INTEGRATED MASTER IN ENVIRONMENTAL ENGINEERING 2019/2020

LCA OF A NOVEL F-T SYNCRUDE PATHWAY USING ADVANCED NETMIX MICROREACTOR TECHNOLOGY

Conversion of associated gas destined for flaring into liquid fuels in offshore FPSO operations

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“We take a handful of sand from the endless landscape of awareness around us and call that handful of sand the world.” – Robert M. Pirsig

Resumo

Uma avaliação de ciclo de vida foi realizada para comparar os impactos ambientais relacionados com a operação de duas cadeias de produção (Dry Methane Reforming, DMR e Steam Methane Reforming, SMR, utilizadoras de sistemas de microreactores NETmix) para converter o gás natural associado destinado à queima sem aproveitamento energético "*flaring*" num produto com valor comercial. Este gás é produzido em plataformas do tipo "*Floating Production Storage and Offloading*" (FPSOs) offshore durante operações de extração de petróleo e gás natural, e foi simulada a sua conversão em crude líquido sintético, para posterior refinação e conversão em Combustível de Aviação Sustentável. Esta operação está associada à produção diária de 500 barris de crude sintético por dia.

Quatro avaliações complementares foram realizadas: uma avaliação berço-ao-túmulo, usando 1 MJ Poder Calorífico Inferior (PCI) como unidade funcional, uma avaliação berço-ao-túmulo usando 1 barril diário de crude como unidade funcional, e duas avaliações porta-a-porta usando 1 MJ PCI como unidade funcional, uma assumindo impactos nulos de extração de gás associado e outra assumindo impactos negativos, contabilizando a redução das emissões diretas. Para ambas as avaliações berço-ao-túmulo, a metodologia de expansão do sistema foi aplicada para alocar a totalidade dos impactos da fase de extração do Petróleo e Gás Natural à extração do gás associado, de forma a avaliar quantitativamente a redução de impactos ambientais na operação de uma FPSO (caso base) associada à aplicação das tecnologias SMR e DMR.

A operação de uma central FPSO hipotética foi estimada usando dados encontrados na literatura (Jungbluth, N., et. Al, 2018), referentes aos dados médios de operação relativos a várias centrais de exploração offshore de Petróleo e Gás Natural no mundo.

Através das avaliações berço-ao-túmulo, foi possível observar uma redução significativa nos impactos de Potencial de Aquecimento Global (PAG) e Oxidação Fotoquímica (OF), embora a última não se devesse à redução do fenómeno de *flaring* mas sim à intensificação de emissões de NO_x. Um aumento dos impactos nas categorias de Depleção Abiótica de Combustíves Fósseis (DACF) e Depleção da Camada de Ozono (DCO) foi verificado, devido ao aumento do consumo de combustíveis fósseis para geração de energia e eletricidade. Similarmente, um aumento na categoria de impacto Ecotoxicidade Marinha (EM) foi observado associado à produção adicional de água residual durante a operação das cadeias de produção. Por outro lado, uma redução relativa ao caso base nos impactos das categorias DACF e DCO existe para cenários de piores operação, mais intensivos em emissões. Um aumento da categoria de Acidificação Potencial (AP) foi também possível de observar, relacionado com o uso de calor gerado em combustão de combustíveis fósseis na etapa de *reforming*, cujo peso no ciclo de vida do produto se sobrepõe à redução do fenómeno de *flaring* na medida em que a combustão gera mais emissões de NO_x do que evita.

A partir das avaliações porta-a-porta assumindo impactos de extração negativos, foi possível concluir com um grau de confiança de 95% que até ao momento, a conversão de gás associado usando estas cadeias produz um crude sintético com um PAG negativo de -0.601 ([-0.599,-0.603]) kg CO_2 eq / MJ PCI e -1.60 ([-1.57,-1.62]) kg CO_2 eq / MJ PCI respetivamente, podendo abater 1200 a 3300 toneladas de CO_2 eq por dia à escala atual de produção.

A cadeia de produção SMR foi considerada como sendo a melhor entre as duas pois o seu desempenho ambiental é melhor que a cadeia DMR em todas as categorias exceto as que estão relacionadas com a redução do *flaring* nas avaliações berço-ao-túmulo, resultados que inerentemente são influenciados pelas suposições tomadas para combater as dificuldades encontradas na gestão de dados para esta ACV.

Abstract

A life cycle assessment study was carried out to compare the environmental impact of using two synthetic crude (syncrude) production pathways (Dry Methane Reforming, DMR and Steam Methane Reforming, SMR, using novel NETmix microreactor technology) to convert associated gas destined for flaring produced in an offshore general Oil & Gas (O&G) Floating Production Storage and Offloading (FPSO) facility into liquid syncrude for later refinement into Sustainable Aviation Fuel. This is associated with a production scale of 500 barrels of syncrude per day.

Four different complementary evaluations were performed: a cradle-to-gate approach using 1 MJ Lower Heating Value (LHV) of syncrude produced as a functional unit, a cradle-to-gate approach using 1 barrel of crude produced as a functional unit, and two gate-to-gate approaches using 1 MJ LHV of syncrude produced as a functional unit, one considering null extraction impacts and the other negative extraction impacts, accounting for avoided emissions. For both cradle-to-gate approaches, system expansion was applied to allocate 100% of the impacts of the O&G extraction phase to the associated gas collection, in order to provide a way to quantify the impact reduction of the SMR and DMR technologies applied to the FPSO's operation.

An hypothetical daily FPSO operation was estimated using data from Jungbluth, N. et. Al, (2018) compiling average data from various offshore O&G extraction facilities in the world.

It was concluded from the cradle-to-gate approaches that a significant reduction in Global Warming Potential (GWP) and Photochemical Oxidation (PO) impacts compared to the FPSO operation baseline was verified for both scenarios, although the latter did not result as a consequence of the reduction of the flaring phenomena but rather from an intensification of NO_x emissions. An increase in the impact categories related to fossil fuel consumption on site for energy and electricity purposes (Abiotic Depletion of Fossil Fuels, ADFF, and Ozone Depletion Potential, ODP) in the Reforming and Amine Scrubbing stages of the life cycle, and marine water pollution related to process wastewater treatment and discharge, (Marine Water Ecotoxicity, MWE), were observed for both scenarios, although impact reduction in the first two categories could be achieved in the worst case scenarios of FPSO operation emissions. An increase of the environmental impact was observed for the Acidification Potential (AP) category, related to the heat supply in the reforming step of the pathways' life cycle, whose negative weight on the life cycle overcomes the positive reduction of the flaring phenomena given the fact that the combustion step generates more NO_x emissions than the pathway offsets.

From the Gate to Gate Approach assuming negative associated gas extraction impact results, it is possible to conclude with 95 % confidence that up to this point, converting associated gas destined for flaring using these pathways produces a syncrude with a negative GWP impact of -0.601 ([-0.599,-0.603]) kg CO_2 eq / MJ LHV and -1.60 ([-1.57,-1.62]) kg CO_2 eq/ MJ LHV

respectively possibly offsetting around 1200 and 3300 tons of CO_2 eq per day at the current production scale.

The SMR pathway was deemed to be the pathway with the best environmental performance as it beat the DMR pathway in every category except the ones related to flaring reduction phenomena in the cradle-to-gate approaches, which inherently had a wrong bias in the results given the methodology LCI assumptions used to tackle the difficulties found in data management for this LCA.

Acknowledgments

There's a great deal of people to be acknowledged for the completion of this thesis – although it was my master thesis, the first thorough scientific work under my name, I was supported by a group of people who helped dealing with my failures, over-enthusiasm and who congratulated me in my successes.

From an early stage in my course I developed a passion for circularity in industry and society – a highly efficient system that maintains our living standards by minimizing the use of resources, and maximizing the re-use of waste. My first acknowledgment is towards Prof. Dr. José Carlos Lopes for the opportunity given to me to develop a life cycle assessment of a technology that can well revolutionize the paradigm of heavy-polluting industries. I could not ask for a better subject for my master thesis. Contributing to a project among many being designed by CoLab Net4CO2 that is steadfastly being developed and improved supplies a motive for me to pour my soul and enthusiasm into my work, which idealistically is all a practitioner in engineering can hope for – an added value (although not as important as the creativity of the engineers designing it) to a technology which I believe is going to be truly beneficial to our future as a sustainable society.

My expressed thanks go to Dr. Mariana G. Domingos and Eng. Lígia Dias for their considerable effort into making the first steps of the LCA project as simple and effective as possible – the special care into clearing all doubts, and supplying the required information for my project with celerity and in the easiest way possible to interpret was deeply appreciated and allowed for an earlier development of the LCA strategy.

My kind regards go also towards Prof. Dr. Aleksandra Zieminska Stolarska, who kindly received me and my colleague Rita in Poland to work together with us, and who continued to provide valuable assistance after the anticipated return to Portugal due to the COVID-19 outbreak. Without her valuable feedback and insights into LCA, this work would never have the refinement of experience in its results.

Further acknowledgment is given to Prof. Dr. Ricardo Santos, for the insights and time spent into the correct presentation and preparation of this thesis for academic standards, which I tried my best to achieve. Doctor Ricardo J. Santos, supervisor of this work, is member of the Associate Laboratory LSRE-LCM funded by national funds through FCT/MCTES (PIDDAC): Base Funding UIDB/50020/2020. Ricardo J. Santos was supported by Project PTDC/EQU-EPQ/30445/2017 - POCI-01-0145-FEDER-030445 - funded by FEDER funds through COMPETE2020 - Programa Operacional Competitividade e Internacionalização (POCI) and by national funds (PIDDAC) through FCT/MCTES.

I would especially like to thank my girlfriend, Diana, for her motivation and comfort, emotional support, and companionship during these rather troubled times of pandemic. Without her, it would have been quite hard to maintain a steady point of equilibrium. I'd also like to thank my parents, my two brothers and my sister for their everlasting presence and acceptance of my decisions during my stay and early departure from Poland.

Last but not least I'd like to thank my colleague (and housemate for one month) Rita Martinho for her insights, discussion of LCA and for the ability to endure my bad mood as we were both handling the forced confinement and an almost 32 hour trip to Portugal.

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Nomenclature

ADFF	Abiotic Depletion of Fossil Fuels
API	American Petroleum Institute
ATJ	Alcohol to Jet
BtL	Biomass to liquid
CCS	Carbon Capture and Storage
CH4	Methane
CI	Carbon Intensity
CO	Carbon Monoxide
CO2	Carbon Dioxide
CORSIA	Carbon Offsetting and Reduction Scheme for International Aviation
CtL	Coal to liquid
DMR	Dry Methane Reforming
EOR	Enhanced Oil Recovery
ETS	European Emission Trading System
F-T	Fischer-Tropsch
FU	Functional Unit
FPSO	Floating production, storage and offloading
GHG	Greenhouse Gases
GtL	Gas-to-liquidH2 Hydrogen
GWP	Global Warming Potential
H2S	Hydrogen Sulfide
HEFA	Hydroprocessed Esters and Fatty Acids
HTFT	High Temperature Fischer Tropsch
IPCC	Intergovernmental Panel for Climate Change
LCA	Life Cycle Assessment
LCAF	Lower Carbon Aviation Fuels
LCI	Life Cycle Inventories
LNG	Liquified Natural Gas
LTFT	Low Temperature Fischer Tropsch
MDEA	N-methyl-diethanolamine
MEA	Monoethanolamine
MWE	Marine Water Ecotoxicity
N2O	Nitrous oxide
NOx	Nitrogen oxides
ODP	Ozone Layer Depletion
OE	Oil Extracted
OECD	Organization for Economic Cooperation and Development
PAH	Polyaromatic Hydrocarbons
PM	Particulate Matter
PO	Photochemical oxidation
RED	Renewable Energy Directive
SAF	Sustainable Aviation Fuel
SIP	Synthesized Iso-Paraffins
SMR	Steam Methane Reforming
SOx	Sulphur Oxides
SOEC	Solid Oxide Electrolysis Cells

TLWP	Tension Leg Wellhead Platforms
TSI	Total Solar Irradiance
VOC	Volatile organic compounds
WGS	Water Gas Shift

Introduction

Climate Change and the Necessary Actions

Climate change has progressively become a reason of concern in the past decades due to the visible changes in the Earth's ecosystems. Although not all observable effects can be attributed to human activity with the same degree of confidence, it is widely accepted that anthropogenic forcing of the Earth's atmosphere has caused consequences that are distinct from those caused by the natural variability of the Earth's climate in the recent past. These include warming of the ocean up to 700 m and even 2000 m in depth (measurement of values of Ocean Heat Uptake Rate increase of 5.31 ± 0.48 ZJ per year and 4.02 ± 0.97 ZJ per year respectively between 2005 and 2017 [1]) , the medium sea level rise, glacier shrinking, mass loss of the Greenland and Antarctic ice sheets, among others. The weight of anthropogenic forcing for these consequences has been modelled and determined with high degrees of confidence. [2]

This effect can be effectively observed in the greenhouse effect phenomena through increased radiative forcing - the change in the radiative flux at the top of atmosphere related to an external driver of climate change. [3]

Natural greenhouse effect phenomena and natural radiative forcing

The greenhouse effect exists naturally as a result of our atmosphere's greenhouse gases (GHG) capability to prevent part of the outgoing thermal radiation from escaping to space. [4] This effect is responsible for maintaining our temperature 33ºC above the average temperature that Earth would have if our atmosphere was inexistent. [5] Natural phenomena such as volcanic eruptions and total solar irradiance changes have an impact on the greenhouse effect.

However, satellite observations of the total solar irradiance (TSI) from 1978 and 2011 display a lower solar cycle minimum than the previous two solar cycles. Even though there's very low confidence in estimating future solar forcing, there's very high confidence that the radiative forcing caused by the variations observed so far in TSI will be "much smaller than the projected increased forcing due to anthropogenic greenhouse gases during the forthcoming decades". [6] Consequently, an intensification of the warming of the Earth's atmosphere is expected in the near future, following the trend that is observable in Figure 1.

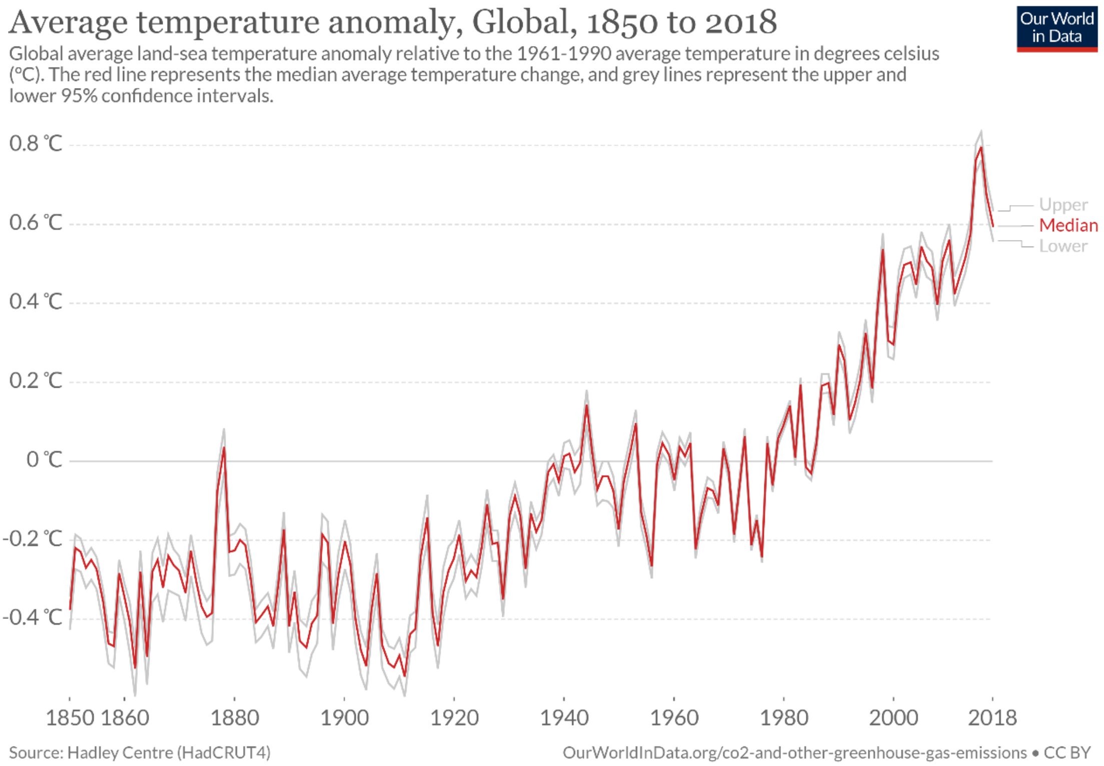


Figure 1 - Recorded global average temperature anomalies since the beginning of the pre-industrial until the present. Source: Richie, H., Roser, M., (2019). [7]

Another thing to bear in mind is that natural radiative forcing caused by volcanic activity is responsible for short term changes (a period of around 2 years) in the observed greenhouse effect. Volcanic eruptions can impact the climate in two ways: the obvious GHG emission that arise from the eruption and through the scattering and absorption of incoming solar radiation due to aerosol volcanic clouds. [8] On the other hand, there have been no major volcanic eruptions since 1991 – and also emissions of CO_2 from volcanic eruptions were determined to be 100 times smaller than anthropogenic emissions of CO_2. [6] Following these observations and other conclusions drawn in their Technical Assessment Reports, The Intergovernmental Panel for Climate Change (IPCC) concluded with very high confidence that the natural radiative forcing observed during the industrial era is a small fraction of the anthropogenic radiative forcing, and even that the former phenomena (namely volcanic aerosol's effects) was responsible for the offset of the latter, likely a substantial fraction of at least 30%.[6]

Anthropogenic greenhouse effect and human induced radiative forcing

Even though the global warming in itself is still hard to pinpoint to human activity alone, as the Earth's Climate depends on a large number of variables besides the aforementioned (some of which hard to model like cloud coverage and water vapor concentration), the latest conclusions of the IPCC indicate that the background concentration of Greenhouse Gases (GHG), and in particular Carbon Dioxide (CO_2), has been a significant indicator of the Earth's warming, "increasing since the pre-industrial era and now higher than ever" [9], and being "extremely likely that they have been the dominant cause of the observed warming since the mid-20th century". [9] This drastic increase can be seen in Figure 2 and 3.

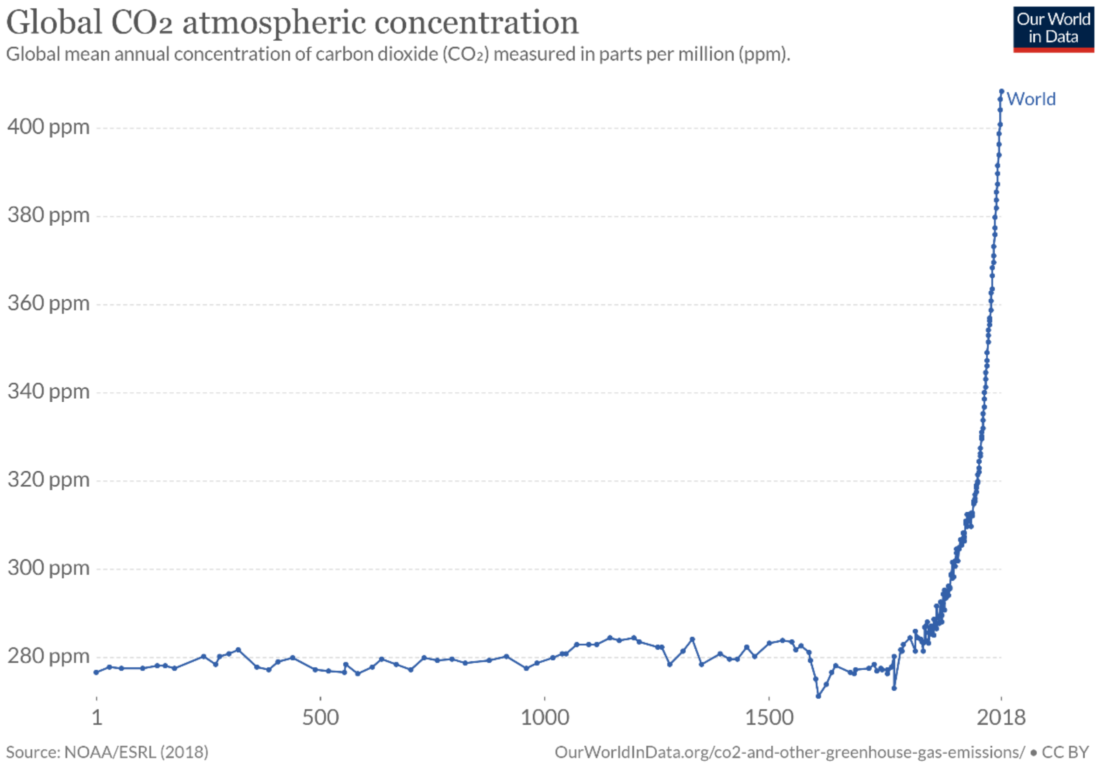


Figure 2 - Global mean annual concentration of Carbon Dioxide in the Atmosphere in the recent geological past. Source: Richie, H., Roser, M., (2019). [7]

As can be seen in figure 2, from 1990 to 2017, the total emissions of CO_2, the most commonly addressed GHG, due to fuel combustion in the world increased by 60% (from close to 20 000 Mt to close to 33 000 Mt) [10], and the average background concentration of CO_2 increased by 14.7 % in the same time period, from 354.39 ppm to 406.55 ppm [11], the latter value unprecedented in 800 000 years of ice-core data. [10] In these 800 000 years of records, it is important to mention that throughout Earth's cycles of ice ages and warmer interglacial periods the background concentration never achieved a value higher than 300 ppm, being fairly stable between 275 and 285 ppm [7] - this can be observed in Figure 3.

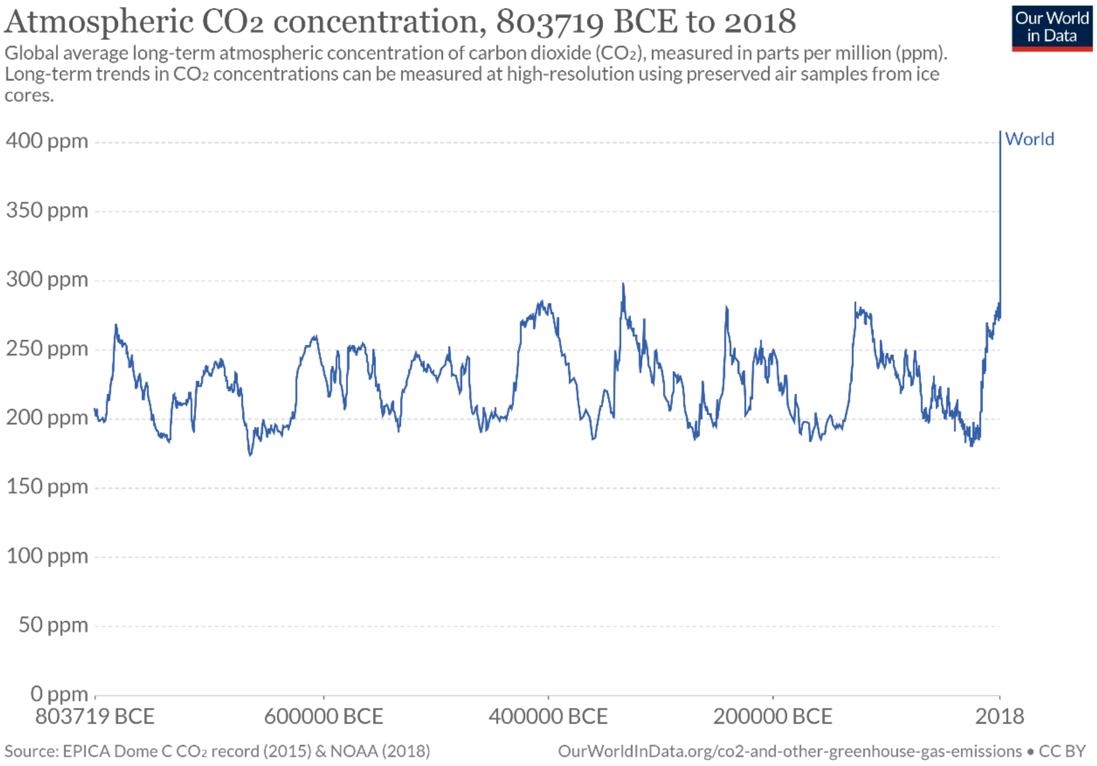


Figure 3 - Long-term atmospheric global average of carbon dioxide concentration observed in ice core data. Source: Richie, H., Roser, M., (2019). [7]

According to the radiative forcing models, CO_2 is currently the component with the largest radiative forcing impact, averaging a growth rate of 0.27 (0.24 to 0.30) W m^{-2} per decade, amounting to a total of 1.82 (1.63 to 2.01) W m^{-2} since the beginning of the industrial era. Since the 1960s, the largest contribution to anthropogenic forcing has been the increasing concentration of CO_2 in the atmosphere, followed by methane (CH_4) with a total of 0.48 (0.43 to 0.53) W m^{-2} and Nitrous oxide (N_2O) with a contribution of 0.17 (0.14 to 0.20) W m^{-2}, all of those emissions related mainly with fossil fuel combustion. [6] The contributions of the different GHG to the observed radiative forcing in the past decades can be observed in Figure 4. In parallel to this CO_2 concentration, positive temperature anomalies were also intensified since the beginning of the industrial era, and especially after the 1960s, as is possible to verify in Figure 1. It is estimated that since the pre-industrial era the average temperature rise consists of approximately 1.1 °C, with a more intense temperature rise in the northern hemisphere relatively to the southern hemisphere. [7]

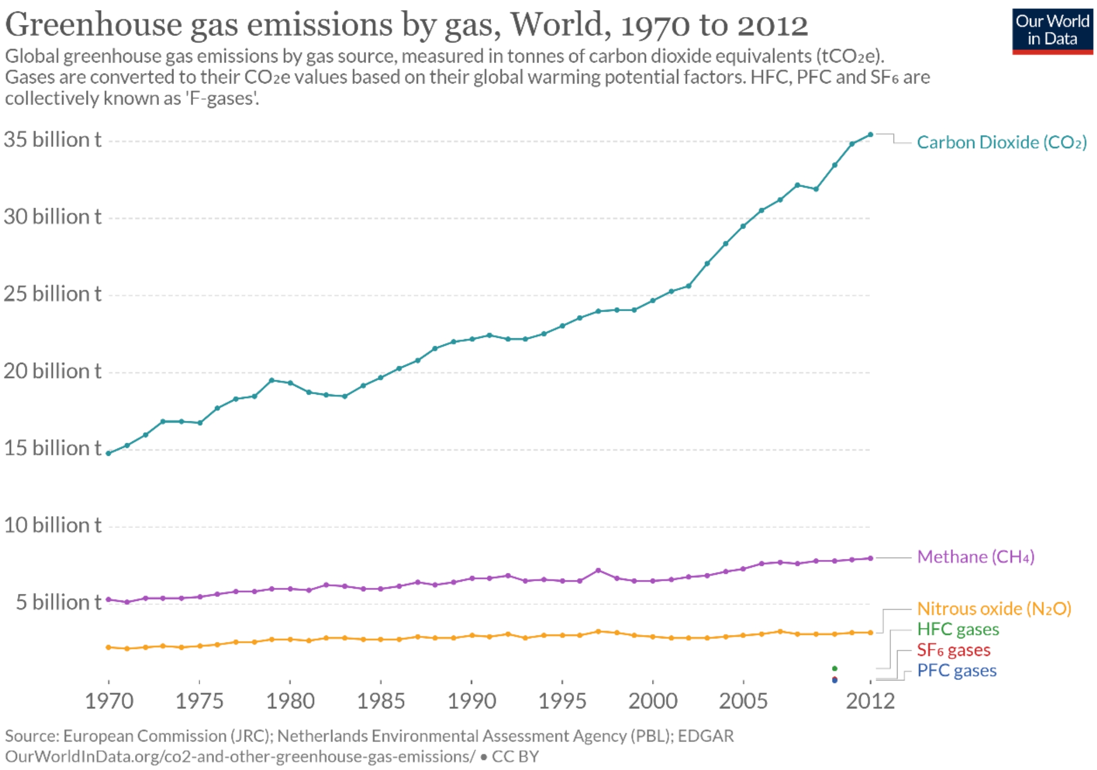
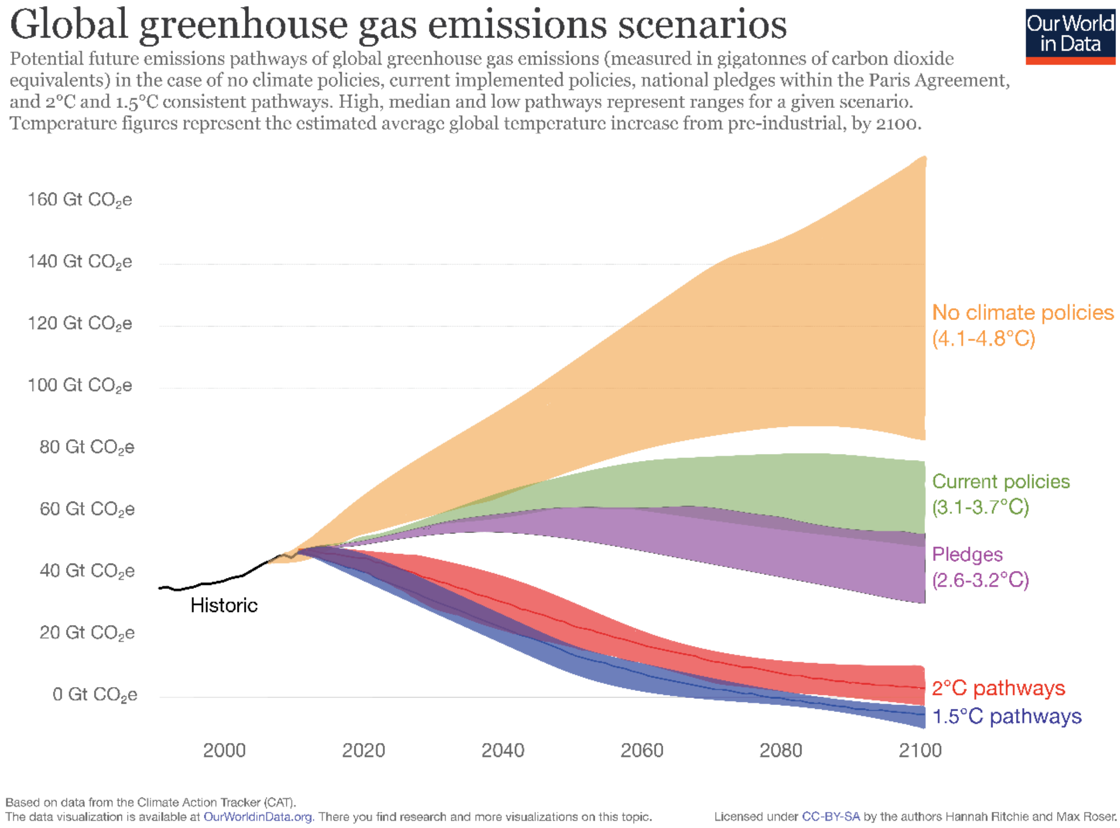


Figure 4 – Global Greenhouse gas emissions by gas type in the world from 1970 to 2012. Source: Richie, H., Roser, M., (2019). [7]

Whilst some might still hold on to the rejection of climate change, it is still a good practice to avoid the destabilization of the Earth's system, and the drastic change of its equilibrium – as such, it is perfectly justifiable that in order to maintain the natural functioning of the ecosystem that we inhabit, we must adapt into a sustainable, carbon-neutral economy that does not compromise the wellbeing of future generations, and to adopt a responsible and efficient use of the fossil fuel resources. [12]

Following these indicators and conclusions, world leaders assumed an objective of keeping the Earth's temperature rise since pre-industrial levels well below 2ºC, with the purpose of limiting the global average of temperature rise to 1.5ºC, in the Paris Agreement of 2015. This was a decision supported by the scientific knowledge gathered and analyzed in the 5th Assessment Report by the IPCC. However, as can be seen in Figure 5, if the commitments to slow down climate change remain as they were defined through international pledges in the Paris Agreement, the average warming of the Earth's temperature by 2100 could achieve values between 2.6 and 3.2 ºC. [7] Moreover, as there's still resistance in the full compliance with the defined objectives, if current not so strict policies were to be adopted permanently, the average warming could achieve even higher values between 3.1 and 3.7 ºC. [7] In order to obtain the desired objective of greenhouse gas reductions, stricter policies providing an incentive to sustainable society and technology need to be addressed, which can be achieved by overall efficiency improvements in energy, industry and technology, a higher share of renewable and nuclear energy in the electricity mix, switching of conventional fuels by less carbon intensive solutions, carbon capture and storage improvements and others. [13]



Based on data from the Climate Action Tracker (CAT).
The data visualization is available at OurWorldinData.org. There you find research and more visualizations on this topic.

Figure 5 - Scenarios for global greenhouse gas emissions until 2100 according to different climate change mitigation policies. Source: Richie, H., Roser, M., (2019). [7]

In the case of the European Union, the Union has committed to cut total emissions (Energy, Industrial Processes and Product Use, Agriculture including forestry and land use change, CO_2 emissions from Biomass, indirect CO_2 and International bunkers and Multilateral Operations [14]) by 40% below 1990 levels of around 5700 Mt, by 2030 [15], in an effort to achieve a carbon neutral, sustainable economy.

One of the policy tools used by the EU to solve this problem is the European Emission Trading System (ETS), which covers around 45 % of the greenhouse emissions in the European Union through a cap and trade system in which a limit is defined to the amount of GHG that can be emitted in installations covered by the system – according to the compliance with the limits imposed, companies can receive or buy emission allowances in open market which can be traded between each other in order to bring flexibility and a collective effort into cutting emissions where it is less expensive. [16]

Impact of the aviation sector in climate change

In 2017, Energy consumption of oil products in transport in the world took a value of close to 2 600 000 ktoe, an increase of 65% since 1971. [17] This growth can be better observed in Figure 6, and it is expected to reach almost 4 000 000 ktoe by 2040, increasing almost exclusively in the non-OECD countries (regions outside the Organization for Economic Cooperation and Development). [18]

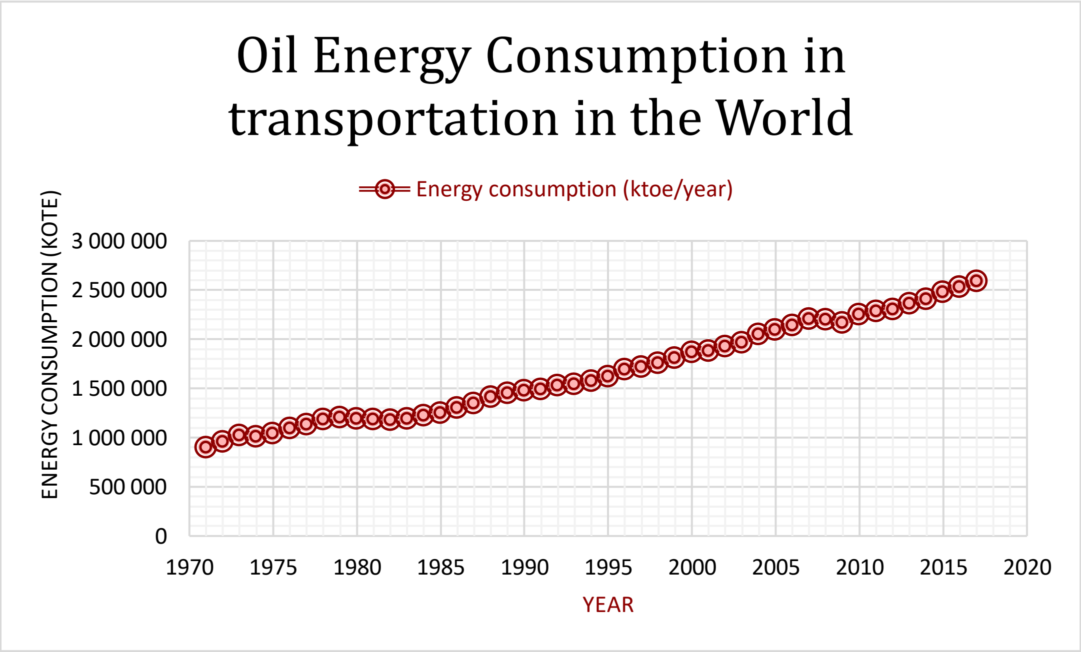


Figure 6 - Fuel energy consumption in the transportation sector in the world. Source: IEA Headline Energy Data. [17]

Similarly, GHG emissions from the aviation sector accelerated visibly in this decade, rising from 710 Mt to 860 Mt from 2013 to 2017, and again to 905 Mt in 2019. [19]
Predictions on total oil demand in all transportation point towards a slowing down during the decade of 2020 before flattening out in 2030, a consequence of the peak of the use of oil derived fuels in passenger cars in 2020, caused by the improvements of fuel efficiency as well as the change in the fuel to electricity based vehicles. [20] The sector where oil demand will continue to grow is in long-distance freight (shipping and aviation) [20] - in the aviation sector, it is projected that transportation energy demand increases to a value of around 250 000 ktoe of jet fuel consumption. [18]

In order to increase capacity whilst maintaining low absolute total emissions, improvements in fuel efficiency, measured in mass of CO_2 per revenue tonne kilometer (a minimum of 1.5% per year from 2009 to 2020 [21]) and fuel pathway optimization, as well as the incorporation of biofuels in the jet fuel mix have been a field of focus in investigation. Also, legislation requires that "all airlines flying within or into the European Region decrease their total GHG emissions by a minimum of 10% or buy CO_2 allowances in the open market"[22], enforcing this policy of reduction of the environmental burden. So far, the ETS was responsible for the reduction of the carbon footprint of the aviation sector in more than 17 million tonnes per year, covering 99 % of all aircraft emissions. [23]

Routes for minimizing the environmental impact in the aviation sector

In 2017, global airlines emitted 859 million tonnes of carbon dioxide[1] – around 2% of the world's global human emissions. [21] Since the beginning of the industry, air transport has made notable improvements in its environmental performance - such as the reduction of CO_2 emissions/seat/km by 80% since the first aircraft and an annual recent CO_2 fuel efficiency improvement around 2.1 % (higher than the initial objective of 1.5 %). [21] Furthermore, it is still investing in the shift towards an environmentally friendly economy, pushing biofuels and alternative renewable fuels forward into fuel blends with conventional fossil based jet fuel. As such, the conditions are favorable for new and sustainable alternative fuels to replace the conventional carbon intensive fossil fuels, promoting sustainable development.

It is expected that shifting to alternative aviation fuels could reduce aviation fuel carbon footprint as much as 80% compared with traditional fuel. [21] This could reduce the impact of the aviation industry significantly in the environment as it progresses into a growing future, as demand in air transport is conservatively predicted to increase in a value of 4.3 % per annum over the next two decades. [21]

Consequently, the aviation industry will focus on the steady incorporation of sustainable hydrocarbon aviation fuels and the optimization of the existing life cycle or fuel pathways of these products. These optimizations will revolve around the: [24]

- Investment in sustainable aviation fuels.
- More efficient aircraft operations.
- Infrastructure improvements.
- Single market based measure in order to achieve a cap on net aviation CO_2 emissions from 2020 and a reduction in net aviation CO_2 emissions of 50% by 2050, in comparison to the levels in 2005.

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[1] 80% of the total emissions made in trips over 1500 kms in length.

Aviation fuels: conventional and alternative – state of the art

As aviation fuel requires higher energy contents per unit volume and an easy handling and distribution, liquid fuels provide the best alternative to gaseous and solid fuels. [4] Furthermore, alternative energy sources such as natural gas or renewable electricity do not comply with the requirements for performance and specifications of aviation fuel. [25] In this section, the various types of jet fuel in current distribution approved by the ASTM D1655 are described, as well as their pathways and associated research in improvement and optimization. However, a special focus is dedicated to conventional jet fuel production (the baseline scenario), and Fischer-Tropsch (F-T) aviation fuel production, as they are more related to the scope of this project more significantly than the other alternatives. Moreover, a special focus was given to the exploration of oil in offshore extraction at the Pre-Salt Santos Basin Cluster since the case study developed refers to that site in particular.

Conventional jet fuel

When looking into oil-derived products such as jet fuel, it is fundamental to understand the full pathway. Oil and natural gas originate from the same source, which is through the geological process of anaerobic decay of organic matter deep under the Earth's surface. [26] Consequently, there are three ways to extract these resources – either co-extraction of natural gas and oil, focused extraction of natural gas or focused extraction of oil. The latter is the most relevant to this process as crude oil is the feedstock used in order to produce conventional jet fuel. However, in these facilities there's a high impact related to the extraction of oil, since the associated natural gas is often not feasible for utilization, being either vented (directly emitted to the atmosphere) or flared (combusted without heat recovery processes). The latter is the most environmentally friendly alternative to handle that effluent. [26] Another issue is the indirect emissions originating from the required energy for extraction, which increases during the lifetime of the oil field.

Flaring is usually done for four main reasons: [27]

- Avoiding operational danger related to the over-pressurization of industrial equipment – Although natural gas can be stored and transported instead of flared, it is a very flammable gas and unless economically favourable, is flared or vented.
- Some natural gas feeds have higher concentrations of hydrogen sulphide (H_2S) in their composition than usual, which makes its safe extraction complicated. Hence, the gas is burned in order to dispose of that gas as a waste.
- Associated natural gas related to oil extraction can occasionally be flared when companies do not possess infrastructure built in site to safely capture and transport natural gas.

- Natural gas production is costlier than petroleum when considering a basis of energy-equivalency – which results in the disposal of natural gas when oil extraction companies are reluctant to invest in the co-extraction of both fossil fuel feeds.

As is displayed in Figure 7, Crude oil and natural gas can be pumped to the surface through primary, secondary and tertiary techniques. [27] When the existent pressure contained in the reservoir is enough to move the oil from the bottom of the borehole, hardly any energy is required to lift the oil to the surface – however, as the oil field ages, ever-increasing energy has to be supplied from the outside, until it is no longer profitable to do so. The primary recovery can be done in two ways, either through gas lift processes (energy supplied in the form of compressed gas, making the oil column lighter) or through deep pump pumping (aid of piston pumps with thermal drive or centrifugal pumps using on-site generated electricity). Whenever primary extraction techniques are not enough to provide the required pressure, secondary techniques such as water flooding are employed – co-produced water from separation is used to displace and/or increase the flow of oil to the surface. Emissions can increase by a factor of 10 to 20 times from the same field during its lifetime, due to the extra energy required to extract the oil.

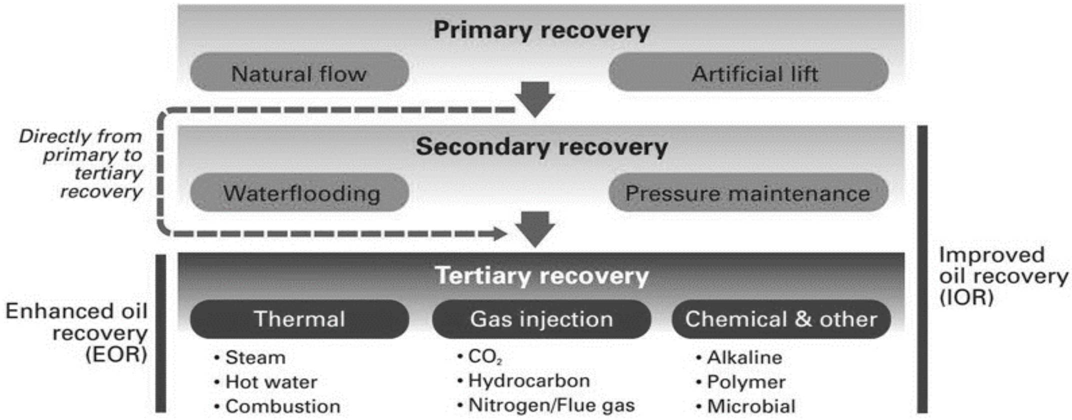

Figure 7 - Distinction between primary, secondary and tertiary recovery of crude oil from reservoir fields. Source: https://marketrealist.com/2015/01/important-know-crude-oil-extraction-process/

Besides reducing energy costs associated with primary and secondary techniques on aging oil fields, tertiary techniques such as enhanced oil recovery (EOR) with CO_2 injection increases the yield of the reservoirs – 30 to 60% of the original oil can be extracted using EOR while only 20 to 40% can be recovered using primary recovery. [27]

In the separation process, maximization of the liquid hydrocarbons' recovery is desired, as well as the removal of dissolved gases from hydrocarbon liquids – this increases the liquid fraction production as well as the API (American Petroleum Institute) gravity. [28] Light hydrocarbons such as methane, ethane and propane should be separated into the gas fraction; butane separation depends on the subprocess pressure, and pentane and above hydrocarbons should be mixed into the oil [28]. This procedure is usually done in a 5 stage process. [27] The produced water contains some of the characteristics of the formation from which it was extracted, requiring treatment in order to remove oil, grease and toxic chemicals before being discharged into the ocean. In offshore facilities, about 80% of the produced water from offshore wells are discharged into the ocean, after the required treatment to comply with environmental legislation. [27]

On the other hand, venting is usually done in industry as an unwanted emission step, resulting from insufficient flaring capacity or leakage in the pipelines. Venting emissions can also occur from the human activities' impact on geological formations, such as emissions from fracking operations. [27] The composition of vented gas relative to flared gas is more discernible in the methane weight in volume – venting releases a lot more methane per m^3 than flaring, which is considerably worse for global warming potential impacts. [27]

The pre-processed crude oil obtained after separation consists of a mixture of hydrocarbons in the paraffinic, naphthenic and aromatic range of hydrocarbons. This mixture is separated into fractions with similar boiling point through atmospheric distillation, vacuum distillation and light ends recovery. [26] The boiling point distribution of the mixture can be observed in Figure 8. In this process the various compounds present in the original crude oil are heated and converted to gases, and later condensed back into liquids. [22]

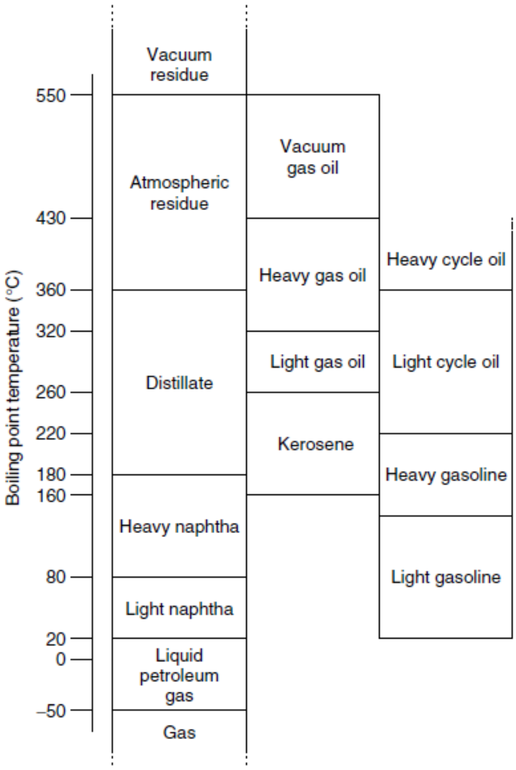

Figure 8 - Boiling point temperature ranges for the hydrocarbon fractions constained in crude oil. Source: de Klerk, A., (2011). [29]

The second distilled fraction taken from the top of the column contains the main raw material for jet fuel production, which still requires processing in a distillate hydrotreater in order to generate and rearrange the hydrocarbons in the boiling range of jet fuel. [22] These petroleum products need treating through stabilization, upgrading and refining in order to remove impurities such as sulphur, nitrogen and oxygen. Upgrading improves the quality of products in crude oil that still require refining. Refining, on the other hand, (which can be partial or stand-alone) converts the crude into the final products or into blending streams. [29] In the final step, various streams from the petroleum treating subunits are blended in order to produce gasoline, kerosene, gas oil, residual oil and specialty items. [26]

The refining step in conventional jet fuel production is simplified, often done only by desulfurization, which is much simpler than for synthetic jet fuel produced from alternative processes due to the low aromatic content of synthetic crude and other properties. [29]

Although it is the dominant technology for the production of jet fuels all over the world [22] the following properties of crude oil have motivated the global economy to search for alternative fuel pathways:

- High cost fluctuation, as can be seen in Figure 9 (a price increase of $1 per barrel of crude oil can cause additional expenses of $425 million to the airline industry). [30]
- High fuel combustion emissions associated with the pathway (electricity generation is done with gas turbines powered by steam obtained from combustion of the process resources explored, which account for 82% of the total GHG emissions in offshore facilities). [31]
- Political pressure to reduce its production volume.

Figure 9 - Barrel of West Texas Intermediate Crude Oil Daily Price Oscillation in the past decade. Source: macrotrends.net [32]

Offshore oil exploration in the Santos Pré-Salt Basin

About 70% of the oil and gas extraction in the world is done onshore. [27] However, new offshore reservoirs are being explored and discovered, such as the highly productive Pre-Salt reservoirs in Brazil. In the Pre-salt Region, 77 wells are responsible for the production of 1.5 million barrels per day, while around 4000 wells in the Post-Salt region produce close to 0.5 million barrels. [33]

This Pré-Salt cluster was a result of the successive deposition of sedimentary rock formed more than 100 million years ago in the gap that resulted from the separation of the Gondwana ancient continent into the current African and South American Continents. Following that separation, large volumes of organic matter were deposited in the lakes risen from the depressions originated in the continent movement. Rivers of both continents flew to the lower regions (e.g. the lakes) which led to the increased deposition of the above-mentioned organic matter, and after the continents drove further apart, a salt layer of about 2000 m was formed, as a result of the coverage of the Atlantic Ocean. This event fixed the organic matter below a solid layer and led to its further conversion into hydrocarbons after long-term thermochemical processes. [33] After the discovery of these oil reservoirs, increased interest in the extraction of the hydrocarbons stored underneath the thick salt layer was observed by the oil and gas industry.

This sort of exploration is proving to be very promising - the production in Brazil's Pre-Salt area tripled from 2014 to 2018, which simultaneously proves the high yield of these wells and represents a significant victory for the oil industry, as it is a breakthrough for ultradeep water exploration. [33] Also, the well drilling operations at such high depths became much faster, becoming almost 3 times faster from 2010 to 2018. In the Santos Basin pre-salt cluster specifically, the average output of oil per well is well above average, adding up to around 25 000 barrels per day – 9 of the 10 most productive wells in Brazil are also in this area.

Among offshore production and drilling facilities existent in the Brazil region, 6 different commonly used types can be distinguished: [34]

- Fixed platforms - suitable for shallow waters up to 300 m, used to drill wells and produce oil too. They are usually designed for long term operations, and its construction involves the use of modular structures made of steel, which are spiked in the seabed.
- Jack-up platforms – suitable for drilling in shallow waters, platforms are able to move around while affording great stability. When there's a necessity to move the location of the structure, the legs made of varying sizes used to reach the seabed are lifted and the platform is towed or self-propelled to a different place.
- Semi-submersible – floating units used to drill wells and produce oil in higher depths (greater than 2000 m). Very mobile, since they consist of one or more decks supported by submerged pontoons, and its stability is maintained by anchoring systems and dynamic positioning systems with thrusters built inside the hull.
- Floating Production, Storage and Offloading facility (FPSO) – these units are used to process, store and offload the crude oil extracted on site, and they operate at great depths (higher than 2000 m) while offering great mobility and an opportunity to explore stranded locations with no conditions to build fixed platform infrastructure.
- Tension Leg Wellhead platforms (TLWP) – a mixture of a floating and fixed platform, this sort of facility has a floating unit on top of a fixed anchored structure fixed on the seabed through tendons fixed by piles, enabling it to operate in ultra-deep waters (2000 m) while being able to control the well at surface like fixed platforms do.
- Drilling Vessel – floating facilities used to drill wells, being able to reach depths greater than 2000 m. Extra stability exists in this equipment due to their usage of acoustic sensors and thrusters which offset the effects of the waves and the wind.

In recap, not all platforms are used for oil exploration (some are only for drilling), and among the platforms that are used for oil exploration only FPSOs are available for on-site storage of extracted crude oil, which makes it an interesting option for stranded reserve valorisation, in which construction of extraction infrastructure might not be economically feasible. Another advantage is its usage in specific Pre-salt wells which contain high volumes of natural gas and CO_2 along with crude oil (such as the wells in the Libra Field and in Sapinhoá Field), [33] since they possess infrastructure to treat the associated gas, and process it efficiently in order to minimize emissions and resource losses as well as to utilize originated CO_2 in enhanced oil recovery processes (EOR).

FPSOs are generally capable of separation, treatment and fluid measurement, as well as the storage of oil, exportation of natural gas and offloading of the obtained oil to transport vessels. A typical FPSO process diagram is displayed in Figure 10, below. Produced crude oil is transported by shuttle vessels from the FPSO to a port of convenience for further refining, and a small part of it is used as fuel for energy purposes. Co-extracted natural gas is used to fuel the common process facilities on the FPSO through electricity and heat generation, and the excess gas is transported from the platform to existing pipeline infrastructure or flared/vented whenever necessity arises to do so. [35] The primary petroleum processing existent in FPSO units generally consists of deep water oil and gas treatment, gas compression for exportation and injection, and water treatment and injection with CO_2 for enhanced oil recovery. [28] When looking at the overall energy consumption in the facility, gas compression systems are responsible for the major weight of consumption during the lifetime of an oil field. [28]

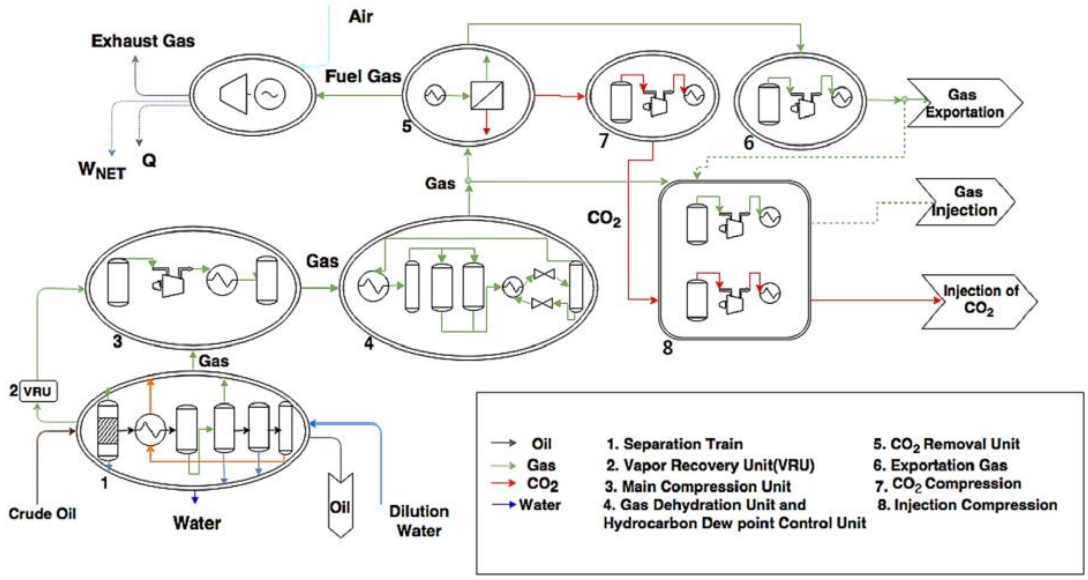

Figure 10 - Typical FPSO process diagram. Source: Allahyarzadeh-Bidgoli et.al (2019). [28]

In this sort of facilities, environmental impacts related to oil spilled during the lifetime of the facility is usually dominated by rare, large spills, rather than frequent small spills as might be the case with other facilities – this has to do with the storage and offloading inherent unique properties of this exploration. [35]

The greatest advantages of this extraction route are: [36]

- Early production and huge storage capacity.
- Easy removal and reuse.
- Reduced capital investment.
- Versatility (can be used in any water depth).
- Lesser abandonment costs when compared to fixed platforms.
- Easy relocation.
- Faster development when compared to fixed platforms enables faster cash-flows.

- Oil spilling risks are minimized due to ample deck space.

Strategies to reduce the environmental impact in global oil and gas exploration consist of: [37]

- Minimizing the venting and flaring of associated gas (which have the potential of achieving around 40% annual carbon intensity reduction in the facilities).
- Increasing the efficiency of conversion processes, and integrating renewable energy along its lifecycle.

Small scale Gas-to-liquid (GtL) facilities offer a possibility to monetize the otherwise vented and flared associated gas [38] (which will be discussed further in this work). Also, renewable energy integration in oil refineries has been an invested field of study resulting in, for example, floating wind turbines in offshore facilities and wave energy harvesting, which reduce future energy expenses related to the increased demand of diesel oil, compensating for the reduced resource availability in aging oil fields. [31] Heat integration of non-condensable fractions of hydrocarbons into combustion for energy purposes or waste heat boilers is also an effective way to reduce hydrocarbon emissions, reported to be a control measure with 99% efficiency. [26]

Alternative fuels

Sustainable Aviation Fuels and Lower Carbon Aviation Fuels are both eligible fuels under the Carbon Offsetting and Reduction Scheme for International Aviation (CORSIA) in order to reduce aviation's environmental impact.

Sustainable Aviation Fuels (SAF) are renewably sourced fuels that can be blended with conventional jet fuels. They do not require technical modifications in the aircraft in order to perform and are able to reduce GHG life cycle emissions significantly. [39]

The reason for this blending is based on safety criteria, as well as energy efficiency – currently, alternative fuels can only be mixed with conventional jet fuel up to 50%. [40] Among the various types of sustainable aviation fuels, the most promising ones are Biomass to Liquid (BtL) F-T jet fuel production, but Hydroprocessed Esters and Fatty Acids (HEFA) currently have the largest production volume, although their limited feedstock availability present a challenge for future scale development. [30]

Lower Carbon Aviation Fuels (LCAF) are fossil-based aviation fuels that meet the CORSIA sustainability criteria (a minimum of 10% Greenhouse gas emission reduction compared to the conventional jet fuel baseline) [37], such as highly carbon efficient coal-to-liquid (CtL) and gas-to-liquid (GtL) feedstocks.

Fischer Tropsch jet fuel

The F-T pathway roughly consists in converting synthesis gas made mainly of carbon monoxide (CO) and hydrogen (H_2) into longer chain hydrocarbons, among them the liquid jet fuel.

Compared to conventional jet fuel, the fuel obtained by this pathway has a number of advantages, such as a higher specific energy an improved thermal stability [22], low content of regulated emissions such as sulphur oxides (SO_x), nitrogen oxides (NO_x), volatile organic compounds (VOC), CO and particulate matter (PM), and low content of non-regulated emissions such as air toxics and polyaromatic hydrocarbons (PAH). [28]

This comes at a cost of efficiency – even though F-T pathways are targeted to generate only high value hydrocarbon products, its overall thermal efficiency is around 60% [28,29] (50% for CtL applications). [45] Also, depending on the feedstock, different pathways have different energy intensities and resource utilization, which can range from an advantageous environmental impact reduction compared to the petroleum baseline to even higher environmental impact than the baseline, as is the case with some conventional CtL F-T facilities. [28,41]
Feedstocks may involve coal (CtL), natural gas (GtL), biomass (BtL) and different kinds of waste. [29] The common essential requirement to all these fuels is that they are a carbonaceous feedstock. [12] Each F-T pathway usually contain 3 main stages as presented in Figure 11.

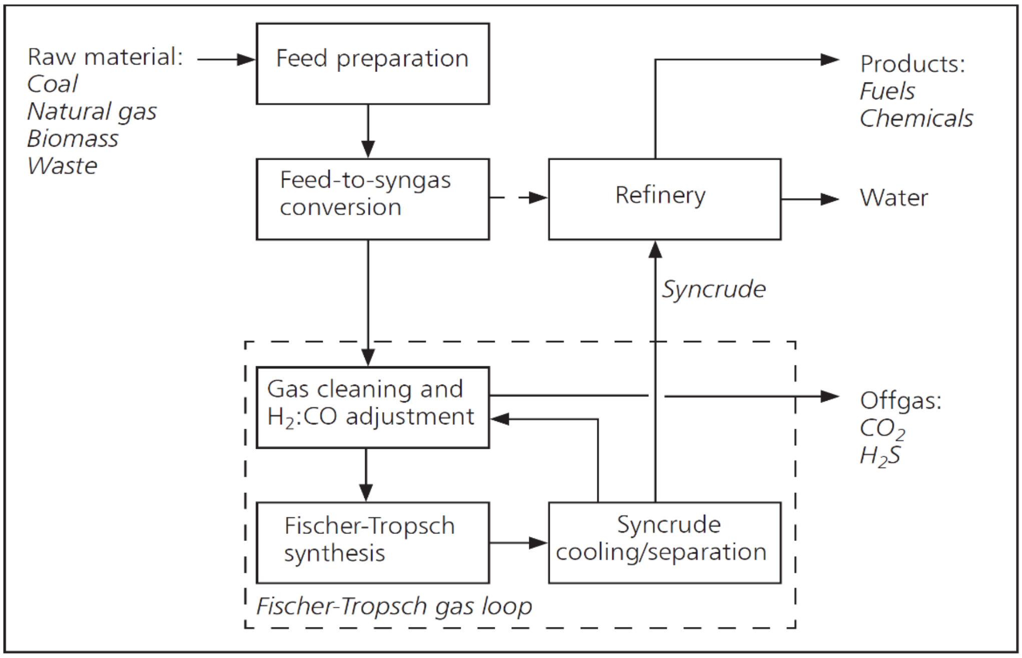

Figure 11 - General Fischer-Tropsch Synthesis pathways for liquid fuel production. Source: http://biofuelsacademy.org/index.html%3Fp=388.html

In the first stage, the generation of syngas, the feedstock is converted to syngas – the choice of feedstock limits the technology that can be used in this step, due to the different feedstock properties and pre-treatment requirements, but not the subsequent processes. [29] Afterwards, in the second stage the generated syngas is conditioned and converted to synthetic crude (syncrude) through F-T synthesis, which nowadays is the most industrially relevant way of converting syngas to syncrude. [29] Following the generation of syncrude, the third stage, refining, is carried through – the syncrude is upgraded and refined to final marketable products. These conversion processes are usually done far from end-use markets but close to the feedstock extraction site. [41]

In the syngas to syncrude conversion, an essential step is the acid gas sweetening, which consists in the removal of CO_2 and H_2S from the process gas originating from the pre-treatment of the feedstock. Among the various options available, the most established process is chemical absorption, more specifically using amine solvents like monoethanolamine (MEA) [42] or N-methyl-diethanolamine (MDEA). In this type of separation, the solvent loaded with the captured CO_2 is transported to a different vessel in which it is heated after a pressure decrease, releasing the CO_2 which can be compressed and stored for further deposit or use in industry, or released into the atmosphere. The solvent is then sent back to the unit in a continuous cycle process after regeneration, requiring a makeup flow to compensate for the natural activity decay and sorbent losses. [43] Energy and resource requirements for the CO_2 capture, including the energy required to compress the CO_2 for transport and storage is much higher than other typical emission control systems. When considering the overall systems' perspective, this has important implications for plant resource requirements and environmental emissions [43], implicating a lower CO_2 reduction per unit of product over the life cycle. That is a result of additional CO_2 emitted in energy and electricity supply for the functioning of the carbon and capture (CCS) unit. Besides these implications to the environment associated with resource depletion, amine life cycle emissions can be a problem in an environmental perspective. Nitrosamines formed in the atmosphere after emission of spent amines might be a risk to aquatic organisms and/or human health, depending on the location of the emission (rural sites have lower probability of conversion of amines into nitrosamines). These compounds are extremely potent carcinogens, and a study evaluated an increase of 200% in human toxicity compared to a baseline scenario with no carbon capture. [44]

Leimbrink (2017) suggested the use of enzymatic reactive absorption to improve the system's functioning and minimizing energy expenditure. This revolves around coupling the high CO_2 loading and low regenerative heating loads and inherently slower reaction rates of MDEA (compared to other sources) with the employment of a carbonic anhydrase enzyme. The result is the decrease of the energy requirement by 40% with a concentration of 30% tertiary amine MDEA and with low operating temperatures in the order of the 25ºC [42].

Moving onto F-T synthesis, F-T can be divided into Low Temperature (LTFT) reactors and High Temperature (HTFT) reactors. The difference is that in HTFT reactors, no liquid phase is present outside the catalyst particles – formation of a liquid phase in fluidized bed HTFT would lead to severe problems since particle agglomeration and loss of fluidization compromise the normal operation of these reactors. [12] That would imply one less phase than LTFT, which has gaseous, aqueous, organic solids and organic liquids. [29] Generally, when the objective is producing long chain waxes, LTFT is preferred, specifically in multi-tubular fixed bed or three phase fluidized bed slurry designs. However, when production of alkenes and straight run fuels is desired, HTFT designs are preferred, using only two-phase fluidized systems. [12] A distinction between the HTFT and LTFT operation modes, catalysts and reactors is displayed in Figure 12.

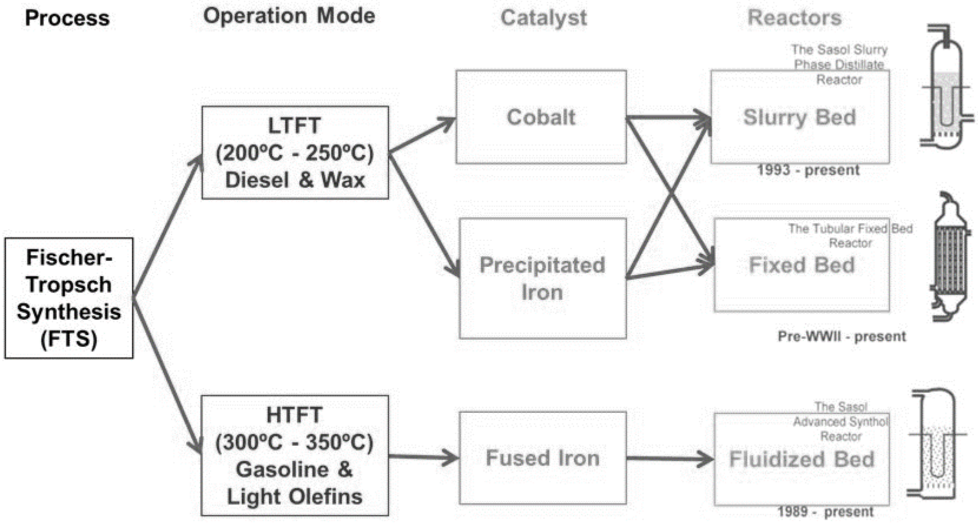

Figure 12 - Operation modes, Catalysts and reactors used in Fischer-tropsch synthesis. Source: https://slideplayer.com/slide/1711043/

After syncrude generation, “less than half of the syncrude from any of the F-T technologies today are available as a liquid organic product” [29], which implies a further upgrading or refining step in order to transform it to useful products. Refining syncrude is different than refining conventional crude oil, since its attributes have a significant impact on refinery technology and refining approach [29], attributes such as:

- Lack of cycloalkanes and aromatics.
- Multiple Product Phases.
- High oxygenate content.
- High alkane content (especially 1-alkane).
- High concentration of linear products.
- Absence of sulphur and nitrogen compounds.
- Presence of Metal Carboxylates.

Regarding refining oriented into jet fuel production, a few guidelines should be present: [29]

- Jet fuel should not have a narrow boiling point distribution, but rather a reasonably distributed one.
- When considering blending synthetic fuels with conventional fuels, it is important to know that fuel systems exposed to aromatics cannot be reliably used with aromatics-free fuels – which requires a minimum amount of aromatics in the final product in order to ensure the necessary properties for its usage (a minimum of approximately 8%).
- Synthetic jet fuel is usually more refined than conventional jet fuel, and therefore has lower lubricity due to its severe reduction after hydroprocessing.

In refining of jet fuel, the carbon number distribution is limited by flash point requirements on the light end, and by freezing point requirements on the heavy end. Jet fuels that are based on isoparaffinic kerosene (oligomerized propane and butene) require aromatic addition, for they have a density that is insufficient to comply with the defined specifications – this often implies that the carbon distribution on the lighter end of the fuel is limited by density requirements too, besides flash point requirements. [29]

Environmental impact reduction techniques employed in F-T processes have many approaches – sequestration of the process CO_2 from acid gas sweetening (removal of CO_2 and sulphur components) and from fuel combustion in the facility, sequestration of process CO_2 that is vented, co-production of different feedstocks (as long as the employed technology allows it) and co-production of fuel and power. [41] However, these solutions have to be analysed carefully, bearing in mind the kind of feedstock produced, the plant location, resource availability and other factors, which can, in some scenarios, bring more harm than good as is the case with excessive energy penalties associated with some CCS technologies, which have to be compensated through added fossil fuel combustion capacity.

Another thing to bear in mind is that an increase of H_2 by-product from the fuel pathway does not compensate for the loss of carbon and subsequent energy loss in F-T liquids. Depending on the job-to-be-done, it might be best to minimize H_2 production unless it is commercially viable, and unless it is used in the facility to supply resources, such as electricity and heat production for the energy utilities or usage of H_2 for refining steps. [45] Other important consideration regarding electricity production is that the share of syngas utilized in electricity production leads to higher carbon dioxide emissions and consequently higher energy penalty associated with CCS solutions. Therefore, it is wiser to use tail gas to generate electricity rather than the syngas, since the latter's usage should be maximized towards liquid fuel production.[45]

Coal-to-liquid FT jet fuel

F-T fuel produced from coal feedstocks are rich in cycloalkanes and hydroaromatic structure dominated aromatic compounds, providing them with a greater thermal stability above 400ºC compared to conventional jet fuel [22] and other jet fuel feedstocks. It is a technology based on the indirect liquification of coal (complete breakdown with gasification to create synthetic gas). In Figure 13 a process diagram distinguishing direct and indirect gasification of coal for CtL applications is depicted.

Coal is extracted through mining, which can be done underground or at the surface. Surface mining generates less solid waste – in underground mining, about 25% of the extracted coal is rejected. [12] Also, surface mining generally has lower rank coals with less weight of coalbed methane – this methane is found in association with the coal seams, absorbed in them. [12] What happens generally is that the methane is released prior to mining using de-gasification wells, and is vented or flared. These emissions are a significant contributor to GHG emissions from coal mining.

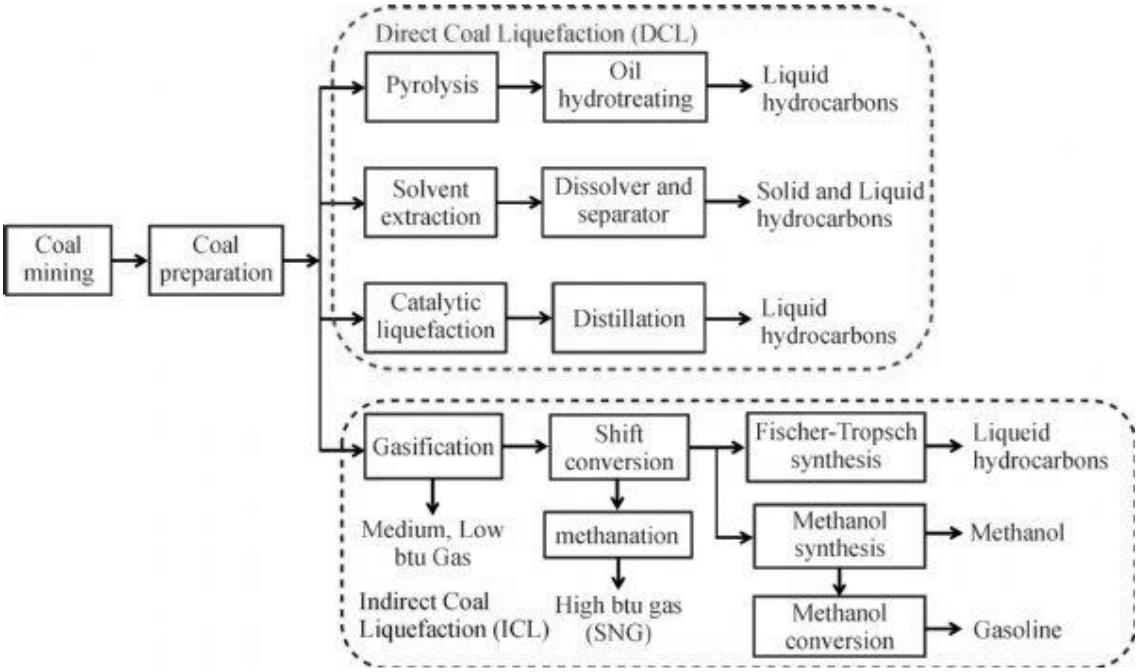

Figure 13 - Direct and indirect liquefaction for coal, for CtL applications in liquid fuel production. Source: Basha Omar M. et. Al (2016). [46]

Huffman, G., (2011) proposed the incorporation of catalytic hydrogenation into F-T synthesis in liquids synthesized from coal. Since water gas shift (WGS) reactions generate a significant amount of CO_2 emissions during processing in order to optimize the H_2/CO ratio in syngas, this study suggested catalytic hydrogenation instead, to generate by-product hydrogen, save water, produce a valuable by-product (multi-walled carbon nanotubes), and substantially reduce CO_2 emissions in syngas production [47].

Gas-to-liquid F-T jet fuel

F-T fuel originated from natural gas feedstock has different advantages in comparison to its competitors.

- Natural gas is the second most abundant fossil fuel, originating from natural gas production wells, associated gas production from oil extraction wells, and methane recovery wells. It has a favorable hydrogen to carbon ratio compared to coal (from around 4 to 0.8 respectively), [12] which is an advantageous feedstock property that simplifies syngas generation towards F-T purposes since this ratio is the property that most affects the severity of the operations required in order to convert the feedstock into liquid fuels. This property affects the efficiency of F-T synthesis and the amount of CO_2 generated in the process. [12]
- Unlike other solid fuels employed in syngas generation, natural gas does not generate ash, tar or other solid effluents related to gasification as the other technologies, and its pre-treatment is simplified requiring only gas conditioning (removal of unsaturated compounds and conversion of sulphur species into hydrogen sulphide) [29] and gas sweetening (removal of H_2S, CO_2 and impurities). [12]
- GtL is overall a feasible technology to synthesize almost any hydrocarbon, and it is a well-established technology with decades of experience and optimization towards

achieving the best results. Compared to coal feedstocks, it requires less cleaning of the initial material inputs, since generally natural gas has a much cleaner composition than coal and does not require more sulphur treatment after reforming, unlike syngas generated from other sources. [12,29]

- It offers an economical advantage since converting natural gas into a liquid solves a cost-efficiency problem related to the other alternative - transport of gaseous natural gas from stranded natural gas reserves through liquified natural gas (LNG). [22] This field of application has been investigated and pursued with interest, following tougher rules and restrictions regarding flaring and fugitive emissions from hydraulic fracturing. [38] There are a lot of options for the fuel pathway for converting natural gas into syngas - each of them valid to specific purposes, like the composition of the final products.
- LTFT reactors for syngas originated from natural gas feedstocks use cobalt catalysts, which are not suitable for coal applications since they are easily poisoned. These catalysts' activity is associated with lower emissions of CO_2 than iron catalysts used in coal applications, due to the absence of WGS activity[2].
- It is technically easier to convert hydrogen rich natural gas than biomass and coal by indirect liquefaction since the syngas conversion process is easier and synthesizes less by-products.

A simple process diagram depicting the stages of F-T liquid hydrocarbon synthesis is shown in Figure 14.

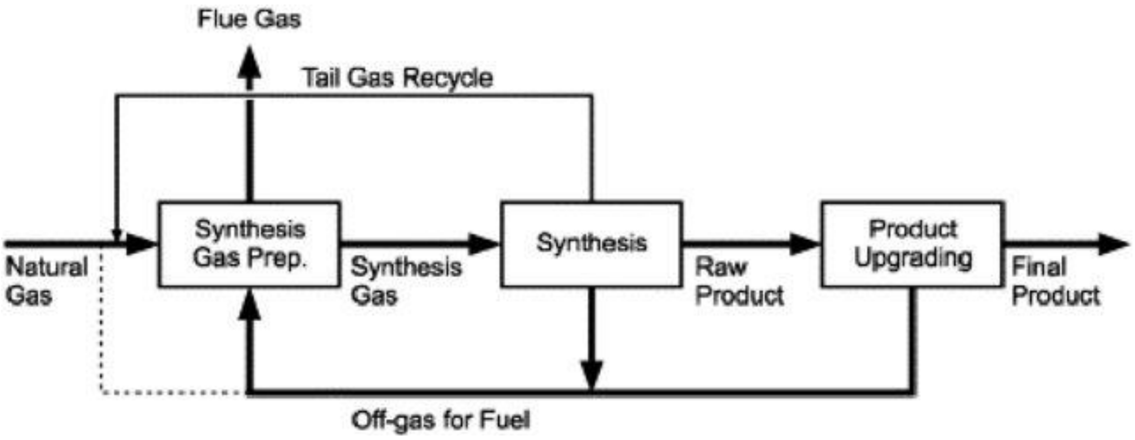

Figure 14 - A simple natural gas feedstock F-T process for liquid hydrocarbon products generation. Source: Rafiee, A., (2012). [48]

Improvements in efficiency can be obtained from utilizing natural gas liquid (heavier hydrocarbons contained in natural gas reservoirs), since this n-alkane rich raw material can be co-refined with syncrude, improving the carbon efficiency of the overall GtL process. [29] However, this implies a natural gas exploration site: if it is possible to transport and distribute this natural gas as an energy carrier, it makes no environmental sense to use it as a raw material for GtL process, since the carbon loss is unjustifiable. [29]

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[2] In HTFT reactors, however, the excess CO_2 generated in the F-T reactor can be consumed using reverse WGS reactors. [12]

Biomass-to-liquid F-T jet fuel

Considering biological feedstocks for renewable fuel production, it is important to denote the difference between the three types of biological feedstocks: [49]

- First generation feedstocks, derived from edible food crops which fell out of popularity as increasing scale of this pathway would compete with current food demand and necessities, cumulatively resulting in indirect land use conversion impacts in longer term.
- Second generation feedstocks, which are produced from non-edible crops and lignocellulosic biomass - among which the hydrogenation of fatty acids (camelina and jatropha oil, used cooking oils and waste animal fats), and gasification followed by F-T (wood and forestry residues, agricultural residues and short rotation woody crops) are the most appropriate long term alternatives.
- Third generation feedstocks, based on algal feedstock, which are a promising alternative due to their relatively high oil content, lower land occupation in comparison to other biological feedstocks and good profile as CO_2 sequestration organisms.

Pre-treatment of biomass can be done by torrefaction or pyrolysis – this is done to handle the heterogeneity associated with the raw material before gasification treatment. Torrefaction consists of the upgrading of the feedstock in order to lower its Oxygen/Carbon ratio and Hydrogen/Carbon ratio, with a milder thermal treatment under inert atmosphere and low temperatures (200-300ºC) upgrading it to a higher quality feedstock, and influencing the subsequent thermochemical conversions to get bio-oil. Pyrolysis, on the other hand, consists of the thermal decomposition of the biomass in the absence of oxygen to produce higher energy density fuel. [50]

One of the pathways for biomass conversion into syncrude for jet fuel that is currently commercially available is the Gasification syngas production pathway followed by F-T. [22] An example of a general biomass to liquid F-T pathway process diagram is represented in Figure 15. In a comparative life cycle assessment, Li, M. et al (2019) determined that although not the pathway with the highest production capacity, it is the one that displayed best economic performance among the studied cases for alternative jet fuel production. [51]

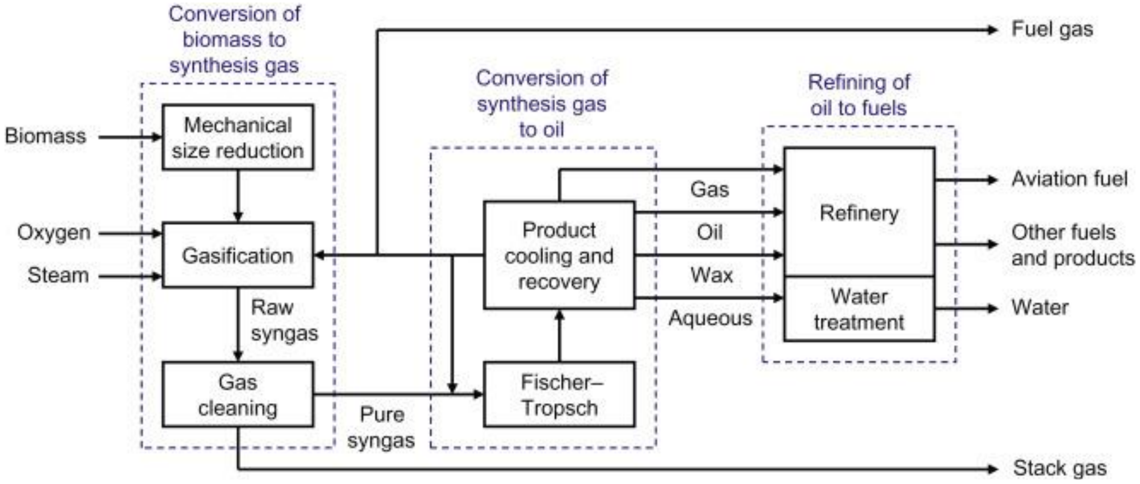

Figure 15 - A general biomass to liquid F-T pathway designed for aviation fuel production. Source: de Klerk, A., (2016). [50]

Gasification consists of a high temperature (700-1500ºC) partial oxidation reaction in which the feedstock reacts with air, steam or oxygen (gasifying agents), converting it into syngas, after which it is cleaned and processed to allow for its further catalytic conversion. [25] The energy required for collecting and harvesting the feedstocks necessary for this pathway are one of the biggest drivers of the emissions of this process, as well as the emissions related to the electricity grid mix in syngas production energy consumption.

Although promising, biorefineries and bio-jet fuel synthesis plants encounter some difficulties regarding operational problems. When the handling of solids is critical for process operations, usually the operability of the facility is around 50% in the first year due to inadequate understanding of the behavior of particle size in these pathways, which is due to the high heterogeneity of the raw material. [30]

Many studies have been performed in order to improve the BtL F-T current overall energy efficiency and environmental performance throughout its life chain. One of them is through excess heat integration. Iribarren (2013) suggested a combined cycle process coupled with BtL F-T in order to coproduce fuels and electricity. [52] This consists in combusting the residual unreacted syngas and fuel gas from subprocesses in order to generate process heat, and processing hot gas stream from heat recovery steam generator to produce electrical energy. This method promotes circularity and reduces the environmental burden of the system.

Another approach to improve the environmental performance of these facilities is by recycling CO_2. Gruber (2019) suggested the use of CO_2 and steam as a gasification agent for biomass feedstocks, and conversion of CO_2 into CO (necessary for syngas production) through reverse WGS reactions when excess electricity is available. [53] Samavati (2018) analyzed the joint use of Entrained Flow Gasification reactors and High Temperature Solid Oxide Electrolysis Cells (SOEC), which consists of using the pure oxygen produced by the SOEC as a gasification agent and CO_2 produced in the Gasification Chamber as an input for the electrolysis reaction. [54]

The choice of feedstocks used for bio-syngas production also plays an important role in impact determination. In a life cycle assessment on diesel fuel production from a BtL process, Jungbluth (2008) concluded that BtL feedstocks originating from agricultural biomass displayed higher impacts than fossil fuel baseline pathways, and that forest wood feedstocks were the best choice among the options available at the date of study. This is corroborated by U.S' Department of Energy report on alternative aviation fuels regarding the example of corn stover as a feedstock. Its low harvester yields, lack of long term regional drought resistance, narrow harvest window for biorefinery standard quality product and the challenges to maintain corn growing soil in good quality and fertility standards make it an unreliable choice for feedstock alongside other edible crop materials. [30] Holmgren (2009) suggested a biomass feedstock mix of peat and biomass originating from forest residues and canary grass, coupling it with CCS for better environmental results, which returns best results of environmental impact reduction for pathways which do not contain significant amounts of peat input from forestry drained peatlands (below 33% without CSS, and up to 90% with CCS). [55]

Transversally to all the above mentioned studies, a collective effort is done in order to both reduce emissions into the environment and to significantly enhance the use of resources and the recycling of reaction sub-products. However, the current barrier for the SAF is not the GHG target emissions, but rather the economic viability of the application of these pathways. [30]

Small scale GtL F-T applications

An interesting field of application of GtL technology is the development of small scale, compact and modular GtL facilities that can be deployed using only associated gas from oil exploration. Although this compact approach does not yet generate on-site production of high value distillates, it avoids flaring or re-injection of feed gas that would otherwise be wasted, obtaining feed gas at no cost. However, these small facilities are technologically simple but less efficient than larger-scale GtL plants. [38]

The company Compact GtL is one of the leaders in running this kind of operational plants, [38] having facilities in, for example, Petrobras' oil exploration in Brazil. The design is focused on a 2 stage F-T process enabling operational cost reduction and catalyst lifetime extension, being compact and modular in reactor designs for the reforming section and F-T section. These reactors have high heat transfer coefficients between streams and a low metal inventory per unit of product, characteristic of their mini channel configuration and plate-fin mechanical construction of the reactor units. [56]

It is especially interesting in offshore exploration of fields with low gas to oil ratios, since the alternative[3] to flaring of gas is the associated gas re-injection, which can be expensive for ultra-deep waters, besides eventually reducing the yield of recoverable reserves, compared to other secondary and tertiary systems of extraction [57], or the liquefaction of the natural gas which has high capital and operational costs at the current date.

Renewable bio-jet fuels

Renewable jet-fuels are typically hydrotreated vegetable oils and animal fats, at very mild temperatures in the range of 350-450ºC and pressures between 4 MPa-15 MPa. [22] One of its big advantages is the low capital process cost, producing Synthetic Paraffinic Kerosene with high quality standards from renewable triglycerides and/or fatty acid feedstocks. This process requires a pre-treatment to remove catalyst contaminants, followed by exothermic hydrogenation and deoxygenation reactions in an hydrotreater to crack the long straight-chain alkanes producing compounds that fall mainly in the kerosene and naphtha boiling range. [22] However, its low concentration of aromatics requires blending with conventional jet fuel and aromatics. Besides, the hydrocarbons that constitute vegetable oil-derived triglycerides have large carbon numbers in their chains (close to 18) which is an appropriate number for diesel fuel but not for jet fuel (between 12 and 14) [40] requiring conversion in an hydrotreater which constitutes a lower fuel yield than that for diesel – these processes include downstream options such as isomerization, cracking or cyclization. [25]

HEFA (Hydroprocessed Esters and Fatty Acids) consists of "various catalytic reactions mechanisms in the presence of hydrogen" [25] in which fats, greases and oils contained in the

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[3] Gas export through pipelines is also an alternative, but hardly feasible in ultra-deep water explorations far from shore.

feedstocks are converted to hydrocarbon mixtures suitable for jet fuel application. Common to the various possible pathways, the hydrogenation step is essential to saturate the double bonds of the lipid chain, through the catalytic reaction with hydrogen. Afterwards, it is necessary to remove the carboxylic acid group from the free fatty acids generated in the hydrogenation reaction, which can be done with an hydro-deoxygenation process, a decarboxylation process or a decarbonylation route. [25] Although processes that are independent of hydrogen could be used, those alternatives are generally less favorable due to their significant consumption of feedstock. [25] Fuel produced by HEFA processes is similar to conventional jet fuel in composition, however it has some advantages such as higher cetane number, lower aromatic content, lower sulfur content and lower GHG emissions. [58] In Figure 16, a general representation of the HEFA pathway is represented in a diagram.

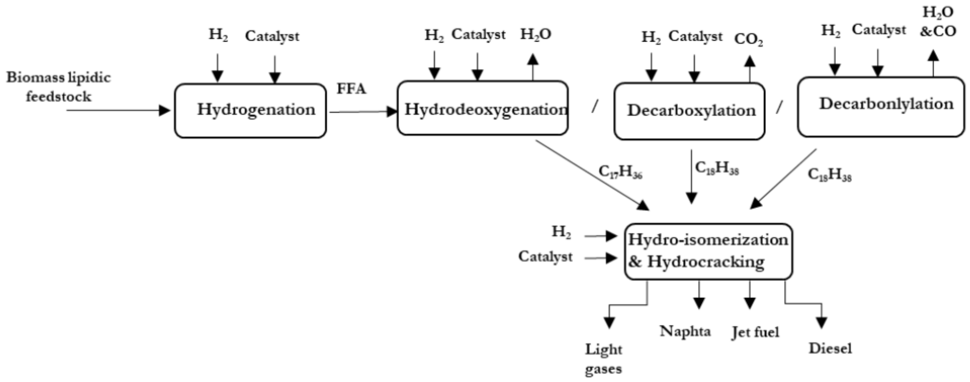

Figure 16 - A general description of an HEFA pathway for liquid fuel production. Source: CORSIA. [25]

Tao, L., et al. (2017) conducted a report in which resource assessment, chemical composition of the oil feedstocks and comparative techno-economic analysis were carried out. The obtained results confirm that generally both edible and non-edible oils are promising alternative fuel feedstocks for HEFA since they can be produced locally and in environmentally friendly ways, besides being renewable. They can also be cost competitive if associated with a strategic and efficient design and integration. Looking into feedstocks specifically, although third generation algae feedstocks have high oil productivity, commercial scale-up is still to be achieved and its price as a biofuel feedstock will be "prohibitively high". On the other hand, most terrestrial oil-sources have feasibility problems – higher yielding oil crops like canola and camelina are controversial since they compete with food purposes. Also, pennycress and jatropha, although receiving a lot of attention in the current biofuel industry, are slow to develop due to a number of factors. The non-terrestrial oil sources, such as animal fats, are an interesting alternative because they have relatively lower prices and are increasingly used in this industry.[58]

Hydroprocessed fermented sugars to SIP (Synthesized iso-paraffins) is based on the biochemical conversion of biological feedstocks in order to synthesize a hydrocarbon molecule called farnesene (see Figure 17), which after upgraded to farnesane can be blended with petroleum based fuel. [25] Sugar for this pathway is usually obtained from sugarcane, but it can be obtained using other sugar plants such as sugar beets, sweet sorghum, and halophytes as well as cellulosic sugars. This is a sort of direct sugar-to-hydrocarbon fermentation pathway which consists of a first step regarding biomass pre-treatment by enzymatic hydrolysis, fermentation of the C5 and C6 sugars to produce farnesene, an hydrogenation process to generate farnesane and a consequent hydrocracking and isomerization to produce the desired jet fuel. [25] Although it is possible to generate aviation fuels or their precursors at industrial scale through microbial production, alternatives to farnesene have to be developed in order to advance from food-resource competitiveness into second or third generation more sustainable feedstocks based on lignocellulosic biomass. [59] This could be achieved by investment into "high-throughput strain engineering" aiming to boost alkane and alkene production to values close to the obtained for farnesene. [59]

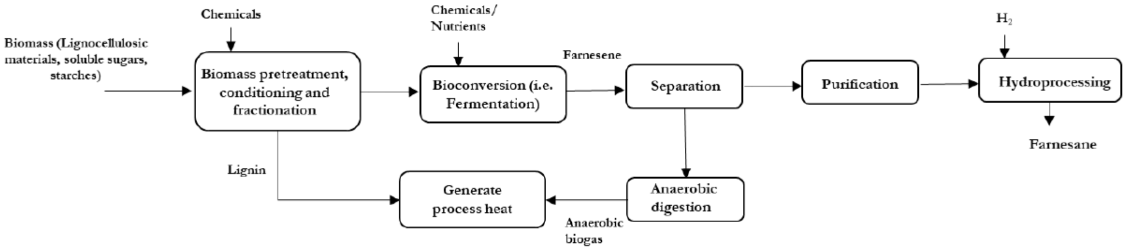

Figure 17 - General descriptive diagram of an SIP pathway for liquid fuel production. Source: CORSIA. [25]

ATJ (Alcohol-to-jet) is also a biochemical conversion process but based on the production of hydrocarbons through ethanol or butanol intermediates, consisting of applying alcohol dehydration, oligomerization and hydrogenation to the fermented and conditioned biomass (see Figure 18), which produces synthetic paraffinic kerosene allowed to be blended at 50% ratios. [25]

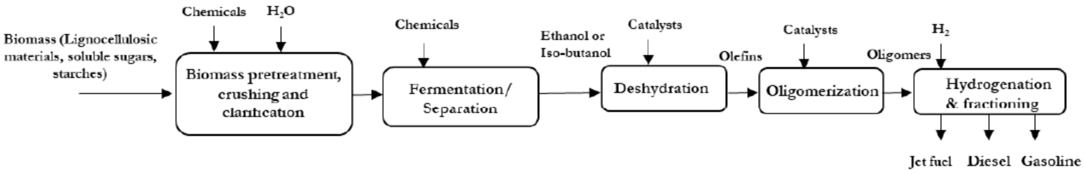

Figure 18 - Simple design for ATJ pathways designed for liquid fuel production. Source: CORSIA. [25]

It provides an opportunity for producing SAF through a wide variety of resources, enabling alcohol producing industries to enter the market of aviation. Fermentation of sugars from edible plants such as corn or corn stover is the most common way to generate alcohol derivates, since fermentation from non-edible plants require other advanced techniques that involve specific pre-treatment, microbes and additional process units. Corn stover usually has higher emission reductions than regular corn (Han, J., (2017) reported 73% GHG emission reduction compared to the petroleum baseline, as opposed to a 16% GHG reduction associated with corn) [60], although its availability might present some challenges to industrial scale production.

In conclusion, alternative jet fuel production pathway sustainability depends on a wide array of factors – not only environmental impact reduction of the baseline conventional jet fuel through its displacement, but also complexity of the operation, feed origin and extraction life cycle impacts and composition, and also system design. In the context of this work, a small-scale GtL unit designed to reduce the impact of the flaring operations in offshore O&G

extraction was studied and evaluated in order to quantify the environmental impact improvement consequent of the application of the system.

The Net4CO2 mission

This work focuses on the comparative life cycle assessment of two novel FT GTL jet fuel pathways (a Steam Methane Reforming and a Dry Methane Reforming route with a novel micro-reactor design applied in reforming and F-T reactions) and the comparison to conventional jet fuel from a conventional petroleum refining pathway.

The novelty resides in the use of an advanced next-generation micro-reactor called NETmix, with a wide variety of advantages such as very high heat transfer coefficient and specific area, key for reactions requiring large amounts of energy supplied or removed (reforming reactions and FT reactions, respectively). Besides removing huge amounts of heat produced during the highly exothermic FT operation, unprecedented even for microreactors, this design is also very flexible since it enhances control of reaction selectivity and therefore product distribution, extremely advantageous for the FT-reaction. Furthermore, the design is simple and compact, presenting a solution for valorization of stranded gas reserves. Further information about the NETmix advanced reactor technology can be found in published papers currently present in the literature [61,62,63,64,65].

These improvements contribute to an increase in the Low Carbon F-T jet fuel pathway options and can reduce environmental impact significantly, enabling it to competitively progress hand-in-hand with renewable bio-jet fuels and reducing the impact of associated gas flaring.

The simulations performed consider a potential implementation offshore, for valorisation of stranded and associated gas, but a critical analysis of the variations expected in an on-shore scenario may be required if a further comparison with certified alternative jet fuels is done.

Methodology

Life cycle assessment (LCA) is defined as the "compiling and evaluation of the inputs and outputs and the potential environmental impacts of a product system during a product's lifetime". [66] It is mainly used to identify improvement opportunities and environmental hotspots of the products or processes at the various points of the life cycle, and it is useful information that can be applied to decision making, marketing, and even to aid in the selection of adequate environmental indicators for impact risk assessment and other environmental impact measurement techniques. [66]

The LCA framework used in the presented thesis was adapted from the environmental life cycle assessment methodology as described in ISO 14040:2006 (Environmental management – life cycle assessment – Principles and framework) and ISO 14044:2006 (Environmental Management – life cycle assessment – requirements and guidelines). As such, fundamental stages of LCA including goal and scope definition; development and analysis of life cycle inventories (LCI); and interpretation of results are comprised in this work.

In the goal and scope definition stage, a number of points have to be addressed, such as: [66]

- The intended application of the study.
- Purpose.
- Audience.
- Usage for comparative analysis.

This stage is essential for establishing a strategy and the methodology for the subsequent steps. System boundaries and the functional unit are defined in this step: the functional unit refers to the "quantified definition of the function of a product" [66], which in the aviation fuel case refers, for example, to the potential energy contained in a unit of mass of the obtained product ready to use in combustion. The same context (aviation) can, however, be approached in different ways through the employment of different functional units and system boundaries, and the correct way to perform a study depends on the defined goal and scope of the given project. The system boundaries, on the other hand, refer to the subprocesses that are contained and that are cut-off from the analysis – which states clearly up to what point the study was carried out, and if whether or not its results can be compared with similar studies. As described in Figure 19, System boundaries can be: [66]

- Cradle-to-grave: inclusion of all the material and energy inputs and outputs along the production, transportation, usage and end-of-life of the given product.

- Cradle-to-gate: inclusion of all the material and energy inputs and outputs up to the “gate” of the factory.
- Gate-to-grave: inclusion of the use and end-of-life phases exclusively, not considering production stage.
- Gate-to-gate: inclusion of processes from the production phase only, not accounting for raw material extraction.

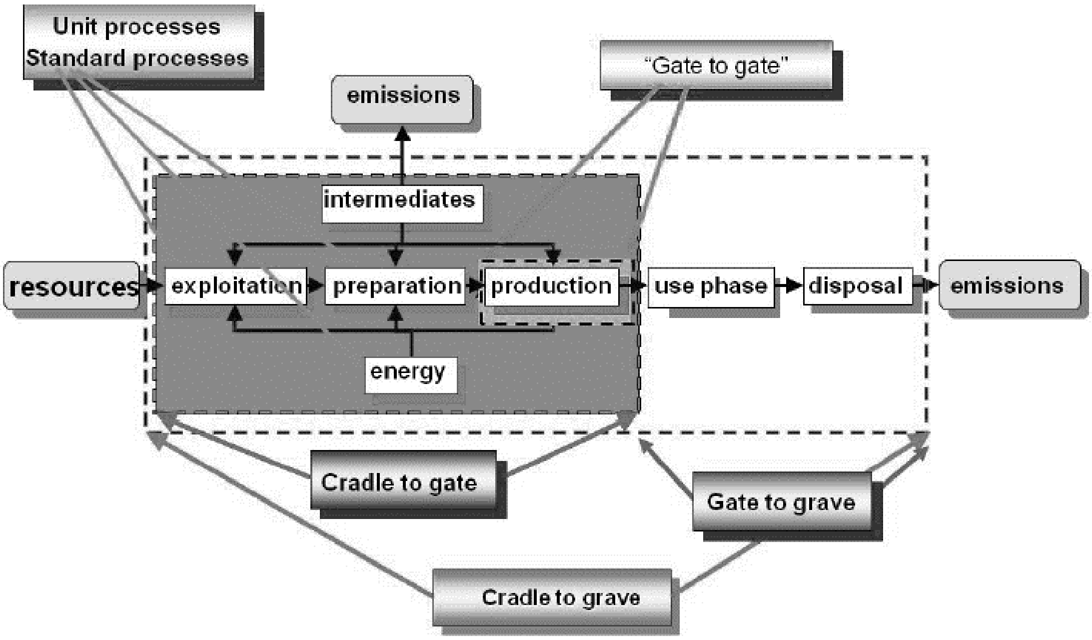

Figure 19 - Types of system boundaries used in LCA evaluations. Source: GaBi [66]

In a consequential approach, both direct and indirect impact of the production system are accounted for, i.e. direct emissions that occur at the facility site, such as energy emissions associated with purchased energy, and indirect impacts related, for example to industry displacement of a product by another, causing positive or negative marginal feedback effects related to its diffusion and proliferation in the market. [40,67] On the other hand, an attributional approach only accounts for the direct impacts in the supply chain, not considering the impacts of the co-products or the reduction in the upstream production displaced by by-products, and simply allocates a portion of the inputs and outputs of the global system to the study object, based on physical properties like mass and energy or economic criteria. [67] Figure 20 schematises both LCA approaches.

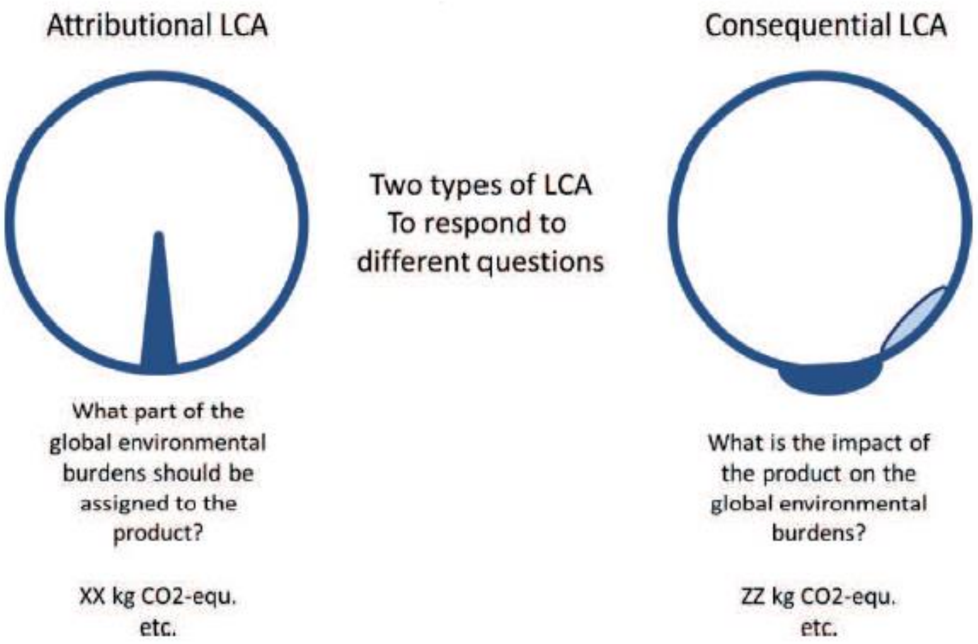

Figure 20 - Visual representation of a consequential and an attributional approach in LCA. Source: Ekvall, T., (2019) [67]

In simple terms, an attributional approach provides an estimation of the part of the global environmental burden of human activity that belongs to the study object, while a consequential approach estimates how the life cycle of the study object affects the global environment burdens and the global market for that study object, marginally developing over a time period (being able to increase or reduce it). However, this does not mean that one approach is superior to the other, rather that they have strengths and weaknesses which enables them to be used in different contexts.

The second step is the Life Cycle Inventory Analysis stage, in which data is collected, validated, related to the unit process in study and aggregated – whenever necessary, insufficient data can be completed through rigorous research in literature and databases.

The third step concerns the Impact Assessment stage. In this step, emissions are classified to a certain impact category, and characterized through adequate revised characterization factors in literature and legislation in order to correctly estimate the potential impact of each direct and indirect emission into the atmosphere of the product’s life cycle.

After all the results are obtained, they have to be interpreted – it is essential that an LCA practitioner takes into account the variability of results obtained in different LCA studies, for they have many degrees of freedom concerning goal and scope definition, quality of data, and impact characterization methods. As such, it is important to interpret the results given with a rigorous background study on the expected results to be obtained, and a critical judgement on whether or not the obtained results are compliant with correct scientific and sensitive evaluations. The steps referred are depicted in Figure 21.

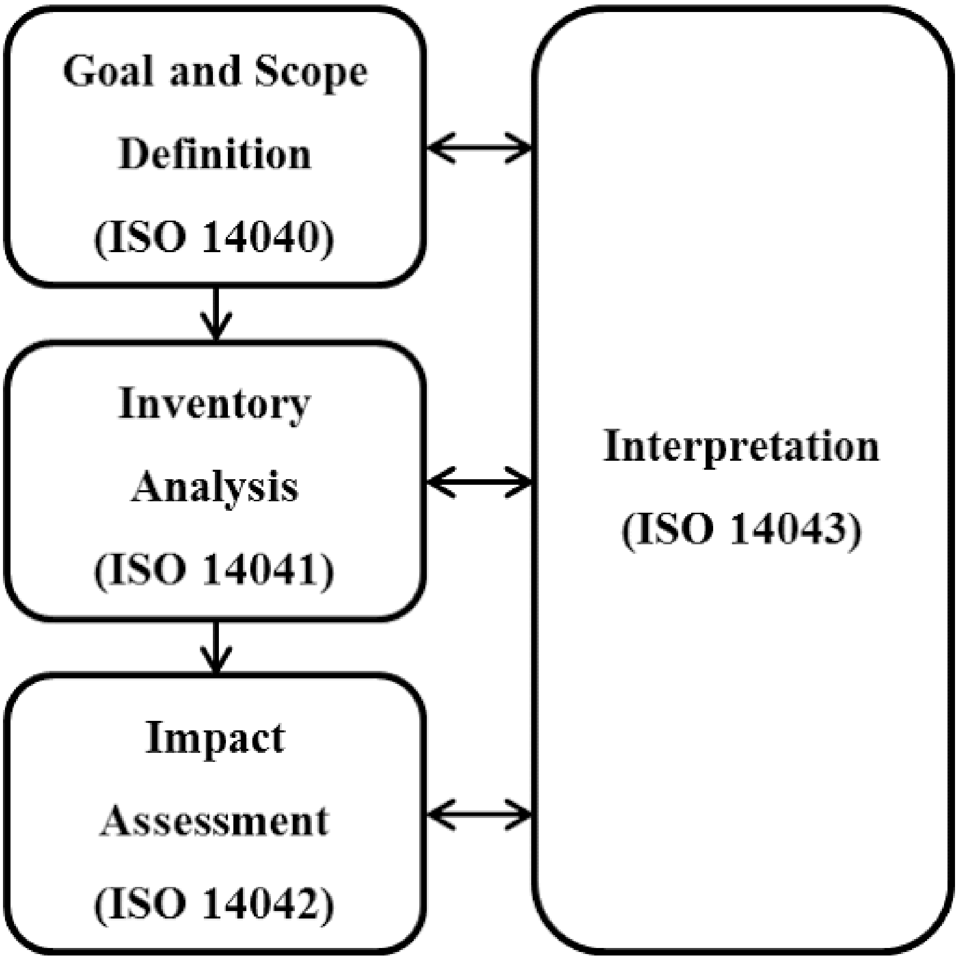

Figure 21 - Life cycle Assessment stages. Source: ISO 14040:2006

Goal and Scope definition

The goal of this study is to effectively compare the environmental performance and environmental hotspots (unit processes with higher environmental impacts and concerns) in two development-stage technologies for alternative F-T synthetic aviation fuel production using novel micro-reactor technology with enhanced heat exchange properties and reaction selectivity, called Net4GtL, developed by Dias, L., and Coelho, F. [92] These two pathways differ in the following points:

- Syngas generation procedure - since one generates syngas through Steam Methane Reforming (SMR Net4GtL) and the other one through Dry Methane Reforming (DMR Net4GtL).
- Pre-treatment – the SMR feed gas is already pretreated while the DMR feed gas is not, which affects its emissions and design in subsequent steps.

- Associated gas composition – The natural gas feed for DMR and SMR come from different oil wells. In the DMR case, a significant amount of CO_2 is present in the composition of the feed, roughly 70%. This has implications in downstream processes (such as CO_2 removal and injection) that could add some bias to the environmental results, as will be discussed later.
- Intermediary steps between reforming and Fischer-Tropsch synthesis – the DMR process has a Water Gas Shift reactor followed by amine scrubbing, while the SMR process has the amine scrubbing process right after the reforming stage and is followed by a Pressure Swing Adsorption unit.

This assessment comes to aid in the decision making of the research and development team in Net4CO_2 as it:

- Compares these two novel fuel pathways to an existing conventional fuel commercialized pathway in order to quantify the improvements in pathway efficiency and resource management associated with this new technology.
- Determines which of the simulations has the best environmental performance, providing decision makers with subprocess specific feedback on emissions and resource consumption.

Since this is a study with an iterative character, focusing on the improvement of a development-stage process, its results **should not yet be disclosed to the general public** – for the results of this study will prompt new considerations and possible changes in the design of the systems, requiring further studying and life cycle assessment improvements before displaying the final results with the best accuracy possible and after a thorough multi-perspective design in mind. Consequently, the audience for this LCA report consists in the designers of these novel processes, decision makers in Net4CO2 and stakeholders who desire to further improve their knowledge into future investment perspectives.

Regarding the scope of the project, the main assessment was carried out in a “cradle-to-gate” approach, including oil and natural gas extraction, separation of the extracted materials, syngas generation, Fischer-Tropsch reaction and separation of the syncrude components. However, the pre-treatment of the feed gas, refining of the liquid syncrude and transport to final user stage was not considered, since the results of the simulations are still not final, and the obtained refined jet fuel does not yet comply with required flash point, freezing point and specific energy requirements in ASTM specification D1655. On the other hand, the choice of previous subprocesses are final, and designed towards a hydrocarbon mixture in syncrude with the appropriate boiling range required for jet fuel production, so it is reasonable that the life cycle assessment from feedstock extraction to syncrude production is done before proceeding to the next step.

Furthermore, a full cradle-to-grave analysis would not be carried out even if the refining stage was present - it would have to include the combustion occurring in the airplanes' turbines, end of "tailpipe emissions", construction, maintenance and disposal of the aircraft, abrasion of the plane landing tracks in airports, and construction and maintenance of these landing tracks. Since this project is focused on the analysis of fuel pathways, and life cycle emissions of the vehicles and infrastructures related to aircrafts have different values throughout the years due to improvements in turbine efficiency and design of infrastructure, it would add significant uncertainty to the analysis besides requiring an extensive data analysis and research.

This first assessment returns results which depict the environmental impact change relative to the baseline O&G operation In the FPSO, clearly showing the quantitative effects of the reduction of the flaring emissions, and the impact of the added energy demand required for the processes to operate. Simply put, it shows whether or not the pathways really reduce the impact of the flaring phenomena in the FPSO facility while producing a valuable resource from the residue, since they consume resources to convert this residue into a product.

Besides the first assessment, gate-to-gate analyses was carried out to better analyse the weight of the different subprocesses in each pathway, independent of the oil and gas extraction phase, since as it will be seen, constitutes the largest share of the environmental impact in the product's life cycle. This is because the impacts of oil extraction were fully allocated to the associated gas destined for flaring which constitutes the feedstock of the pathways. However, this does not necessarily correspond to the truth, as the impact of extraction of this otherwise flared gas would actually constitute a zero or even negative impact, since its alternative fate would be combustion and emission into the atmosphere. To this effect, two Gate-to-Gate analysis were performed, one assuming null associated gas extraction impacts and another which accounts for the avoided emissions related to the capture of the associated gas which would be ultimately flared.

On the other hand, as purely attributional analysis is being done in this project, it was decided to couple four attributional analysis together in order to correctly interpret this problem at hand. That is why a fourth assessment was carried out, a cradle-to-gate analysis like the first one, with the same system boundaries, but with one barrel of crude as the functional unit. In summary, interpreting the fourth analysis at the same time provide the following related conclusions:

1. First analysis – cradle to gate, functional unit: 1 MJ LHV of syncrude produced – analysis focused on the syncrude production solely, as it is suggested by the RED directive. This analysis is independent of the impact of crude barrel production in the facility, and not

as sensitive to scale production as the fourth assessment, but it reveals the weight of the facilities in the global environmental impact of the FPSO's operation.

2. Second analysis – gate to gate, 1 MJ LHV of syncrude produced, null extraction impacts – analysis that unlike the cradle-to-gate analyses, does not return impact reduction related to the reduction of the flaring phenomena in the facility, but offers more sensitive results regarding the weight of the different subprocesses in each pathway, returning results which are easy to communicate to the designers of the pathways in NET4CO2, in terms of environmental hotspots and improvement possibilities.
3. Third Analysis – gate to gate, 1 MJ LHV of syncrude produced, negative extraction impacts – this reflects the values which should be used for a further certification, as they represent the correct estimation that takes into account the avoided emissions in the flaring event, its strongest environmental benefit.
4. Fourth analysis – cradle to gate, 1 barrel of crude produced – this analysis accounts for the incremental barrels of oil recovered from the injected CO_2 coming from the syncrude pathway activities and the syncrude barrels produced, returning results which show whether or not these pathways offer a reduction of the impacts per unit of product, suggesting a primary insight into bigger scale production if the results are positive, as well as tackling the concern that producing barrels of syncrude in this facility could be worse than carrying out the conventional production of crude oil.

This evaluation considers only environmental impacts, and not social-economic impacts necessary for the so called "sustainability assessment" – since the nature of this project is still a development stage array of simulations that needs further practical testing.

The functional unit chosen was 1 MJ LHV of fuel combustion energy (considering the Lower Heating Value of the fuel at hand) as it is typical of a multi-product aviation fuel production system and according to the Renewable Energy Directive (RED) guidelines for aviation fuel life cycle assessment, [68] as well as previous reports in similar subjects. [69,70,71,72,73] The barrel of crude oil was defined as the functional unit in the fourth analysis only to aid in the result interpretation.

The system boundaries for the novel GtL processes described in this study are described in the next subchapters. For in-depth subprocess description, consult the "Data Quality Requirements and Life Cycle Inventory Analysis" Chapter.

SMR Net4GTL (Process 1)

The first step of the life cycle is the extraction of the natural gas originating in Pre-salt oil and gas reservoirs from the seabed to the off-shore platform in which the facility is located, using enhanced oil recovery through CO_2 and water alternating injection. This natural gas feedstock can be obtained in two ways – either direct extraction of the natural gas from the well, or usage of the excess on site natural gas which is destined to flaring in oil exploration facilities. The latter significantly decreases the overall emissions of the pathway since it converts a residue into a resource, maintaining it inside the Technosphere. Consequently, it was considered that the natural gas feedstock used for the production of liquid fuels fully consisted of gas destined for flaring – besides the obvious impact reduction at which this technology aims for, using extracted natural gas for liquid fuel production when it can be used for energy or electricity generation is an inherent waste of the full potential of the natural gas as a fuel [29]. Afterwards, the natural gas is pre-treated to remove unsaturated hydrocarbon compounds and natural gas impurities that could affect the pathway. As will be explained further in the document, pre-treatment was not included in the scope of this analysis.

After pre-treatment, the gas is reformed in a Catalytic Steam Methane Reformer operating at 860ºC and 20 bar in a catalysed reaction by rhodium coated in the NETmix reactors, enabling a 79 % hydrocarbon conversion.

Following this reforming stage, excess water is removed in a flash vessel and recovered, whilst CO_2 is removed later in an amine scrubbing reactor using MDEA solvent in an aqueous solution with 40% wt concentration to sweeten the acid gas coming out of reforming stage, from which a 97% purity CO_2 flow is originated. This high purity CO_2 is then used in oil enhanced recovery or released in the atmosphere (both scenarios were tested in a sensitivity analysis[4], and the injection was assumed to happen in this study). MDEA is recovered through evaporation, and the syngas free of CO_2 is next sent to a pressure swing absorption reactor, in order to adjust the H_2/CO ratio for optimal F-T conditions – this results in an 80% H_2 recovery, generating a H_2 flow with 99.5% wt concentration, from which a portion is sent to the F-T reactor (since the recovery is larger than needed) and the rest is sent for co-combustion with the light-gases generated after F-T, designed for heat integration which shall be explained later.

Next the syngas undergoes F-T reaction in NETmix reactors, coated with cobalt and operating at 250ºC and 30 bar. In this reactor, a conversion of 88 % CO conversion is achieved, processing roughly 500 barrels per day of F-T syncrude after separation from water and light hydrocarbons, generating wastewater and fuel for heat integration.

The last step is the refining of this syncrude, which results in a multi-product array of Aviation fuel (kerosene), naphta and solid wax. After refining, the fuel is shipped to the end user. As mentioned before, these steps are not included in the analysis.

Regarding heat integration, H_2 and light gases generated from the other unit processes are burned in a furnace to generate enough heat for the SMR reactor and other heat duties of the facility. Also, cooling water required for the highly exothermic F-T reaction is converted to

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[4] See Appendix II – Sensitivity Analyses

steam during the heat transfer phenomena, which is applied in other subprocesses as process steam. The process steps and the system boundaries of this technology are represented in Figure 22.

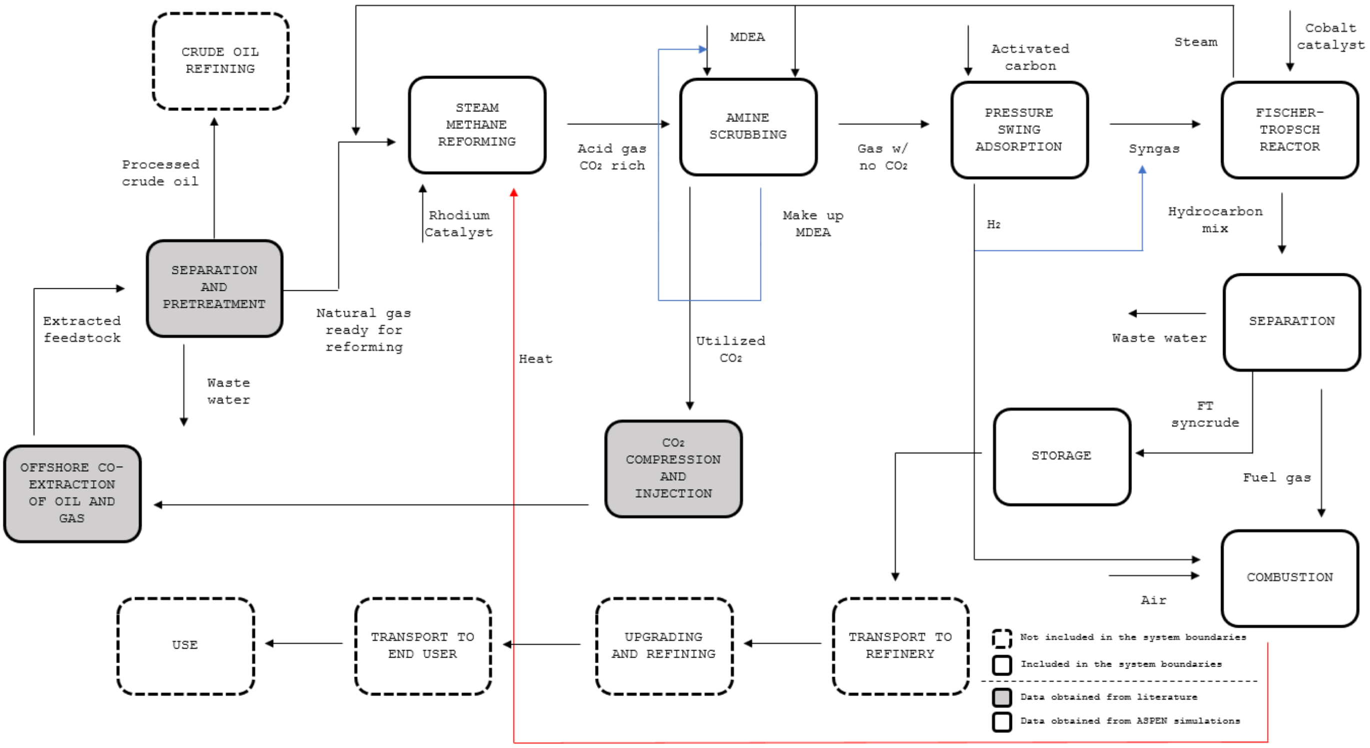

Figure 22 - SMR (Steam Methane Reforming) and Fischer Tropsch (FT) fuel pathway system boundaries considered in this study. Black lines represent linear mass flows, red lines represent heat flow and the blue lines represent circular loops.

DMR Net4GtL (Process 2)

The Natural Gas composition was assumed to have a high weight of CO_2 in its composition, as it was reported by the data suppliers, who stated that coming from a certain undisclosed Pre-salt reservoir, would possess that ratio of CO_2. Likewise process 1, it was assumed that the gas used in this process is the gas that is destined to otherwise be flared.

After collection, it undergoes de-pressurizing to 5 bar and pre-heating to avoid condensation and enters the DMR reformer which operates at 900 °C and 4 bar, in which 98% of the methane reacts with an associated heat expenditure of 16 MW.

Following the reforming section, this gas is mixed with water in order to proceed to the low temperature water gas shift which operates at 180°C and 3 bar. This section is responsible for raising the H_2/CO ratio to the adequate value for the F-T reactor. 90% of the water used in the reaction is recovered in a flash vessel and recirculated in order to minimize water expenditure. Next the Syngas is pressurized to 33 bar and sent to the amine scrubbing section, in which the gas is rid of its remnant CO_2 composition. 96% of the CO_2 is recovered in this stage, and MDEA is recovered through a stripper column for solvent recovery, which returns 99% of the original solvent to the system. Similar to the first scenario, this high purity CO_2 is then used in oil enhanced recovery.

Afterwards, the syngas is sent to the F-T reactor operating at 250°C and 29-30 bar - which results in a conversion of 87% of the carbon monoxide to synthetic liquid hydrocarbons, among them the syncrude, which is further separated from water and lighter hydrocarbons, (the latter used in combustion for heat integration in the facility), yielding approximately 500 barrels per day of liquid syncrude.

The last step is refining, in which syncrude is improved and separated into its various co-products among them the desired aviation fuel that is stored and transported to its final destination. These steps were not included in the life cycle.

Similarly to the previous process, heat integration is realized in order to improve pathway efficiency, but no excess hydrogen is produced, resulting in heat excess. Steam produced in F-T is also used as process steam in other subprocesses. In Figure 23, system boundaries and subprocesses of this pathway are depicted in graphic form.

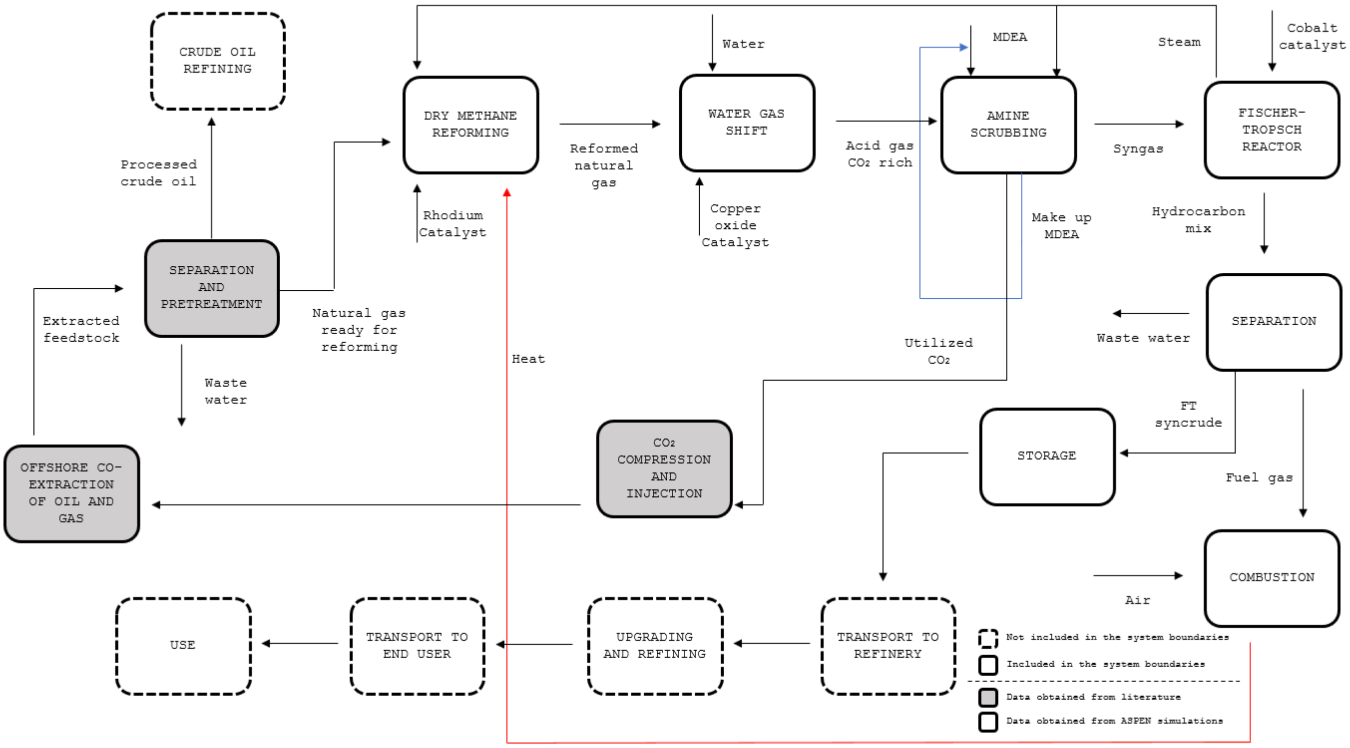

Figure 23 - DMR (Dry Methane Reforming) and Fischer Tropsch (FT) fuel pathway system boundaries considered in this study. Black lines represent linear mass flows, red lines represent heat flow and the blue lines represent circular loops.

Allocation Procedures

The comparison between the two simulated processes designed by the NET4CO2 company was done with an attributional approach, as is suggested by RED and CORSIA framework [25] since it is not a biomass feedstock technology, but a natural gas feedstock pathway – problems related with indirect land use conversion are not an issue in fossil-fuel pathways. Consequential calculations assuming a marginal increase of capacity in F-T derived from small-scale applications and a marginal decrease of conventional jet fuel associated with the increase of the alternative pathway would associate greater uncertainty to the results which would not justify a trade-off for significance of results – there's no point in developing such an assessment over a technology that still requires final design improvements and commercial tests.

Impact categories and Impact Assessment Method

The characterization method was the CML_IA baseline contained in SimaPro v.8.50, the program used for the modelling of this LCA study. This model is an elaboration of the problem-oriented midpoint approach, focusing on a series of environmental impact categories expressed in terms of emissions to the environment. Midpoint impact categories are identified by "an indicator placed at the location in the impact pathway up to which a common mechanism exists for the main contributing substances within that specific impact category". [74] To put it more simply with a practical example, in the case of GHG emissions the midpoint indicator is chosen at the increase of the radiative forcing of the atmosphere, since before that point the pathways differ from one GHG to the other, but from that point their impact is modelled to be identical around the globe, and possible to relativize to an unitary emission (CO_2 eq). Examples of midpoint and endpoint impact categories are depicted in Figure 24.

It was developed by the Center of Environmental Science of the Leiden University in the Netherlands. It includes 3 impact assessment categories, divided in obligatory, additional and other impact categories, the obligatory impact categories being used in most LCAs.

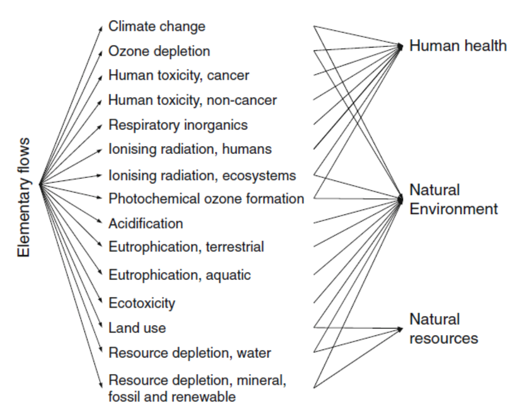

Figure 24 - Mid Point and Endpoint impact category characterization. Source: Hauschild et. al (2013). [74]

The life cycle categories that are going to be assessed in this work are the following:

- Global Warming Potential (GWP) measured in kg CO_2eq - this is an indicator of the contribution of a given activity to the emission of greenhouse gases believed to be a big anthropogenic driver of climate change. It makes sense to compare the pathways as GHG emission reduction is the biggest driver in the environmental performance of fuels and environmental impact reduction. The characterization model is developed by the IPCC, and is expressed for a 100 year time horizon. [75]
- Ozone Depletion Potential (ODP), measured in kg CFC-11-eq - there are many gaseous emissions that contribute to the depletion of stratospheric ozone in the atmosphere, which increases radiative forcing in Earth's climate, reflecting in an increase of temperature and an intensification of global warming. Cleaner synfuels provide a better alternative when they do not have a high concentration of emissions related to ozone depletion, such as some VOCs. The characterization model is developed by the World Meteorological Organization, which defines the ozone depletion potential of various gases. [75]
- Acidification of Soil and Water Potential (AP), measured in kg SO_2eq - the emission of NO_x and SO_x are associated with the increase of acidity in water and soils, regionally and globally. Quantifying the emissions of these compounds through the life cycle of the systems enables a significant advantage of alternative jet fuels compared to conventional aviation fuel with a lot of acidifying emissions associated. The model is developed by Huijbregts. [75]
- Photochemical Ozone Creation Potential (PO), measured in kg ethene eq - some gaseous emissions affect the synthesis of Ozone in lower layers of the atmosphere, a reaction catalysed by sunlight. This is a step which has more significance in the life cycle end (combustion) of the jet fuels, since different fuel compositions with distinct aromatics concentrations will produce objectively different emissions, constituting distinct quantifiable impacts. This potential is calculated with the UNECE Trajectory model, with a time span of 5 days. Geographical scale and regional specificity are included. [75]
- Abiotic Depletion of Fossil Fuels (ADFF), measured in MJ LHV - related to the depletion of natural fossil fuel resources. This is a step which reveals the advantage of alternative renewable fuels in contrast with conventional fossil non-renewable fuels.
- Marine Water Ecotoxicity (MWE), measured in 1,4-dichlorobenzene equivalents/kg) - relates to the impact on marine ecosystems of emissions of toxic substances to the air, soil and water. USES-LCA calculations describing fate, exposure and effects of the toxic substances are done to obtain the necessary Eco-toxicity potential and characterization factors. This indicator can be applied for different spatial specificity. [75]

Other impact categories that can be used to assess the environmental impact are:

- Depletion of abiotic elements - non fossil fuels (measured in kg Sb eq) - an indicator related to the use of natural non-fossil resources in a given activity, very significant in land use impact characterization. This is an indicator connecting the extraction rate of the resources used with their scarcity – in this particular case, since there is no infrastructure involved in the life cycle inventory, the results are extremely sensitive to the metals used in the catalysts – the databases associated with these metals have large uncertainty associated, and besides that, the lifetime of the catalysts is information that is hard to come by and differs according to the operation conditions, reagent composition, etc..

- Human toxicity (measured in 1,4-dichlorobenzene equivalents/ kg emission) – this category refers to the effects of the exposure to toxic substances in human health. Toxic compound discharge during an activity can adversely affect the human health, and it is important to address subprocesses with relevant emissions into the environment for it concerns public health as well as the safety and wellbeing of the working staff. The characterization factors, Human Toxicity Potentials, fate, exposure and effects of the toxic substances are all included in the calculations using USES-LCA methodology included in the CML_IA baseline. [75] This category was dropped since in offshore exploration, the emissions do not affect human health significantly (low population density, high distance from shore). Fresh water ecotoxicity and terrestrial ecotoxicity were also not considered for the same reason.
- Eutrophication (measured in kg PO4-3 eq) – eutrophication is a measurement of the enrichment of an aquatic system with nutrients derived from human activity emissions. Since agriculture is a significant step of the biofuel life cycle, it is wise to measure quantitively the contribution of that step to the overall life cycle impact of water courses associated with the bio jet fuel production deriving from, for example, fertilizer use. The model is developed by Heijungs et. Al. In this particular case, however, eutrophication emissions are very low, and the results were sensitive to the NO_x airborne emissions, which in equilibrium could eventually reach freshwater aquatic water bodies and cause eutrophication. Consequently, this category would not bring useful information either.

Sources of uncertainty in impact characterization

Jet fuel and syncrude pathways are associated with a large uncertainty in the characterization of impacts associated with the life cycle inventory due to a number of factors. Life Cycle Associates [40] presents a framework in which uncertainty sources for this LCA application are described. They are the following:

- Petroleum baseline determination methods differ from one study to another, ranging from assigning just the refinery emissions (GREET model) associated with crude distillation to jet, to methods involving linear programming models to obtain the marginal emissions[5] from refining and crude oil. [40]

- The allocation of emissions to fuels and co-products - after refining there are a lot of co-products besides jet-fuel, such as naphtha, lubricant base oil, other hydrocarbons and electrical energy- and the two pathways for allocation of emissions (substitution credit for co-products vs allocating emissions by energy or market value) constitute radically different results between studies, specially “when the jet-fuel is a minor product and the credit for co-products results in very low or even negative GHG emissions”. [40] This problem can be tackled with system expansion.
- Different LCA models for biomass-feedstock jet-fuels return different values for direct and indirect land use emissions from agriculture required to produce biomass feedstock jet fuels. This is because land conversion impacts are different according to the different biomass feedstocks, geographical position, agriculture operations and the possible displacement of one food crop for a jet fuel feedstock cultivation. [40] For this reason, and due to time and resource constraints, a choice was made to not include a comparative analysis to bio-jet fuel pathways until there is sufficient data to justify that endeavour.
- Since there is no generalized approach to jet fuel sustainability assessment through LCA, methodologies, data sourcing, assessment scope, baseline comparison thresholds and treatment of co-products vary from region to region and even from country to country. [40]

Besides these cautionary measures, one should also be careful around some LCA assumptions such as:

- Considering a lower refining energy intensity for jet fuel over diesel (since kerosene can be considered a straight run product) - Substitution of petroleum by renewable feedstocks in jet fuel production changes the refinery operations consequently changing its energy intensity. [40]
- Agricultural N_2O emissions from nitrogen fixing plants (a high impact greenhouse gas) are significant and constitute a significant share of the fuel life cycle’s emissions in bio-jet fuel pathways. Different models to estimate the N_2O emissions have large biased differences. [40]
- Jet Fuel yields from different hydroprocessing technologies are proprietary and generally not available to the general public. [40]

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[5] Marginal emissions reflect the future potential emissions associated with the activity at hand. In the case of refineries, for example, the fact that oil wells are becoming depleted and sourer in acid composition increases the emissions associated with extraction related with energy and electricity expenditure through time.

- In a substitution approach for co-product carbon intensity (CI) determination, one should be very cautious when attributing impacts to naphtha – generally, “the average carbon intensity for petroleum naphtha is larger than that of renewable jet fuel”. [40] As such, when using substitution credits for co-products, in CI calculations comparatively lower GHG intensities are obtained for the same pathway as the jet fuel yield is lower, a significant error corrected by a combination of the former mentioned approach with a consequential analysis of oil refining. [40]

Data quality requirements and Life Cycle Inventory Analysis

It is wise to focus on a methodology appropriate to the scope of the project and to compare studies with equal scope and statistical significance, as is recommended by the ISO standard 14040:2006 and 14044:2006.

The inventory data for each pathway was compared using the SimaPro impact characterization model CML-IA baseline which allows for the relative comparison of the environmental performance of these pathways under the same impact characterization methodology. All of the inventory data relates to a continuous phase operation, which in practical terms suggests that some of the circular feeds are not accounted for in the analysis, as they stay inside the system boundaries throughout the life cycle of the product without interacting with their environment.

According to statistics and data science’s good practices, every LCI step with insufficient data should be handled accordingly, with a sample big enough to draw solid results associated with a high degree of significance and minimizing errors. Whenever it is impossible to collect the desired data and approximations are deemed to be risky and meaningless, the subprocess units related to that inventory data in particular should be dropped from the system boundaries. Alternatively, the life cycle categories to be evaluated can be also re-adjusted, in the case of trace emissions.

Oil and gas extraction, separation, and pre-treatment of crude oil

Oil and gas extraction was assumed to be done in an FPSO facility located in the Santos Basin, in the pre-salt ultradeep water area. The data listed in Table 1 was collected from 6 FPSO facilities among the operating facilities in this area under Petrobras’ [76], which are focused in ultradeep water exploration:

Table 1 - FPSO facilities under Petrobras' and Modec's operation in the Santos Basin, Pre-Salt.

FPSO facility	Distance to shore (km)	Depth (m)	Oil production (thousand bpd)	Oil production (Mton/day)	Natural gas production (million m³/d)	Storage capacity (thousand barrels)	Storage capacity before offloading (thousand barrels)	Field
Cidade de Ilhabela	310	2140	150	23.8	6.0	1600	550	Sapinhoá
Cidade de Baraty	300	2120	120	19.0	5.0	1600	760	Lula
Cidade de São Paulo	300	2140	120	19.0	5.0	1600	760	Sapinhoá
Cidade de Mangaratiba	240	2200	150	23.8	8.0	1600	550	Iracema
Cidade de Itaguai	240	2240	150	23.8	8.0	1600	550	Iracema
Cidade de Saquarema	300	2120	150	23.8	6.0	1600	550	Lula

The relevant data such as distance from shore, depth, oil and natural gas production and storage capacity was obtained from Petrobras' and Modec's website.

As can be observed, oil production in barrels per day is between 120 and 150 thousand bpd, and the storage capacity is the same for every vessel, regardless of any other variable. As will be mentioned further, LCI data from crude oil extraction and processing is related to kg of oil extracted, so a conversion step of barrels into a mass unit had to be done in order to carry out the inventory data collection. A value of 136 kg per barrel of oil was considered, based on the worldwide average gravity of crude oil. [77]

As such, it was presumed that the extraction facility consisted of a general FPSO vessel with an oil production capacity of 150 000 bpd (which amounts to approximately 24 thousand metric tonnes of oil per day) and a storage capacity of 1 600 000 barrels. It was also presumed that these facilities operate with enhanced oil recovery based on CO_2 injection and water flooding, as is common in the Santos Basin operations. Furthermore, it was presumed that an offloading frequency of 1 week was to be done, as is customary for FPSO facilities after the first year. [35] Following that assumption, calculation of the leftover space available for F-T syncrude storage was done, in order to assess how much capacity can be installed in future investigations.

Concerning the crude oil extraction, separation from water and natural gas and production/processing, LCI data on a unitary basis (unit/kg OE) was obtained from Jungbluth (2018) [27], and the data collected included direct and indirect emissions to air and water resulting from the offshore operation at hand. All the relevant data necessary to convert unitary data values into the total daily emissions is included in Table 2.

Table 2 - Relevant information to the calculation of the missing Life Cycle Inventory Data related to Oil and Gas extraction phase.

	Unit	Baseline	SMR	DMR
Extra Barrels of oil produced[6]	Barrels per day	0	817	1 413
Mass of Oil extracted from depth	kg/day	2.04 x 10^7		
Flared Gas[7]	Nm^3/day	8.65 x 10^5	6.56 x 10^5	3.51 x 10^5
Vented Gas	Nm^3/day	2.98 x 10^5		
Total produced water	kg/day	2.04 x 10^7		
Discharged water	kg/day	1.63 x 10^7		
Total Storage capacity	Thousand barrels	1 600		
Storage Left After one week		550	544	540

Global average values were extracted since no specific data related to Brazilian Pre-salt exploration was supplied. Produced water in the facility can be discharged, treated for injection and subsequently injected for improved oil recovery or treated for discharge, meeting environmental ocean discharge regulations. It was considered that 80% of the water is discharged after treatment, according to what can be found in literature for offshore exploration. [27] The remaining body of water was assumed to be treated into water for injection regulations and consequently injected along with CO_2. Electricity generation in the facility was assumed to take place in gas turbines using a mix of sweet and sour natural gas explored on site, and diesel fuel oil burned in a diesel electric generating set. The gas turbine electrical efficiency was fixed at 35.2%, as it is the turbine electrical efficiency associated with Titan 130 Gas Turbines, typically used in offshore explorations[8]. A natural gas mass balance was carried out, as well as two hypothesis tests to assure that the daily produced natural gas was enough to supply the demanded energy for the operation. The conclusion was positive, and can be verified in the Appendix I.

The construction of the infrastructure related to well drilling and oil extraction as well as the infrastructure related to the FPSO was not considered for this life cycle assessment, since the impacts related to construction and maintenance of the reactors and infrastructure of the plants are not important to the scope of this project – insufficient experimentation has been done in order to determine the lifetime of the NETmix micro-reactors in this specific application, which would render results with added uncertainty.

The difference between the baseline and proposed Net4GtL scenarios related to the extraction stage of the life cycle is in the flaring emissions. It was assumed that the gas feed input in the reforming stage, calculated from the simulations, is completely made up of associated gas destined for flaring, and consequently the application of the proposed system would reduce

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[6] This is the sum of normal operation crude oil extracted, incremental crude oil extracted from Enhanced Oil Recovery operations and syncrude production

[7] Calculated using unitary values per kg of OE found in the same database

[8] Source: Wall, M., Lee, R., Frost, S., "Offshore Gas Turbines (and major driven equipment) integrity and inspection guidance notes)".

the Oil and Gas Extraction Phase direct emissions to the atmosphere. This difference can be observed in Table 3.

Since there is a large uncertainty associated with the feed gas pre-treatment operation and emissions, the same flare gas and vent gas composition contained in the database found in Jungbluth et. al. was assumed for all three scenarios, even though technically the flared and vented gas emissions from the three scenarios would be different, as the composition of the feed gas in the reforming stage differs from the SMR case to the DMR case. The sensitivity analysis associated with this assumption can be found in Appendix II, but the main point of this assumption was to minimize the bias in the conclusions, in order to draw better information from the obtained results. Vent gas emissions were considered to be the same for all scenarios since they consist of unwanted emissions, unlike flaring which is done for safety.

However, it is also very important to mention that because of this assumption, the DMR feed gas which is 3 times higher in mass flux than the SMR case will return better values for the reduction of total flare volume reduction, even though it is not necessarily true. It is also logical that if the total mass of associated gas destined for flaring was collected and further converted into liquid syncrude, for the same mass of associated gas consumption a higher yield of barrels would be obtained for the SMR case.

Another thing to have in mind is that the hydrocarbons content in the SMR natural gas is larger than the hydrocarbons content in the DMR natural gas, for the same barrels produced. This is because the carbon dioxide in the DMR case also acts as a reactant, contributing to the number of barrels produced. Therefore, if the starting natural gas had exactly the same composition, with a large content in carbon dioxide, and the choice in question was to use the gas directly to DMR or to perform a gas treatment to eliminate carbon dioxide prior to SMR, the reduction in flaring per barrel could be lower for the SMR case if the pre-treatment contribution is significant, assuming the increase in the number of barrels is similar to the impact increase. Although the DMR has a higher CO_2 concentration, it also has a higher CH_4 absolute mass, which is the reagent – so that would mean that the previous comment made before on the yield of barrels is not true either since the associated gas feed is not entirely made of reagent for the syngas generation operation.

Reflecting upon the choices made, a few conclusions can be dealt with:

- Converting the volume of flared gas into a mass using its density at normal temperature and pressure conditions and assuming that its usage in the reforming reactor reduces the mass of emissions to tackle data unavailability doesn't incur in significant data bias and mistakes, even if the carbon dioxide content may vary for different natural gas compositions. This is because stoichiometrically the combustion of the natural gas would result in a chemical reaction ultimately possessing a similar mass of product and reagents. Consequently, it's possible to estimate the avoided emissions by assuming that the mass of associated gas used in the reforming reactor would otherwise be flared and generate combustion emissions as calculated in the database, on an unitary base per Nm^3 of flared gas.

- Using this data obtained from real facilities also has the advantage of having included in it the disparity between natural gas compositions, flaring combustion conditions (some more incomplete than others), and even flaring origin conditions, since not all associated gas being combusted comes from the same place.
- The reduction in the flaring emissions will be apparently lower for the SMR case since it is pretreated – consequently it would have a higher mass of CO_2 than the one that is assumed in this work if it had not been pretreated before. If that mass was present, and subtracted to the total associated gas production in the facility, it would render higher emission avoidance than the one that's calculated. This means that the reduction of emissions in the SMR case is in fact a calculation done by defect, and not by excess, as is the case in the DMR case, where there's a much higher mass of CO_2 that would have been removed earlier in the pretreatment stage. This invasive "impurity" mass of CO_2 makes the subtraction of total associated gas a calculation done by excess. Hence, the pretreatment step which is not evaluated in this assessment is the subprocess step with the largest result bias associated.

Bearing these concepts in mind, it is fundamental that the reader analyses the 4 complementary results with clinical eye and bearing in mind these assumptions that were used inevitably to tackle data unavailability. Consequently, all assumptions and uncertainties must be taken into account to better understand the final results.

The life cycle inventory data for the O&G Extraction Phase is described in Table 3.

Table 3 - Inventory data related to Oil and Gas Extraction phase, for the three scenarios.

SCENARIO	DATA	VALUE	UNIT	ONE DAY OF OPERATION[9]	UNIT	NOTES
				INPUTS		
				Energy use		
Common to all scenarios	Diesel burned in electrical generator	0.150	MJ/kg OE	3.06×10^6	MJ/day	-
	Heavy fuel oil, burned in equipment	0.150	MJ/kg OE	3.06×10^6	MJ/day	-
	Sweet gas, burned in gas turbine	1.020	MJ/kg OE	2.08×10^7	MJ/day	Data adapted to better fit the case study. Original database had a grid electricity share, which does not exist in FPSO offshore typical exploration in stranded reserves – this supply was switched to the burning of the sweet gas.
	Sour gas, burned in gas turbine	0.100	MJ/kg OE	2.04×10^6	MJ/day	-

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[9] A daily operation mass of 2.04×10^7 kg of Oil Extracted was assumed based on the 150 000 bpd production volume assumed, alike the volume of flared gas and vent gas, calculated as 8.65×10^5 Nm^3 and 2.98×10^5 Nm^3 respectively. Volume of produced water was calculated using the same methodology, obtaining a value of 2.04×10^7 kg.

SCENARIO	DATA	VALUE	UNIT	ONE DAY OF OPERATION	UNIT	NOTES
Water in extraction operations						
SMR	Saltwater sourced	-	-	2.06 x 10^{5}	m3/day	Assuming 1.03 x 10^{-2} m^{3}/kg OE and the usage of treated produced water (see water balance in Appendix I).
DMR		-	-	2.07 x 10^{5}		
OUTPUTS						
Flaring emissions into the atmosphere						
Baseline	Methane, fossil	7.07 x 10^{-4}	kg/Nm^{3}	612	kg/day	Standard deviations included in the dataset.
SMR				404		
DMR				101		
Baseline	Carbon dioxide, fossil	3.71	kg/Nm^{3}	3.21 x 10^{6}	kg/day	Standard deviations included in the dataset.
SMR				2.12 x 10^{6}		
DMR				5.29 x 10^{6}		
Baseline	Carbon monoxide, fossil	1.00 x 10^{-3}	kg/Nm^{3}	865	kg/day	Standard deviations included in the dataset.
SMR				572		
DMR				143		
Baseline	NMVOC, non-methane VOC, unspecified origin	1.96 x 10^{-4}	kg/Nm^{3}	170	kg/day	Standard deviations included in the dataset.
SMR				112		
DMR				28		
Baseline	Nitrogen oxides	1.63 x 10^{-3}	kg/Nm^{3}	1.41 x 10^{3}	kg/day	Standard deviations included in the dataset.
SMR				9.32 x 10^{2}		
DMR				2.32 x 10^{2}		
Baseline	Dinitrogen monoxide	2.00x10^{-5}	kg/Nm^{3}	17.3	kg/day	Standard deviations included in the dataset.
SMR				11.4		
DMR				2.85		
Baseline	Particulates <2,5 um	5.40 x 10^{-4}	kg/Nm^{3}	467	kg/day	Standard deviations included in the dataset.
SMR				309		
DMR				77.0		
Baseline	Sulfur Dioxide (minimum)	0	kg/Nm^{3}	0	kg/day	Depends on the NG composition. This was accounted for in an uncertainty analysis.
SMR						
DMR						
Baseline	Sulfur Dioxide (maximum)	0.170	kg/Nm^{3}	1.47 x 10^{5}	kg/day	
SMR				9.72 x 10^{4}		
DMR				2.42 x 10^{4}		
Baseline	Mercury	2.00x10^{-7}	kg/Nm^{3}	0.173	kg/day	Standard deviations included in the dataset.
SMR				0.114		
DMR				0.029		
Baseline	Radon-222	0.400	kBq/Nm^{3}	3.46 x 10^{5}	kBq/day	Standard deviations included in the dataset.
SMR				2.29 x 10^{5}		
DMR				5.71 x 10^{4}		
Baseline	Heat - waste	36	MJ/Nm^{3}	3.11 x 10^{7}	MJ/day	Standard deviations included in the dataset.
SMR				2.06 x 10^{7}		
DMR				5.13 x 10^{6}		
Venting emissions into the atmosphere						
Common to all scenarios	Carbon Dioxide, fossil	1.40 x 10^{-2}	kg/Nm^{3}	4.17 x 10^{3}	kg/day	Standard deviations included in the dataset.
	Helium	1.00 x 10^{-3}	kg/Nm^{3}	298	kg/day	Standard deviations included in the dataset.
	Mercury	1.50 x 10^{-8}	kg/Nm^{3}	4.47 x 10^{-3}	kg/day	Standard deviations included in the dataset.
	Methane, fossil	0.585	kg/Nm^{3}	1.74 x 10^{5}	kg/day	Standard deviations included in the dataset.
	NMVOC, non-methane VOC, unspecified origin	0.271	kg/Nm^{3}	8.07 x 10^{4}	kg/day	Standard deviations included in the dataset.
	Radon-222	0.100	kBq/Nm^{3}	2.98 x 10^{4}	kBq/day	Standard deviations included in the dataset.
Emissions to marine water						
Common to all scenarios	Water discharge after treatment	-	-	1.63 x 10^{7}	kg/day	80% of the total produced water, which was estimated using unitary data of 1 kg/OE according to Jungbluth (2018).

SCENARIO	DATA	VALUE	UNIT	ONE DAY OF OPERATION	UNIT	NOTES
Common to all scenarios	Total Oil Discharge	4.05×10^{-5}	kg/kg OE	826	kg/day	Generic value - average IOGP data plus breakdown of 5 biggest non-war related oil spills on oil platforms between 1900 and 2010.
	Low active radioactive waste	2.00×10^{-7}	m^3/kg OE	4.08	m3/day	Standard deviations included in the dataset.
Common to all scenarios	Disposal, municipal solid waste, 22,9% water	1.00×10^{-4}	kg/kg OE	2.04×10^3	kg/day	Standard deviations included in the dataset.
Outputs to the technosphere						
SCENARIO	**DATA**	**VALUE**	**UNIT**	**RELATED TO THE F. UNIT**	**UNIT**	**NOTES**
SMR	Associated gas produced	6.16×10^5	kg/day	0.29743	kg/MJ	The allocation of the total flared gas in the impact assessment was done in order to avoid penalizations associated with the different reforming feed flows. The different values in relation to the MJ functional unit have got to do with the small discrepancy of the number of barrels generated in the separation stage. See the Appendix III for further explanation. What differs between the two is that for the same mass of associated gas produced, different masses of associated gas is captured and consequently, different environmental impacts are related to this stage.
DMR				0.29666	kg/MJ	

SMR Net4GtL and DMR Net4GtL inventory data

The inventory data related to energy consumption, material inputs and outputs and emissions existent for all stages of our system from reforming up to syncrude production and separation was obtained via computer modelling and simulation in Aspen Plus [92] - considering the system is still being developed and the engineers/designers/decision-makers are still optimizing the system and its energy intensity and environmental impact. As such, it has some limitations which can bring substantial uncertainty. The composition of the feed gas and its subsequent transformations are confidential and are not to be revealed in this life cycle inventory of this document.

The natural gas composition was supplied by GALP, and the production capacity of 500 barrels per day with a desired 60% global efficiency was fixed in order to be consistent with the capacity from other small modular GtL facilities such as the one developed by ENVIA GtL Velocys, which produces around 250 bpd. [78] This is because the target of this GtL technology is the monetization of stranded gas reserves and the usage of excess associated gas destined for flaring.

Life cycle inventory data of MDEA, rhodium, cobalt and copper-oxide catalysts was retrieved from EcoInvent's Databases. MDEA specifically was considered to have a similar life cycle inventory data as MEA, since it has been assumed that MEA can act as a proxy for other solvent amines when a lack of data arises. [79] Rhodium, cobalt and copper-oxide catalyst life cycle data is also very difficult to come by – however, a significant share of the life cycle impacts of the metal catalysts is due to mining operation. In the rhodium case, a platinum group metal, the low grade of the mined ore, difficult mining operations and the fossil fuel intensive energy mix related to the mining location (South Africa, 90% electricity generated from hard coal) constitute a much higher impact than its secondary production. [80] A longevity of 3 years was assumed for every catalyst, in order to allocate a portion of its mass corresponding to a daily operation[10]. The choice of 3 years is the fact that in two-phase reforming in similar small scale GtL operations, the longevity of cobalt catalysts improves significantly [56] when compared to a two-phase reforming design.

Pre-treatment of natural gas LCI data gathering and subsequent impact calculation was not carried out for two reasons:

- The composition of the feedstock for the F-T process was supplied in different forms. In the DMR process, the feedstock has a much bigger CO_2 weight than the feedstock used in the SMR process. Furthermore, the SMR process is already pretreated, while the DMR process is not, which besides influencing the simulation results substantially, makes the assessment of the pre-treatment of natural gas meaningless.
- Pre-treatment depends on the composition of the given natural gas feedstock at hand. A consequence of that is that the designs of pre-treatment are more or less specific to the feedstock under study. Assuming a generalized pre-treatment for both of these feedstocks would add unnecessary uncertainty and bias to the final results that do not bring a positive trade-off in significance.

Wastewater generated in the subprocesses is assumed to be treated internally and injected for enhanced oil recovery along with the produced on-site CO_2 (Appendix I). However, the discharge of this water was still included in the impact calculation, to avoid an assessment calculated by defect – this is because the treatment of this water before injection would have non-null impacts, and it is still wise to include the negative impacts of the CO_2 EOR operation if one includes its positive impacts (incremental barrel of oil recovery and CO_2 emission avoidance).

The electricity demand for this facility was assumed to be supplied by the fuels already being explored in the facility, in the existing electrical gas turbines. As such, a mix of sweet and sour natural gas was assumed to be burned and converted to electricity with 35.2 % efficiency.

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[10] The logic behind this is the fact that summing the impacts of the mass portions on a daily basis over the course of 3 years would be equal to the total life cycle impacts of the undivided mass. This is true since the characterization model associated with these SimaPro databases calculates impacts associated with the output in mass of these metals related to technosphere.

The data from the simulations are aged 2 years, obtained from 2018 to 2020. Recent data from literature, such as the data collected from Jungbluth et. Al (2018) [27] was compiled so this study was significant regarding its time reference.

Reforming operation

The reforming operation consists of the conversion of methane in the gas to hydrogen and carbon monoxide. This requires an heat input, which is supplied by the furnace fed with the gas mix from the separation after F-T reaction in both pathways, surplus hydrogen from the PSA in the case of the SMR pathway and natural gas in the DMR pathway. The emissions related to the combustion of these fuels for heat production were allocated to each subprocess on an energy demand basis.

Regarding electricity consumption, the DMR pathway has no electricity consumption in this step, unlike the SMR pathway which has more compressors then the SMR pathway, due to design requirements.

The SMR pathway also uses fresh water in order to produce steam, unlike the DMR pathway, which, as the name suggests, performs a dry reforming operation.

The life cycle inventory related to this stage can be found in Table 4.

Table 4 - Inventory data related to the reforming phase, for the two scenarios.

SCENARIO	DATA	VALUE	UNIT	NOTES
		INPUTS		
		Energy use		
SMR	Sweet gas, burned in gas turbine	3.54 x 10^{3}	MJ/day	Considering Titan 130 efficiency (35.2%).
	Sour gas, burned in gas turbine	3.54 x 10^{2}		Considering Titan 130 efficiency (35.2%).
		Inputs from technosphere		
SMR	Rhodium consumption	2.57 x 10^{-3}	kg/day	Considering 3 year life expectancy.
DMR		1.96 x 10^{-4}		Considering 3 year life expectancy.
		Inputs from nature		
SMR	Fresh water consumption	241	m^3/day	Water needed to generate steam.
		OUTPUTS		
		Emissions to the atmosphere		
SMR	Water Vapour	4.66 x 10^{5}	kg/day	100% of all the on-site furnace heat.
DMR		1.10 x 10^{5}		93.8% of all the on-site furnace heat.
SMR	Carbon dioxide, fossil	2.69 x 10^{5}	kg/day	100% of all the on-site furnace heat.
DMR		3.11 x 10^{5}		93.8% of all the on-site furnace heat.
SMR	Carbon Monoxide, fossil	3.24 x 10^{3}	kg/day	100% of all the on-site furnace heat.
DMR		1.55 x 10^{3}		93.8% of all the on-site furnace heat.
SMR	Nitrogen, atmospheric	2.38 x 10^{6}	kg/day	100% of all the on-site furnace heat.
DMR		7.69 x 10^{5}		93.8% of all the on-site furnace heat.
SMR	Oxygen	1.44 x 10^{5}	kg/day	100% of all the on-site furnace heat.
DMR		2.31 x 10^{4}		93.8% of all the on-site furnace heat.
SMR	Methane, fossil	1.52 x 10^{-14}	kg/day	100% of all the on-site furnace heat
DMR		1.79 x 10^{-14}		93.8% of all the on-site furnace heat
SMR	Nitrogen monoxide	1.44 x 10^{3}	kg/day	100% of all the on-site furnace heat
DMR		2.79 x 10^{3}		93.8% of all the on-site furnace heat
SMR	Nitrogen dioxide	1.87	kg/day	100% of all the on-site furnace heat
DMR		2.70		93.8% of all the on-site furnace heat
SMR	Dinitrogen monoxide	1.27	kg/day	100% of all the on-site furnace heat
DMR		0.27		93.8% of all the on-site furnace heat

SCENARIO	DATA	VALUE	UNIT	NOTES		
SMR	Hydrogen	17.2	kg/day	100% of all the on-site furnace heat		
DMR		21.6		93.8% of all the on-site furnace heat		
			Outputs to the technosphere			
SCENARIO	**DATA**	**VALUE**	**UNIT**	**RELATED TO THE F.UNIT**	**UNIT**	**NOTES**
SMR	Reformed Gas	4.51×10^5	kg/day	0.21780	kg/MJ	
DMR		5.14×10^5	kg/day	0.24775	kg/MJ	

Water Gas Shift

The water gas shift reaction is exclusive to the DMR process, and its purpose is the enrichment of the H_2 and the reduction of CO in the syngas. It is an exothermic reaction, so its heat also contributes to the heat integration of the system. In this reactor, a water feed is mixed with the reformed gas in the presence of a copper oxide catalyst. There's no generation of wastewater in this subprocess as the water is later removed in the amine scrubbing process through a flash vessel. Life cycle inventory data related to the Water Gas Shift subprocess step is represented in Table 5.

Table 5 - LCI data relevant to the water gas shift subprocess, exclusive to the DMR pathway.

SCENARIO	DATA	VALUE	UNIT	NOTES		
			INPUTS			
			Energy use			
DMR	Sweet gas, burned in gas turbine	172	MJ/day	Considering Titan 130 efficiency (35.2%).		
	Sour gas, burned in gas turbine	17.2		Considering Titan 130 efficiency (35.2%).		
			Inputs from technosphere			
DMR	Copper oxide consumption	8.82×10^{-3}	kg/day	Same logical procedure as it was done with rhodium (see footnote 10).		
			Inputs from nature			
DMR	Fresh water consumption	82	m^3/day			
			OUTPUTS			
SCENARIO	**DATA**	**VALUE**	**UNIT**	**RELATED TO THE F. UNIT**	**UNIT**	**NOTES**
DMR	Reformed gas, shifted	5.96×10^5	kg/day	0.28699	kg/MJ	

Amine Scrubbing

In the amine scrubbing stage, the CO_2 in the feed gas (negative to the subsequent FT operation as it alters the FT end product mixture distribution) is removed by the use of chemical absorption using the tertiary amine MDEA. Research was conducted to obtain proper LCI data for this product, however no relevant data was obtained other than patent data and general information about the process. As such, a different approach was considered using the methodology proposed by Hischier R. et. Al (2005) [81] in which facing nearly inexistent LCI data of a given chemical, input materials would be estimated using the stoichometric equation and a 95% efficiency assumption. Energy and water consumption, as well as emissions to the air, water and soil and waste generated would be estimated using average data from the chemical industry. However, given the fact that the information is very scarce, this methodology was dropped out in favor of assuming MEA's production life cycle impacts as a proxy for all amine production systems, as was previously done in similar research. [79]

Common to both scenarios, a makeup feed of amine and fresh water has to be supplied in continuous operation to replace the spent amine that cannot be regenerated. MDEA and MDEAH+ emissions present in the wastewater flow as programmed in ASPEN Plus were modelled as general tertiary amine emissions into the water, as it is the most appropriate emission model available in SimaPro databases for this problem at hand. Represented in Table 6 is the inventory data related to the amine scrubbing subprocess step.

Table 6 - Inventory data related to the amine scrubbing phase, for both scenarios.

SCENARIO	DATA	VALUE	UNIT	NOTES
		INPUTS		
		Energy use		
SMR	Sweet gas, burned in gas turbine	2.94 x 10^5	MJ/day	Considering Titan 130 efficiency (35.2%).
	Sour gas, burned in gas turbine	2.95 x 10^4		Considering Titan 130 efficiency (35.2%).
DMR	Sweet gas, burned in gas turbine	8.59 x 10^5	MJ/day	Considering Titan 130 efficiency (35.2%).
	Sour gas, burned in gas turbine	8.60 x 10^4		Considering Titan 130 efficiency (35.2%).
		Inputs from nature		
SMR	Freshwater consumption	22	m^3/day	
DMR		12	m^3/day	
		Inputs from the technosphere		
SMR	MDEA make up feed	2.90 x 10^1	kg/day	Much higher amine demand due to the significantly higher CO_2 concentration in the DMR feed gas.
DMR		2.48 x 10^4	kg/day	
		OUTPUTS		
		Emissions into marine water		
SMR	Water discharge after treatment	1.95 x 10^4	kg/day	Value is higher for DMR since there is a flash vessel removing water from the untreated feed gas. One would expect a higher water discharge since there is a higher water feed.
DMR		5.29 x 10^4	kg/day	
SMR	Amine, tertiary	29	kg/day	MDEAH+ emissions constitute 99% of the total amine emissions into the water.
DMR		101		
		Outputs into the technosphere		

SCENARIO	DATA	VALUE	UNIT	RELATED TO THE F. UNIT	UNIT	NOTES
SMR	Syngas cleansed of CO_2	3.29 x 10^5	kg/day	0.15900	kg/MJ	DMR value is lower since it undergoes Water Gas Shift Reaction before, unlike the feed gas in the SMR pathway which undergoes Amine Scrubbing right after reforming.
DMR		2.31 x 10^5		0.11134		

CO_2 compression and reinjection

Although in the Life Cycle Assessment model developed in SimaPro the inputs of CO_2 compression and reinjection were associated with the Amine Scrubbing Step (to reduce the number of subprocesses, simplifying the analysis), this chapter is separated from the Amine Scrubbing chapter in order to better explain the assumptions and estimations conducted in this step.

A value of 400 kg of CO_2 per barrel recovered was assumed, according to Godec, M., et. Al (2016). [82] As such, for each pathway tested the total amount of barrels recovered per day was obtained dividing the CO_2 recovered during amine scrubbing by the 400 kg/barrel of OE defined[11]. This is relevant for the typical value found in literature associated with oil lifting with enhanced oil recovery which was 1.795 kWh/incremental barrel recovered. [83]

Afterwards, a value of CO_2 compression energy of 56 kWh/ton CO_2 was assumed. [84] This makes it possible to calculate the energy required for compression of the necessary mass of CO_2 for the EOR process. A value of 0.0132 m^3 water injected/kg crude oil was assumed according to Jungbluth (2018). The water was assumed to be generated in the facility and treated for injection – hence it is not considered as an input or an output in this step, as in continuous operation this water never leaves the system. Including it in this life cycle stage would be double counting of impacts. The compression energy associated for water compression was assumed to be 4 kWh/incremental barrel of oil. [82] Energy required for capturing and transporting gas destined for flaring was not considered in the scope of this project.

Summarizing – the number of barrels of oil recovered through EOR is obtained dividing the mass of CO_2 extracted in amine scrubbing by the unitary necessity of CO_2 per barrel extracted (400 kg/barrel). Afterwards, the energy required for oil lifting is calculated multiplying the value 1.795 kWh/barrel by the amount of oils recovered, obtained in the previous step. All that is left is calculating the required energy for compression, which obtained by multiplying the mass of CO_2 used for injection by the energy required for compression per ton of CO_2 (56 kWh/ton CO_2). The treated data to obtain the LCI information for this step and the LCI data are represented in Table 7 and 8 respectively.

In reality, this approach is an approximation. It was necessary to use generalized values because no information was given about the depth, pipe length, porosity of the oil field, compounds present in the reservoir, etc., which are relevant variables for the required energy for pumping. Moreover, as energy intensity related to extraction changes with time, a marginal model would have to be applied in order to simulate the increase of energy intensity during the aging of the oil field. This over-complicates the project, which scope and lack of definitive information do not justify such procedures.

Table 7 - Relevant data for LCI estimation in the CO_2 injection for EOR operation, for the CO_2 generated in the Amine Scrubbing subprocess step.

	SMR	**DMR**
Mass of CO_2 generated in the Amine Scrubbing step (kg/day)	1.24×10^5	3.62×10^5
Incremental barrels of oil recovered (bpd)	311	904
Volume of water used for EOR (m^3/day)	435	1266
Power required for CO_2 compression and injection (kWh/day)	6.96×10^3	2.03×10^4
Power required for Oil Lifting (kWh/day)	5.58×10^2	1.62×10^3

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[11] Although this was assumed, it is not necessarily true. CO_2 usage per incremental barrel of oil is a known information, but incremental barrels of oil per ton of CO_2 is not necessarily the inverse of this value, unless we know beforehand the bulk of total incremental barrels of oil recovered.

	SMR	DMR
Power required for Water compression and injection (kWh/day)	1.24×10^3	3.62×10^3

Table 8 - LCI data for the CO_2 injection and EOR step, included in the Amine Scrubbing life cycle stage in the model.

SCENARIO	DATA	VALUE	UNIT	NOTES
		INPUTS		
		Energy use		
SMR	Sweet gas, burned in gas turbine	22.6	MJ/day	Considering Titan 130 efficiency (35.2%).
	Sour gas, burned in gas turbine	2.26		Considering Titan 130 efficiency (35.2%).
DMR	Sweet gas, burned in gas turbine	65.8	MJ/day	Considering Titan 130 efficiency (35.2%).
	Sour gas, burned in gas turbine	6.59		Considering Titan 130 efficiency (35.2%).

Pressure Swing Adsorption

The pressure swing adsorption subprocess consists in the adjustment of the H_2/CO ratio to the optimal ratio of 4 and removing the excess hydrogen for combustion in the furnace. This adsorption is done with an activated carbon catalyst. This process is exclusive to the SMR process. LCI data for this subprocess step is displayed in Table 9.

Table 9 - LCI data relevant to the PSA (Pressure Swing Adsorption) process, exclusive to the SMR pathway.

SCENARIO	DATA	VALUE	UNIT	NOTES		
			INPUTS			
			Energy use			
SMR	Sweet gas, burned in gas turbine	3.44×10^4	MJ	Considering Titan 130 efficiency (35.2%).		
	Sour gas, burned in gas turbine	3.44×10^3		Considering Titan 130 efficiency (35.2%).		
			Inputs from the technosphere			
SMR	Granular Activated Carbon consumption	142	kg	Same logical procedure as it was done with rhodium (see footnote 10).		
			OUTPUTS			
			Outputs into the technosphere			
SCENARIO	**DATA**	**VALUE**	**UNIT**	**RELATED TO THE FUNCTIONAL UNIT**	**UNIT**	**NOTES**
SMR	Syngas, adjusted	2.97×10^5	kg/day	0.14321	kg/MJ	

Fischer Tropsch

The Fischer-Tropsch reaction constitutes of the conversion step of the syngas produced from the associated gas destined for flaring into the desired syncrude, for later refining into jet fuel. This process is common to both pathways. Being an exothermic reaction, its reaction heat is integrated into steam production, steam which is consumed along the pathway, maximizing the circularity of the resources in the pathways. The product flow that exits the FT reactor is further separated to obtain the desired syncrude, as described in the next subchapter. Although the SMR process does not need any external preheating energy expense, the DMR process requires an heat input from the furnace. Similarly to what was done in the reforming stage, 6.2 % of the total combustion emissions were allocated to the FT process in the DMR pathway. The LCI data for the Fischer-Tropsch subprocess step is represented in Table 10.

Table 10 - Life Cycle Inventory Data Related to the Fischer-Tropsch subprocess step of the life cycle, common to both scenarios.

SCENARIO	DATA	VALUE	UNIT	NOTES		
INPUTS						
Inputs from the technosphere						
SMR	Cobalt consumption	0.680	kg/day	Same logical procedure as it was done with rhodium (see footnote 10).		
DMR		0.736				
Inputs from nature						
SMR	Fresh water consumption	355	m³/day	Water used to generate steam for on-site usage.		
DMR		424				
OUTPUTS						
Emissions into the atmosphere						
DMR	Water vapour	7.18×10^3	kg/day	6.2% of all the on-site furnace heat.		
	Carbon Dioxide	2.03×10^4	kg/day	6.2% of all the on-site furnace heat.		
	Carbon Monoxide	101	kg/day	6.2% of all the on-site furnace heat.		
	Hydrogen	1.41	kg/day	6.2% of all the on-site furnace heat.		
	Methane, fossil	1.17×10^{-15}	kg/day	6.2% of all the on-site furnace heat.		
	Nitrogen Monoxide	182	kg/day	6.2% of all the on-site furnace heat.		
	Nitrogen Dioxide	0.177	kg/day	6.2% of all the on-site furnace heat.		
	Dinitrogen Monoxide	1.74×10^{-2}	kg/day	6.2% of all the on-site furnace heat.		
	Nitrogen, atmospheric	5.03×10^4	kg/day	6.2% of all the on-site furnace heat.		
	Oxygen	1.51×10^3	kg/day	6.2% of all the on-site furnace heat.		
Outputs into the technosphere						
SCENARIO	**DATA**	**VALUE**	**UNIT**	**RELATED TO THE FUNCTIONAL UNIT**	**UNIT**	**NOTES**
SMR	Liquid F-T product	2.97×10^5	kg/day	0.14321	kg/MJ	
DMR		2.31×10^5	kg/day	0.11134	kg/MJ	

Separation

After the F-T synthesis subprocess, the liquid F-T product is separated into three fractions:

- A wastewater fraction (treated and used for injection in on-site EOR).
- A light gas mixture fraction (burned in the furnace which supplies the necessary heat for the operation).
- The liquid syncrude fraction (stored in the form of barrels).

There are no emissions to water since all of this process water is injected. Atmospheric emissions related to the combustion of the light gases are split according to an energy allocation procedure as it was earlier explained in Table 4 and 10. This process does not have any external heat or electricity expenses. The LCI data for this step is described in Table 11.

Table 11 - Life Cycle Inventory Data related to the Separation stage post F-T, common to both scenarios.

SCENARIO	DATA	VALUE	UNIT	NOTES		
OUTPUTS						
Co-products						
SMR	Wastewater	117	m³/day	Used in injection for the EOR process.		
DMR		110	m³/day			
SMR	Light Gas Mixture	1.31×10^5	kg/day	Used for on-site heat demand supply as combustion fuel.		
DMR		7.29×10^4	kg/day			
Outputs into the technosphere						
SCENARIO	**DATA**	**VALUE**	**UNIT**	**RELATED TO THE FUNCTIONAL UNIT**	**UNIT**	**NOTES**
SMR	Syncrude	5.61×10^4	kg/day	0.02709	kg/MJ	506 barrels per day according to the Aspen Plus Conversion.
DMR		5.63×10^4		0.02712		508 barrels per day according to the Aspen Plus Conversion.

Heat generation and integration

These processes (SMR and DMR) were designed to minimize the supply of outside energy for the functioning of the system in continuous phase by:

- Taking advantage of the FT reaction's highly exothermic character to supply the necessary heat for steam generation.
- Using the light gases, hydrocarbons and hydrogen obtained in the separation stage as fuel for combustion in the furnace which supplies the required energy for the reforming stage.

In the DMR case, heat created in the WGS reaction is also integrated, even though it constitutes only around 25% of the heat generated in the FT reaction.

In the case of the SMR pathway, there is an excess of heat due to co-combustion of hydrogen with the other fuel gases. This heat cannot be further integrated, and it is released into the atmosphere. In the case of the DMR pathway, however, combustion of the light gases is not enough to supply the energy demand in reforming and pre-heating in the FT reactor, so an additional mass of natural gas has to be burnt in the furnace to supply the required energy.

A thermal efficiency in heat transfer from the furnace to the necessary subprocesses of 85% was admitted during the design for both pathways. The total combustion emissions were allocated to the pathway subprocesses according to the energy use of the furnace heat per subprocess. In the SMR pathway, 100% of the heat is utilized by the reforming reactor, as it requires no pre-heating before Fischer-Tropsch, and all the necessary heat required for steam production comes from the FT exothermic heat – consequently the emissions from combustion are fully allocated to the reforming stage. However, in the DMR pathway, 93.8 % of the heat is supplied to the Reforming reactor, while the remaining 6.2% is fed to the pre-heater before FT. As for the SMR pathway, all the necessary heat for steam production is provided by the FT exothermic reaction. The fresh water used to create steam was included in the FT stage as in input (see Table 10). These manoeuvres in system boundary designs were made to simplify the modelling of the system and to avoid the creation of a subprocess just for combustion, which would not bring valuable conclusions regarding the weight of the reforming stage in the overall emissions of the facility. The data related to the Heat Generation and Integration is depicted in Table 12.

Table 12 - Life Cycle Inventory Data related to the heat generation and integration in both facilities.

SCENARIO	DATA	VALUE	UNIT	NOTES
INPUTS				
Inputs from nature				
DMR	Natural gas consumed	2.94 x 10^5	MJ	Considered to be a part of the natural gas extracted on site, so it was not included in the impact assessment at this stage as it would be double counting of impacts.
SMR	Total combustion emissions	3.26 x 10^6	kg	100% of the emissions allocated to the reforming stage. See the reforming Life Cycle Inventory table for composition of the combustion flue gas.
DMR		1.30 x 10^6	kg	93.8 % of the emissions allocated to the reforming stage, and 6.2% allocated to the FT stage. See the reforming and FT stage for the composition of the combustion flue gas.

Electricity generation and consumption

The baseline scenario consists of an FPSO facility which consumes 2.93 x 10^7 MJ/day of fuel energy, consisting of a power consumption of 118 MW/day assuming turbine electrical efficiency of 35.2%. With the additional workload of the SMR and DMR facilities, the power consumption sums up to a total of 120 and 122 MW respectively, an increase of 1.26% and 3.26% in the power demand. These shares can be visually observed in Figure 25. Concerning electricity demand solely in the DMR and SMR facilities, Table 13 provides information in the shares of consumption, demonstrating the dominating weight of the amine scrubbing stage related to the other subprocesses.

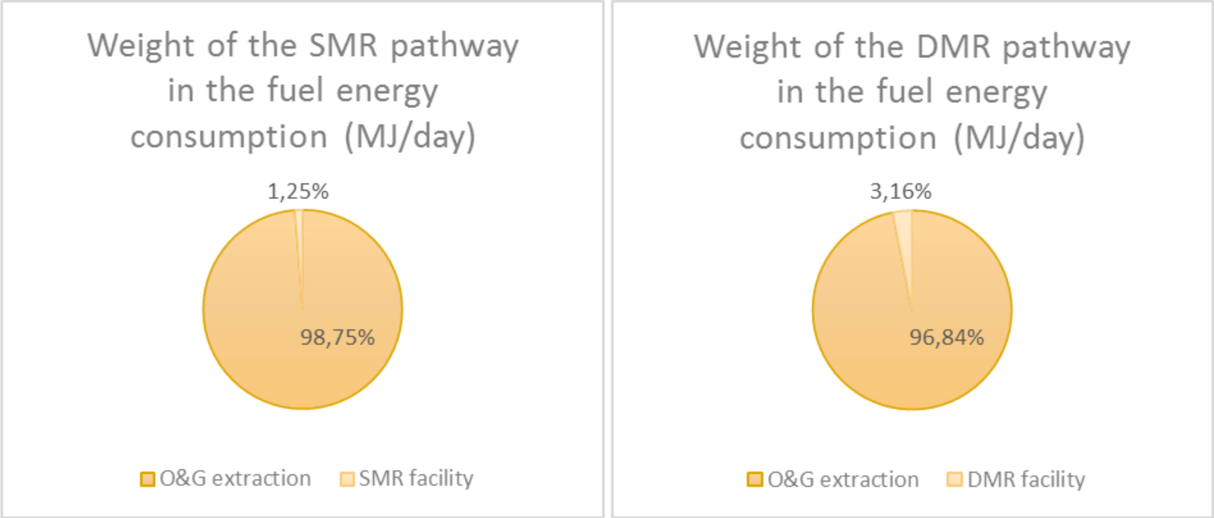

Figure 25 - Fuel energy consumption shares in the facility for both scenarios, on a daily basis.

Table 13 - Electricity consumption share, SMR and DMR facilities only.

	SMR		DMR	
	MJ/day	**%**	**MJ/day**	**%**
Reforming	3.89 x 10^3	1.06%	-	-
Water Gas Shift	-	-	1.89 x 10^2	0.02%
Amine Scrubbing	3.24 x 10^5	88.57%	9.45 x 10^5	99.97%
CO_2 injection for EOR	2.49 x 10^1	0.01%	7.24 x 10^1	0.01%
PSA	3.79 x 10^4	10.36%	-	-

A sensitivity analysis was carried out in order to verify the impact of the fuel supply mix in the generation of electricity in the gas turbines (Appendix II).

Interpretation of the results

The final stage of the LCA is the interpretation of the results. As was mentioned before, four different analyses were performed:

1) Cradle-to-gate LCA, Functional Unit: 1 MJ LHV syncrude production.
2) Gate-to-gate LCA, Functional Unit: 1 MJ LHV syncrude production, null extraction impacts.
3) Gate-to-gate LCA, Functional Unit: 1 MJ LHV syncrude production, negative extraction impacts (avoided emission impacts).
4) Cradle-to-gate LCA, Functional Unit: 1 Daily Barrel produced.

Each analysis was studied individually, and a final interpretation was done in the conclusions that connects the four analyses together. For both the cradle-to-gate LCAs, system expansion was applied to allocate 100% of the daily impacts of O&G extraction to the associated gas extraction (although it would have 0 or negative impacts since it is a residue that would otherwise be combusted without heat recovery). This step is explained further. The four LCA results are complementary.

Cradle-to-gate LCA, Functional Unit: 1 MJ syncrude production

In this evaluation, all the system boundaries considered in the methodology are included for both processes. Every subprocess step in the life cycle of the pathways underwent a mass allocation method in order to allocate the impacts of each subprocess to the production of 1 MJ of the syncrude – the value of the allocated masses per subprocess unit are described in Table 14. The main objective of this analysis is to display simultaneously the weight of the O&G extraction phase in the life cycle of the syncrude, its reduction potential using the different pathways, and the relative weight between the subprocesses included in the pathway and the existing O&G extraction operation. It is worth to remember that the feed gas extraction (associated gas destined for flaring) should be considered to have a null impact on the environment as capturing it would stop it from being released into the atmosphere – this leads us to the second and third LCA results. However, this LCA's results allow for a quantitative value for impact reduction – it answers the question "what's the magnitude of the weight of the pathway subprocesses compared to the O&G extraction impacts?".

Table 14 - Mass allocation done to perform the LCA over a MJ LHV of syncrude production as a Functional Unit.

	Subprocess step	SMR	DMR
Subprocess output mass (kg) per MJ of syncrude produced	O&G extraction	0.297425	0.296666
	Reforming	0.217804	0.247745
	Water Gas Shift	-	0.286995
	Amine Scrubbing	0.159004	0.111348
	PSA	0.143214	-
	FT	0.143214	0.111348
	Separation	0.027093	0.027123

An example calculation of the mass portions is done in the Appendix III for clarification into the procedure.

The obtained results are represented in Figure 26. This representation of impacts relates the lower impactful scenario to the highest polluting scenario (example, ODP of SMR is 96% of the ODP of DMR). It proves a useful visualization tool, however provides an incomplete analysis that must be sustained by the absolute impacts in the form of a table. For absolute values of impact, the results are displayed in Table 15.

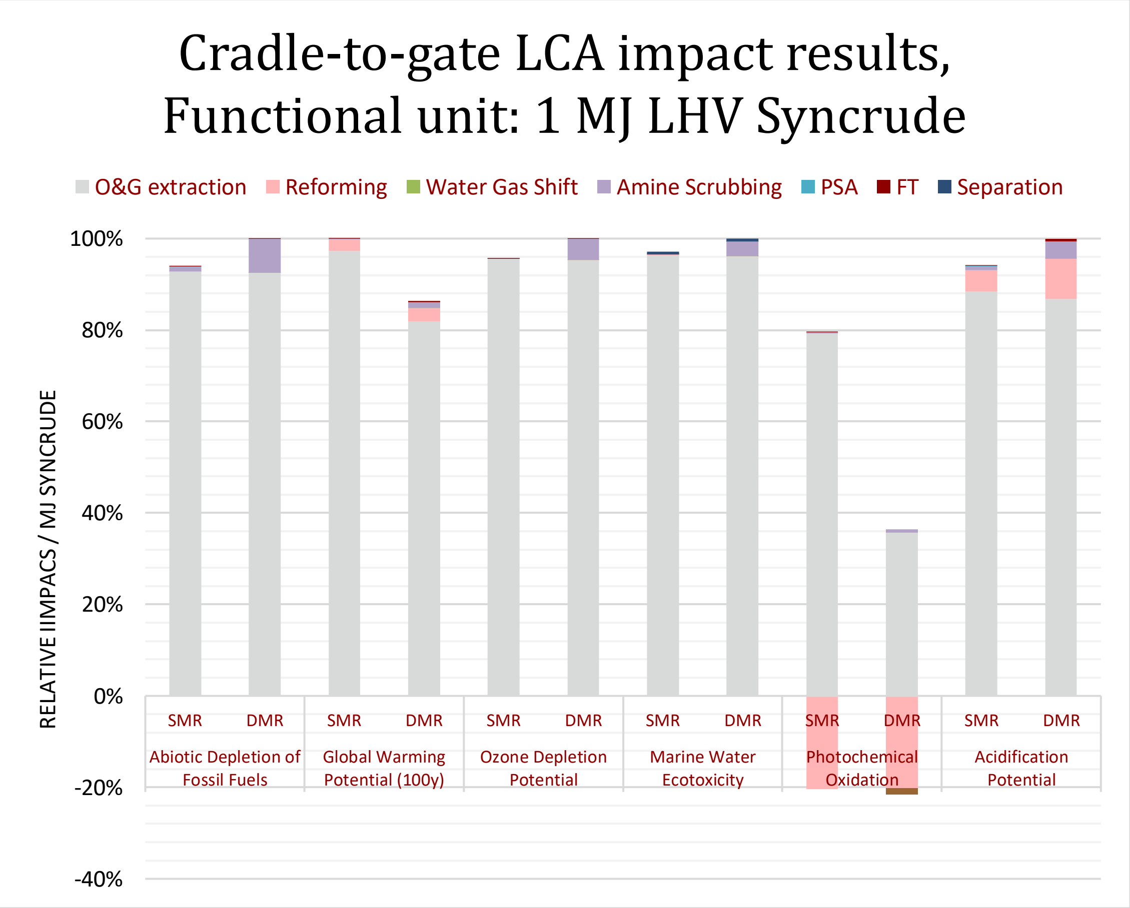

Figure 26 - Cradle-to-gate Life Cycle Impact Relative Impact Comparison for production of 1 MJ LHV of syncrude using the novel SMR and DMR pathways.

The absolute impact result values are described in Table 15.

Table 15 - Life Cycle Assessment Absolute Results for both pathways (Cradle-to-gate, Functional Unit 1 MJ LHV syncrude production)

IMPACT CATEGORY	**UNIT**	**PATH WAY**	**LIFE CYCLE STAGE**						
			O&G	Reforming	WGS	Amine Scrubbing	PSA	FT	Separation
ADFF	MJ/MJ	SMR	15.6	2.53×10^{-3}	-	0.167	2.65×10^{-2}	3.98×10^{-5}	0
		DMR	15.6	3.96×10^{-5}	9.76×10^{-5}	1.260	-	3.67×10^{-5}	0
GWP	kg CO_2 eq/ MJ	SMR	4.99	0.130	-	1.06×10^{-2}	1.87×10^{-3}	3.69×10^{-6}	0
		DMR	4.21	0.150	6.21×10^{-6}	6.42×10^{-2}	-	9.80×10^{-3}	0
ODP	kg CFC-11 eq/ MJ	SMR	4.02×10^{-8}	1.34×10^{-12}	-	3.52×10^{-12}	8.90×10^{-12}	3.28×10^{-13}	0
		DMR	4.01×10^{-8}	1.01×10^{-13}	2.33×10^{-14}	1.96×10^{-9}	-	3.02×10^{-13}	0
MWE	kg 1.4-DB eq/MJ	SMR	792	3.46×10^{-1}	-	0.971	0.608	5.26×10^{-3}	5.05
		DMR	790	2.63×10^{-2}	7.05×10^{-4}	27.3	-	4.85×10^{-3}	4.70
PO	kg C_2H_4 eq/MJ	SMR	9.87×10^{-4}	-2.55×10^{-4}	-	3.94×10^{-6}	6.49×10^{-7}	9.13×10^{-10}	0
		DMR	9.78×10^{-4}	-5.54×10^{-4}	2.35×10^{-9}	2.01×10^{-5}	-	-3.61×10^{-5}	0
AP	kg SO_2 eq/MJ	SMR	1.02×10^{-2}	5.31×10^{-4}	-	9.86×10^{-5}	1.56×10^{-5}	3.45×10^{-8}	0
		DMR	9.96×10^{-3}	1.02×10^{-3}	5.88×10^{-8}	4.34×10^{-4}	-	6.67×10^{-5}	0

The LCA results for this particular case study show that the DMR pathway has a better environmental performance in GWP and PO impacts (14 % and 45% lower), which are related to the reduction of the associated gas flaring phenomena occurring in the normal O&G extraction operation and with the reforming furnace emissions, respectively. In the PO case, it might appear that the O&G extraction phase is much more impactful in the SMR case than in the DMR case – but in Table 15 it is possible to see that it is in fact not. The same can be said for the impacts in the reforming stage. The reason why the graphic image does not represent the actual state is due to the relativization done to compile all the impact categories in the same graph, in which the scenario with the lowest total absolute emissions is attributed a fraction of the scenario with the highest absolute emissions.

Summarizing, although visually it might seem that the O&G extraction phase has much lower impacts in the DMR case compared to the SMR case, which could lead one to think the reduction in PO impact had anything to do with the flare gas reduction, in fact it is not relevant to this impact category, and the subprocess step responsible for the reduction of impacts in the DMR case is the reforming stage, rather than the O&G phase, as can be seen from the other LCA results which are displayed in the following subchapters of the Interpretation.

In emissions related to additional energy expense (ADFF, ODP, and AP) DMR has a worse performance (7%, 5% and 6% higher impacts) as it is more energy intensive than SMR. The amine scrubbing and reforming stage are the subprocess steps inside the pathway boundaries that are linked to the biggest differences between the two scenarios, as will be possible to observe better in the second LCA results.

Regarding MWE, the production of wastewater during the Amine Scrubbing and Separation subprocesses increments the already existing impact with additional burdens on the environment, as is expected. Since a higher mass of CO_2 has to be removed in the DMR case, a higher flow rate of wastewater is generated, and a higher amine concentration in the wastewater is discharged into the ocean, resulting in 3% higher impacts for DMR.

The differences observed between the amine scrubbing impact assessment results are attributed to the different energy intensities of CO_2 removal (it is almost 3 times higher for DMR).

The differences observed between the reforming stage impact assessment results, however, relate to the different furnace combustion conditions between the two pathways – while the SMR pathway uses the light gas mixture produced in the separation step and the excess hydrogen absorbed in the PSA stage to feed the heat utility for the reforming stage, the DMR process requires the combustion of additional natural gas in the furnace to supply the demanded heat of the reforming stage, besides having no excess hydrogen to combust. The higher emissions related to this stage can be observed specially in the AP Impact Results, which are almost 2 times higher in the reforming stage of the DMR phase comparing to the SMR.

The negative PO impacts associated with the reforming stage in both processes are caused by the NO_x emissions, that rather than synthesize tropospheric ozone destroy it – this also means that the emissions in VOCs during reforming stage responsible for ozone synthesis in the troposphere are not enough to overcome the nitrogen oxide emissions, which means that they are rather small.

Gate-to-gate LCA, Functional Unit: 1 MJ LHV syncrude production, null extraction impacts

This analysis only evaluates the performance of the pathways not accounting for its impact reduction on the existing facility – the associated gas that serves as the feed gas for the liquid fuel production is assumed to have null extraction impacts, and as such the quantitative results here answer the questions “Which one of the pathways has the higher operational environmental impacts?” and “What subprocesses are the most impactful in which categories for both pathways”. These results also allow for the first environmental impact results on the various categories for the pathway as they are designed to be compared – over a MJ LHV basis and with a null or negative impact on raw material extraction. Consequently, after inclusion of the refining and combustion step and an adequate cradle-to-grave analysis (infrastructure and natural gas pretreatment impact calculations), these and the results of the third analysis could be used to disclose whether or not the aviation synfuel generated through these pathways is eligible as a LCAF or even a SAF.

The mass allocation used for this LCA is described in Table 16:

Table 16 - Mass allocation done to perform the LCA over a MJ LHV of syncrude produced, gate-to-gate analysis, null extraction impacts.

	Subprocess step	SMR	DMR
Subprocess output mass (kg) per MJ of syncrude produced	Reforming	0.217804	0.247745
	Water Gas Shift	-	0.286995
	Amine Scrubbing	0.159004	0.111348
	PSA	0.143214	-
	FT	0.143214	0.111348
	Separation	0.027093	0.027123

The obtained results are in Figure 27:

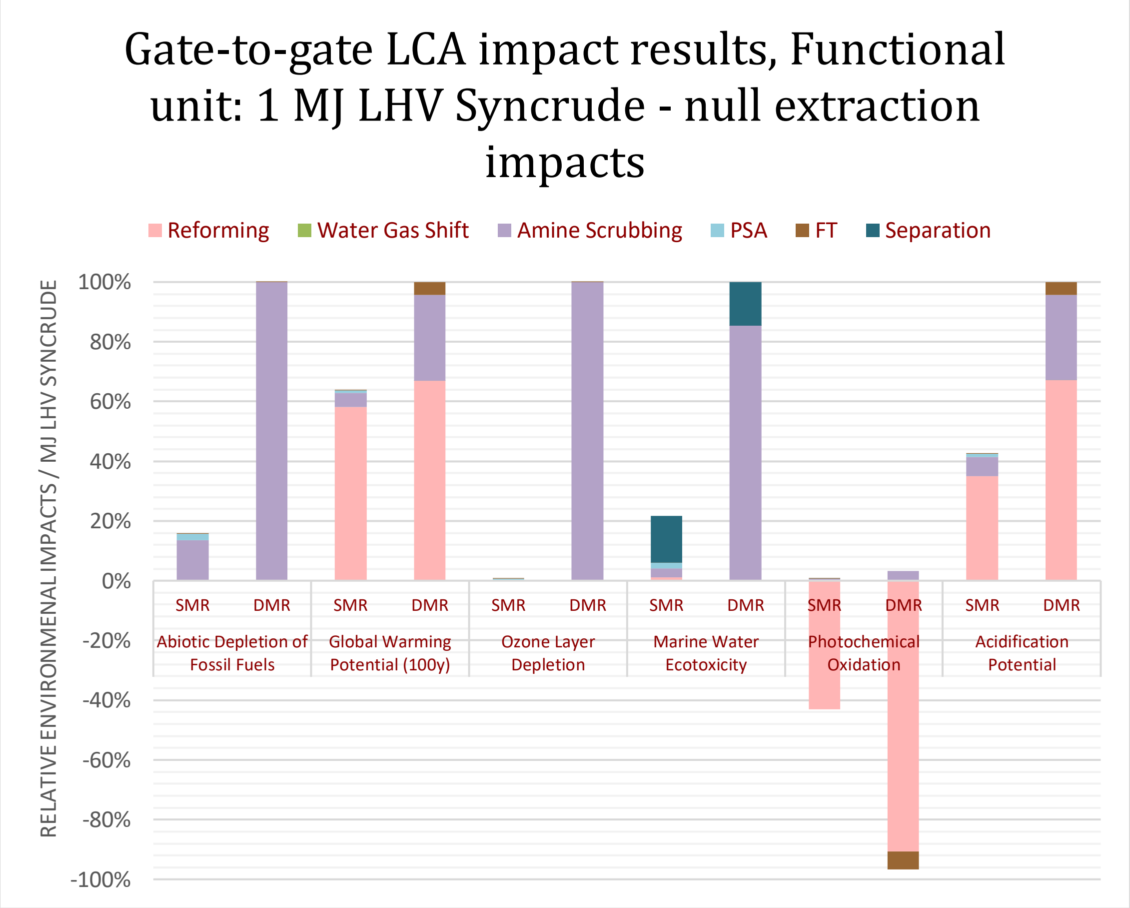

Figure 27 - Life Cycle Impact Relative Impact Comparison for production of 1 MJ LHV of syncrude for the SMR and DMR pathways, assuming null extraction impacts

The absolute impacts for the subprocesses in every category are the same as the ones found in Table 15, withdrawn the O&G extraction phase.

The most impactful life cycle stages of the pathways are the Amine Scrubbing Stage and the Reforming Stage for most impact categories (Separation is also relevant in the MWE impact). The reforming stage is environmentally worse for the DMR case in AP and GWP impacts (92% and 15% worse) due to its worse furnace combustion emissions for heat generation. This can also be observed in the FT stage, for it requires heat generated in the furnace. In PO the reforming stage has better environmental performance (117% better) because of the higher

NO_x emissions – but this conclusion needs to be handled with care as it will be further discussed in this chapter.

The amine scrubbing stage is environmentally worse in every category for the DMR case due to its higher energy intensity and necessity of more fossil fuel energy for electricity generation.

Gate-to-gate LCA, Functional Unit: 1 MJ LHV syncrude production, negative extraction impacts

This analysis is similar to the previous one, with the exception that the extraction impact results, rather than being null, are negative – semantically this could raise some eyebrows since negative environmental impacts are usually associated with sequestration phenomena. However, in this case, the situation at hand is an emission step which cannot be avoided in other ways – the usage of associated gas would only not have negative impact results if the O&G extraction industry ceased to be a necessity in modern society. As the oil and gas extraction will not stop for several decades, since we depend on it not only for energy purposes but also for plastic production and other industries, the flaring phenomena will not stop either for the reasons previously mentioned in this report, such as safety reasons. Following this logic thread of thought, for every barrel that is produced through these pathways, a certain volume of emissions is retained and avoided – what this LCA results show is precisely how much higher or lower these avoided emissions are related to the added emissions due to pathway operation, and also they provide the final environmental impact results to be communicated to third parties. However, without the other three complementary analysis, we would be left with a very one-dimensional and partial view of a complex problem.

The mass allocation step and the total mass of captured associated gas destined for flaring related with this LCA results are shown in Table 17. The avoided emissions correspond to the subtraction of the total baseline emissions by the emissions existent after application of the DMR and SMR pathway, which can be done using the values in Table 3. The absolute impact results are the same as the ones in Table 15, except for the O&G extraction impacts which are replaced by the values used in Table 18.

Table 17 - Mass allocation done to perform the LCA over a MJ LHV of syncrude produced, gate-to-gate analysis, negative extraction impacts.

	Subprocess step	**SMR**	**DMR**
Subprocess output mass (kg) per MJ of syncrude produced	Associated gas Capture	0.141628	0.347957
	Reforming	0.217804	0.247745
	Water Gas Shift	-	0.286995
	Amine Scrubbing	0.159004	0.111348
	PSA	0.143214	-
	FT	0.143214	0.111348
	Separation	0.027093	0.027123

	SMR	DMR
Mass of captured associated gas destined for flaring (kg/day)	2.09×10^5	5.14×10^5

Table 18 - Impacts of the Associated Gas Capture in the life cycle of the syncrude, assuming negative extraction impacts and 1 MJ LHV as a functional unit.

	Impact Categories					
	ADFF	GWP	ODP	MWE	PO	AP
Unit	MJ/MJ	kg CO_2 eq/MJ	kg CFC-11 eq /MJ	kg 1,4-DB eq/MJ	kg C_2H_4 eq/MJ	kg SO_2 eq/MJ
SMR	0	-0.744	0	-4.77×10^{-2}	-6.20×10^{-6}	-1.62×10^{-4}
DMR	0	-1.830	0	-1.17×10^{-1}	-1.53×10^{-5}	-3.99×10^{-4}

The obtained results are represented in Figure 28:

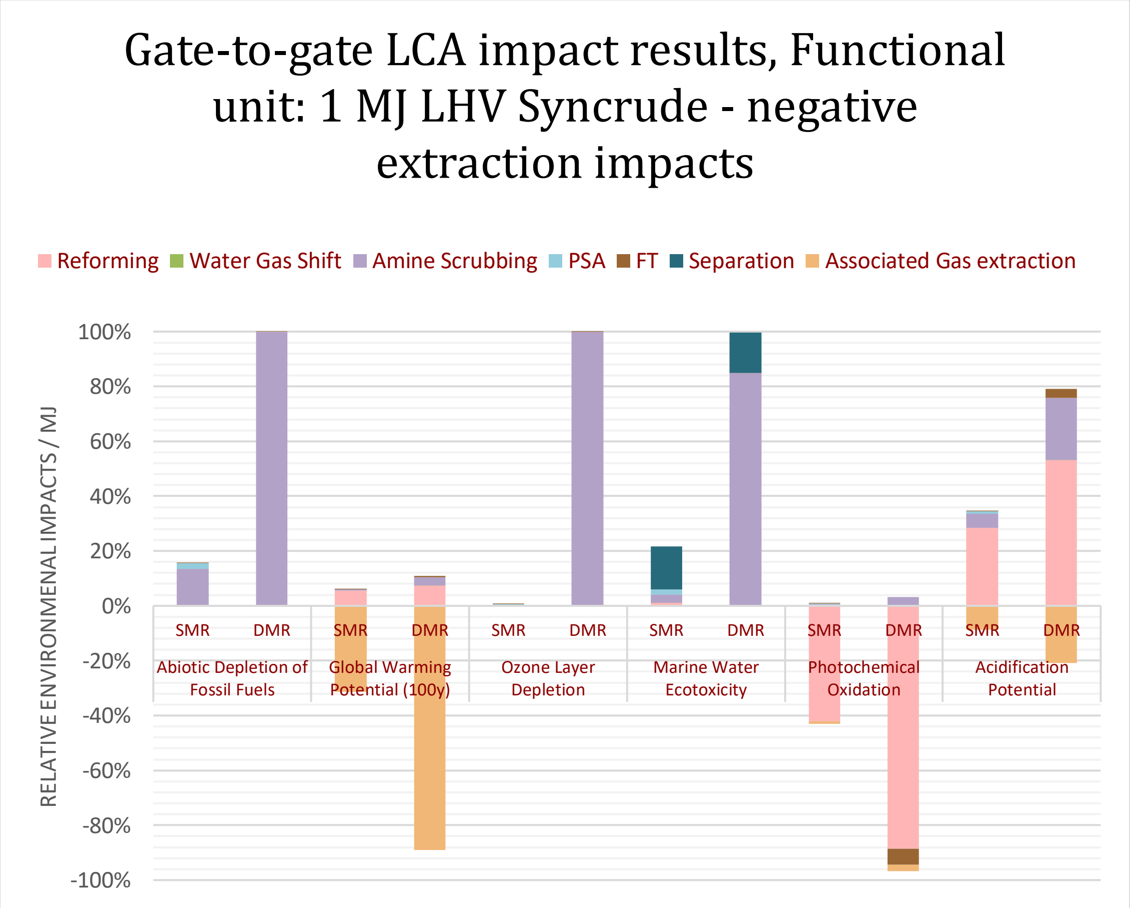

Figure 28 - Life Cycle Impact Relative Impact Comparison for production of 1 MJ LHV of syncrude for the SMR and DMR pathways, assuming negative extraction impacts.

It can be concluded that the global warming potential offset from the associated gas capture is much higher than the emissions associated with the pathway operation (8 times higher for DMR, 5 times higher for SMR), which suggests that this process of converting associated gas into syncrude not only improves the operation of the facility in environmental terms, but it also contributes to the reduction of the global environmental impacts significantly.

Another interesting remark is the fact that the offsetting of PO related emissions is almost insignificant compared to the negative impacts already occurring in the reforming reactor. This implies that the positive emissions which can be seen in the cradle-to-gate scenarios occur from the energy production in the gas turbines of the facility rather than the flaring phenomena. Consequently, this pathway does not in fact reduce the Photochemical Oxidation Impacts related to the flaring phenomena, and that illusion is created from the fact that the NO_x emissions in the reforming furnaces are much higher than Tropospheric Ozone formation responsible emissions occurring throughout the pathway.

Cradle-to-gate LCA, Functional Unit: 1 Daily Barrel produced

This LCA results are complementary of the first, as they display the impacts per barrel calculated over the life cycle of the facility – despite it being a conventional crude oil barrel, an incremental oil barrel recovered with EOR technology, or a syncrude barrel. As such the total impacts of the daily operation in the FPSO facility were divided by the number of barrels produced per day, which quantitatively answers the question "is the installation of these pathways beneficial for the reduction of the overall impacts in the FPSO per barrel produced?", or rather "does the production of syncrude and EOR incremental barrels have beneficial impact results coupled to the conventional crude oil barrels produced?".

For this analysis, the total daily mass output of every subprocess step was assumed in the life cycle assessment calculation methodology, and the obtained total daily impacts were then divided by the total amount of daily barrels. This is displayed in the following table:

Table 19 - Mass allocation done to perform the LCA over a daily barrel of crude oil produced.

	Subprocess step	**Baseline**	**SMR**	**DMR**
Subprocess output mass (kg) per day for total daily barrels produced	O&G extraction	6.16×10^5	6.16×10^5	6.16×10^5
	Reforming	-	4.51×10^5	5.14×10^5
	Water Gas Shift	-	-	5.96×10^5
	Amine Scrubbing	-	3.29×10^5	2.31×10^5
	PSA	-	2.97×10^5	-
	FT	-	2.97×10^5	2.31×10^5
	Separation	-	5.61×10^4	5.63×10^4
Extra Barrels per day produced		0	817	1 413

The output mass in the O&G extraction subprocess step is the same for the three scenarios, since it corresponds to the total mass of associated gas destined for flaring that is generated in the FPSO facility on a daily basis. Consequently, the emissions related to energy production in the facility are the same for the three of them, since those emissions are independent of the amount of gas that is flared or used in syncrude production. However, the flaring emissions associated with this mass of associated gas produced are different, since a part of the direct combustion of this gas is avoided when applying the SMR and DMR pathways. This difference in emissions can be better observed in Table 3. The obtained results are found in Figure 29:

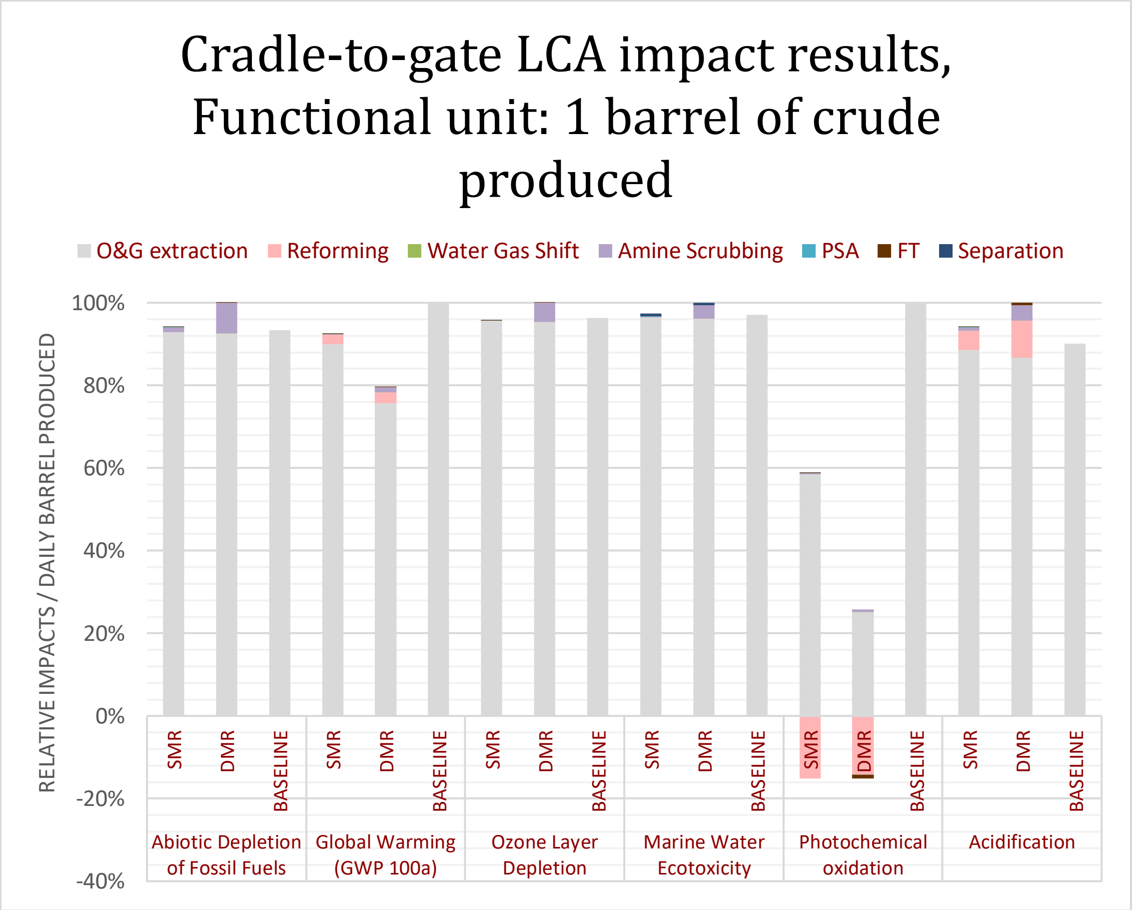

Figure 29 - Life Cycle Impact Relative Comparison for production of 1 daily barrel of crude oil between the SMR, DMR and conventional O&G crude oil production.

The absolute results of this LCA are reflected in Table 20:

Table 20 - Life Cycle Assessment Absolute Results for both pathways and the baseline O&G extraction (Cradle-to-gate, Functional Unit 1 daily barrel production)

IMPACT CATEGORY	UNIT	PATHWAY	LIFE CYCLE STAGE						
			O&G	Reforming	WGS	Amine Scrubbing	PSA	FT	Separation
ADFF	MJ/bpd	SMR	214	3.47×10^{-2}	-	2.30	3.63×10^{-1}	5.47×10^{-4}	0
		DMR	214	5.43×10^{-4}	1.34×10^{-3}	17.2	-	5.03×10^{-4}	0
		BASELINE	216	-	-	-	-	-	-
GWP	kg CO_2 eq/ bpd	SMR	68.6	1.79	-	0.146	2.56×10^{-2}	5.06×10^{-5}	0
		DMR	57.7	2.05	8.51×10^{-5}	8.80×10^{-1}	-	1.34×10^{-1}	0
		BASELINE	76.3	-	-	-	-	-	-
ODP	kg CFC-11 eq/ bpd	SMR	5.53×10^{-7}	1.84×10^{-11}	-	4.83×10^{-11}	1.22×10^{-10}	4.50×10^{-12}	0
		DMR	5.50×10^{-7}	1.38×10^{-12}	3.20×10^{-13}	2.69×10^{-8}	-	4.14×10^{-12}	0
		BASELINE	5.56×10^{-7}	-	-	-	-	-	-
MWE	kg 1.4-DB eq/bpd	SMR	1.09×10^{4}	4.75	-	13.3	8.35	7.23×10^{-2}	69.3
		DMR	1.08×10^{4}	0.360	9.67×10^{-3}	374	-	6.65×10^{-2}	64.4
		BASELINE	1.09×10^{4}	-	-	-	-	-	-
PO	kg C_2H_4 eq/bpd	SMR	1.36×10^{-2}	-3.50×10^{-3}	-	5.41×10^{-5}	8.91×10^{-6}	1.25×10^{-8}	0
		DMR	1.34×10^{-2}	-7.59×10^{-3}	3.22×10^{-8}	2.76×10^{-4}	-	-4.95×10^{-4}	0
		BASELINE	1.37×10^{-2}	-	-	-	-	-	-
AP	kg SO_2 eq/bpd	SMR	0.139	7.29×10^{-3}	-	1.35×10^{-3}	2.14×10^{-4}	4.73×10^{-7}	0
		DMR	0.137	1.40×10^{-2}	8.07×10^{-7}	5.94×10^{-3}	-	9.15×10^{-4}	0
		BASELINE	0.142	-	-	-	-	-	-

The results allow for the comparison of the conventional operation with the pathways installed to the baseline production of O&G.

Reductions in the environmental burden of the facility can be found in the GWP and PO impact categories (7% and 20% for the SMR and DMR respectively), the GWP reduction relating to the reduction of the flaring of the associated gas.

Since an extra consumption of resources is needed to convert this associated gas into liquid fuel, a higher ADFF impact is observed for both pathways in comparison to the baseline (0.7% and 7% higher), the highest for DMR almost exclusively because of the extra energy expense in amine scrubbing. The ODP, related to the increase of natural gas combustion for electricity generation is higher for the DMR process compared to the baseline (3.9%), and the SMR impact is lower (0.5% lower).

Regarding AP, the reduction of the flaring phenomena does not imply an improvement in this impact category, as the extra NO_x emissions in the Reforming Stage and the extra SO_x emissions related to sour gas combustion for electricity generation in the pathways overcome the impacts of the conventional production (total emissions 4.5% and 11% higher than the baseline).

Conclusions and future work

A Life Cycle Assessment study was carried out to compare the environmental impact of using two syncrude production pathways (Dry Methane Reforming and Steam Methane Reforming using novel NETmix microreactor technology) to convert associated gas destined for flaring produced in an offshore general O&G FPSO facility into liquid syncrude for later refinement into Sustainable Aviation Fuel, a production scale of 500 barrels of syncrude per day.

Four different complementary evaluations were performed: a cradle-to-gate approach using 1 MJ LHV of syncrude produced as a functional unit, a cradle-to-gate approach using 1 barrel of crude produced as a functional unit, and two gate-to-gate approaches using 1 MJ LHV of syncrude produced as a functional unit, one considering null extraction impacts and the other negative extraction impact results, accounting for avoided emissions. For both cradle-to-gate approaches, system expansion was applied to allocate 100% of the impacts of the O&G extraction phase to the associated gas collection, in order to provide a way to quantify the impact reduction of the SMR and DMR technologies applied to the FPSO's operation.

An hypothetical daily FPSO baseline operation was estimated using data from Jungbluth, N. et. Al, (2018) compiling average data from various offshore O&G extraction facilities in the world. It was concluded that the operation of the SMR and DMR technologies (an increment of 506 + 311 and 509 + 904 syncrude and incremental barrels of oil respectively to a daily operation of 150 000 barrels per day of oil produced) could reduce impacts per daily barrel in GWP impacts due to the significant reductions in CH_4 and CO_2 atmospheric emissions related to the decrease of the flaring of the associated gas, which is a positive trade-off for the added impacts of the SMR and DMR units operation (between 7.4 and 7.5 % and between 20.1 and 20.6 % respectively) and PO impacts (between 21 and 29 % and between 44 and 66 % respectively) although the latter is due to an increase in NO_x emissions and not necessarily a reduction in PO responsible emissions.

In ADFF, ODP and MWE impacts, increases of the environmental burdens of the FPSO were verified due to the increase in energy demand in SMR and DMR operations (an increase of 1.26% and 3.26% in the power demand respectively) and wastewater generation related to the syncrude production pathways operation – mainly the Amine Scrubbing and Reforming life cycle stages. At most, these increases could amount to 6.7% in ADFF, 10% in ODP, and 21% in MWE in the DMR case (the worst performing pathway among the two), related to the bottom bound of the error bars in the uncertainty analysis – the less polluting FPSO operation scenario.

However, in worst case scenarios of FPSO operation emissions (the upper bound of the error bars in the uncertainty analysis), reductions in the environmental impact per barrel could be verified for both ODP and MWE impacts (6.8 and 0.9 % in ODP impacts and 4.4 and 3.1 % in MWE impacts respectively).

The AP impacts are higher for both scenarios (between 0.2% and 12% in the SMR case and between 11% and 50% in the DMR case) given the fact that the reforming operations require heat supply, which is produced through the combustion of the light gas mixture generated in the FT separation process, plus hydrogen in the SMR case and natural gas in the DMR case which ultimately increase NO_x emissions in the life cycle more than they mitigate through flaring reduction. However, in the worst case scenario of emissions, an impact reduction per barrel was verified in the DMR case (8.4%), since its associated gas flaring reduction is higher in volume and the acidification potential impacts are largely due to the composition in sulphur of the associated natural gas.

Although hard to conclude in a first glance which technology in specific is better than the other, due to some unfortunate LCI data bias in the results, it is possible to conclude with 95 % confidence that so far, converting associated gas destined for flaring using these pathways synthesizes a syncrude with a negative GWP impact of -0.601 ([-0.599,-0.603]) kg CO_2 eq / MJ LHV and -1.60 ([-1.57,-1.62]) kg CO_2 / MJ LHV respectively – this value will, of course, increase once infrastructure, transport, associated gas pre-treatment, refining and combustion life cycle impacts are integrated, but that proves the pathways are conclusively a very promising future alternative jet fuel production pathway, possibly offsetting around 1200 and 3300 tons of CO_2 per day at the current production scale. The SMR pathway seems to be the best pathway for synfuel generation since it beats DMR's performance whenever the results are not conditioned by the reduction in total flare gas volume, which are too influenced by the assumption undertaken in the methodology relative to the feed gas compositions.

Looking at the system as it is, an impact category specific analysis was performed in order to suggest improvements to the operation of the pathways:

- ADFF: minimizing fossil fuel expenditure for energy, heat and electricity demands, incorporating alternative energy sources whenever economically viable.
- GWP and PO: reducing as much associated gas flaring as possible, maximizing syncrude production – the tradeoff is positive to the environment.
- ODP: using another chemical other than Halon 1301 for fire suppression in gas turbines.
- AP: Optimizing the combustion step in the furnace in order to the minimize NO_x emissions as much as possible.
- MWE: Using a different chemical solvent for amine scrubbing, in order to minimize spent amine emissions into wastewater.

Looking into future system design options:

- Integrate Solar, wind and wave energy for the external energy supply requirements related to the syncrude production operation – this will achieve optimal GWP results which can benefit further on once other life cycle stages are included.

- Using an HGtS (a post combustion CO_2 capture and storage hydrate-based technology designed by NET4CO2) system instead of an amine scrubbing system for CO_2 removal, separation, and conversion to solid hydrates, reducing energy consumption per unit of mass of CO_2 removed and minimizing MWE impacts.
- Using Hydrogen Turbines in the SMR pathway in order to convert the excess hydrogen separated in the PSA subprocess step into electricity rather than excess heat.
- Combination of CO_2 and H_2 generated in the process for synthetic natural gas production using methanation technology.

If a further LCA is to be developed, site-specific data must be correctly measured, especially water composition data and associated gas composition if a thorough evaluation is to be performed. Also, the remaining life cycle stages of the syncrude production should be added to the evaluation if a certification for alternative jet fuel production is desired.

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APPENDIX I – MASS BALANCES ON SITE

Natural gas mass balance

Since this analysis was built assuming an average hypothetical FPSO facility with oil and gas extraction operations, a natural gas mass balance was conducted in order to verify whether or not the assumption that the natural gas used on site for electricity generation and the SMR/DMR pathways would be available on site.

As such, the sum of the mass of flared gas, the gas used in gas turbines and the gas used in the furnace (in the case of DMR) had to be at least lower than the daily average production of the FPSO facilities based in the Pre-salt area. Furthermore, in order to achieve a more solid conclusion, since the sample relating to the Brazilian Pre-salt FPSO exploration was a small sample, an hypothesis test was carried out using plant facility data from the U.S Energy Information Administration. These procedures are described in detail in this appendix.

A noteworthy consideration is the fact that the values used in this mass balance are values related to an average turbine efficiency of 30% - as such, it is an analysis conducted on excess, for an higher turbine efficiency as the one used in this LCA would lead to less natural gas being burned – a lower natural gas demand and required capacity, as well as more leftover natural gas. These values can be observed in Table 21, and graphically in Figure 30.

Table 21 - Natural gas mass balance in the facility, for both scenarios.

	SMR	DMR	Notes
Natural Gas extracted (m3)	6.33×10^{6}		Using Petrobras' and Modec's FPSO data (see table 1).
Natural Gas extracted (kg)	4.51×10^{6}		Assuming a density of 0.712 at Normal Temperature and Pressure Conditions [85].
Flared Natural Gas (kg)	4.07×10^{5}	1.02×10^{5}	
Flare Gas used in the pathway (kg)	2.09×10^{5}	5.14×10^{5}	-
Natural gas burned in gas turbine (kg) -extraction phase	4.68×10^{5}		Assuming a medium LHV of 48 MJ/kg [86].
Natural gas burned in gas turbines (kg) - pathway	8.93×10^{3}	2.31×10^{4}	Assuming a density of 0.712 at Normal Temperature and Pressure Conditions; Assuming a medium LHV of 48 MJ/kg[12].
Natural gas fed to the furnace (kg)	-	1.56×10^{5}	
Leftover natural gas (kg)	3.42×10^{6}	3.25×10^{6}	Calculated as the difference between the extracted natural gas and all the consumed natural gas in the facility (turbines, processes, and flaring).
Higher capacity then: (kg)	1.09×10^{6}	1.26×10^{6}	Sum of the flared natural gas, associated natural gas, and the total natural gas burned in gas turbines.
Higher capacity then: (Nm^3)	1.53×10^{6}	1.77×10^{6}	Assuming a density of 0.712 at Normal Temperature and Pressure Conditions [85].

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[12] For the calculation of the mass of natural gas burned in gas turbines for the pathway, the electricity demand calculated in the simulations was divided by an efficiency of 30%, and then the corresponding total energy in MJ was divided by the Medium Lower Heating Value of natural gas.

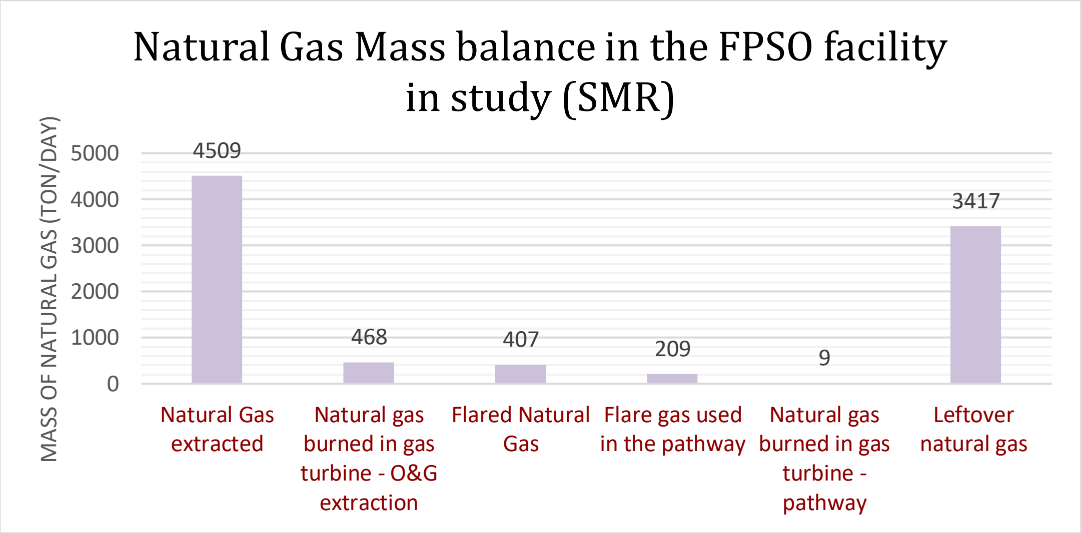

Figure 30 - Natural Gas mass balance in the FPSO facility in study, SMR case.

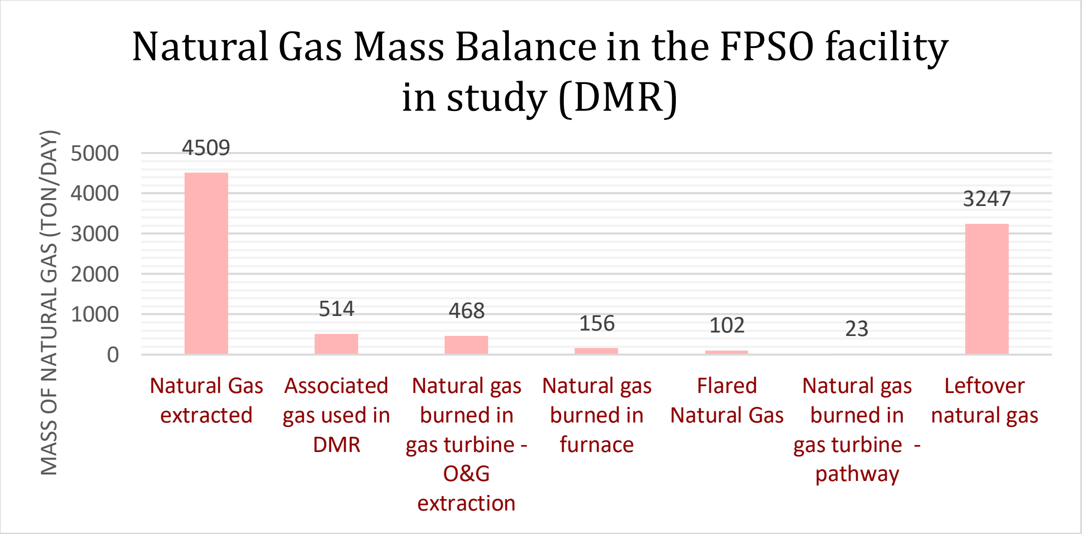

Figure 31 - Natural Gas Mass Balance in the FPSO facility in study, DMR case.

Afterwards, the following hypothesis was formulated: The capacity of the plant is **not higher** than the minimum capacity needed (1.77 x 10^6 Nm^3/day). This hypothesis was tested:

- Using natural gas extraction facility data from 478 O&G exploration facilities in the US [87] using a z-statistic method (assuming the population data in the Brazilian production is similar to the North American one)
- Using the facility data from 6 FPSO operating in the Brazilian Pre-Salt, using a t-statistic method.

The information from the hypothesis tests are described in the tables below. A normal distribution of the sample means was assumed in the hypothesis test according to the central limit theorem, which enables the use of the z-statistic and t-statistic to formulate this hypothesis testing.

As it is possible to observe in Table 22, the p value is much lower than 0.01, which suggests that we can reject the null hypothesis with a degree of confidence of 99%. Further graphical information on the US O&G operation data can be found in Figure 32.

Table 22 - Statistical information about the sample collected of oil and gas extraction in the US and the Pre-Salt and result of the hypothesis test about natural gas production.

	US EPA Data	Pre-Salt Petrobras Exploration data
Mean (Nm^3/d)	4.69 x 10^6	6.33 x 10^6
Standard Deviation (Nm^3/d)	6.95 x 10^6	1.37 x 10^6
Standard Error	3.18 x 10^5	5.58 x 10^5
Null Hypothesis (H_0)	Plant capacity is not higher than 1.77 x 10^6 m^3/d	
Alternative Hypothesis (H_1)	Plant capacity is higher than 1.77 x 10^6 m^3/d	
z-score	9.18	-
t-score	.	8.44
p-value (99% confidence)	<0.0001	0.000193

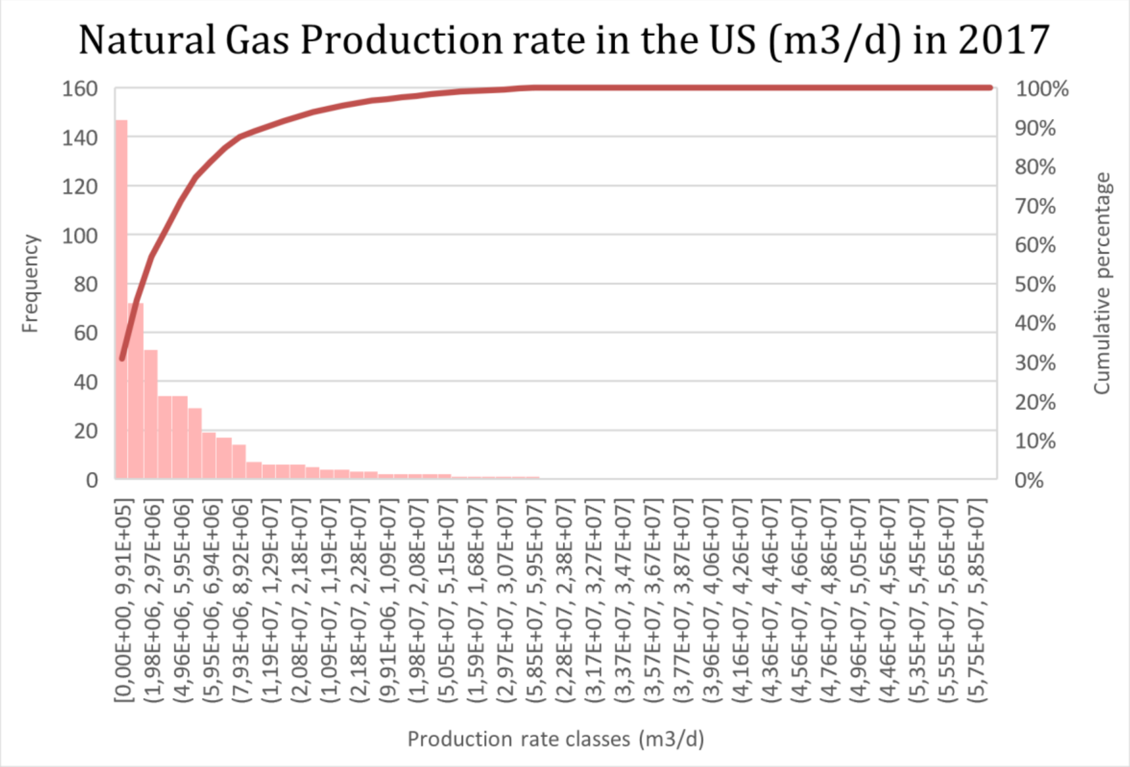

Figure 32 - Histogram depicting the distribution of the production rate of natural gas in the US region.

Water volume balance

As was discussed before, water produced on site can be treated for either injection or discharge, the latter constituting 80% of the total amount of produced water. It was assumed that the water produced during the syncrude production process would be treated for injection, since they are water flows with much lesser contaminant concentrations than the typical produced water from separation of the crude oil after extraction. In summary, the water used for injection that is produced on site corresponds to the sum of the total amount of water produced during the syncrude synthesis process and 20% of the water produced during separation. The remaining body of water necessary for the water and CO_2 injection process would be supplied by saltwater, as it is an offshore exploration facility. The estimation of the saltwater necessary to extract from the ocean to perform the oil recovery is described in the following expression:

$$V_{saltwater} = V_{demand\ in\ regular\ operation} + V_{demand\ related\ to\ additional\ CO_2\ production} \\ - V_{treated\ produced\ water} - V_{wastewater\ generated\ in\ pathway}$$

The total water balance in this facility is described in the Table 23:

Table 23 - Total water balance in the facility, m3/day, for both pathways

	SMR	DMR
Volume of wastewater generated in the pathway	1.37×10^2	1.64×10^2
Wastewater generated in amine scrubbing	1.96×10^1	5.32×10^1
Wastewater generated in FT separation	1.17×10^2	1.10×10^2
Volume of wastewater generated in the extraction phase	2.04×10^4	
Treated produced wastewater	4.08×10^3	
Volume of water demand in injection (normal operation)	2.10×10^5	
Additional demand of water in injection due to the pathway	4.35×10^2	1.27×10^3
Saltwater used in injection	2.06×10^5	2.07×10^5

APPENDIX II – SENSITIVITY ANALYSES

Sensitivity analyses were carried out in order to infer the impact of the assumptions assumed in the hypothetical FPSO situation on the environmental impact results obtained through the chosen methodology. They are described in detail in this appendix.

Injecting CO_2 produced in the Amine Scrubbing Step vs releasing it

Not as much a sensitivity analysis on assumptions but rather a decision making tool, this analysis was carried out in order to verify if the extra electricity expense associated with the CO_2 injection for Enhanced Oil Recovery would compensate for the emission abatement of the generated CO_2 during amine scrubbing into the atmosphere, considering the total impacts of the FPSO. This is because given the circumstances of electricity generation by natural gas combustion in turbines, the trade-off could have a negative impact on the environment rather than the desired positive one. In other words, the indirect emissions associated with the CO_2 injection could win over the direct emissions associated with its release. Since this sensitivity analysis is most relevant to the amine scrubbing step, results were also calculated inside the boundaries of the amine scrubbing step alone to better visualize the differences in the obtained results. The MWE impact category was not included in this analysis as it was not relevant.
Figure 33 and 34 represent the results of this sensitivity analysis.

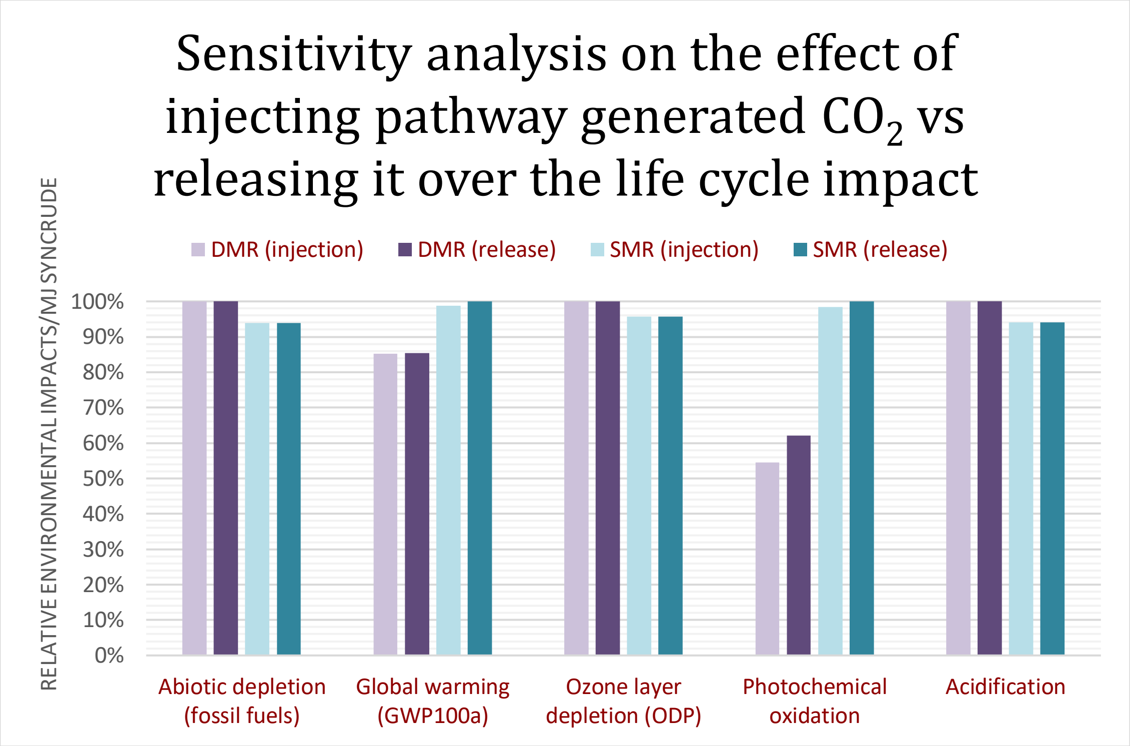

Figure 33 - Sensitivity analysis - Effect on the product life cycle's environmental impact of injecting CO_2 generated in amine scrubbing versus releasing it.

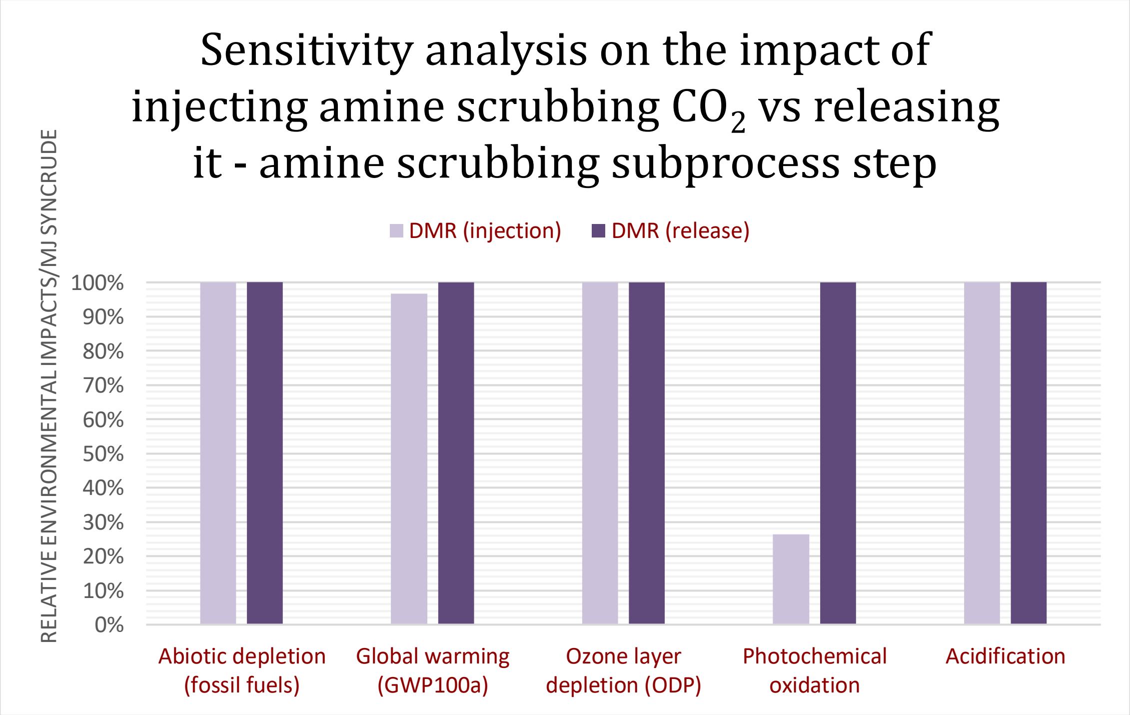

Figure 34 - Sensitivity analysis on the impact of injecting CO_2 vs releasing it on the environmental impact of the DMR amine scrubbing process.

Looking deeper into the Photochemical oxidation impact calculation, we can observe the contribution of the different substances in the calculated environmental impact in Figure 35.

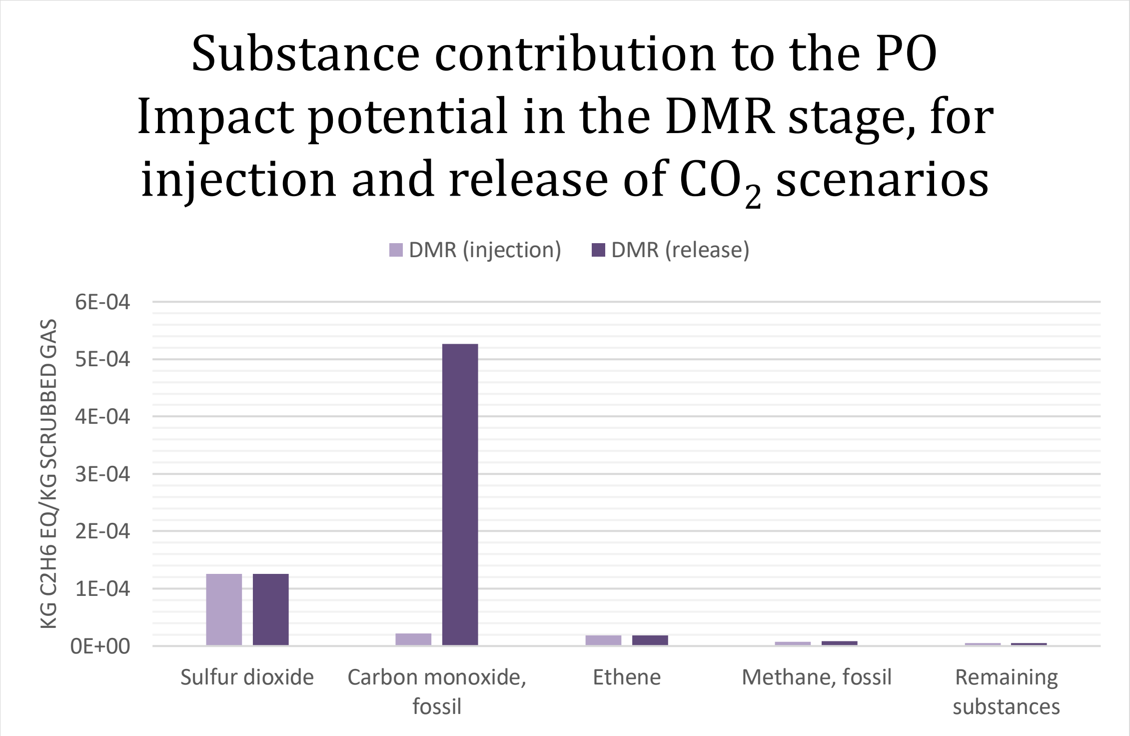

Figure 35 - Substance contribution to the photochemical oxidation potential impact in the DMR amine scrubbing stage - injection of CO_2 vs release scenarios.

As it can be observed, the main impact differences associated with the release of CO_2 are related to the photochemical oxidation potential impact – and it can also be observed that the most impactful compound in the difference of the results is the emission of Carbon Monoxide into the atmosphere if it is released, that is otherwise retained on ground when it is injected. One important conclusion to withdraw from this analysis is that the extra energy expense associated with the injection of this relatively small mass of CO_2 increments an insignificant contribution of impacts in both the total life cycle impacts and the specific amine scrubbing process impacts, but the atmospheric emissions associated with the presence of Carbon monoxide in the CO_2 flux coming out of the amine scrubbing increases the PO impact enough to be perceptible on the total life cycle impacts, which ultimately means that the injection should be considered environmentally beneficial in the case study under the scope of this project.

Using the latest EcoInvent database for Water Discharge after treatment vs using database in literature

The composition of the discharged water can have a meaningful impact on the ecosystem where it is discharged into – in this specific case, the marine water ecosystem, the ocean. Consequently, it is important to get the most solid measurements possible in order to effectively compare the performance of this toxicity indicator in comparison with the performance of other facilities, operating with different discharge compositions. Since the evaluation of the environmental impacts of the water discharge depends a great deal on this composition, a sensitivity analysis was conducted to observe the differences in the calculated impacts of marine water ecotoxicity (MWE) related to the choice of different databases, using the same volume of water discharge. All other impact categories were not included in this analysis as the water discharge is relevant to this impact category most significantly. The ecoinvent database contained in Simapro for produced water discharge in offshore petroleum exploration was compared with the values calculated over a unitary base of kg/OE found in Jungbluth (2018), and the results can be observed in Figure 36:

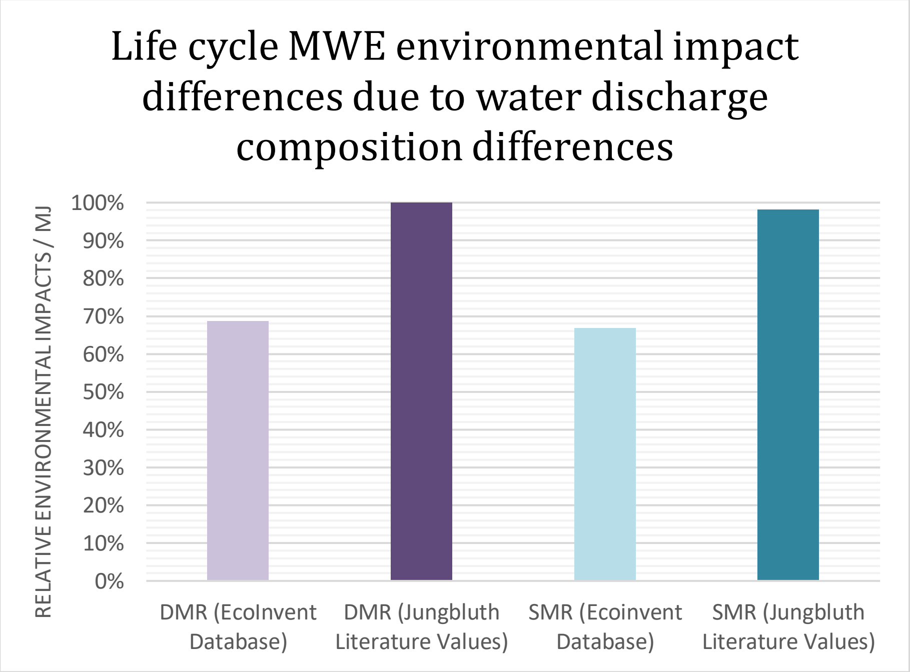

Figure 36 - Impact of the discharge water composition differences in the calculated results for the life cycle's marine water ecotoxicity impact.

It is possible to observe that there is a significant difference in the calculated impacts for the same volume of water discharged. In order to better understand what substances or compounds are affecting the results more significantly, a graph displaying the calculated environmental impact per substance can be found in Figure 37.

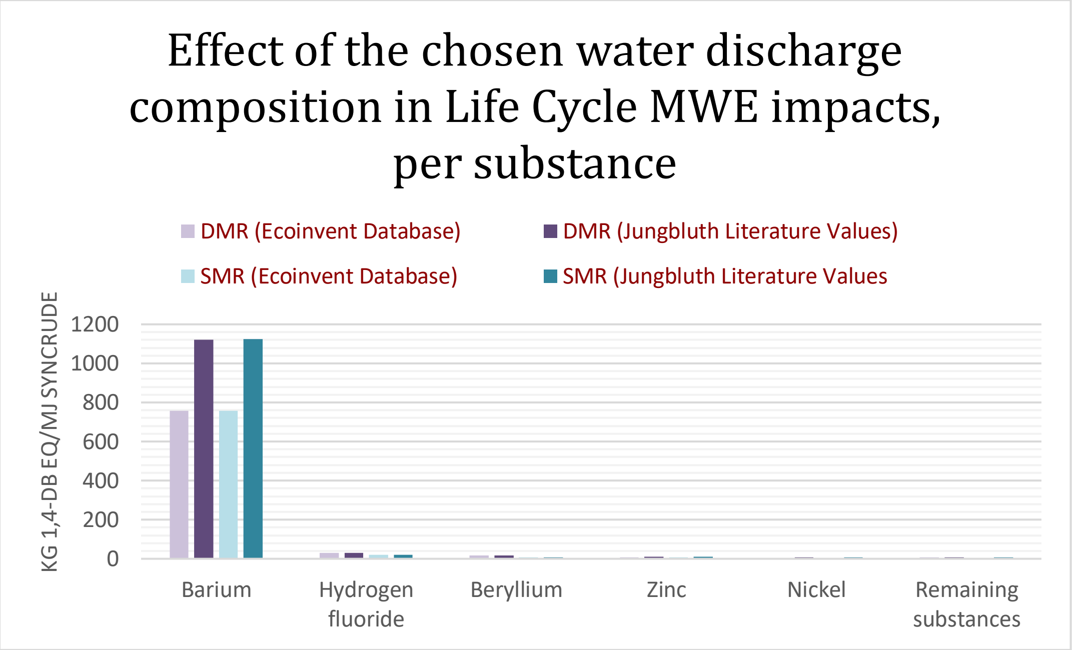

Figure 37 - Life Cycle Marine Water Ecotoxicity impacts calculated per substance for both water discharge compositions used in the sensitivity analysis.

It can be concluded that the compound most responsible for the calculated MWE environmental impacts in the life cycle using the two databases assessed in this sensitivity analysis is barium, in both cases. The discrepancy observed between the results obtained using different water discharge compositions leads to the conclusion that a rigorous on-site measurement must be done in order to effectively compare different O&G extraction facilities as well as the studied SMR and DMR pathway to other liquid fuel synthesis facilities, for the usage of average values can result in significant calculation errors and uncertainties. Particular attention should be given to the measurement of barium in water discharge, as it is associated with the lion share of the impacts in both scenarios.

The fact that this happens is that typically in offshore water treatment, a simplified treatment is done in which the toxic residue sludge is sent onshore for further treatment, and the post-treatment water is discharged [88]. This was considered in an LCA to be the most beneficial of the various O&G extraction facility water treatment options (in comparison to onshore treatment and injection) in terms of environmental impact [88].

The fact that barium has such a high marine water environmental impact has to do with the fact that the produced water generated after separation from the crude oil post-extraction has a high concentration of dissolved barium, which is not removed in the water treatment. In seawater the solubility of barium is significantly lower than the concentration of discharge, which prompts its precipitation into solid barite after association with sulfate ions, which are in a very high concentration in saltwater. However, the complexation of barium ions with organic acid anions can slow its precipitation rate leading to a longer exposure time in its dissolved form [89].

In sea water, the toxic barium ion concentrations are in excess of barium solubility, and consequently it affects only embryos and larvae of marine invertebrates as it bioaccumulates in their organism. Besides solid bioaccumulation in these life forms, it can also deposit in deep sea sediments in smaller water columns (solubility increases with depth, and consequently most of the barite precipitated in the upper water column dissolves at high depths [89]).

Thus, it can be concluded that the high ecotoxicity potential calculated for the wastewater impacts in the ecosystems can be attributed to the impact of barite and barium complexes in the lower eutrophic levels of the ecosystem.

Assuming European production versus global average production in outsourced material inputs

As the FPSO operates, it must purchase material inputs that it itself cannot produce, which implies the outsourcing of these materials. Although the mass or volume of them are estimated using simulations or average global data, the life cycle impacts associated with the production of its materials before their usage is something that also has to be accounted for, as the production of a functional unit of a given material such as a kilogram of rhodium catalyst does not have the same environmental impacts in Europe and in the rest of the world, due to, for example, the energy efficiency of the production chain.

Since the life cycle inventory data of the catalysts and the MDEA production were obtained using the ecoinvent databases present in the SimaPro software, and since it was assumed that the production was done with life cycle inventory data obtained through global average values of the corresponding industries, a sensitivity analysis was conducted to verify the impact of the choice of production source of the rhodium, copper oxide and activated carbon materials as well as the production of MDEA (in this case, MEA since its LCI proxied that of MDEA) over the calculated results for the relevant impact categories in the life cycle impacts of the syncrude. The results are depicted in Figure 38.

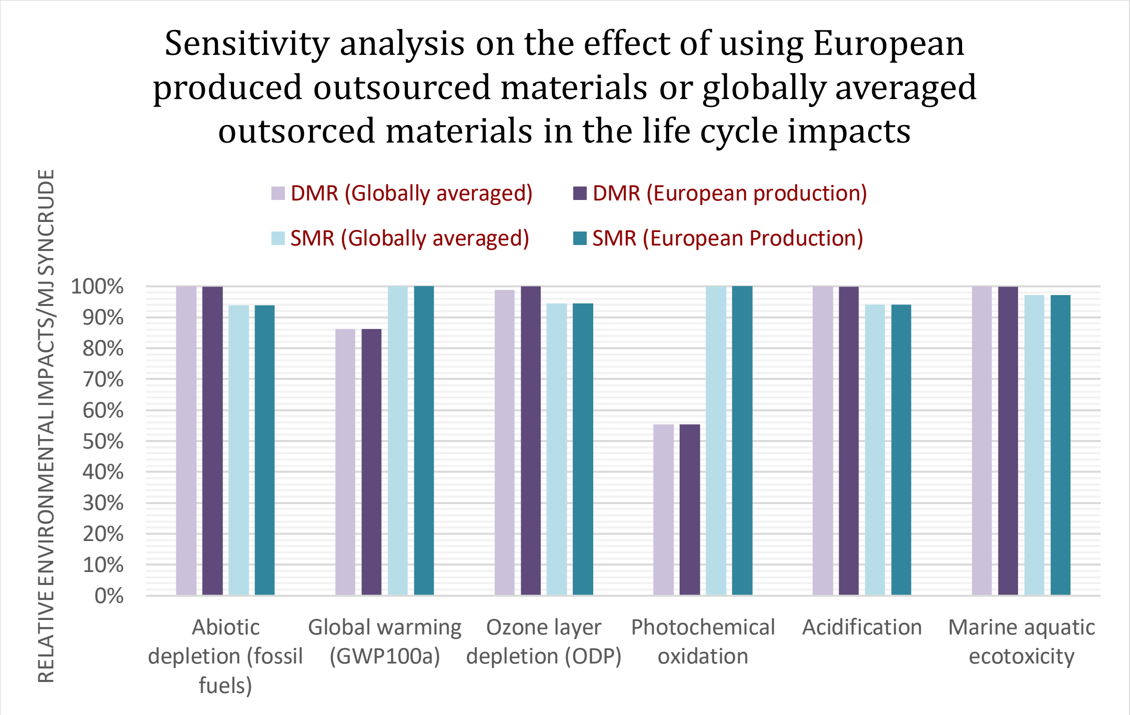

Figure 38 - Sensitivity analysis on the effects of the assumption in source of production of the outsourced inputs used in the facility over the life cycle impacts of the syncrude.

As it is possible to observe, the impacts of the choice of the production source between the two selected possibilities for this sensitivity analysis proves that it does not bring significant changes in the life cycle impacts of the syncrude. However, it is worth noticing that if infrastructure impacts had been accounted for, the disparities would probably be observable.

Flare and vent gas composition effects on the life cycle of the syncrude product

As it was mentioned before, the composition of the feed gases at the entrance of the reforming stage is different for both scenarios. This severely affects the results of the simulations, and the weight of the subprocesses in the total life cycle impact as is the case with the amine scrubbing stage, in which a higher energy expense and amine use is employed in the DMR case. Since the purpose of the assumptions taken over the course of this project was to minimize the errors that could bias the interpretation of the calculated results towards one or the other pathway, a problem was formulated as follows: what is the difference in the results associated with the usage of a common flaring and venting composition in both scenarios (although it is not necessarily the truth), compared to using specific different flaring and venting for both the scenarios? Before moving on to the sensitivity analysis, it is worth to go over some key points:

- The venting composition is relatively easy to simulate, since they are unwanted emissions into the atmosphere resulting from operational mis-steps. As such, they could be assumed for sensitivity analysis purposes to have roughly the same composition (%w/w) as the feed gas at the entrance of the reforming reactor.

- The flaring emissions relate to the combustion of the associated gas without the integration of its heat, in a flare. For that reason, a simulation was carried out in ASPEN Plus for the combustion of the feed gases in an ideal combustion setting, to obtain these combustion emissions, at 1100, 1400 and 1700 K. Since this combustion is complete, it has an inherent physical error when compared to the database found in Jungbluth et. Al (2018). The combustion emissions at 1400 K conditions were selected.

The sensitivity analysis on the impact of the choice of the composition of the flare and vent gas are presented in Figure 39:

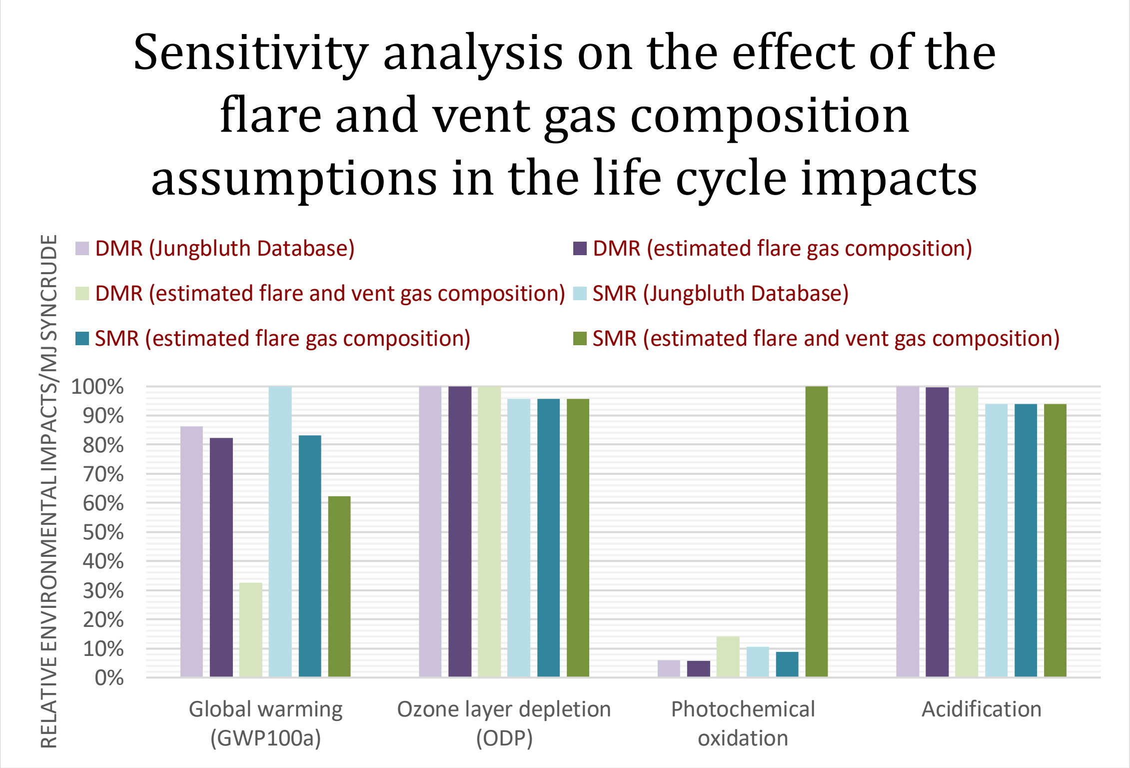

Figure 39 - Sensitivity analysis on the effect of the flared and vented gas compositions in the life cycle impacts of the syncrude.

The largest differences can be found in the global warming potential and the photochemical oxidation potential. A specific analysis per category was also carried out, as can be observed in Figures 40 and 41.

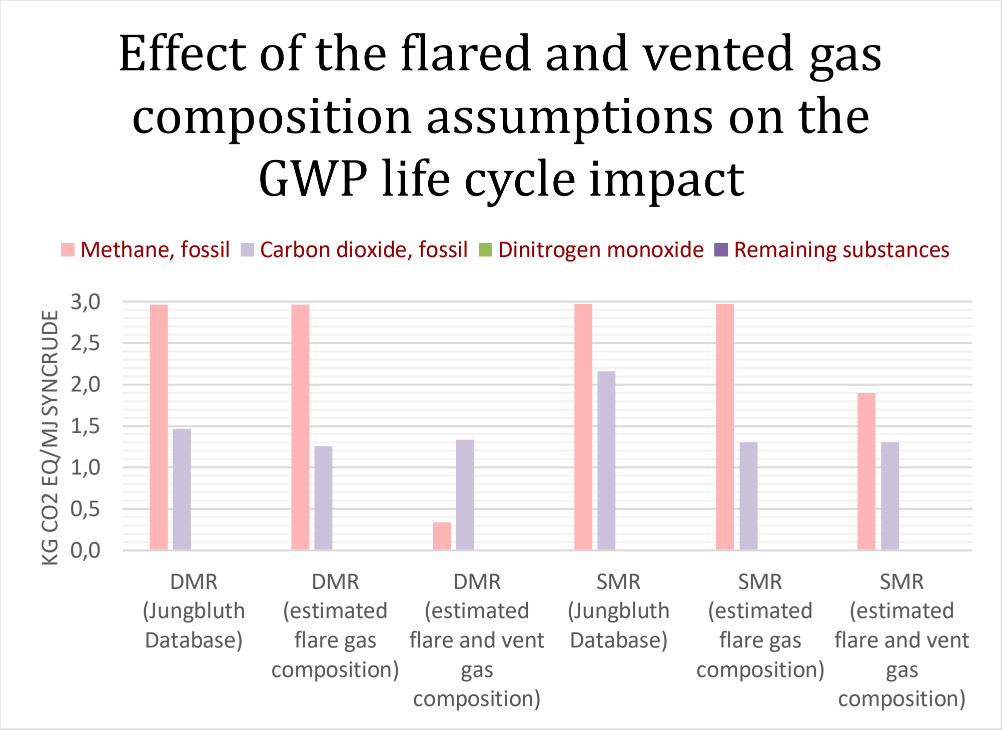

Figure 40 - Effect of the flared and vented gas composition assumptions on the life cycle GWP impact.

In the case of the global warming potential, the biggest differences to be found are in the methane emission in the vented gas (more evidently in the DMR pathway) and the higher emissions of carbon dioxide in the SMR pathway when compared to the DMR (4th group of columns vs 1st group of columns).

In the 2nd and 5th groups of columns this difference in the carbon dioxide emissions is not as discernible as it is in the 1st and 4th columns, as in the former the larger composition of CO_2 in the DMR feed gas evens out the lower flare gas combustion reduction that exists in the SMR case - which means that even though flaring is much more reduced in total volume in the DMR case, the flaring that does exist is comparable in environmental impacts to that of the flaring emissions of the SMR case, which combusts more flare gas, but a flare gas with a much lower CO_2 composition in volume.

The difference observed in the methane emissions from the 3rd column to the 1st and 2nd columns has got to do with the difference in %(w/w) composition of the feed gas in comparison to the one found in the Jungbluth database for the vent gas, since the DMR pathway feed gas has a 70% CO_2 concentration, which implies that for the same mass of the gas mixture, a much higher CO_2 mass rather than CH_4 will be calculated assuming that it has the same composition as the reforming gas composition and a much lower CH_4 mass. We could not use this data as it is known from literature that the vent gas has a much higher methane concentration than the flared gas.

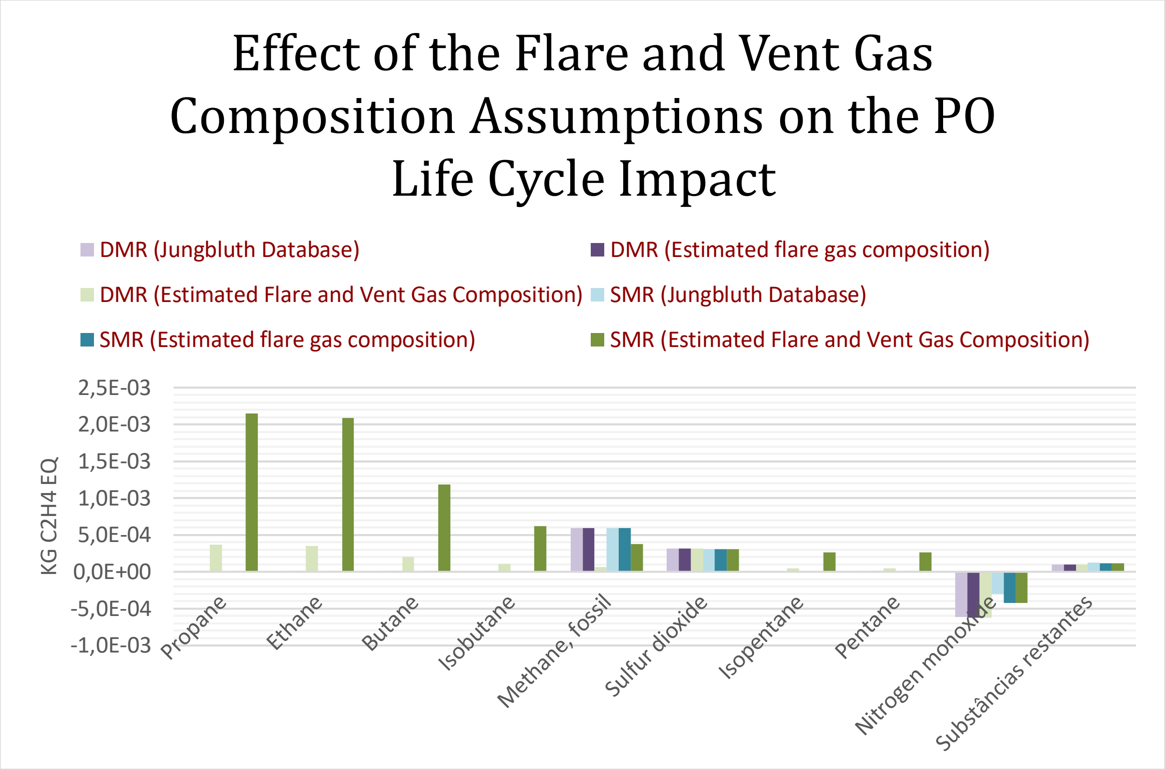

Figure 41 - Effect of the flare and vent gas composition assumptions on the Photochemical Oxidation Potential Life Cycle Impacts.

Looking into the Photochemical Oxidation Impacts, it is possible to observe the big discrepancy in Figure 39 that can be justified by Figure 41. The natural gas feed that reaches the reforming reactor has a significant mass of longer-chain alkanes as opposed to the venting gas composition assumed in Jungbluth et. Al. This has got to do with the fact that the previously mentioned database does not differentiate between the different volatile organic compounds emitted, and uses a generalized emission instead called "NMVOC, unspecified origin" as it can be seen in Table 3. The negative impact related to Nitrogen Monoxide emissions demonstrates the Ozone Depletion potential, which is negative, rather than the "positive" potentials associated with this impact category that refer to the hazardous ozone formation in the troposphere.

Looking over these results, it was considered that the composition found in the Jungbluth database would be the best assumption choice to withdraw valuable information from this life cycle assessment – although it compromises the existence of a single conclusion in which one pathway is deemed to be environmentally better than the other, it can however quantitatively demonstrate the impact of the reduction of the total existing flaring intensity that these technologies can offer, and reduce the global uncertainty related to the inherently different pathways by committing to the same uncertainty range for both of them in subprocesses that are not simulated in Aspen but rather estimated from literature.

Effect of the energy supply mix in the Life Cycle Impacts of the syncrude

This analysis reflects on the impact of the energy supply source in the life cycle impact of the syncrude. The O&G extraction taking place in FPSO facilities is very energy intensive, and as such the energy mix has very impactful results in the life cycle impacts of the syncrude, as the indirect emissions related to the production chain can vary greatly according to the energy mix supply. Two scenarios were tested for this analysis – for a constant total energy fuel energy supply, different shares of fossil fuel energy generated in gas turbine combustion were assumed in order to test its influence in the final results. The share of heavy fuel oil was maintained constant in the O&G extraction phase since it refers to fuel burnt in equipment, and the sweet and sour natural gas consumption rate was maintained at a ratio close to 10%, assumed to decrease together in response to an increase in diesel fuel oil increments. These shares can be found in Table 24, and the results are depicted in Figure 42.

Table 24 - Fuel energy shares used in the sensitivity analysis related to the impact of the energy supply mix in the life cycle impacts.

SMR and DMR Pathway fuel energy shares				
Share in energy mix	Sweet Natural Gas	Sour Natural Gas	Diesel fuel oil	Heavy Fuel Oil
Baseline scenario	91 %	9 %	0 %	0 %
Scenario 2	68 %	7 %	25 %	0 %
O&G extraction Phase fuel energy shares				
Share in energy mix	Sweet Natural Gas	Sour Natural Gas	Diesel fuel oil	Heavy Fuel Oil
Baseline scenario	71 %	7 %	11 %	11 %
Scenario 2	60 %	7 %	22 %	11 %

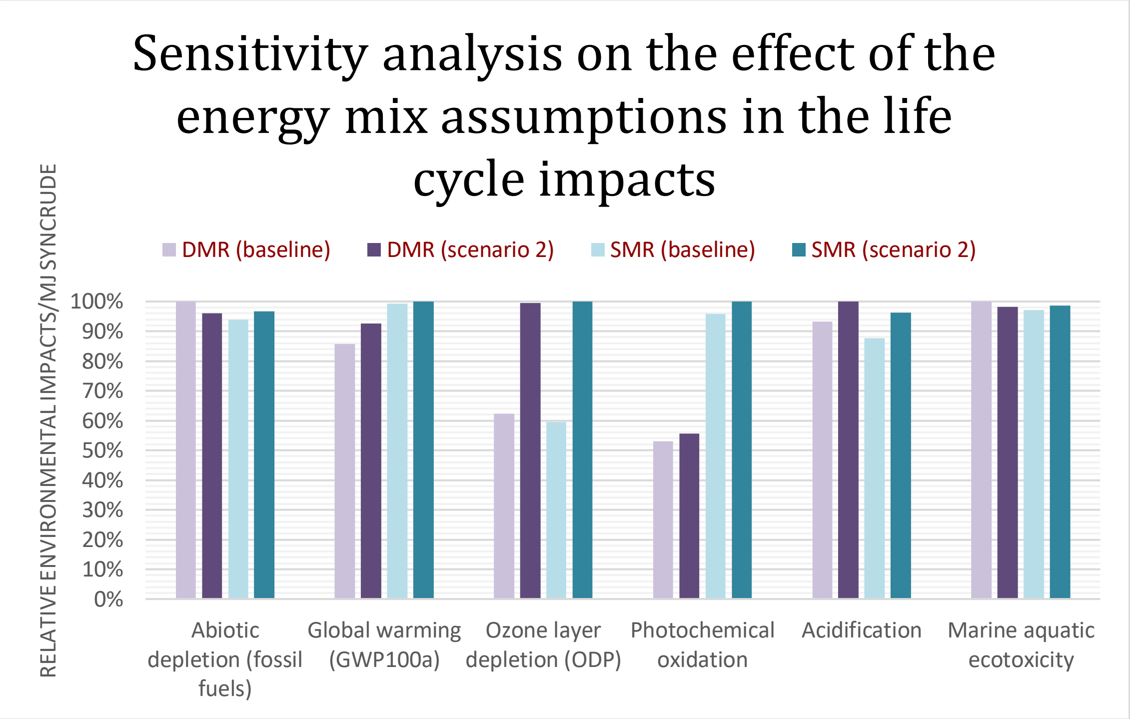

Figure 42 - Sensitivity analysis on the effect of the energy mix assumption in the life cycle impacts of the syncrude.

Besides the results obtained for the greenhouse gas emissions, reflected in the global warming potential, the obtained results are not very intuitive as we see ascending patterns in DMR opposed to descending patterns in SMR, and vice-versa – this has not only to do with the different energy intensity between pathways (DMR is more energy intensive than SMR) but also with the fact that the percentage shares are not exactly the same for the O&G extraction phase and the pathways, since there is an heavy fuel oil share in the O&G extraction phase that remains constant between scenarios, and does not exist in the studied pathways. Consequently, a separate analysis was given to the all the impact categories except marine water ecotoxicity as can be observed in the figures below.

In Figure 43, it is possible to observe the effect that the energy supply mix has in the abiotic depletion of fossil fuels, related to the scarcity of the fossil fuel resources used in this facility. Since the energy consumption is constant, and the variable that changes between scenarios is the share in the total energy supply, one can infer that the different results arise from the fact that the different fuels have different scarcity factors as well. It is expected that the scarcity factor for diesel is lower since there are well-established technologies for biodiesel and alternative diesel production besides the conventional diesel production using crude oil as a feedstock that significantly alter its resource regeneration rate[13].

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[13] The characterization model for abiotic resource depletion is based on reserves and annual de-accumulation, the latter defined as the annual production subtracted by the annual regeneration.

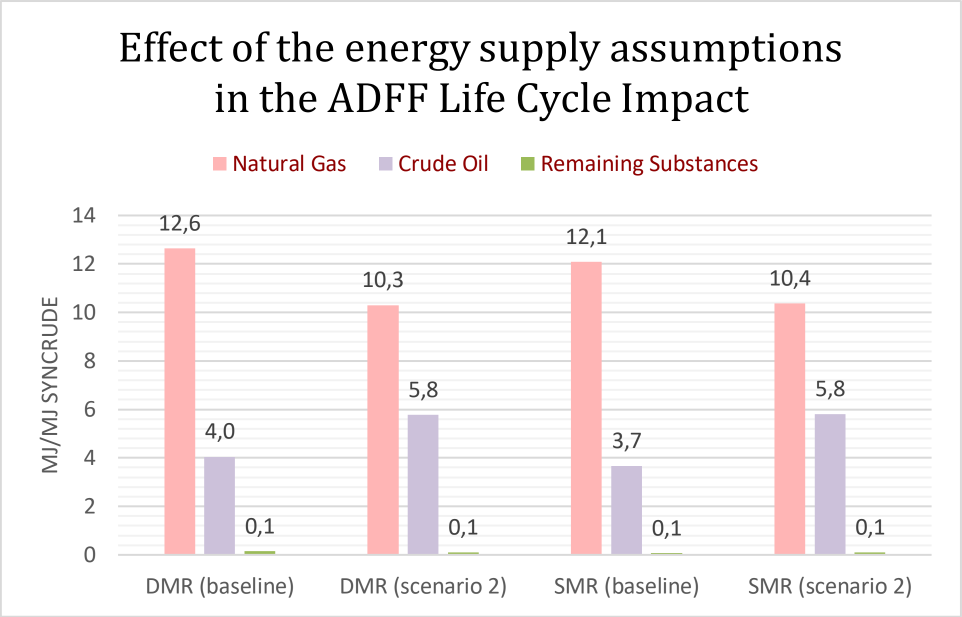

Figure 43 - Effect of the energy supply assumptions on the Abiotic Depletion of Fossil Fuels Life Cycle Impact, for both pathways.

In the case of the Global Warming Potential Impacts, it is possible to observe in Figure 44 that an increase in the diesel fuel oil share in the energy mix results in a higher impact related to CO_2 emissions, since diesel fuel oil has higher CO_2 emissions per unit of energy.

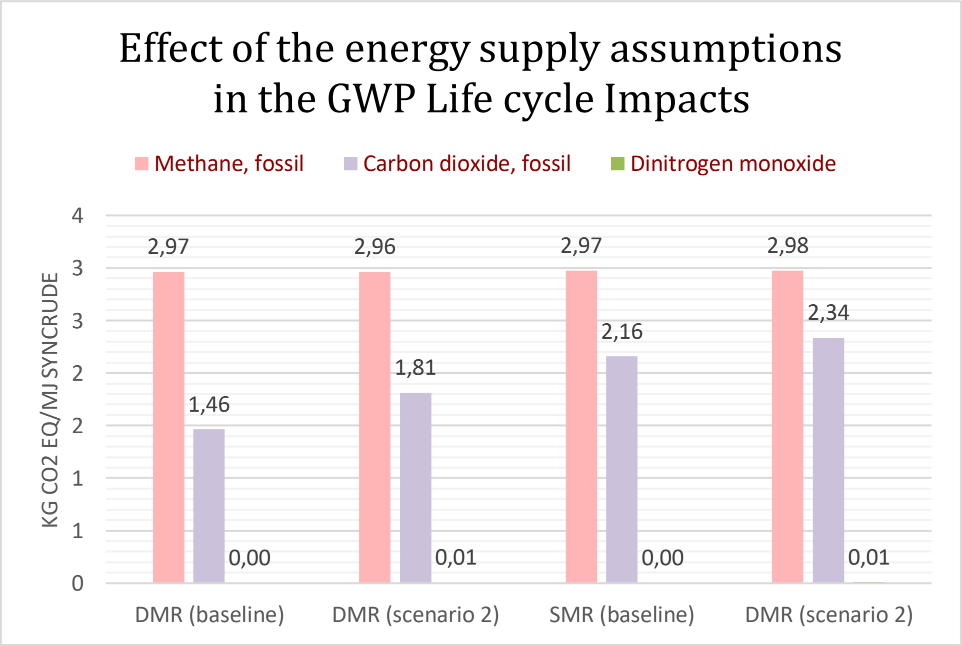

Figure 44 - Effect of the energy supply assumptions in the GWP Impacts over the life cycle of the syncrude, for both pathways.

In Figure 45, it is possible to observe the impacts related to the ODP impacts in the life cycle associated to both scenarios. The differences are exclusively related to the different emissions of Halon 1301, or bromotrifluoromethane.

Halon 1301 has been typically used as an extinguishing agent of choice for gas turbines, auxiliary components and generators in packet units. It has been preferred over CO_2 as a fire extinguisher chemical since the concentrations at which it acts as a fire suppressor are significantly lower than those for CO_2, the latter being at toxic concentration levels and constituting a safety operational hazard (7% vs 34%). However, after Halon 1301 acts upon a fire or is exposed to temperatures above around 480 ºC it breaks down into corrosive and toxic byproducts, among them compounds related to ozone layer depletion [90].

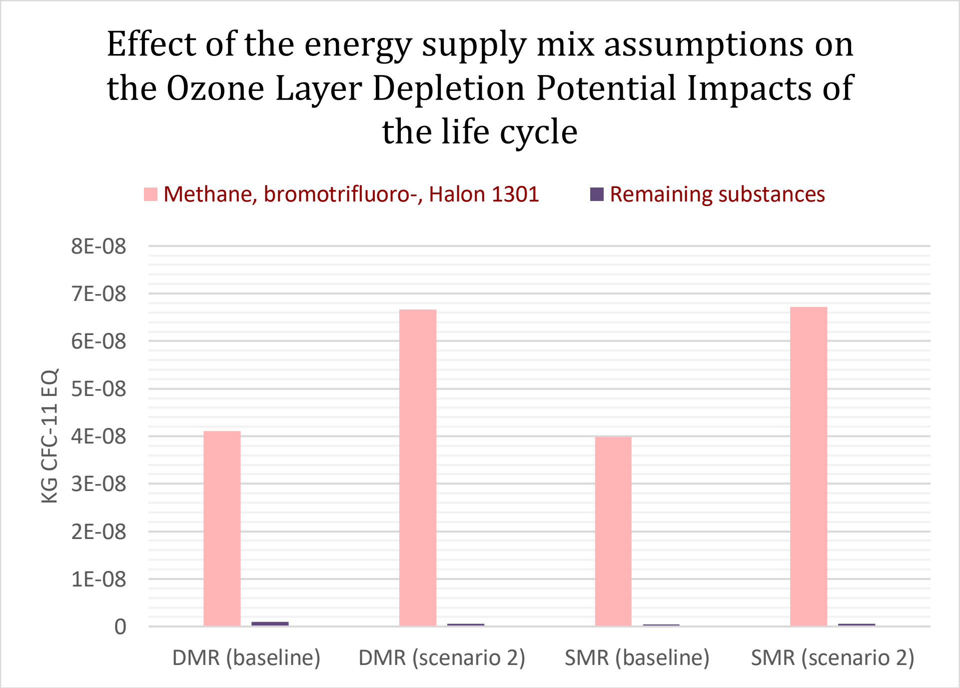

Figure 45 - Effect of the energy supply mix assumptions on the obtained Ozone Layer Depletion life cycle impact results of the syncrude, for both pathways

In Figure 46, the differences observed between energy scenarios are due mostly to carbon monoxide emissions, which are slightly higher for the scenarios with a higher diesel fuel oil contribution to the energy mix. Regarding Acidification Potential Impacts as depicted In Figure 47, the differences are related to the Nitrogen Oxide emissions - NO_x emissions are higher per unit of energy when diesel fuel is burned than the NO_x emissions for natural gas.

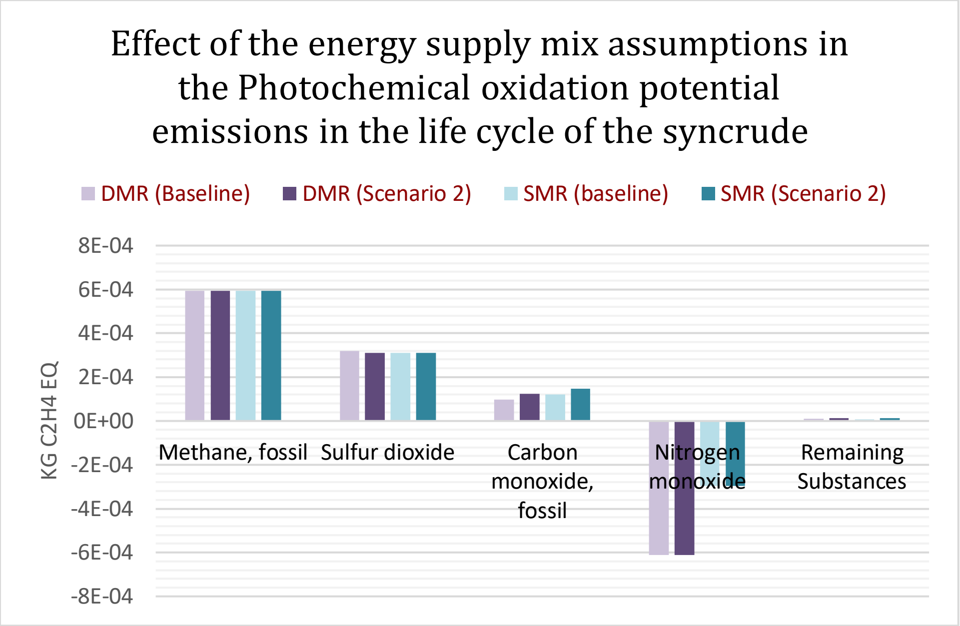

Figure 46 - Effect of the Assumptions done on energy mix supply over the Photochemical Oxidation Impact Potential in the life cycle of the syncrude, for both scenarios.

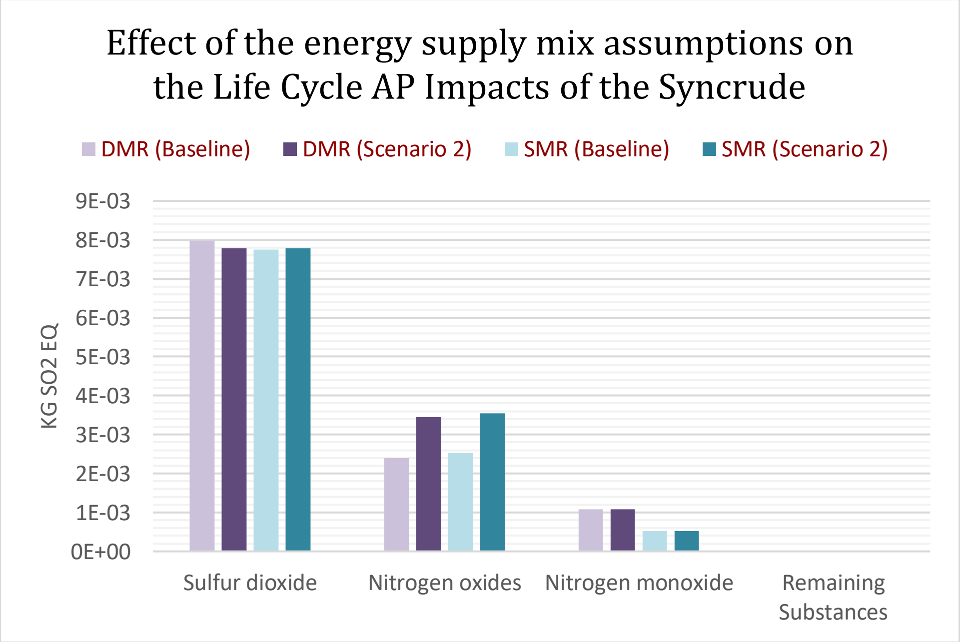

Figure 47 - Effect of the energy mix assumptions on the Acidification Potential Impacts over the life cycle of the syncrude.

Given these analyses, it is somewhat difficult to point out definitive conclusions regarding the energy mix impact changes in the life cycle regarding abiotic depletion of fossil fuels - however, it is easy to state that in the case of GWP, ODP and PO impact categories an aggravation of the environmental impacts exist given the fact that per unit of energy, diesel fuel oil is more emission intensive than natural gas, and that these emissions are significant enough in the life cycle to require a thorough measurement procedure if future work is desired. This claim is backed up by the knowledge that "specific fuel consumption for natural gas is lower than that of diesel by about 13.5% at the same power output” [91] in marine gas turbine applications – consequently its emissions per unit of energy are also higher.

The reflections on data quality requirements for further work can be found in the Conclusions.

APPENDIX III – MASS ALLOCATION PROCEDURES

As it was previously mentioned, it is necessary that the impact assessment results are calculated according to the functional unit – 1 MJ LHV of synfuel. Since the LCI data is related to the total daily operation inventory data, it is necessary to allocate a fraction of the total mass output of each subprocess step to the impacts related to the production of 1 MJ of syncrude.

Thus, one must start at the final subprocess, the separation of the crude from the light gas fraction and the water. What is desired is the percentage of the total daily mass output of each subprocess that is required to produce 1 MJ LHV of synfuel. Therefore, the mass percentage is calculated as such:

$$\%_{allocated\ mass} = \frac{Mass\ of\ syncrude\ (kg)\ contained\ in\ 1\ MJ\ LHV}{Total\ Daily\ Mass\ of\ Syncrude\ produced\ (kg)}$$

To obtain the mass of syncrude in 1 MJ LHV, $m_{syncrude\ in\ 1\ MJ\ LHV}$,

$$m_{syncrude\ in\ 1\ MJ\ LHV}\ (kg/MJ) = \frac{Total\ Daily\ Mass\ of\ Syncrude\ produced\ (kg)}{Total\ Energy\ contained\ in\ the\ syncrude\ output\ (MJ)}$$

And in order to obtain the total energy contained in the syncrude output, $E_{total\ daily\ syncrude\ output}$:

$$E_{total\ daily\ syncrude\ output} = Total\ Daily\ Mass\ of\ Syncrude\ produced\ (kg)\ \times LHV\ (15^{o}C)_{syncrude}$$

After the mass percentage of the daily mass output of the subprocesses is calculated, the contribution of each subprocess' output mass to the production of 1 MJ LHV is calculated as:

$$m_{subprocess\ output,1\ MJ\ production} = m_{subprocess\ output,total\ production} \times \%_{allocated\ mass}$$

For the O&G extraction phase, the mass output of the subprocess was considered to be the total produced associated gas destined for flaring, which is the same for all subprocesses – although the emissions of this step are not the same, for there is a trade-off between the emissions in this step with the emissions associated with the steps related to liquid syncrude production.

APPENDIX IV – UNCERTAINTY ANALYSES

Uncertainty Analyses were carried out for each of the LCA conducted in this thesis, in order to know the uncertainty associated for each impact category related to the total aggregated impacts for each scenario. Monte Carlo Simulations were performed in order to assess the confidence intervals of our calculated impacts using 95% confidence criteria.

The obtained results are found in Figures 48, 49, 50 and 51:

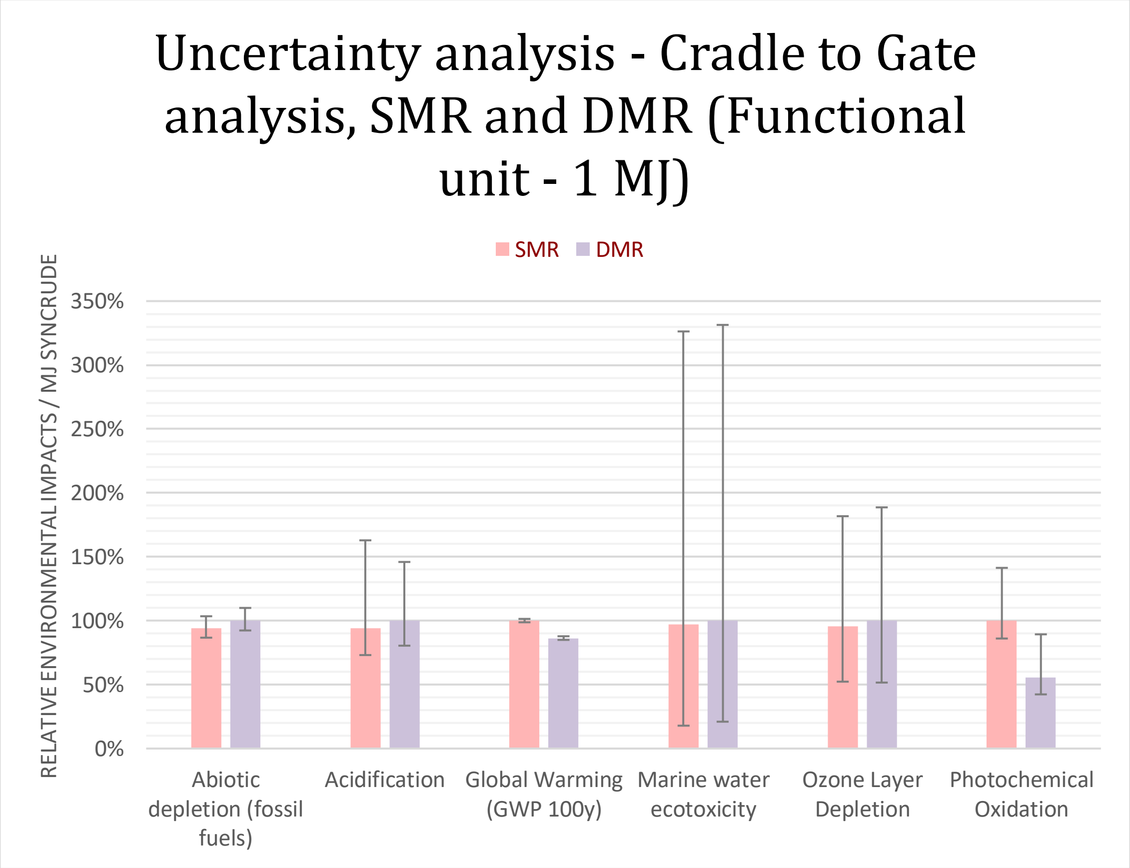

Figure 48 - Uncertainty analysis - Cradle to Gate analysis, SMR and DMR (Functional unit - 1 MJ)

It is possible to observe that the Impact Category with less uncertainty is GWP, oscillating no more than 2% from the calculated results, and that the impact category with largest uncertainty is MWE, possibly achieving impacts more than 3 times higher than the one calculated. This is related to the very large uncertainty related to discharged water composition in offshore O&G exploration.

AP impacts could also be potentially higher around 1.5 times than the one obtained in the LCA results, due to the fact that different associated natural gas compositions can have different sulphur compositions (and consequently SO_x emissions) and given the fact that different flaring combustion conditions can influence the formation of NO_x emissions greatly. Similarly, PO impacts share this behaviour associated with the differing flare and vent gas compositions. This AP uncertainty is more observable in the SMR case, since a lower volume of associated gas flaring is avoided when compared to the DMR case.

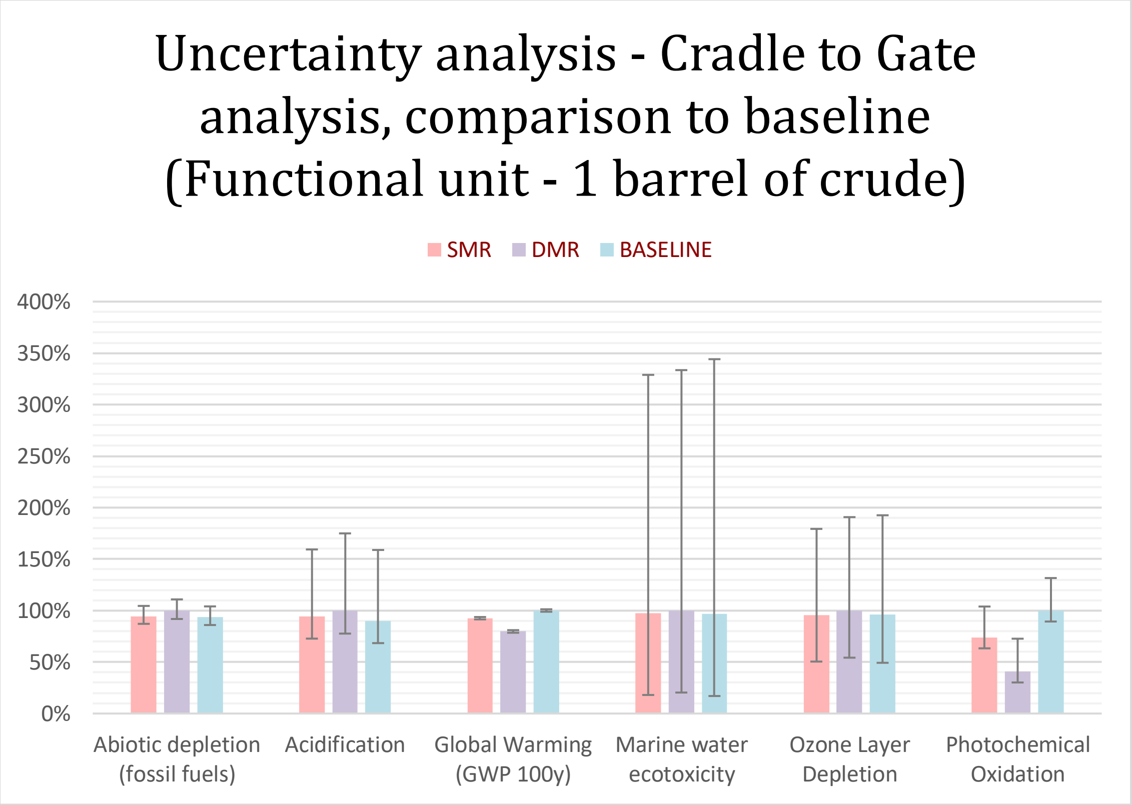

Figure 49 - Uncertainty Analysis - Cradle to Gate Analysis, comparison to baseline (Functional Unit - 1 barrel of crude)

The results for the baseline scenario follow the same patterns as the obtained for the SMR and DMR case, which is o be expected since the largest share of the global impacts is due to the O&G extraction stage, where the uncertainties are quantified. The AP impact is, however, different (no longer the uncertainty range is higher for SMR), which is probably due to the fact that the allocation of impacts and uncertainties to the functional unit is done diferently when the functional unit is a barrel contrary to the 1 MJ LHV.

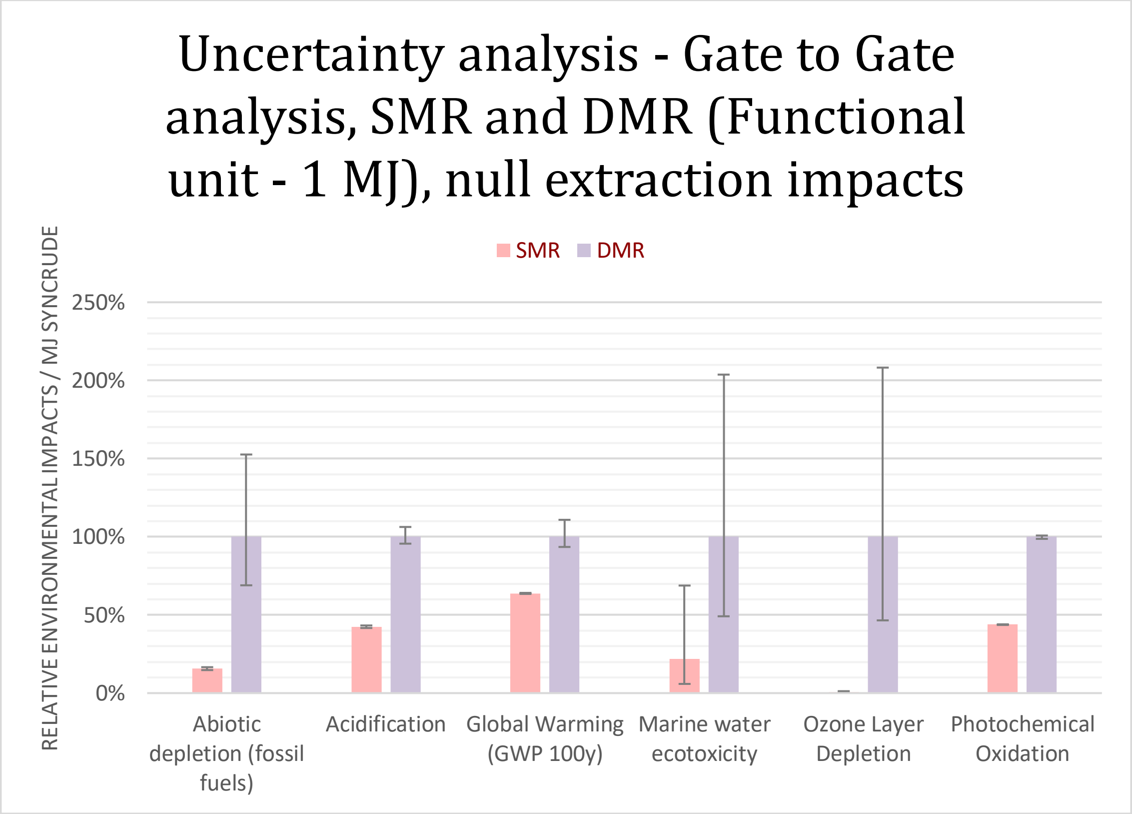

Figure 50 - Uncertainty analysis - Gate to Gate analysis, SMR and DMR (Functional Unit - 1 MJ), null associated gas extraction impacts.

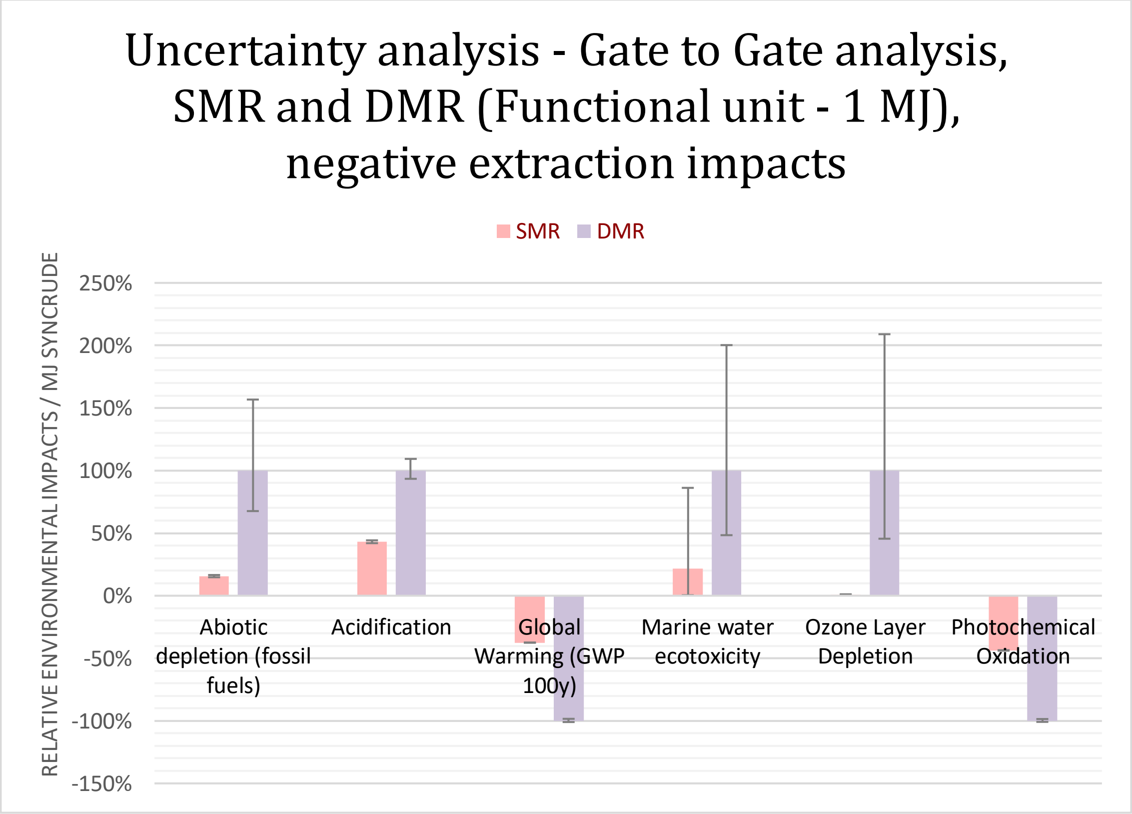

Figure 51 - Uncertainty analysis - Gate to Gate analysis, SMR and DMR (Functional Unit - 1 MJ), negative associated gas extraction impacts.

Looking into the uncertainty for the Gate to gate analyses, smaller uncertainty ranges are found in AP, GWP and PO impact categories when comparing to the other analysis, given the fact that most of the uncertainty relates to the associated gas flaring phenomena which is inexistent in this analysis.