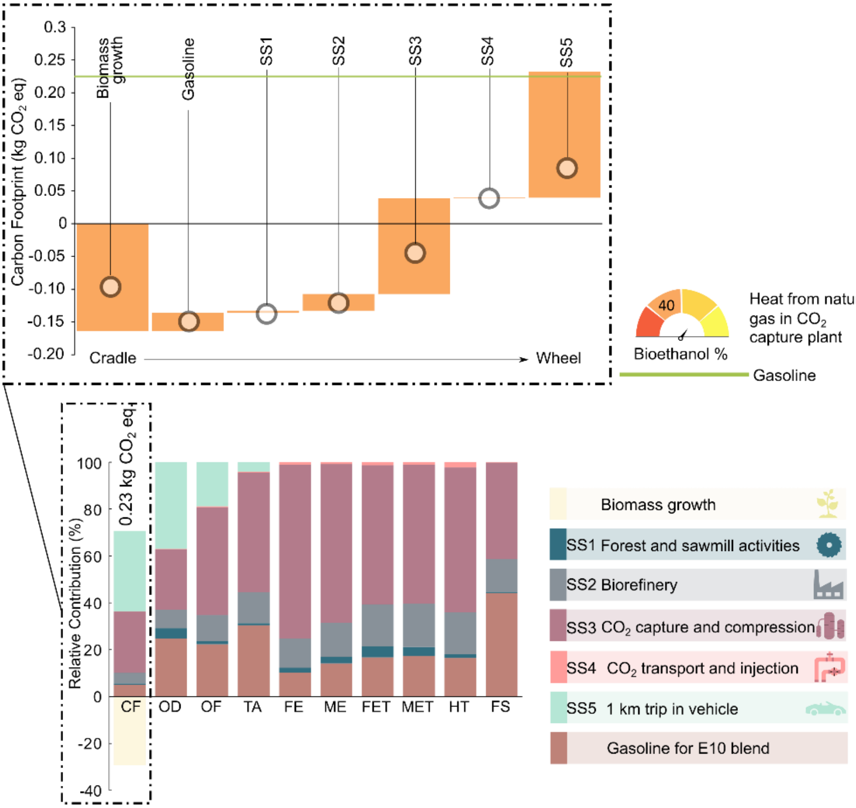

Figure A12 Breakdown of contributions to the Carbon Footprint for scenario E40 NG and environmental profiles (bar-graph plots) displaying characterization results for 1 km travelled in an E40 ethanol (40%) and gasoline (60%)-fueled vehicles in which heat from natural gas is used in the CO$_2$ capture plant.

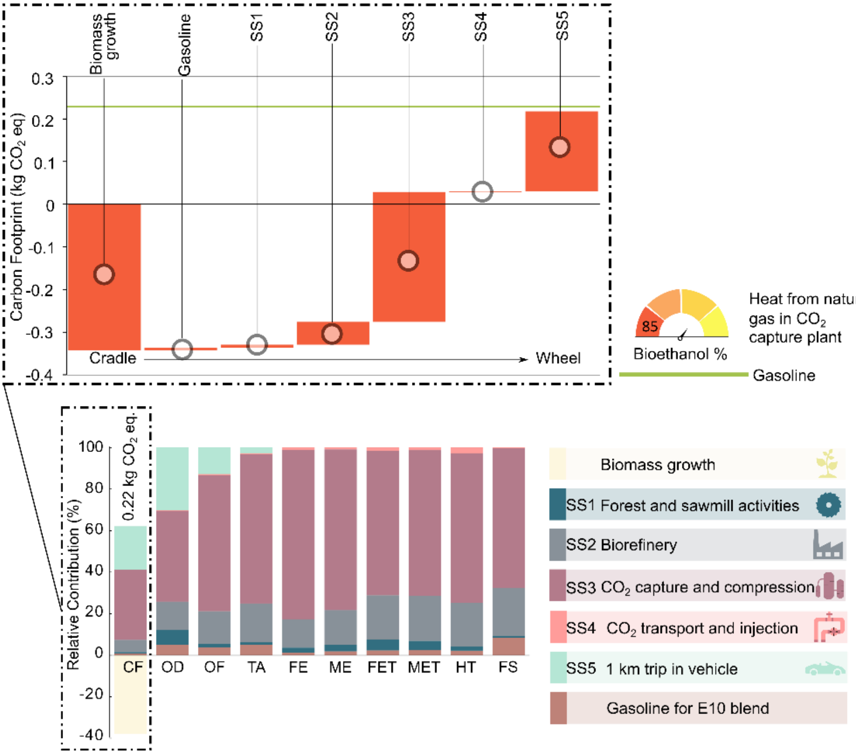

Figure A13 Breakdown of contributions to the Carbon Footprint for scenario E85 NG and environmental profiles (bar-graph plots) displaying characterization results for 1 km travelled in an E85 ethanol (85%) and gasoline (15%)-fueled vehicles in which heat from natural gas is used in the CO_2 capture plant.

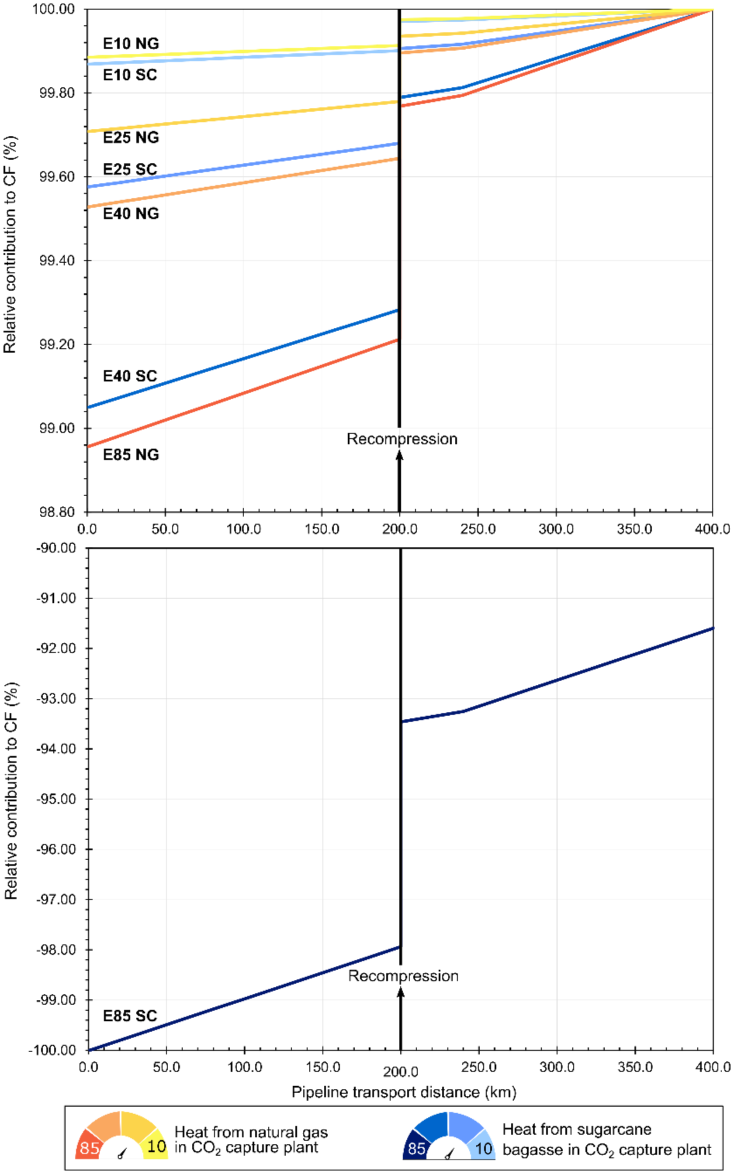

Figure A14 Sensitivity assessment of the pipeline transport distance in the range of 1-400 km (recompression was considered at 200 km) and effect in the relative contribution to the Carbon Footprint for scenarios E85 NG, E40 NG, E25 NG, E10 NG, E40 SC, E25 SC, E10 SC in subplot A and E85 SC in subplot B.

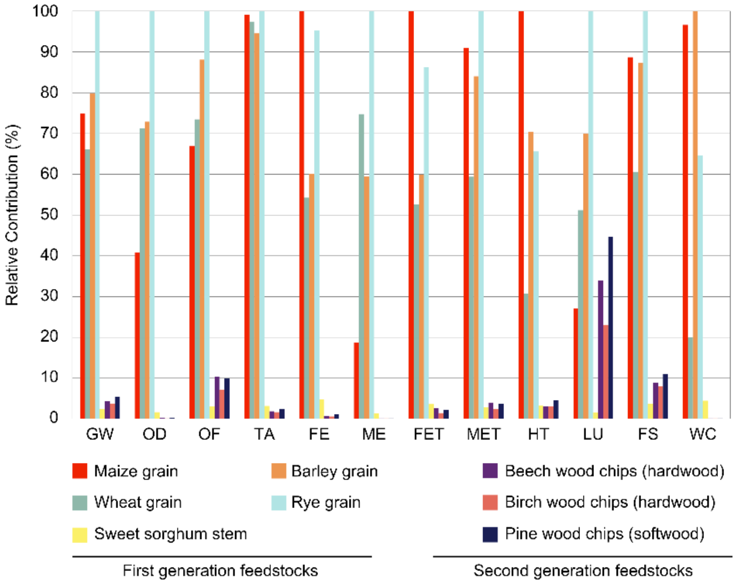

Figure A15 Relative contribution per kg of feedstock (first generation and second generation) from the ecoinvent v3.5 database available processes displaying the impact in GW (ReCiPe 2016 methodology): global warming, OD: ozone depletion, OF: ozone formation, terrestrial ecotoxicity, TA: terrestrial acidification, FE: freshwater eutrophication, ME: marine eutrophication, FET: freshwater ecotoxicity, MET: marine ecotoxicity, HT: human toxicity, carcinogenic, LU: land use, FS: fossil resource scarcity, WC: water consumption

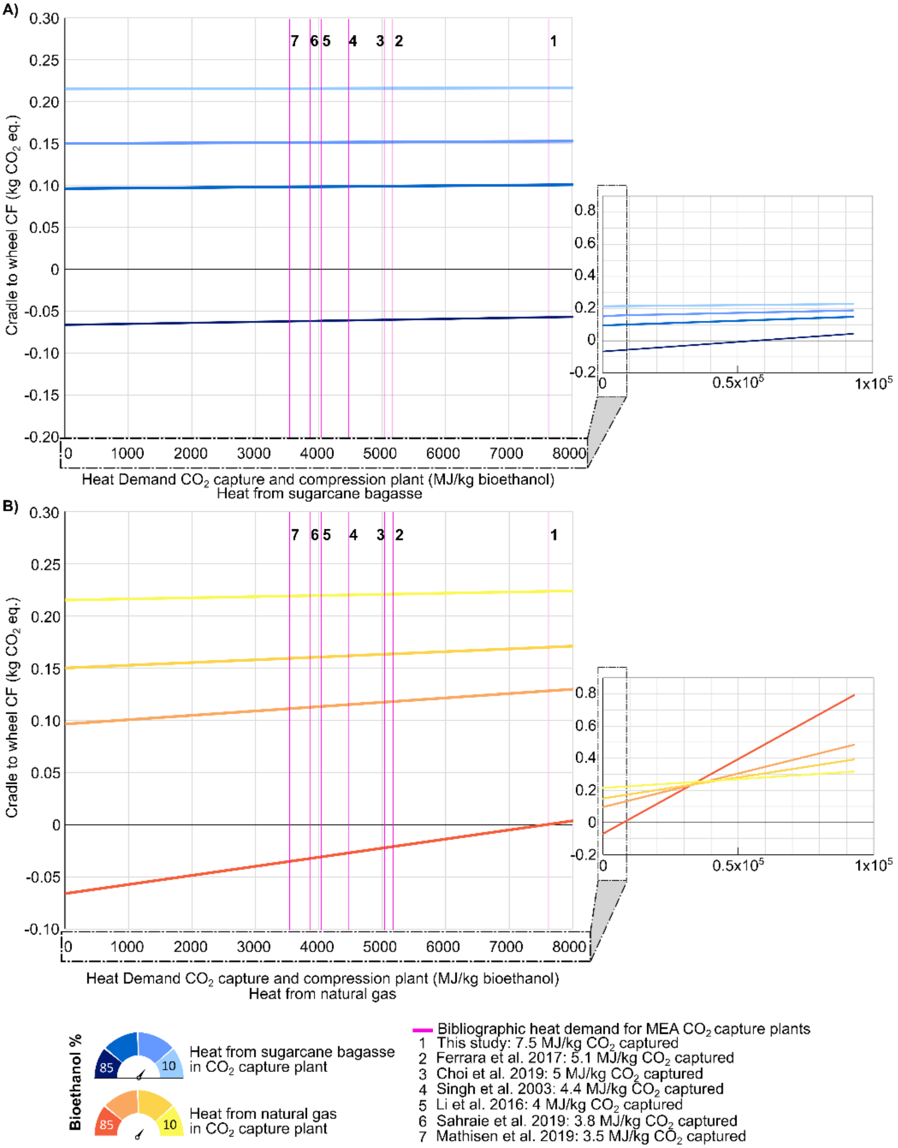

Figure A16 Sensitivity analysis on the carbon footprint (kg CO_2 eq/km) and benchmark of the heat requirement values using different bibliographic sources. Subplot A corresponds to the scenarios considering heat from sugarcane bagasse while subplot B considers heat from natural gas. Each scenario is represented with one line, the darker the color, the higher the bioethanol content in the blend (E85, E40, E25 and E10).

Additional characterization results in absolute terms for all impact categories and scenarios are presented below in Table A34 and Table A35. Table A34 includes the results for scenarios dealing with sugar cane as a heating source in SS3 (SC scenarios), again benchmarked against the gasoline fossil counterpart. In the case of SC scenarios, all impact categories show worse results per functional unit compared with gasoline, except for CF which was studied in detail in Chapter 4, and the fossil resource scarcity, which presents improved results for all scenarios when compared to gasoline. In the case of particulate matter formation, and ozone formation categories, two scenarios present better results than gasoline: E25 SC and E10 SC. Terrestrial acidification depicts an improvement in the results with respect to gasoline in E40 SC, E25 SC and E10 SC.

Table A34 Environmental impact results per scenario for the midpoint ReCiPe 1.1 (Huijbregts et al., 2016) categories per km travelled in a passenger car. The scenarios correspond to sugar cane heating in CCS and are compared to the gasoline fuel benchmark. Red indicates impact values above double the value of the BAU. Yellow indicates values above the BAU. Green indicates values below the impact of the BAU scenario. CF: carbon footprint, OD: ozone depletion, IR: ionizing radiation, OF$_{HH}$: ozone formation, human health, PMF: particulate matter formation, OF: ozone formation, terrestrial ecotoxicity, TA: terrestrial acidification, FE: freshwater eutrophication, ME: marine eutrophication, TET: terrestrial ecotoxicity, FET: freshwater ecotoxicity, MET: marine ecotoxicity, HT$_C$: human toxicity, carcinogenic, HT$_{NC}$: human toxicity, non-carcinogenic, LU: land use, MS: mineral resource scarcity, FS: fossil resource scarcity, WC: water consumption

Acronym	Units	E85 SC	E40 SC	E25 SC	E10 SC	Gasoline
CF	kg CO$_2$ eq	$-2.74\cdot10^{-2}$	$1.15\cdot10^{-1}$	$1.62\cdot10^{-1}$	$2.20\cdot10^{-1}$	$2.23\cdot10^{-1}$
OD	kg CFC11 eq	$2.37\cdot10^{-7}$	$1.71\cdot10^{-7}$	$1.48\cdot10^{-7}$	$1.29\cdot10^{-7}$	$8.30\cdot10^{-8}$
IR	kBq Co-60 eq	$1.55\cdot10^{-2}$	$9.27\cdot10^{-3}$	$7.07\cdot10^{-3}$	$5.17\cdot10^{-3}$	$4.44\cdot10^{-3}$
OF$_{HH}$	kg NO$_x$ eq	$3.26\cdot10^{-4}$	$2.69\cdot10^{-4}$	$2.47\cdot10^{-4}$	$2.35\cdot10^{-4}$	$2.65\cdot10^{-4}$
PMF	kg PM2.5 eq	$2.21\cdot10^{-4}$	$1.73\cdot10^{-4}$	$1.54\cdot10^{-4}$	$1.44\cdot10^{-4}$	$1.71\cdot10^{-4}$
OF	kg NO$_x$ eq	$3.36\cdot10^{-4}$	$2.78\cdot10^{-4}$	$2.56\cdot10^{-4}$	$2.44\cdot10^{-4}$	$2.76\cdot10^{-4}$
TA	kg SO$_2$ eq	$5.90\cdot10^{-4}$	$4.81\cdot10^{-4}$	$4.38\cdot10^{-4}$	$4.20\cdot10^{-4}$	$5.10\cdot10^{-4}$
FE	kg P eq	$3.74\cdot10^{-5}$	$2.08\cdot10^{-5}$	$1.51\cdot10^{-5}$	$9.82\cdot10^{-6}$	$7.10\cdot10^{-6}$
ME	kg N eq	$3.55\cdot10^{-5}$	$1.74\cdot10^{-5}$	$1.11\cdot10^{-5}$	$5.06\cdot10^{-6}$	$8.37\cdot10^{-7}$
TET	kg 1,4-DCB	$3.13\cdot10^{-1}$	$1.85\cdot10^{-1}$	$1.39\cdot10^{-1}$	$1.00\cdot10^{-1}$	$8.26\cdot10^{-2}$
FET	kg 1,4-DCB	$1.95\cdot10^{-3}$	$1.16\cdot10^{-3}$	$8.75\cdot10^{-4}$	$6.30\cdot10^{-4}$	$5.06\cdot10^{-4}$
MET	kg 1,4-DCB	$2.78\cdot10^{-3}$	$1.71\cdot10^{-3}$	$1.32\cdot10^{-3}$	$9.99\cdot10^{-4}$	$8.74\cdot10^{-4}$
HT$_c$	kg 1,4-DCB	$3.55\cdot10^{-3}$	$2.14\cdot10^{-3}$	$1.64\cdot10^{-3}$	$1.21\cdot10^{-3}$	$9.93\cdot10^{-4}$
HT$_{nc}$	kg 1,4-DCB	$7.50\cdot10^{-2}$	$4.28\cdot10^{-2}$	$3.14\cdot10^{-2}$	$2.14\cdot10^{-2}$	$1.61\cdot10^{-2}$
LU	m^{2}a crop eq	$5.58\cdot10^{-2}$	$2.70\cdot10^{-2}$	$1.71\cdot10^{-2}$	$7.48\cdot10^{-3}$	$6.74\cdot10^{-4}$
MS	kg Cu eq	$2.19\cdot10^{-4}$	$1.46\cdot10^{-4}$	$1.20\cdot10^{-4}$	$9.92\cdot10^{-5}$	$9.38\cdot10^{-5}$
FS	kg oil eq	$5.32\cdot10^{-2}$	$6.80\cdot10^{-2}$	$7.18\cdot10^{-2}$	$8.09\cdot10^{-2}$	$1.09\cdot10^{-1}$
WC	m^3	$1.33\cdot10^{-2}$	$6.60\cdot10^{-3}$	$4.28\cdot10^{-3}$	$2.05\cdot10^{-3}$	$5.64\cdot10^{-4}$

Table A35 includes the environmental results for the fossil-heating alternatives (scenarios NG). In this case, E40 NG, E25 NG and E10 NG perform worse than gasoline in CF. In FS, E85 NG performs worse than gasoline. The rest of the impact categories, again, get worse when compared to conventional fueling options. Land use occupation and water consumption impact categories present worse results than gasoline in all scenarios, mainly due to the more intensive use for cropping and silviculture activities, both for the woodchips exploited for the production of bioethanol, but also for the sugar cane bagasse assumed to be used in half of the presented scenarios.

Table A35 Environmental impact results per scenario for the midpoint ReCiPe 1.1 categories per km travelled in passenger car. The scenarios correspond to natural gas heating in CCS and are compared to the gasoline fuel benchmark. Red indicates impact values above double the value of the BAU. Yellow indicates values above the BAU. Green indicates values below the impact of the BAU scenario. CF: carbon footprint, OD: ozone depletion, IR: ionizing radiation, OF_{HH}: ozone formation, human health, PMF: particulate matter formation, OF: ozone formation, terrestrial ecotoxicity, TA: terrestrial acidification, FE: freshwater eutrophication, ME: marine eutrophication, TET: terrestrial ecotoxicity, FET: freshwater ecotoxicity, MET: marine ecotoxicity, HT_C: human toxicity, carcinogenic, HT_{NC}: human toxicity, non-carcinogenic, LU: land use, MS: mineral resource scarcity, FS: fossil resource scarcity, WC: water consumption

Acronym	Units	E85 NG	E40 NG	E25 NG	E10 NG	Gasoline
CF	kg CO_2 eq	$2.18\cdot10^{-1}$	$2.32\cdot10^{-1}$	$2.35\cdot10^{-1}$	$2.51\cdot10^{-1}$	$2.23\cdot10^{-1}$
OD	kg CFC11 eq	$1.71\cdot10^{-7}$	$1.40\cdot10^{-7}$	$1.28\cdot10^{-7}$	$1.20\cdot10^{-7}$	$8.30\cdot10^{-8}$
IR	kBq Co-60 eq	$2.24\cdot10^{-2}$	$1.26\cdot10^{-2}$	$9.13\cdot10^{-3}$	$6.04\cdot10^{-3}$	$4.44\cdot10^{-3}$
OF_{HH}	kg NO_x eq	$5.71\cdot10^{-4}$	$3.86\cdot10^{-4}$	$3.20\cdot10^{-4}$	$2.66\cdot10^{-4}$	$2.65\cdot10^{-4}$
PMF	kg PM2.5 eq	$3.48\cdot10^{-4}$	$2.33\cdot10^{-4}$	$1.92\cdot10^{-4}$	$1.60\cdot10^{-4}$	$1.71\cdot10^{-4}$
OF_{TE}	kg NO_x eq	$5.84\cdot10^{-4}$	$3.97\cdot10^{-4}$	$3.30\cdot10^{-4}$	$2.75\cdot10^{-4}$	$2.76\cdot10^{-4}$
TA	kg SO_2 eq	$1.01\cdot10^{-3}$	$6.82\cdot10^{-4}$	$5.64\cdot10^{-4}$	$4.72\cdot10^{-4}$	$5.10\cdot10^{-4}$
FE	kg P eq	$6.19\cdot10^{-5}$	$3.26\cdot10^{-5}$	$2.24\cdot10^{-5}$	$1.29\cdot10^{-5}$	$7.10\cdot10^{-6}$
ME	kg N eq	$4.97\cdot10^{-6}$	$2.72\cdot10^{-6}$	$1.94\cdot10^{-6}$	$1.22\cdot10^{-6}$	$8.37\cdot10^{-7}$
TET	kg 1,4-DCB	$6.25\cdot10^{-1}$	$3.34\cdot10^{-1}$	$2.33\cdot10^{-1}$	$1.39\cdot10^{-1}$	$8.26\cdot10^{-2}$
FET	kg 1,4-DCB	$2.65\cdot10^{-3}$	$1.49\cdot10^{-3}$	$1.08\cdot10^{-3}$	$7.18\cdot10^{-4}$	$5.06\cdot10^{-4}$
MET	kg 1,4-DCB	$4.29\cdot10^{-3}$	$2.43\cdot10^{-3}$	$1.77\cdot10^{-3}$	$1.19\cdot10^{-3}$	$8.74\cdot10^{-4}$
HT_c	kg 1,4-DCB	$5.39\cdot10^{-3}$	$3.02\cdot10^{-3}$	$2.19\cdot10^{-3}$	$1.44\cdot10^{-3}$	$9.93\cdot10^{-4}$
HT_{nc}	kg 1,4-DCB	$7.68\cdot10^{-2}$	$4.37\cdot10^{-2}$	$3.20\cdot10^{-2}$	$2.16\cdot10^{-2}$	$1.61\cdot10^{-2}$
LU	m^2a crop eq	$4.32\cdot10^{-3}$	$2.33\cdot10^{-3}$	$1.64\cdot10^{-3}$	$1.00\cdot10^{-3}$	$6.74\cdot10^{-4}$
MS	kg Cu eq	$2.14\cdot10^{-4}$	$1.44\cdot10^{-4}$	$1.18\cdot10^{-4}$	$9.87\cdot10^{-5}$	$9.38\cdot10^{-5}$
FS	kg oil eq	$1.38\cdot10^{-1}$	$1.09\cdot10^{-1}$	$9.73\cdot10^{-2}$	$9.16\cdot10^{-2}$	$1.09\cdot10^{-1}$
WC	m^3	$7.46\cdot10^{-3}$	$3.80\cdot10^{-3}$	$2.53\cdot10^{-3}$	$1.32\cdot10^{-3}$	$5.64\cdot10^{-4}$

A4. Supplementary information Chapter 5

The supplementary information for Chapter 5 includes further details on the simulation for the process section regarding the production of FDCA from HMF, and the Aspen Plus® optimization procedure.

A4.1 GENERAL DESCRIPTION OF THE PROCESS TO PRODUCE FDCA FROM HMF

The oxidation of HMF to FDCA has been examined by the scientific patent for hydroxymethyl furfural oxidation (Lilga et al., 2012). The chemical transformation of HMF to FDCA, according to the patent, can be performed through the oxidation with the use of air and a solid metal catalyst (platinum) supported on ZrO_2. In a fixed bed continuous reactor, the HMF feedstock is added in a ratio of 0.5% wt. to an acidic aqueous solution (acetic acid solution in water, 40:60).

Triebl et al. (2013) proposed the same transformation of HMF to FDCA and its separation through two different procedures. In the first case, the authors considered an approach involving the separation of FDCA through a crystallization unit and filter, from this point forward, scenario 1. The second approach was based on the separation of the components with the use of a liquid-liquid extraction unit and subsequent distillation for the recovery of the extractant, hereafter scenario 2. However, in the case of this chapter, a critical evaluation of the proposed configurations has been contemplated. The first modification of scenario 1 was the simplification of the process by eliminating air recirculation. It was considered that the energy demand for the compressing power to perform air recirculation was not essential considering the amount of residual O_2 released. On the other hand, the high content of inert (N_2) in the air recirculation requires a larger volume of the plant, even if there is a purge. However, due to the high boiling points of both compounds, the energy consumption of the separation is expected to be high. This leads to the possibility of exploring vacuum distillation, which would allow working at lower temperatures. From an environmental point of view, this approach aims to reduce the high toxicity values of the use of organic solvents such as trioctylamine. The European Regulation on Registration, Evaluation, Authorization and Restriction of Chemicals (REACH) of the European Chemicals Agency (ECHA) (European Chemicals Agency, 2018) has determined that trioctylamine is very toxic to aquatic ecosystems and humans. In the case of air recirculation (2013), it has been avoided, once again, in the new configuration for scenario 2. A more detailed explanation on the simulation arrangement for both cases is given below.

A4.2 ASPEN PLUS® MODELLING APPROACH

The Aspen Plus® V9 process simulator was the commercial software selected to model the FDCA production and separation route according to the conditions defined in the previous section (Lilga et al., 2012; Triebl et al., 2013). The modelling of the upstream section of the configuration is common to both case studies. The definition of the input flow was made according to the specified composition required for the reaction mechanism. Fresh water, acetic acid, HMF and air are the inputs to the system, which enter the process at ambient temperature and pressure, 25°C and 1 bar. The input streams must be conditioned to reach the operating temperature and pressure of the reactor, which are 10 bar and 100°C. The pressure increase of the liquid stream is carried out with a pump, while the air is introduced into the reactor with a 3-stage isentropic compressor with a discharge pressure and a temperature of 10 bar and 100°C respectively. The discharge pressure of the pump is also 10 bar, and then a heat exchanger raises the temperature of the liquid stream to the required value of 100°C.

It is key to ensure the reaction conditions and compositions that will enter the reactor due to the nature of the block selected to model the reactions. A stoichiometric reactor block functions as a black box model, basing the calculations for the output products on the specified yields achieved under specific temperature and pressure values. It was considered that impurities in the reactor (co-products and by-products) do not affect the performance of the reaction.

Scenario 1: FDCA production and recovery by crystallization

depicts the flowchart developed for scenario 1. In scenario 1, the separation sequence starts with an expansion valve working at a discharge pressure of 3.5 bar. The objective is to condition the output flow of the reactor (stream 7) to milder conditions, i.e., closer to ambient pressure and temperature. Heat exchanger E-2 contributes to the same purpose, aiming at an output temperature in stream 9 of 30°C. The adiabatic flash unit F-1 has the function of performing liquid-vapor separation at. The vapor stream exits the unit with a composition rich in air and steam, along with residual acetic acid fractions. Most of the air (89% of the input stream) is removed through the vapor stream 10. The liquid stream (stream 11) is pumped to the crystallizer with P-2. In the crystallizer, at 2.5 bar and 25°C, the $FDCA^{-2}$ anion and H^+ yield FDCA. The solid product (stream 17) is separated with a 98% wt. solid fraction in the filter cake using the rotatory vacuum filter FI-1. The filtrate (stream 14) is recirculated and mixed with the feed stream (stream 1), a purge of 5% of this stream is included to prevent inert accumulation throughout the system (stream 16).

A design specification and a balance variable have been included in block M-1 to assist in the appropriate convergence of the model. Through these specifications, the model is able to update the flow of the make-up stream in the recycle calculations. The HMF concentration at the reactor inlet was set at 0.5% wt. through the design specification.

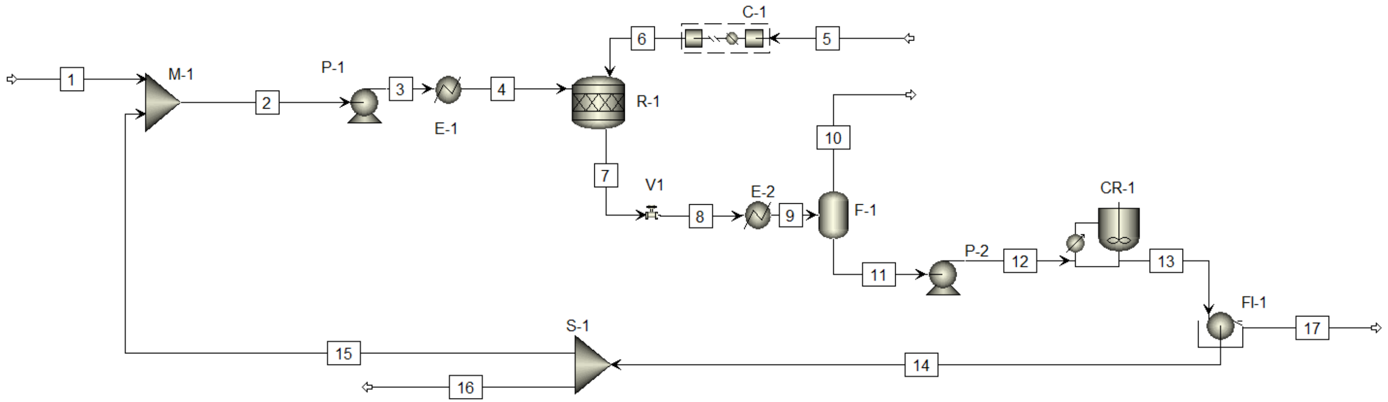

Figure A17. Aspen Plus flowsheet for the production of FDCA through scenario 1

Scenario 2: FDCA production and recovery by vacuum distillation

Figure A18 depicts the flowchart developed for scenario 2. In the case of scenario 2, the first unit operation after reactor R-1 is flash F-1. This unit operates at 100°C, decreasing the output pressure of 10 bar from the reactor outlet to 1 bar. The objective of F-1 is to separate in the vapor phase as many of the most volatile components in stream 9. The separated vapor stream (stream 10) exits through the top of the unit containing mainly water, acetic acid and air (as O_2 and N_2). The liquid fraction contains the target product (FDCA) and other by-products and chemicals (water, acetic acid, HMF, DFF and FFCA). Reducing the working pressure and volume of the flow to be treated in the downstream separation unit will reduce energy requirements. Stream 11 continues to the vacuum distillation column D-1, which works at 0.55 bar. The boiling point of the compounds would imply an intensive energetic demand for their separation (FDCA: 420°C). Reducing the working pressure by applying vacuum distillation lowers the boiling point of the compounds. The vacuum distillation column selected was a DSTWU block with a total condenser and 10 stages. HMF was set as the light key with a recovery of 0.99 and FDCA was set as the heavy key, with a recovery value of $1 \cdot 10^{-6}$. The energy demand required to decrease the operation pressure to vacuum values would be reached through the use of a vacuum pump. However, in this chapter, this energetic requirement was not considered. Stream 17 contains the final FDCA with a mass fraction of 99.7%. In this scenario, streams 10 and 16 contain a mixture of air, water and acetic acid as main components. The objective is to recover the water and acetic acid and recirculate it to the reactor and, on the other hand, to remove air. This is performed through the F-2 (37.5ºC and 1 bar) and F-3 (81ºC and 1 bar) flash units respectively. The simulation included the purge of the recirculation streams in a ratio of 5% to prevent inert accumulation throughout the system.

In the same way as in the previous scenario a design specification and a balance variable were included in block M-1 for the calculations of the recycle flows. Table A36 presents a compilation of Aspen Plus flowsheet unit operation blocks and conditions included in scenarios 1 and 2.

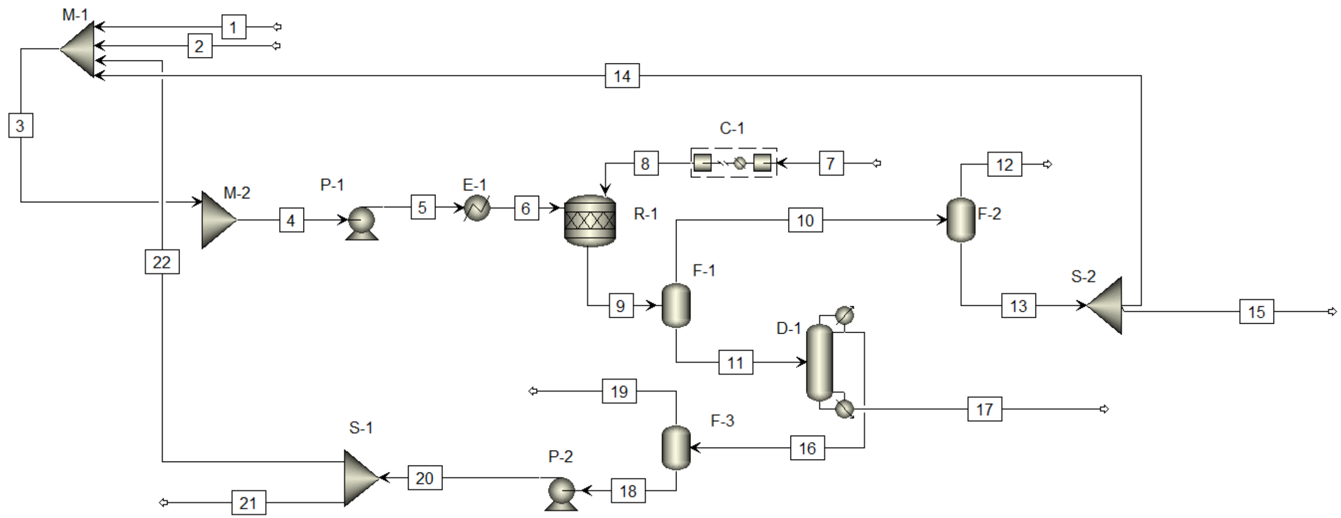

Figure A18. Aspen Plus flowsheet for the production of FDCA through scenario 2

Table A36 Aspen Plus® used operation blocks in the flowsheets of scenarios 1 and 2

Common unit operation blocks		
Equipment name	Aspen Plus name	Description
P-1	Pump	Pump for liquid input stream Discharge pressure 10 bar
E-1	Heater	Heat exchanger to heat liquid input stream Discharge temperature 100°C (use of hot utility)
C-1	MCompr	Isentropic 3-stage air compressor Discharge pressure 10 bar
M-1, M-2	Mixer	Mixers
R-1	RStoic	Stoichiometric reactor It models reactions attending to specified conversion
Unit operation blocks scenario 1		
Equipment name	Aspen Plus name	Description
V-1	Valve	Expansion valve Outlet pressure of 3.5 bar to perform adiabatic flash
E-2	Heater	Heat exchanger to cool reactor output stream Discharge temperature 30°C (use of cold utility)
F-1	Flash2	Two phase flash unit operating at 1.5 bar and 30ºC
P-2	Pump	Pump for liquid stream 11 Discharge pressure 3 bar
CR-1	Crystallizer	Crystallizer Operating temperature 25ºC and pressure 2.5 bar
FI-1	Filter	Drum rotary vacuum filter Brownell filtration model
S-1	FSplit	Stream splitter to purge
Unit operation blocks scenario 2		
Equipment name	Aspen Plus name	Description
F-1	Flash2	Two phase flash unit operating at 1 bar and 100ºC
F-2	Flash2	Two phase flash unit operating at 1 bar and 37.5ºC
D-1	DSTWU	Vacuum distillation unit Total condenser Reflux ratio 0.13 10 stages Operating pressure 0.55 bar
S-1, S-2	FSplit	Stream splitters to purge
F-3	Flash2	Two phase flash unit operating at 81ºC and 0.55 bar
P-2	Pump	Pump for stream 18 Discharge pressure 1 bar

Thermodynamic model

The selection of the thermodynamic properties model, among the options available in the simulator, was performed with the algorithm proposed by Carlson (1996). In the case of crystallization (scenario 1 involving $FDCA^{-2}$ and H^+ ions), the Electrolyte NRTL model was used. In the case of vacuum distillation, scenario 2, the NRTL model was selected. For the estimation of the properties of the components involved, the simulator allows to directly introduce the components of its database, except for the reaction intermediates: DFF, FFCA and $FDCA^{-2}$, which were not available. Their properties were estimated according to their molecular structure, imported through files with extension (*mol*).

A4.3 ASPEN PLUS® SENSITIVITY ANALYSIS

As a complement to the study, a sensitivity analysis of key parameters was performed with the support of the Aspen Plus Sensitivity Model Analysis Tool. Considering the degrees of freedom in the process simulation, there is a need to evaluate certain variables attending to the final objectives of the process. In this case, the overall objective was to minimize the energy consumption of the process units and maximize the purified FDCA obtained. Each parameter was evaluated in a single step and varied within the operation limits. The parameters analyzed were kept constant at their optimal value to evaluate the effect of the related variables. The sensitivity assessment focused mainly on downstream separation operations. It was carried out to analyze whether minimization of energy requirements through optimization of a selection of relevant parameters could be effective. The analyzed variables were the operating pressure at unit F-1 for scenario 1 and the operating pressure of units F-1 and D-1 for scenario 2. These variables were analyzed in the range of feasible operation, with the ranges corresponding to minimum and maximum pressure. This range of operation has been retrieved from the limiting pressure values computed by the simulation without any errors in the flowsheet diagram. A constant increment was considered to obtain equidistant points in the selected range of operation.

Sensitivity analysis of scenario 1

The analysis of scenario 1 was focused on the effect of the pressure variation in F-1 on the separation efficiency. The pressure was assessed in the operation range of 0.1-1.5 bar. The sensitivity analysis of the flash unit was studied considering the resulting value of the energy demands of the equipment that can be found before or after F-1 in the production line. This was due to the fact that F-1 was simulated as an adiabatic flash with no heat duty. The effect produced was studied on the cooling required in the previous heat exchanger E-2. It was also found that the operating pressure of F-1 indirectly affected the energy consumed by the pump P-2 Figure A19-A. The needed energetic consumption that would be derived from the pressure decrease to 0.2 bar was not considered. An additional unit such a vacuum pump or an ejector would be required in that case. The mass flow of FDCA in the final output stream was also plotted to simultaneously evaluate the positive yield in the production of the main chemical and the potential decrease in the energy consumption.

It can be observed that the net energy required for the heat exchanger and the pump tend to decrease as the operation pressure of F-1 increases. The main objective of the F-1 unit is to eliminate the maximum amount of residual inert fractions, i.e., N_2, which enters the system together with O_2, for the oxidation of HMF. It can be deduced that, as the pressure of the liquid-vapor separation unit increases, the separation is improved, resulting in a reduction of the overall plant recirculating-flow. Hence, the pump P-2 and the heat exchanger E-2 require slightly lower energy consumption. Venting the spent air prior to the crystallization unit through F-1 ensures the correct operation of CR-1. However, the decrease of the volume in the plant has also an effect on the product flow obtained in stream 17. In general, the change of pressure in F-1 has shown that the energy consumption of E-2 could have a maximum reduction of 5%. However, the reduction in energy consumption within the operating range studied amounts to 48%. The energy consumption of P-2 is more sensitive to pressure change than the cooling needs of the previous heat exchanger. If we consider that the best scenario for energy consumption was implemented, the FDCA mass flow would be reduced by 4% from the value corresponding to the minimum pressure considered within the range. The baseline scenario corresponds to the pressure of 1.5 bar and 30ºC, for which inventory tables have been provided.

Sensitivity assessment of scenario 2

The sensitivity analysis performed for scenario 2 is based on the minimization of the energy requirements for the separation process. The two process units considered were the first separation unit, flash F-1 and the vacuum distillation column D-1.

For the pressure of the flash unit, the values of energy consumption and mass fraction of the separation were discussed. The objective of this unit is to maximize the amount of FDCA present in the output flow, as well as to simultaneously separate as much N_2 as possible leaving the column at the top. Furthermore, the separation performance in F-1 determines the extent to which recirculation of raw materials (acetic acid, water, HMF) can be achieved. For economic and environmental reasons, the overall objective of optimization should be to minimize the energy consumption of the unit, provided that the operational requirements are met. The pressure in F-1 has been evaluated in the range of 0.1-1 bar. The needed energetic consumption that would be derived from the pressure decrease to vacuum values was not considered. An additional unit such a vacuum pump or an ejector would be required in that case. Figure A19 B) displays the results of the first sensitivity analysis for scenario 2.

In this case, the trend for the energetic duty of the unit is to decrease as the pressure increases. Regarding nitrogen leaving the unit through the top, it tends to slightly increase as the pressure increases while acetic acid decreases. In this case, the trends of the evaluated variables behave with a somewhat stabilized response until reaching the pressure of 1 bar, at which most of the changes occur. In this unit, the optimal value of energy demand should be minimal, as expected. The nitrogen mass fraction should be maximized and, finally, the mass fraction of acetic acid in stream 10 should be minimized. The optimum operation point in this case occurs at a pressure of 1 bar (100ºC), which is again the pressure of the base case scenario considered for the simulation presented. The maximum reduction that can be achieved in the energy consumption of the F-1 flash within the temperature range studied is 9% based on the minimum pressure of 0.1 bar. A 5% reduction in the mass fraction of acetic acid can be observed in the range of pressure evaluated over the range of studied pressures. The mass fraction of nitrogen increases at a rate of 11% over the studied pressure variation.

The performance of the D-1 distillation column was analyzed by studying its operating pressure in a variable range of 0.0001-0.999 bar. On this occasion, the parameters evaluated were the heating and cooling requirements for the reboiler and column condenser respectively. In addition, the FDCA mass fraction leaving the column through the bottoms as product was represented.

The results of the sensitivity analysis are presented in Figure A19 C). In this case the trends show a considerable shift of the evaluated variables in the change from 0.0001 to 0.05 bar. From 0.05 bar, the values remain somewhat constant. The direction of change in the energy consumption of the column is to decrease with increasing pressure. In other words, as pressure is lower, global net energy demand increases. However, the mass fraction of the FDCA increases as the pressure increases, reaching a maximum for pressures in the range of 0.42-0.63 bar. The increase of FDCA in the outflow presents a very slight increase (0.6%). However, the decrease in energy needs is comparatively greater, reaching 61% decrease values for both heating and cooling duties. The optimal operation would be within the aforementioned pressure range (0.42-0.63 bar), since for these values, the mass fraction of the FDCA is at its maximum, while the energy demand is within the expected reduction. The base case scenario was simulated for a column pressure of 0.55 bar, which is within the optimum range of operation.

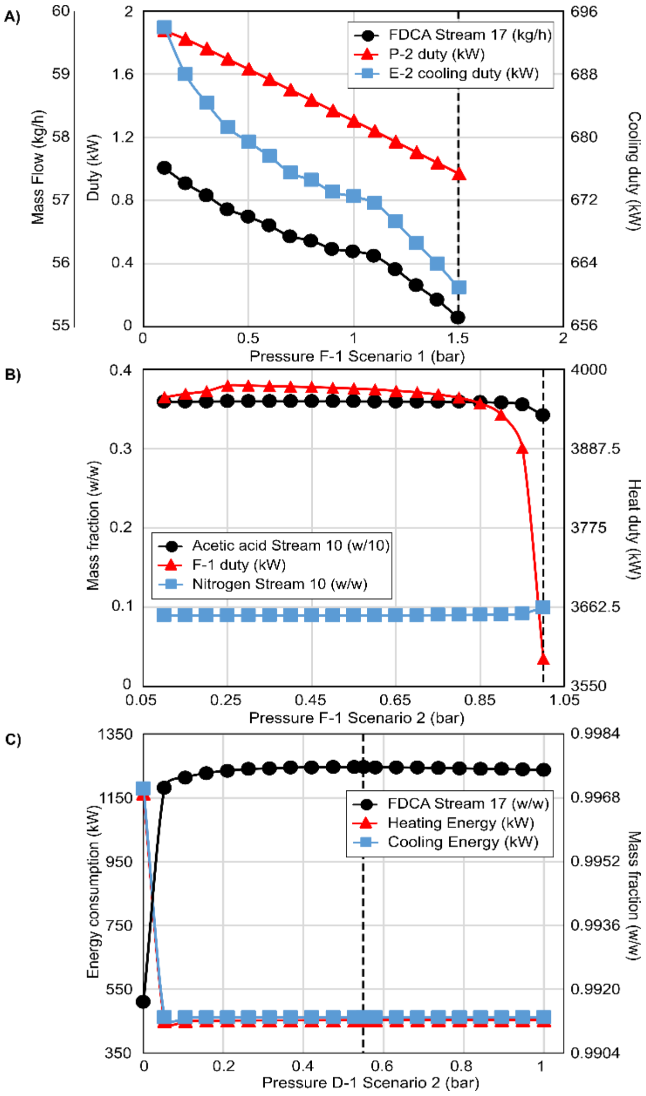

Figure A19 A) Sensitivity analysis for scenario 1. Effect of the pressure of flash F-1 in the energy consumption of P-2 and E-2 units and the FDCA product obtained in stream 17. B) Sensitivity analysis for scenario 2. Effect of the pressure of the F-1 flash on the mass fraction of the products present in the vapor stream (w/w) and the heating energy consumption of the unit (kW). C) Sensitivity analysis for scenario 2. Effect of the pressure of distillation column D-1 in the purity of FDCA obtained (w/w) and the net energy consumption of the unit (kW). The dashed lines represent the base case scenario conditions.

A5. Supplementary information Chapter 7

This section contains the supplementary information and results of Chapter 7. The Life cycle inventory (LCI) tables for the system under study (production of 1 kg of biobased succinic acid from SSL), the results for succinic acid market growth and marginal mix estimations as well as the inventories for Consequential LCA are detailed. The figures presenting further results, complementary to the main manuscript are depicted here as well.

A5.1 DETAILS OF THE METHODOLOGY

Attributional LCA

For SS1 and SS2 the impacts were assigned to the two main products exiting SS2, the pulp and the pre-processed SSL. For economic allocation, since we are dealing intermediate products, it was estimated that the economic value of SSL and pulp was that of their further processed end products (i.e., fermentable sugars and dissolving pulp respectively) (Nitzsche et al., 2020; Parra-Ramírez et al., 2018).

In SS3 (nanofiltration) the allocation was performed among the two main valuable products obtained, pre-treated SSL —which would be one of the main substrates carried forward into fermentation— and lignosulfonates. The economic value of lignosulfonates is based in their potential application as plasticizing additives in cement mixtures (Holladay et al., 2007).

Especially in the case of CO_2, which experiences a shift from emission to input flow (technical flow), the consideration of allocation rather than considering zero background emissions is pertinent, as to account correctly for emissions in CCU. In this case, as in every input for LCA its background impacts in a cradle-to-gate perspective should be accounted for. Allocation was performed between CO_2 and clinker (McKinsey Climate Change Initiative, 2008) and CO_2 and bioethanol (Gnansounou, 2010) in the fossil and biogenic CCU scenarios (Zimmermann et al., 2018). For economic allocation, the cost of capturing CO_2 from diverse point sources, evidently differs, which was considered (Bains et al., 2017). The BAU biobased scenario impacts have been allocated to succinic acid and ammonium sulfate respectively, for comparability reasons (Biddy et al., 2016; Independent Commodity Intelligence Services (ICIS), 2003).

Consequential LCA

The first step in C-LCA is to determine the reference product and co-products of the system. The products of the system under study are SA and lignosulfonates. Lignosulfonates are the dependent co-product, since their revenue does not exceed 80% of the total revenue of the system following the identification of the determining product criterion. Therefore, the system is expanded to include the co-product (lignosulfonates) which is considered as an avoided burden of another market (i.e., plasticizer additive in the cement industry) (Schmidt, 2014). The production of SA from sorghum as the first-generation biomass conversion scenario (BAU) produces ammonium sulfate, considered as avoided product in C-LCA (Pinazo et al., 2015).

The case of SSL displays a constrained market meaning that it is a dependent by product of the pulp and paper industry. The system boundaries are thus expanded to include its use or treatment. Analyzing its current market, bioethanol is the main product derived from SSL —stream rich in sugars apt for any fermentation. However, the shift of producing SA from SSL rather than the state-of-the-art production of bioethanol results in the need to compensate the bioethanol produced by SSL with the corresponding marginal technology that will be able to absorb the demand. The identification of marginal suppliers was performed on the basis of the 5-step procedure developed by Weidema et al. (1999) resulting in the identification of the suppliers that would be able to change their production capacity in response to a change in demand. In a growing market such as that of bioethanol, the marginal technology is that with the greatest historical production growth (i.e., bioethanol produced from maize) (Bittencourt Sydney et al., 2019). The sugar contents in SSL and sugar consumption patterns for the production of bioethanol were considered for the estimation of the amount of bioethanol per functional unit that should be compensated (Pateraki et al., 2016a; Xavier et al., 2010).

Obtaining CO_2 from point sources, to produce bio-SA from SSL would lead to an intrinsic change of the clinker and bioethanol industries. These are industries with the feasibility to absorb the increase of demand of CO_2, however they would experience a shift in which the current BAU production with carbon emissions to the environment will be substituted by an identical production with a carbon capture plant and with the consequent elimination of 90% of the carbon emissions to the environment (Thonemann and Pizzol, 2019). The result, in our system, is a process substitution in which the reduction or increment of indirect and direct emissions will be accounted as a difference and included in the inventory.

The production of SA with SLL as carbon source will lead to displacing the BAU production methods in the current market. The affected suppliers in this study are part of the selection of a marginal supply mix obtained by extrapolating available market trends. The use of a marginal supply mix makes sense for newer markets with less availability of data or increased uncertainty due to their biobased nature, which makes difficult to predict their evolution. The SA market is expected growth with an annual rate of anywhere from 7 to 49% in the next years (Garcia-Aguirre et al., 2020; Nghiem et al., 2017; Saxena et al., 2017; Tan et al., 2017).

A5.2 LIFE CYCLE INVENTORY

Table A37 Inventory for silviculture activities (SS1) per m^3 of eucalyptus wood and their CO_2 uptake estimation (González-García et al., 2012; Morales et al., 2015b; Phyllis2 ECN, 1998)

SS1. Production of eucalyptus wood chips (1m^3)		
Item	***Amount***	***Units***
Mass inputs from technosphere		
Land use (forest extensive occupation)	0.091	ha·a
E. globulus stems	22	stems
Diesel	0.68	kg
Petrol	7.78	g
Lubricants	30	g
Herbicide (glyphosate)	87	g
Ternary fertilizer (16%N 8%P_2O_5 12%K_2O)	0.14	kg
Diammonium phosphate (18%N 46%P_2O_5)	1.33	kg
Lorry 3.5 t	0.52	tkm
Inputs from nature		
CO_2 uptake from Eucalyptus Woodchips	1.16	kg CO_2/kg wood
Outputs to technosphere		
Wood chips	1	m^3
Emissions to air		
SO_2	7.26	g
NO_x	40	g
CO_2	2.38	kg
CO	9.17	g
VOC	5.4	g
N_2O	24	g
Pentane	0.24	g
NMVOC	24	mg
CH_4	97	mg
Particulates	0.89	g
N_2	70	g
NH_3	59	g
Emissions to water		
NO_3^-	1.51	kg
PO_4^-	12	g

Table A38 Inventory for the wood pulping (SS2) with calcium bisulfite (in a pulp and paper factory (no bleaching or further pulp processing included) (Chen et al., 2016; Modahl et al., 2015)

SS2. Pulp and paper factory (per kg SSL)		
Item	***Amount***	***Units***
Mass inputs from technosphere		
Eucalyptus woodchips	$9.99\cdot10^{-4}$	m^3
Sulfur	$1.20\cdot10^{-2}$	kg
Calcium carbonate	$1.18\cdot10^{-2}$	kg
Process water	12.19	kg
NaOH	$3.64\cdot10^{-4}$	kg
Transport (lorry)	105	kgkm
Energy inputs from technosphere		
Electricity	$6.55\cdot10^{-2}$	kWh
Steam	0.26	kg
Outputs to technosphere		
SSL	1.00	kg
Pulp	0.78	kg
Emissions to air		
Water (vent)	$4.73\cdot10^{-3}$	kg
CO_2 (vent)	$2.91\cdot10^{-3}$	kg
SO_2 (vent)	$8.00\cdot10^{-6}$	kg
NaOH (vent)	$4.73\cdot10^{-4}$	kg
Steam out	$7.03\cdot10^{-2}$	kg
Emissions to water		
COD	$4.10\cdot10^{-3}$	kg
BOD	$1.67\cdot10^{-3}$	kg
Total P	$6.39\cdot10^{-4}$	kg
Total N	$3.62\cdot10^{-3}$	kg

Table A39 Inventory for the pretreatment of SSL (SS3), through nanofiltration obtaining lignosulfonates as co-products, continuous operation (Pateraki et al., 2016a)

SS3. Pretreatment (per kg SA)		
Item	***Amount***	***Units***
Energy inputs from technosphere		
Electricity filtration	0.01	kWh
Outputs		
SSL	4.25	kg
Lignosulfonates	2.15	kg

Table A40 Inventory for the pretreatment of SSL (SS3) through nanofiltration, obtaining lignosulfonates as co-products, fed batch operation (Pateraki et al., 2016a)

SS3. Pretreatment (per kg SA)		
Item	***Amount***	***Units***
Energy inputs from technosphere		
Electricity filtration	0.06	kWh
Outputs to process and technosphere		
SSL	4.25	kg
Lignosulfonates	2.15	kg

Table A41 Inventory for the sterilization of inputs to the fermentation (SS4), continuous operation (Ladakis et al., 2018)

SS4. Sterilization (per kg SA)		
Item	***Amount***	***Units***
Energy inputs from technosphere		
Steam for sterilization	0.27	kg

Table A42 Inventory for the sterilization of inputs to the fermentation (SS4), fed batch operation (Ladakis et al., 2018)

SS4. Sterilization (per kg SA)		
Item	***Amount***	***Units***
Energy inputs from technosphere		
Steam for sterilization	0.20	kg

Table A43 Inventory for continuous fermentation for the production SA (SS5)

SS5. Fermentation (per kg SA)		
Item	***Amount***	***Units***
Mass inputs from technosphere		
Water	1.00	kg
Yeast extract	0.25	kg
NaH_2PO_4x H_2O	$5.91\cdot10^{-2}$	kg
Na_2HPO_4	$1.58\cdot10^{-2}$	kg
NaCl	$5.09\cdot10^{-2}$	kg
$MgCl_2$ x 6 H_20	$1.02\cdot10^{-2}$	kg
$CaCl_2$ x 2 H_2O	$1.02\cdot10^{-2}$	kg
NaOH	1.00	kg
CO_2	0.37	kg
Process water cooling	4.00	kg
Energy inputs from technosphere		
Electricity agitation	1.43	kWh
Electricity cooling	$3.10\cdot10^{-2}$	kWh

Table A44 Inventory for fed batch fermentation for the production SA (SS5)

SS5. Fermentation		
Item	***Amount***	***Units***
Mass inputs from technosphere		
Water	0.59	kg
Yeast extract	$1.48 \cdot 10^{-1}$	kg
$MgCO_3$	$1.48 \cdot 10^{-1}$	kg
NaH_2PO_4x H_2O	$3.40 \cdot 10^{-2}$	kg
Na_2HPO_4	$9.20 \cdot 10^{-3}$	kg
NaCl	$2.96 \cdot 10^{-2}$	kg
$MgCl_2$ x 6 H_20	$5.90 \cdot 10^{-3}$	kg
$CaCl_2$ x 2 H2O	$5.90 \cdot 10^{-3}$	kg
NaOH	1.20	kg
CO_2	0.30	kg
Process water cooling	4.00	kg
Energy inputs from technosphere		
Electricity agitation	2.07	kWh
Electricity cooling	$3.10 \cdot 10^{-2}$	kWh

Table A45 Inventory for the separation sequence of SA in continuous operation (SS6)

SS6. Downstream (per kg SA)		
Item	***Amount***	***Units***
Mass inputs from technosphere		
Activated carbon, columns	$1.20 \cdot 10^{-3}$	kg
Resin, ion exchange	$4.00 \cdot 10^{-4}$	kg
HCl	0.90	kg
Energy inputs from technosphere		
Electricity centrifugation	$5.40 \cdot 10^{-2}$	kWh
Electricity evaporation	1.60	kWh
Electricity crystallization	0.19	kWh
Outputs to technosphere		
Wastewater	1.45	kg
Succinic acid	1	kg
Waste to treatment		
Bacterial biomass to incineration	0.12	kg
Spent activated carbon	$1.20 \cdot 10^{-3}$	kg
Spent ion exchange resin	$4.00 \cdot 10^{-4}$	kg

Table A46 Inventory for the separation sequence of SA in fed batch operation (SS6)

SS5. Downstream		
Item	***Amount***	***Units***
Mass inputs from technosphere		
Activated carbon, columns	$1.20{\cdot}10^{-3}$	kg
Resin, ion exchange	$4.00{\cdot}10^{-4}$	kg
HCl	1.1	kg
LP steam evaporation	0.29	kg
Energy inputs from technosphere		
Electricity centrifugation	$3.16{\cdot}10^{-2}$	kWh
Electricity evaporation	0.94	kWh
Electricity crystallization	0.19	kWh
Outputs to technosphere		
Wastewater	1.74	kg
Succinic acid	1	kg
Waste to treatment		
Bacterial biomass to incineration	0.15	kg
Spent activated carbon	$1.20{\cdot}10^{-3}$	kg
Spent ion exchange resin	$4.00{\cdot}10^{-4}$	kg

Table A47 Inventory for the capture of CO_2 from the production of clinker assuming 90% capture rate (SS5) (García-Gusano et al., 2015)

Carbon capture and utilization (fossil alternative)		
CO_2 from fossil point source, long-term supplier, cement industry (per ton clinker)		
Item	***Amount***	***Units***
Mass inputs from technosphere		
Clinker (no CC)	1.00	kg
Ammonia	$2.00{\cdot}10^{-3}$	kg
MEA	$2.60{\cdot}10^{-3}$	kg
Limestone	$1.40{\cdot}10^{-3}$	kg
Energy inputs from technosphere		
Electricity	$7.00{\cdot}10^{-5}$	MWh
Heat	$2.25{\cdot}10^{-3}$	GJ
Outputs to technosphere		
Clinker (with CC)	1	kg
CO_2 (90% captured)	0.76	kg
Emissions to air		
CO_2 (10% not captured)	0.084	kg

Table A48 Inventory for the capture of CO_2 from the production of bioethanol assuming 90% capture rate (SS5) (Carminati et al., 2019)

Biobased carbon capture and utilization		
CO_2 from biogenic point source, near-term supplier, bioethanol fermentation		
Item	***Amount***	***Units***
Mass inputs from technosphere		
Bioethanol from wood (no CC)	1.00	kg
Energy inputs from technosphere		
Electricity	0.11	kwh/kg CO_2
Outputs to technosphere		
Bioethanol (with CC)	1	kg
CO_2 (90% captured)	1.16	kg
Emissions to air		
CO_2 (10% not captured)	0.13	kg

Table A49 Inventory for the petrochemical production of SA used as business as usual (fossil BAU) (Pinazo et al., 2015)

Petrochemical SA (1kg)		
Item	***Amount***	***Units***
Mass inputs from technosphere		
Maleic anhydride	0.89	kg
Hydrogen	0.25	kg
Water	0.30	kg
Nitrogen	$7.29 \cdot 10^{-2}$	kg
Palladium catalyst	$1.0 \cdot 10^{-5}$	kg
Natural gas	0.10	kg
Energy inputs from technosphere		
Electricity	0.36	kWh
Outputs to technosphere		
Succinic acid	1	kg
Waste to treatment		
Waste (generic)	0.32	kg

Table A50 Inventory for the biobased production of SA used as business as usual (biobased BAU) (Moussa et al., 2016)

First generation SA (1kg)		
Item	***Amount***	***Units***
Mass inputs from nature		
CO_2	2.01	kg
Cooling water	1.23	m^3
Mass inputs from technosphere		
Sorghum grain	1.66	kg
Sulfuric acid	1.11	kg
Ammonia	0.41	kg
Tap Water	1.67	kg
Ultrapure water	25.3	kg
Glucose	$1.30 \cdot 10^{-2}$	kg
Energy inputs from technosphere		
Electricity	2.67	kWh
Heat	14.77	MJ
Outputs to technosphere		
Succinic acid	1	kg
Ammonium sulfate	1.49	kg
Waste to treatment		
Wastewater	$1.1 \cdot 10^{-2}$	m^3
Biowaste (incineration)	$8.2 \cdot 10^{-1}$	kg
Sorghum bagasse	$3.95 \cdot 10^{-1}$	kg
Emissions to air		
Water	2.72	kg
Volatile organic compounds	$2.00 \cdot 10^{-3}$	kg
Carbon monoxide	$1.50 \cdot 10^{-2}$	kg
Nitrogen oxides	$5.00 \cdot 10^{-3}$	kg
Particulates µm<10	$1.00 \cdot 10^{-3}$	kg
Ammonia	$1.72 \cdot 10^{-4}$	kg
Lead	$5.20 \cdot 10^{-6}$	kg
Sulfuric acid	$8.06 \cdot 10^{-5}$	kg

Table A51 Prices for outputs in the life cycle for the production of SA (Considered in economic allocation calculations)

Product	Price	Unit	Average €/kg	Reference
Bioethanol	0.47	$/l	0.524	(Gnansounou, 2010)
Clinker	37	€/t	0.0370	(McKinsey Climate Change Initiative, 2008)
CO_2 from clinker	26-42	$/ton	0.0299	(Bains et al., 2017)
CO_2 from ethanol	14	$/ton	0.0123	(Bains et al., 2017)
Lignosulfonates	300	$/ton	0.240	(Holladay et al., 2007)
SSL (assuming price of fermentable sugars- xylose)	0.4	$/kg	0.320	(Parra-Ramírez et al., 2018)
Pulp (assuming price of dissolving pulp)	1350	€/t	1.35	(Nitzsche et al., 2020)
Ammonium sulfate	0.137	$/kg	0.121	(Independent Commodity Intelligence Services (ICIS), 2003)
Succinic acid			2.8	(Biddy et al., 2016)

Table A52 Economic and mass allocation factors in A-LCA

Subsystem	Outputs	Mass allocation (%)	Economic allocation (%)
SS2	Pulp	43.90	84.35
	SSL	56.10	15.65
SS3	SSL rich in sugars	66.41	72.49
	Lignosulfonates	33.59	27.51
SS5 (CO_2 from biogenic point emission source)	Bioethanol	46.20	97.30
	CO_2	53.80	2.66
SS5 (CO_2 from fossil point emission source)	Clinker	57.00	62.10
	CO_2	43.00	37.90
BAU biobased SA	SA	40.20	93.96
	Ammonium sulfate	59.80	6.04

A5.3 MARKET TRENDS AND MARGINAL MIXES FOR SA

Table A53 Historic market data for SA production volume

Year		1990[a]	2010[b,c]	2011[d]	2015[d]
Fossil	(ton/year)	17,000	25,000	25,000	25,000
Biobased 1st generation	(ton/year)	1	1,250	10,000	180,000
Total	(ton/year)	17,001	26,250	35,000	205,000

a (Nghiem et al., 2017)
b (Gallezot, 2012)
c (Moussa et al., 2016)
d (Pinazo et al., 2015)

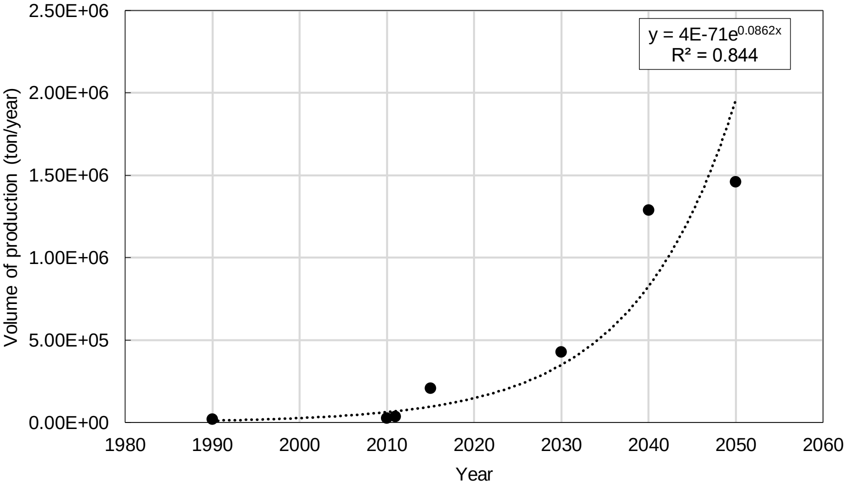

Figure A20 Estimated projection of growth for succinic acid production from data in table A53

Table A54 Current mix of production of SA, year 2015

	Current mix
Fossil	12%
Biobased 1st generation	88%

Table A55 Marginal mix estimation for short-term scenarios in timeline 1 (LT1 scenarios)

	Fossil	**Biobased 1st generation**
Annual trend	1.88	719,996
Technology lifetime	40	40
Capital replacement rate (%)	-2.5	-2.5
Net annual trend (%)	4.38	719,999
Net annual change	7,450	7,200
Marginal mix (%)	50.85	49.15

Table A56 Marginal mix estimation for short-term scenarios in timeline 2 (LT2 scenarios)

	Fossil	**Biobased 1st generation**
Annual trend	1.88	2,860
Technology lifetime	40	40
Capital replacement rate (%)	-2.50	-2.50
Net annual trend (%)	4.38	2,863
Net annual change	7,450	35,781
Marginal mix (%)	17.23	82.77

Table A57 Marginal mix estimation long-term scenarios (LT)

	Fossil	**Biobased 1st generation**
Annual trend	0	2,860
Technology lifetime	N/A	40
Capital replacement rate (%)	N/A	-2.5
Net annual trend (%)	N/A	28,623
Net annual change	N/A	35,781
Marginal mix (%)	0	100

A5.4 LIFE CYCLE INVENTORY FOR CONSEQUENTIAL LCA

Table A58 Current scenario (no change in current mix of SA)

Current scenario	Value	Units
SA fossil (12%) + SA biogenic (88%)	1	kg
Avoided ammonium sulfate	1.31	kg

Table A59 Consequential LCA inventory for short term scenarios (TL1)

Short term scenario, B-ST-TL1	Value	Units
SA (present study, no allocations, biobased CO_2)	1	kg
Displaced ethanol (from corn)	0.322	kg/kg SA
Substituted bioethanol industry (now with CC)	0.296	kg/kg SA
SA avoided (50.9% fossil, 49.1% biobased)	1	kg
Lignosulfonates (avoided additives-plasticizer for cement)	2.15	kg/kg SA
Short term scenario, F-ST-TL1		
SA (present study, no allocations, fossil CO_2)	1	kg
Displaced ethanol (from corn)	0.322	kg/kg SA
Substituted clinker industry (now with CC)	0.494	kg/kg SA
SA avoided (50.9% fossil, 49.1% biobased)	1	kg
Lignosulfonates (avoided additives-plasticizer for cement)	2.15	kg/kg SA

Table A60 Consequential LCA inventory for short term scenarios (TL2)

Short term scenario, B-ST-TL2	Value	Units
SA (present study, no allocations, biobased CO_2)	1	kg
Displaced ethanol (from corn)	0.322	kg/kg SA
Substituted bioethanol industry (now with CC)	0.296	kg/kg SA
SA avoided (17.2% fossil, 82.8% biobased)	1	kg
Lignosulfonates (avoided additives-plasticizer for cement)	2.15	kg/kg SA
Short term scenario, F-ST-TL2		
SA (present study, no allocations, fossil CO_2)	1	kg
Displaced ethanol (from corn)	0.3216	kg/kg SA
Substituted clinker industry (now with CC)	0.4940	kg/kg SA
SA avoided (17.2% fossil, 82.8% bio)	1	kg
Lignosulfonates (avoided additives-plasticizer for cement)	2.15	kg/kg SA

Table A61 Consequential LCA inventory for long term scenarios (LT)

Long term scenario, B-LT	Value	Units
SA (present study, no allocations, biobased CO_2)	1	kg
Displaced ethanol (from corn)	0.322	kg /kg SA
Displaced bioethanol industry (now with carbon capture)	0.296	kg /kg SA
SA avoided (0% fossil, 100% bio)	1	kg
Lignosulfonates (avoided additives-plasticizer for cement)	2.15	kg
Long term scenario, F-LT		
SA (present study, no allocations, biobased CO_2)	1	kg
Displaced ethanol (from corn)	0.322	kg /kg SA
Displaced clinker industry (now with CC)	0.494	kg /kg SA
SA avoided (0% fossil, 100% bio)	1	kg
Lignosulfonates (avoided additives-plasticizer for cement)	2.15	kg

A5.5 SUPPLEMENTARY RESULTS

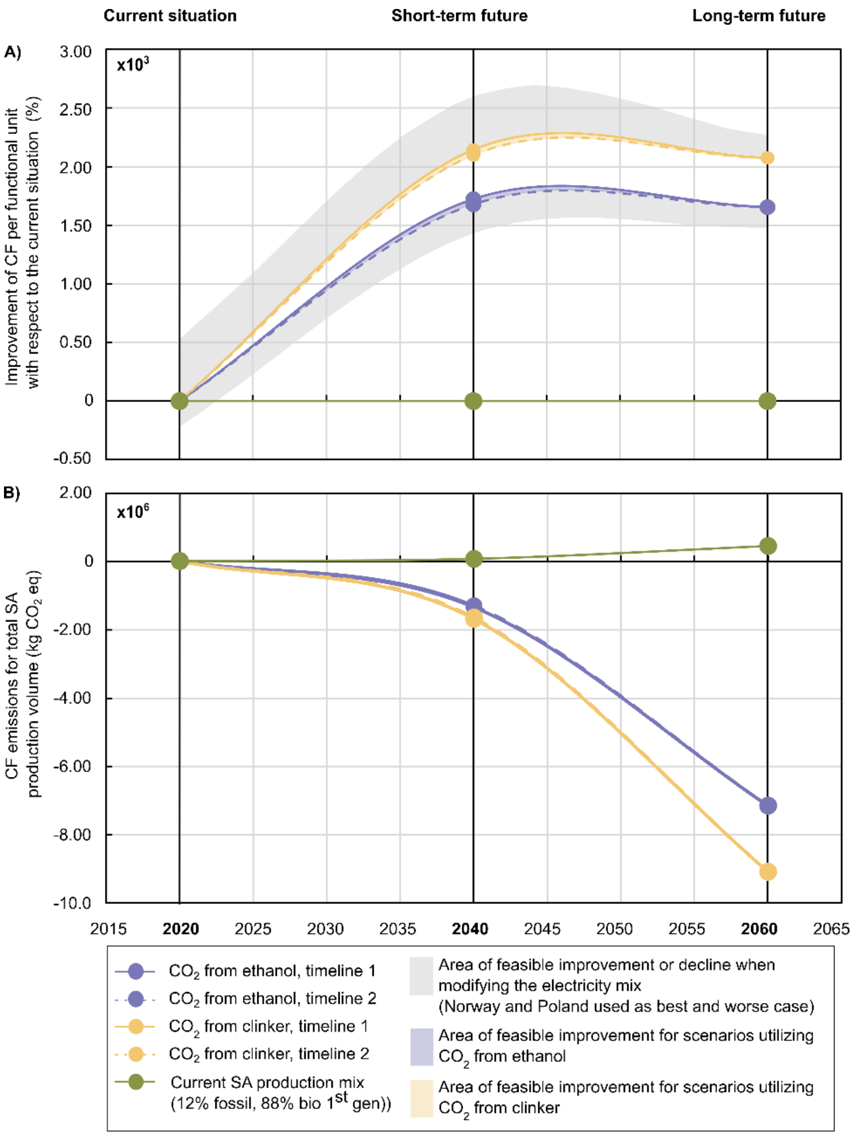

Figure A21 Projection of C-LCA impacts in Carbon Footprint (CF) to 20 and 40 years from the current situation. SA is produced in fed-batch operation. A) Displays the percent improvement of the CF with respect to the current SA scenario per functional unit B) Displays the total CF of SA market considering a growth in the SA production volume

Percent-improvement calculations for consequential values

The maximum value for the percent-improvement in each CCU scenario corresponds to that of TL1 (short-term, timeline 1), which are, for fossil and biogenic CO_2 the best scenarios with respect to the BAU. The percent-improvement was obtained as follows:

$$\mathrm{Improvement}\ (\%) = \frac{\left(\frac{\mathrm{CF}}{\mathrm{FU}}\right)_{\mathrm{BAU}} - \left(\frac{\mathrm{CF}}{\mathrm{FU}}\right)_{\mathrm{SCEN}}}{\left(\frac{\mathrm{CF}}{\mathrm{FU}}\right)_{\mathrm{BAU}}} \times 100\% \qquad \text{Eq. 1}$$

Where $\frac{\mathrm{CF}}{\mathrm{FU}}$ is the carbon footprint per functional unit for each scenario, BAU is the business-as-usual case (current scenario), and SCEN represents any of the scenarios in the current study. For 1465%, SCEN= F-ST-TL1, for 1023%, SCEN= B-ST-TL1.

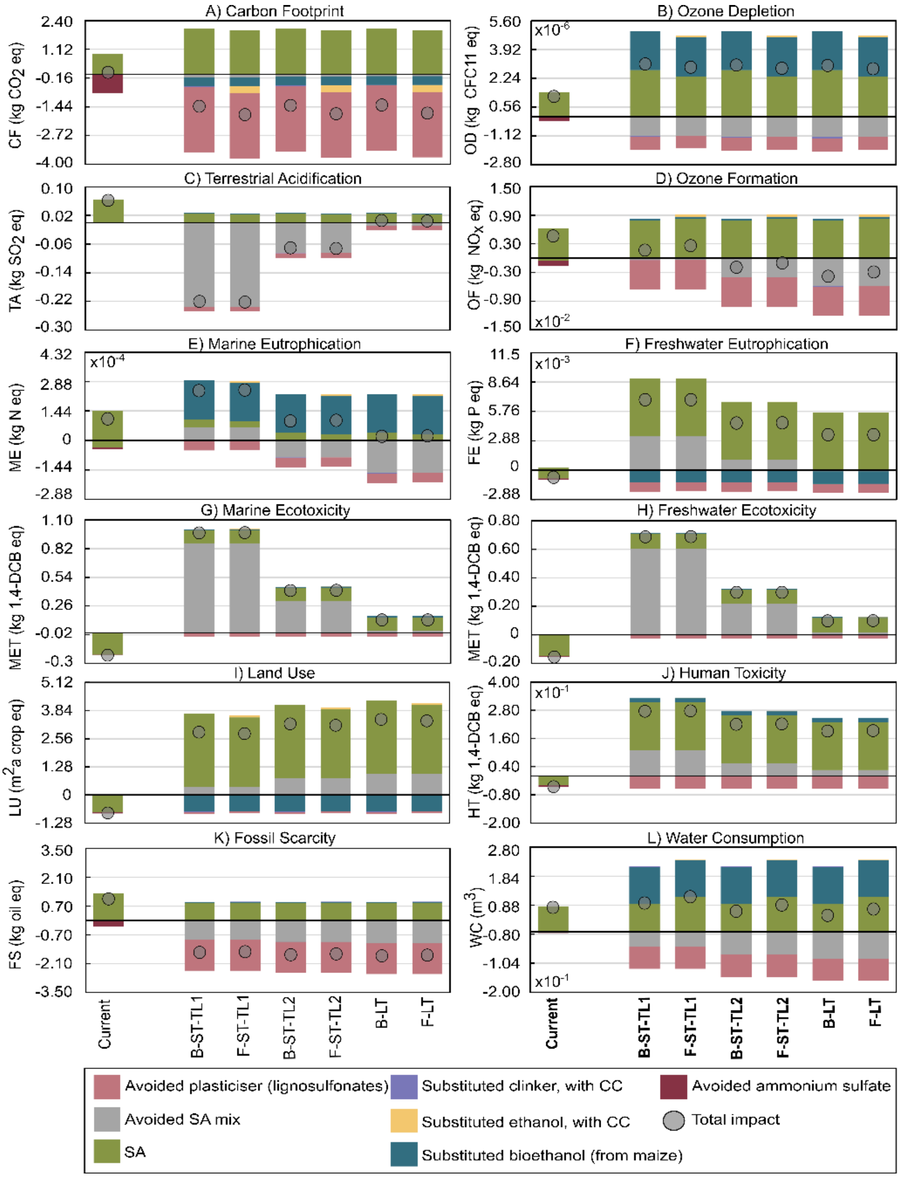

Figure A22 Comparative evaluation and breakdown of environmental profiles through C-LCA for SA produced in fed-batch operation. A) Carbon footprint B) Ozone depletion C) Terrestrial acidification D) Ozone formation E) Marine eutrophication F) Freshwater eutrophication G) Marine ecotoxicity H) Freshwater ecotoxicity I) Land use J) Human toxicity K) Fossil scarcity L) Water consumption.


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Annex III

Abbreviations

ABBREVIATIONS

A-LCA	attributional life cycle assessment
ALO	agricultural land occupation
BAU	business-as-usual
BECCS	bioenergy with carbon capture and storage
CCS	carbon capture and storage
CCU	carbon capture and utilization
CDR	carbon dioxide removal
CF	Carbon footprint
CFCs	chlorofluorocarbons
C-LCA	consequential life cycle assessment
DACCS	direct air carbon capture and storage
DALY	Disability-Adjusted Life Years
DCM	dichloromethane
DFF	diformylfuran
DMSO	dimethyl sulfoxide
EA	economic allocation
FDCA	2,5-furandicarboxylic acid
FE	freshwater eutrophication
FET	freshwater ecotoxicity
FFCA	5-formyl-2-furancarboxylic acid
FS	fossil scarcity
FU	functional unit
GW	global warming
HMF	hydroxymethyl furfural
HMFO	hydroxymethylfurfural oxidase
HT	human toxicity
IPCC	Intergovernmental Panel on Climate Change
IR	Ionizing radiation
ISO	International Organization for Standardization
LCA	life cycle assessment
LMW lignin	low molecular weight lignin
LU	land use
MA	mass allocation
ME	marine eutrophication
MET	marine ecotoxicity
NET	negative emission technology
NREU	non-renewable energy
OD	ozone depletion
OF	ozone formation
PA	Polyamide
PBS	polybutylene succinate

PE	polyethylene
PEF	polyethylene furanoate
PEG	polyethylene terephthalate
PET	polyethylene terephthalate
PHA	polyhydroxyalkanoates
PMF	Particulate matter formation
PS	polystyrene
PVA	polyvinyl alcohol
PVC	polyvinyl chloride
REPA	Resource and environmental profile analysis
SA	succinic acid
SETAC	Society of Environmental Toxicology and Chemistry
SPOLD	Society for the Promotion of life cycle analysis
SS	subsystem
SSL	spent sulfite liquor
TA	terrestrial acidification
TOPO	triocyphosphine oxide
TPA	terephthalic acid
ULO	urban land occupation
UPO	unspecific peroxygenase
VSLS	very-short-lived substances
WC	water consumption


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Annex IV

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The defossilization of the chemical industry, together with negative emission technologies like carbon capture and storage and carbon capture and utilization have been defined as essential contributors to curb the climate crisis.

To reach climate goals, it will also be necessary to support the sustainable development of biorefining pathways.The objective of this thesis is to determine the environmental weaknesses and strengths of second generation biorefineries.

The analysis of different renewable carbon opportunities to reach climate neutrality goals and objectives beyond decarbonization was achieved through the life cycle assessment methodology.

Studying different modelling systems allowed to support the consistent development of recommendations and best practices in regulations and standards of biorefineries.