Life cycle assessment of feedstock recycling processes

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Content

Nomenclature

AEC	Alkali electrolysis cell
ALCA	Attributional life cycle assessment
AGR	Acid gas removal
BAT	Best available technique
BFW	Boiler feed water
BTX	Benzene, toluene, xylenes
CC	Carbon capture
CCU	Carbon capture and utilization
CHP	Combined heat and power
CLCA	Consequential life cycle assessment
CO_2eq	CO_2 equivalent, quantification unit of global warming impact
E/e	High/low energy efficiency
eChem	Electrically heated chemical process
fHTR	Full hydrotreating
EoL	End of Life
FEI	Framework energy integration
FR / FeedRec	Feedstock recycling
FRD	Fossil resource depletion
FRDI	Fossil resource depletion impact
FSQ	Framework status quo
FT	Fischer-Tropsch
GHG	Greenhouse gas
GW	Global warming
GWI	Global warming impact
HCR	Hydrocracking
HDO	Hydrodeoxygenation
HHV	Higher heating value
HP	High pressure
HT	High temperature
HTR	Hydrotreating

IEC	Institute of Energy Process Engineering and Chemical Engineering
INC	Incremental process application scope
IP	Intermediate pressure
IPCC	Intergovernmental Panel for Climate Change
KPI	Key performance indicator
kt	Kilo ton = 10^6 kg
LCA	Life cycle assessment
LCI	Life cycle inventory
LCIA	Life cycle impact assessment
LHV	Lower heating value
LP	Low pressure
LPG	Liquefied petroleum gas
LSC	LPG steam cracking
LT	Low temperature
LWP	Light-weight packaging
M/m	High/low material efficiency
MBT	Mechanical biological treatment
MeOH	Methanol
MP / MPW	Mixed plastic waste
MR / MRF	Material recovery
MSW	Municipal solid waste
Mt	Mega ton = 10^9 kg
MTA	Methanol-to-aromatics
MTO	Methanol-to-olefins
NGR	Natural gas reforming
NR	Naphtha catalytic reforming
NSC	Naphtha steam cracking
PEMEC	Proton exchange membrane electrolysis cell
pHTR	Partial hydrotreating
POX	Partial oxidation
PSA	Pressure swing adsorption
PTH	Power-to-heat
PTX	Power-to-X

Ref	Reference process
RMP	Recyclable materials rich in plastics
RP	Refuse-derived fuel from plastic-rich waste
RR	Refuse-derived fuel from residual waste
SOEC	Solid oxide electrolysis cell
STP	Standard temperature and pressure
TOC	Total organic carbon
TRL	Technology readiness level
WW	Waste water
σ	CHP electric-thermal output ratio

Indices

e	Electrically heated chemical process
h	Syngas-based process with hydrogen integration
waf	Water and ash free
wf	Water free

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Chapter 1

Introduction and outline

Germany is facing great challenges to achieve the defined target of climate neutrality by 2045 from a societal and economic, but also technological perspective. While decarbonization is a viable option in key emission-intensive sectors like energy generation and mobility to reduce their climate impact, it is less applicable for the production of carbonaceous products. As an example, plastics play an integral role in our society due to their versatility and unique application features, but pose the intrinsic risk of emitting the containing carbon in form of greenhouse gases (GHG). Their sustainable application requires the establishment of a circular economy and its key elements, including the utilization of renewable feedstock, the maximization of the product life time and recycling after utilization, while maintaining safe handling and treatment to prevent direct plastic emissions into the environment [1].

Currently, conventional treatment of non-biodegradable carbonaceous waste in Germany consists primarily of material recycling and thermal treatment. Material recycling aims at the direct recovery of recyclable materials (especially various plastic fractions) from waste by physical separation. The practicality of material recycling is limited by the applicable waste fractions, the recovery efficiency and the quality of recovered materials [2–5]. For Germany, 47% of total used plastics were accounted as recycled in 2019. Due to diminished quality and limited applicability (downcycling), only 13.7% of total processed plastics were covered by recyclates [6]. The upper limit for the plastic recycling rate based on conventional material recycling in an optimized system is estimated at 72% [5], so complete circularity is not expected to be feasible even under optimal conditions. On the other hand, thermal treatment by incineration is applicable to most waste fractions, but only enables the recovery of energy from carbonaceous waste with limited efficiency, while emitting the containing carbon. Greenhouse gases of 12 Mt CO_2eq were emitted from waste-to-energy plants (waste incineration and RDF power plants) in Germany in 2015 [7]. The prioritization of methods for waste prevention and management for policy and legislation in the European Union is defined by the waste hierarchy in the Waste Framework Directive [8], including prevention, preparing for re-use, recycling, recovery and disposal. Alternatively, material recycling, chemical recycling and energy recovery are considered as secondary, tertiary and quaternary recycling [9].

Focusing on the feedstock side, the chemical industry faces major challenges under the pressure to reduce greenhouse gas emissions. Base chemical processes rely predominantly on fossils as material feedstock (15.5 Mt naphtha and 2.3 Mt natural gas in Germany in 2017 [10]) and fuel for the supply of high-temperature process heat. Direct greenhouse gas emissions currently comprise 28 Mt CO_2eq from process heat and onsite energy generation and 5 Mt CO_2eq from process emissions [11]. Options for emission reduction include the integration of biomass and renewable energy (directly by process electrification or indirectly by hydrogen integration), but are restricted by technology readiness and availability of applicable biogenic feedstock and renewable energy [11]. With combined direct greenhouse gas emissions of 45 Mt, waste-based energy production and fossil-based chemical production caused 5.6% of the total German greenhouse gas emissions in 2019 [12].

A possible alternative or addition to the described conventional processes is *chemical recycling*. The term describes a range of processes and process chains that target to integrate carbonaceous waste fractions into material value chains by means of chemical conversion on vastly different pathways in relation to waste applicability, conversion principle and product application [13]. The objective of their application is the improvement of material and/or carbon beyond the possibilities of conventional waste treatment and chemical production options and thereby reduce fossil resource demand and emission of greenhouse gases. A generalized overview of chemical recycling processes and pathways is shown in figure 1. Solvent-based purification aims to directly recover polymers without breaking them down to monomer level. Since this is performed by physical dissolution and precipitation, the process is often considered as an enhancement to mechanical recycling instead of a chemical recycling process. The objective of depolymerization processes is the direct recovery of monomer compounds of the applied plastic waste via thermal or thermo-catalytic conversion [14, 15]. Both process types primarily target the utilization of plastic fractions with high material purity, especially manufacturing residues or pre-sorted plastics, which limits the applicable waste quantities. Further, it potentially rivals the direct utilization as directly recyclable plastics, which contradicts the waste hierarchy prioritization.

Pyrolysis processes are primarily considered for the conversion of mixed plastic-rich waste fractions to a liquid product oil. Gasification is applicable with a wide range of carbonaceous feedstock for the production of synthesis gas. Both processes do not address the direct recovery of plastic components in the converted waste feed, but the production of chemical feedstock for a range of possible applications and can therefore be described as *feedstock recycling processes*. By rerouting large-volume waste fractions that are currently incinerated, feedstock recycling processes have a significant quantitative potential to lower the fossil feedstock demand of chemical production, either by directly replacing conventional feedstock, especially crude oil-based naphtha, or by replacing conventional base chemical production processes [13, 14, 16].

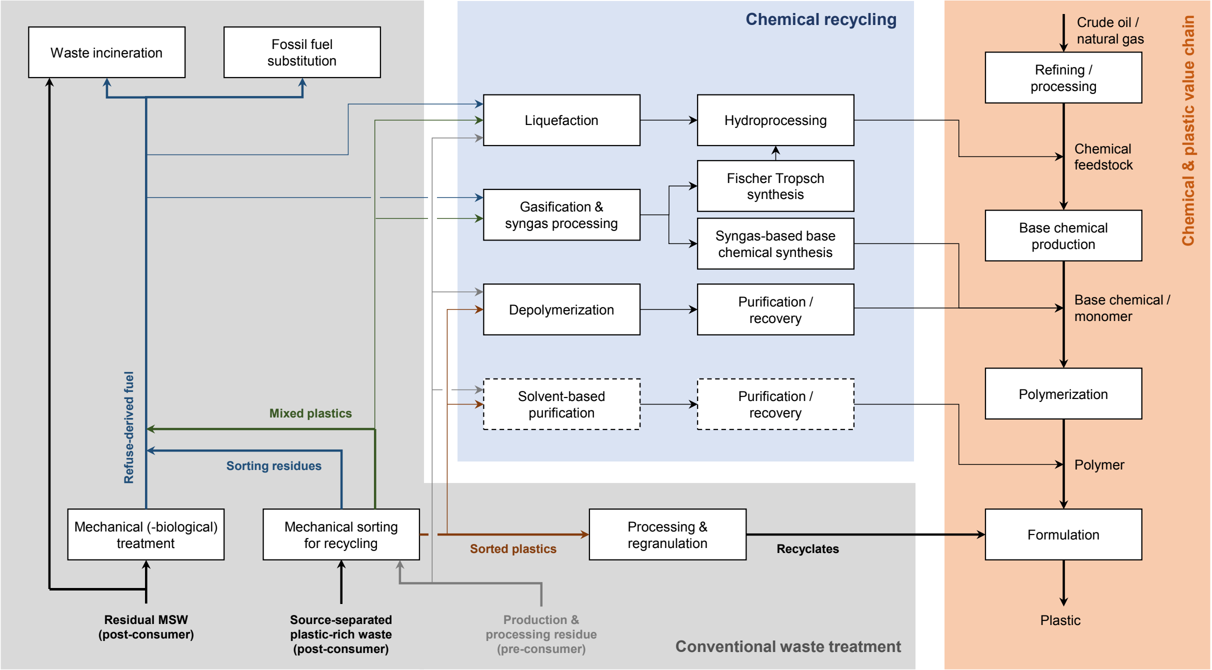

Figure 1: Overview of pathways for chemical recycling application (adapted from [17])

Still, feedstock recycling is a controversial topic in public, corporate and political discussions. Frequently addressed focus points of critique include missing or unsuccessful examples of industrial implementation, high emissions and energy demand, high costs and the inhibition of developments in mechanical recycling [1, 18, 19]. The evaluation of the practical feasibility and sustainability of chemical recycling in general and feedstock recycling in particular is essential to determine how the concerning legislative framework will be structured in the near future. Regulatory elements that are currently not clearly defined in this regard include the classification in the waste hierarchy, integration in the emission trading system and ratification and certification of products as renewable or recycled materials [20–22].

Currently, the sustainability of the application of feedstock recycling processes is not sufficiently assessed, despite the significant public, corporate and legislative interest. There are several aspects that make the assessment challenging. First, core processes in waste gasification and pyrolysis are broadly still under development, meaning that process data from industrial-scale applications are scarce and the achievable process performance and process implementation time are unclear. Second, the primary products from gasification and pyrolysis (syngas and pyrolysis oil, respectively) are non-uniform and not standardized. Their yield and composition vary depending on the applied waste feedstock, the conversion technology and the process configuration. For both syngas and pyrolysis oil, various utilization pathways (including processing and base chemical production) are possible, which lead to significant shifts in base chemical production pathways and differing environmental impacts. Last, as a perspective technology option for chemical production, feedstock recycling needs be assessed in context with other emerging technologies that are currently under consideration for the future transformation towards a sustainable production system.

The presented thesis targets to holistically investigate the environmental impact of two exemplary feedstock recycling processes based on validated modelling data by applying two different assessment frameworks. In chapter 2, life cycle assessment as a methodology for sustainability evaluation is reviewed, with focus on aspects that are specific for feedstock recycling technologies and previously existing investigations in the field. In chapter 3, the existing lack of applicable process inventory data is addressed by means of validated process modelling and balancing, in order to provide a sound data foundation for the contextual evaluation of feedstock recycling processes. The balanced processes cover: (1) gasification and pyrolysis-based feedstock recycling, including the quantified impact of potential key technological shortcomings, (2) conventional processes on waste treatment and base chemical production, and (3) processes and process configurations that enable the integration of electricity and hydrogen for process efficiency improvement and emission reduction. In chapter 4, gasification and pyrolysis are evaluated in a process-focused assessment to determine critical aspects and quantify the consequences of feedstock recycling application at varying development status. Chapter 5 provides an environmental potential analysis of feedstock recycling in common context of both waste treatment and chemical production in a novel assessment approach. For that, an integrated assessment system is defined, including the treatment of major post-consumer waste fractions and production of major base chemicals in Germany. By integrating feedstock recycling technologies in this system, their effect in terms of potential application scope and environmental impact depending on the chemical integration pathway can be assessed with minimal methodological uncertainty due to varying assessment scopes and framework assumptions. The approach is applied for a short-term situation, as well as a future setting under the availability of limited quantities of renewable energy, to assess feedstock recycling in context of other emerging chemical production processes, including hydrogen-based power-to-X and processes applying direct high-temperature electric heating.

The investigation is conducted with the objective to determine the environmental impact of feedstock recycling processes in dependence of its development status, the applied waste feedstock and the application of its products in chemical production, identify possible focus points for further technology development, and quantify its potential impact on sustainable industrial production systems. It aims to contribute to the factual discussion on the environmental effectiveness of feedstock recycling and the corporate and legislative decision process, to determine if development and industrial implementation of feedstock recycling is worth incentivizing or not.

Chapter 2

Life cycle assessment methodology

Life cycle assessment (LCA) is a methodology for the evaluation of direct and indirect environmental impacts of products, processes or services throughout the life cycle. The process of conducting an LCA and its elements are standardized in ISO 14040 and 14044 [23, 24]. Accordingly, the LCA process is structured into four phases:

- goal and scope definition,
- life cycle inventory analysis,
- life cycle impact assessment,
- interpretation.

The goal definition should encompass all relevant information on the reason for carrying out the study, the intended audience and further utilization of the results. The scope of the study describes all methodological assumptions and conditions that are applied for conducting the study to ensure transparency, comparability and conclusiveness of the study and its results. It includes the definition of the assessed system (i.e. system boundaries, functional unit), sources and requirements of the applied data, methodological conditions (i.e. applied allocation rules and impact categories) and limitations of the assessment and its utilization.

In the life cycle inventory (LCI) phase, required data are collected and interconnected, in order to quantify associated energy and material streams within the system (intermediate flows) and streams extracted from or emitted to the environment (elementary flows). The structure of an LCI model is visualized in figure 2. The involved processes are divided into a foreground system and a background system. The foreground system involves the processes that are specific to the production system and that are affected by decisions within. Foreground processes are mostly subject of individual modelling and balancing. The background system includes the processes that are not specific to the production system, that are included in numerous production systems and that are not significantly affected by its changes (e.g. electricity supply). Background processes are usually not modelled in detail but applied from averaged or projected supply data, for example from LCI databases [25].

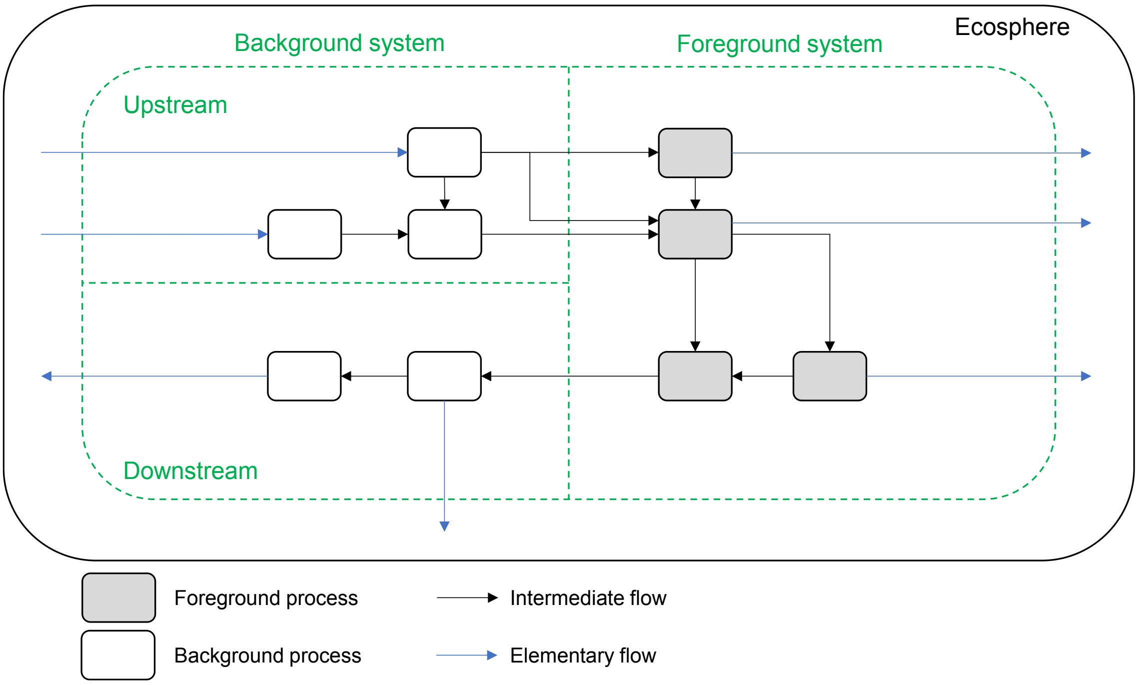

Figure 2: Schematic structure of life cycle inventory model (adapted from [25])

In the life cycle impact assessment (LCIA) phase, the environmental impact of the investigated system is quantified with regards to specific environmental impact categories, that can include global warming, fossil resource depletion, acidification and others. The determined elementary flows are multiplied with individual characterization factors for specific chemical components or component groups in each impact category. The total impact in each category is determined by the sum of all individual impacts of the elementary flows. Conclusive sets of characterization factors are available in form of characterization models (e.g. IPCC characterization factors for the impact concerning climate change [26]). Further, sets of complementary characterization models in various impact categories are summarized and maintained in characterization methodologies (e.g. Product Environmental Footprint PEF, CML 2001 and ReCiPe 2016) [27]. Finally, in the interpretation phase, the acquired results are evaluated in perspective of the defined goals of the investigation and recommendations may be derived. The interpretation further considers the robustness and uncertainty of the results, sensitivity of key parameters and limitations of the applicability of the results.

Conducting an LCA is not a linear process, but requires an iterative approach between the different phases. The cited ISO standards provide a structural orientation to the process of conducting an LCA, but are not specific enough to give a methodical guideline [28]. More extensive and detailed guideline documents are available to specify possible approaches on how to conduct LCAs in general [29, 30] or for specific applications in waste treatment [31, 32] or chemical production [33]. In the following, previous LCA investigations on feedstock recycling are reviewed and categorized and specific aspects in LCA methodology are addressed, that are relevant for the evaluation of feedstock recycling processes.

2.1. Previous LCA investigation on feedstock recycling

Gasification and pyrolysis are frequently addressed in LCA investigations as advanced thermal treatment processes for the production of electricity and/or heat [34–38]. Studies assessing their implementation as alternative recycling processes for chemical and fuel production are summarized in table 1. Pyrolysis for the conversion of mixed plastic waste streams is the most frequently addressed feedstock recycling process, with pyrolysis product oil being considered primarily for substitution of crude oil or crude oil-based processing fractions and fuels. Gasification is most often assessed for conversion of municipal solid waste-based fractions. Considered gasification-based products for fossil feedstock substitution include syngas with a defined H_2-CO ratio, lower olefins by means of MTO synthesis or steam cracking of Fischer-Tropsch (FT) products, ammonia, methanol and liquid fuels from FT synthesis. Two investigations [39, 40] conduct simplified screenings for the environmental impact for the application of various polymer types and treatment technology without specification of practical waste fractions.

Determined by the broad applicability of syngas and pyrolysis oil, a clear distinction between LCA for chemical feedstock and fuel production solely based on the applied primary waste conversion process is hardly possible. The majority of the studies address the substitution of a petrochemical intermediate or a fuel without consideration of a specified product quality or composition. Specific chemicals with uniform compositions are less often addressed in the reviewed feedstock recycling studies. Base chemical production LCA is more frequently available from other non-fossil sources for the production of olefins [41–47], aromatics [45, 48], methanol [49–54], ammonia [55–58] and hydrogen [59–62]. Other methodological differences concerning the applied assessment framework and the generation of life cycle inventories are addressed in the following.

Table 1: Overview of LCA investigations on feedstock recycling for chemical and fuel production

Source	Year	Scope	Waste fraction	Process	Main product substitution	Process data source	Ref. waste treatment
[63]	2003	Attr; WP	EoL vehicle parts	Gasification	Methanol	Literature	MR, INC, LF
[64]	2005	Attr; WP	PE, PET	Hydrocracking Pyrolysis	Crude oil Atm. residue, naphtha, LPG	Literature	MR, INC, LF
[65]	2008	Attr; WP	MPW	Pyrolysis	Paraffins, naphtha, diesel	Literature	MR, INC, LF
[66]	2013	Attr; PP	RDF (MSW)	Gasification	Ethylene	Literature	MR, INC
[67]	2014	Attr; WP	MPW	Pyrolysis	Atm. residue, naphtha, LPG	Literature	MR
[68]	2014	Attr; WP	RDF (MSW)	Gasification	Liquid fuels	Literature	
[69]	2015	Attr; WP	MSW	Pyrolysis	Diesel, gasoline	Literature	INC, LF
[70]	2017	Attr; WP	MPW	Pyrolysis	Diesel, naphtha	Literature	INC, LF
[71]	2018	Attr; WP	MPW	Pyrolysis	Wax, naphtha, crude oil, fuel oil	Industry	INC, LF
[72]	2019	Attr; WP	MPW	Pyrolysis Gasification	Diesel Ethanol	Literature	INC
[73]	2019	Cons; WP	MPW	Pyrolysis	Crude oil	unclear	MR
[74]	2019	Attr; WP	Sorting residue; MPW	Pyrolysis Gasification Hydropyrolysis	Syngas, diesel Syngas Diesel, syngas	unclear	MR, INC
[75, 76]	2020	Attr; WP, PP, Cr-Gr	MPW	Pyrolysis	Naphtha	Industry	MR, INC, CK
[40]	2020	Attr; WP	Pure polymers	Pyrolysis	Crude oil, liquid fuels	Modelling	MR, INC, CK
[77]	2020	Attr; WP, PP	MPW	Pyrolysis	unclear	Industry	INC, LF
[78]	2020	Attr; PP	RDF (MSW)	Gasification	Olefins	Modelling	INC
[79]	2020	Attr; WP	MPW	Pyrolysis	Naphtha, LPG	Literature	INC
[80]	2021	Attr; WP	MR plastic fractions	Pyrolysis / depolymerization	Naphtha, slack wax, styrene	Industry	MR
[81]	2021	Attr; WP	Recycling residue	Pyrolysis / depolymerization	Naphtha, cracker gas	Experimental	MR
[39]	2021	Attr; WP	Pure polymers	Pyrolysis Gasification	Paraffins, diesel Syngas	Modelling	MR, INC
[82]	2021	Attr; WP	MSW	Gasification	Liquid fuels	Modelling	INC, LF
[83]	2021	Cons; WP	HDPE	Pyrolysis	Olefins, aromatics, naphtha, fuels	Experimental, modelling	
[84]	2021	Attr; WP	RDF (MSW)	Gasification	Olefins	Literature	INC
[85]	2021	Attr; WP, PP	MPW	Pyrolysis	Polyolefins	Unclear	INC
[86]	2022	Cons; WP	RDF (MSW)	Gasification	Olefins	Literature	INC
[87]	2022	Attr; PP	RDF	Gasification	Methanol	Modelling	
[88]	2022	Attr; WP	MPW	Pyrolysis	Crude oil	Modelling	LF, INC, MR
[89]	2022	Attr; PP	RDF (MSW)	Gasification	Ammonia	Modelling	
[90]	2022	Attr; WP	MR plastic fractions	Pyrolysis / depolymerization	Naphtha, slack wax, styrene	Industry	MR, INC
[91]	2022	Integrated system	RDF	Pyrolysis Gasification	Naphtha, methanol Methanol, olefins, ammonia	Modelling	INC

Attr – attributional LCA, Cons – consequential LCA, WP – waste perspective, PP – product perspective, Cr-Gr – Cradle-to-Grave, MPW – mixed plastic waste, MSW – municipal solid waste, RDF – refuse derived fuel, FT – Fischer-Tropsch synthesis, INC – thermal treatment, MR – material recycling, LF – landfilling, CK – cement kiln

2.2. Assessment scope

The life cycle of any product can generally be divided in four phases: feedstock supply, production, utilization and disposal. The product life cycle phases and nomenclatures of varying scopes that can be covered by an LCA are visualized in figure 3. If the whole life cycle of a product is investigated, the assessment scope is defined as *cradle-to-grave*. Based on the intention of the specific assessment, it is practical to restrict the scope to relevant phases to limit the assessment complexity und maintain the focus on relevant aspects. The *functional unit* is defined as a reference unit that quantifies the performance of a product system [24] and needs to be adapted to the respective scope. For the assessment of feedstock alternatives for a chemical product with a defined composition, it is practical to limit the scope to *cradle-to-gate* (also considered as *product perspective*), as the ensuing further processing and utilization are uniform and do not deviate between the compared alternatives. The functional unit in this case is the production of the chemical product in a defined quantity and quality. For comparison of waste treatment alternatives for a specific waste stream, it is practical to limit the assessment to an *end-of-life scope* or *waste perspective*, with the functional unit being the treatment of a quantity of a specific waste fraction with a defined composition [32]. In this case, a *zero-burden approach* is applied [92, 93], meaning that the formation process of the waste is not relevant. Similar to the defined product quality in cradle-to-gate investigations, the waste composition definition is essential in end-of-life assessments, as the composition significantly impacts the applicability and conversion characteristics of waste treatment processes [32, 94].

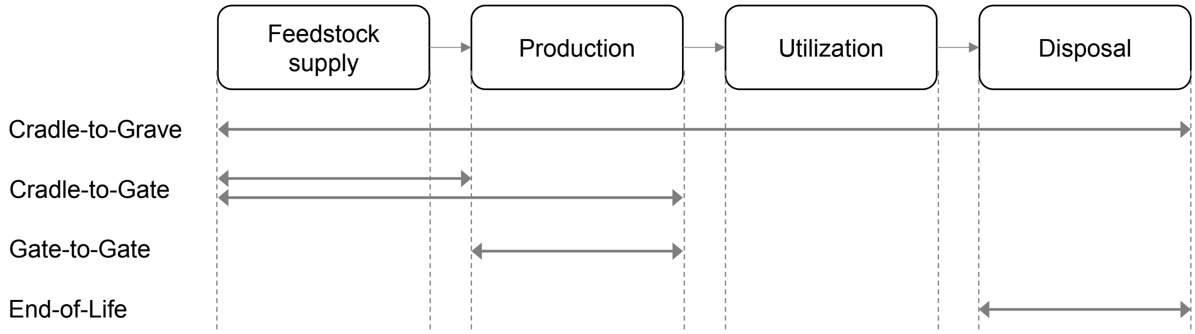

Figure 3: Product life cycle phases and life cycle assessment scopes

Feedstock recycling processes in general are characterized by their multifunctionality, meaning they address both the functions of chemical production and waste treatment. In the assessment scope definition, this can be incorporated by system expansion. The principle is illustrated in figure 4 for the application of chemical recycling in the plastic life cycle for the waste and product perspective and includes possible definitions of functional units, the conventional reference und the respective possible scopes for system expansion. Both perspectives encompass the same process steps. Depending on the investigated chemical recycling process, the functional unit differs. In the waste perspective, the primary or normative functional unit is defined by the quantity and type of waste treated, while the product system is expanded to include the corresponding chemical product as a secondary or expanded functional unit. In contrast, under the product perspective, the functional unit is defined by the produced chemical quantity and expanded to include the corresponding waste amount.

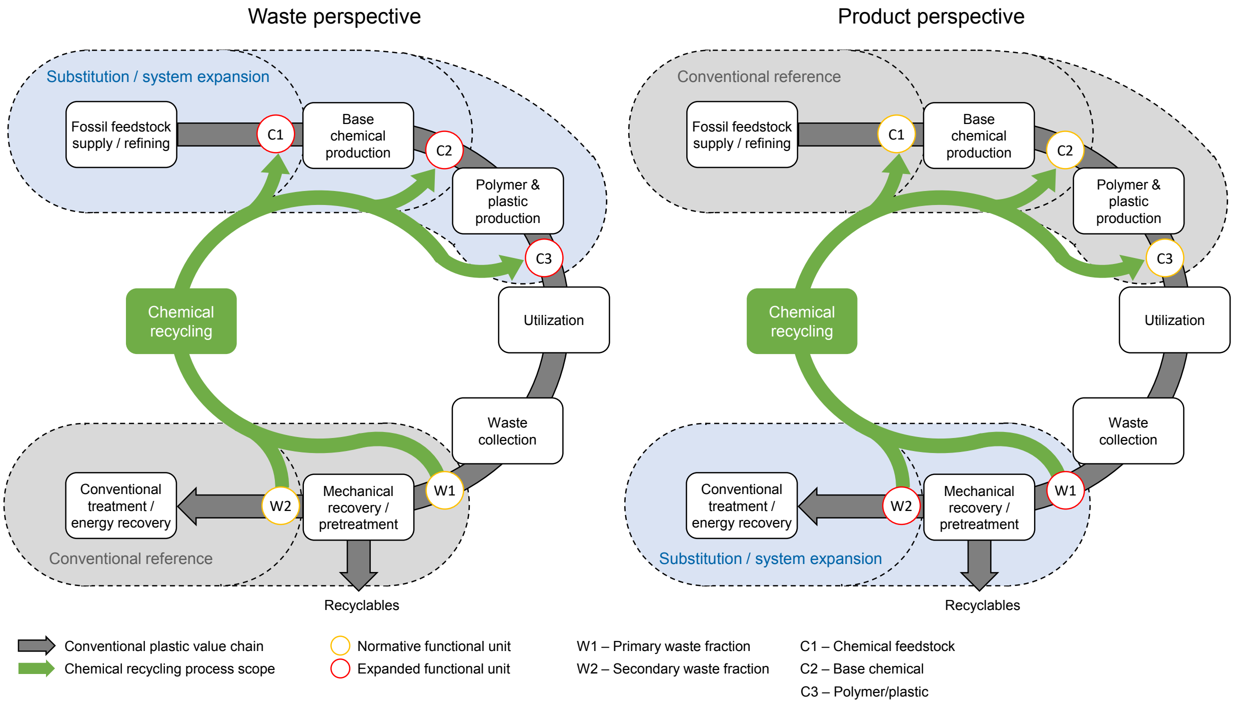

Figure 4: Illustration of waste and product perspective for chemical recycling [17]

Both perspectives can be assumed, with possibly significant differences in assessment results due to variations in considered processes. Exemplary, Jeswani et al. [76] apply a waste perspective and a product perspective in the assessment of mixed plastic waste pyrolysis. In the waste perspective, produced pyrolysis oil is assumed to substitute fossil naphtha, with the further naphtha utilization not being relevant in the assessment. In the product perspective, fossil naphtha supply is not considered, but a steam cracker balance for the production of ethylene from pyrolysis oil is included. The application of an end-of-life scope is most commonly applied in existing feedstock recycling LCAs (compare table 1). The application of a cradle-to-grave scope over the full life cycle is not useful for the assessment of feedstock recycling technologies, due to the high dissipation of base chemicals during subsequent chemical processing and the utilization of chemical products. Modelling the bridge between produced base chemical and applicable waste fraction can only be performed by significant simplification and assumptions, which influence the assessment results without a functional basis.

2.3. Attributional vs. consequential LCI modelling

Generally, there are two possible approaches to model life cycle inventories in attributional and consequential LCI. Both approaches are not in conflict, but rather should be applied to answer different questions. The difference is visualized in figure 5.

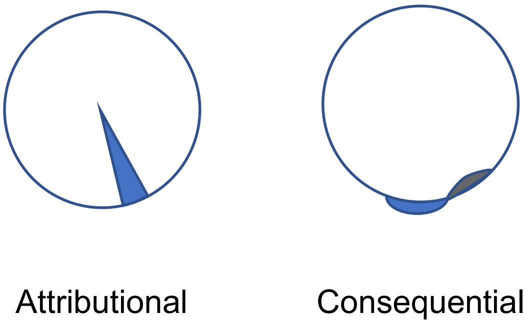

Figure 5: Visualization of the attributional and consequential modelling concept [95]

In attributional LCI, the aim is to describe relevant flows to and from a reference process and its associated processes under a normative rule. The approach is applicable to quantify the environmental impact and the distribution within the system, but is less suitable for perspective decision support. It addresses the question *“What part of the global environmental impacts is associated with a product or process?”* by describing the status quo of a defined system [96–98]. Practically, the concept is characterized by the application of average data for background processes, e. g. an average electricity production mix of a country. Secondly, allocation is applied to consider multifunctionality of processes. An application example is the mass balance approach [99, 100], which associates single products of a multi-output process (e.g. naphtha steam cracking) with fractional environmental burdens of the process with limited or no causality and independency.

In consequential LCI, the objective is the prediction of consequences of choices within a defined system based on developed scenarios, thereby addressing decision support. This requires a more complex modelling approach to reflect interactions of processes within the system and also associated markets. Consequently, the addressed questions is *“What effects on a defined system does a decision have?”* [96–98]. Practically, changing application of background processes (e. g. an increase in demand) is met by marginal processes instead of average processes. An example of the differentiation in terms of energy supply is given in chapter 3.6. Further, allocation of multifunctional processes is avoided by system expansion to include all associated processes that are affected by a decision. For the example of steam cracking, the focus is extended from the main products in ethylene and propylene to other products and their further processing (including hydrogen, C4 olefins and pyrolysis gasoline).

If marketed product quantities or qualities are subject to change, changes in the associated markets are considered as well, which requires the integration of economic aspects.

Attributional LCI modelling is applied for the majority of the reviewed investigations, with consequential LCI being applied in three cases. Faraca et al. [73] apply a marginal process mix for electricity substitution and perform a life cycle costing analysis for the pyrolysis of mixed plastic waste for crude oil substitution. Required conditions for positive net costs are discussed but no discrete market effect is considered. Generally, two prominent approaches are available for market impact modelling [101], each being applied once in the reviewed literature. Zhao and You [83] apply a partial equilibrium modelling approach to integrated the market impact of various pyrolysis-based products on an abstract level. Voss et al. [86] develop an discrete agent-based system model for an assessment framework of Germany to simulate a competitive market for MSW treatment between thermal treatment and gasification-based olefin production.

2.4. Inventory modelling consistency

Maintaining consistency in inventory modelling is essential to derive realistic and applicable results from LCA and to prevent false conclusions. Due to the generalized and interdisciplinary approach in LCA, detailed balancing and technological aspects are often neglected, but can have significant impact on the assessment results. Specific aspects with relevance for the assessment of feedstock recycling processes are highlighted in the following.

As for general waste treatment LCA, waste specific aspects are of critical importance. Waste fractions are not uniform, but vary significantly in their material and elementary composition, which impacts applicability to treatment processes and process balancing in terms of material and energy yields and emissions. Pyrolysis [64, 67, 73] and gasification [63, 66, 74] processes are balanced by generalized mass-based yields of pyrolysis oil and syngas from literature sources in multiple instances, despite differences in the applied waste compositions. Both gasification [102, 103] and pyrolysis [104, 105] product yields and compositions vary significantly depending on the applied feedstock. For thermal treatment, general benchmarks for electrical and thermal efficiency based on the feedstock heating value are commonly applied, despite significant impact of other waste characteristics, especially the waste moisture content [106].

The second focus point is feedstock recycling product substitution. Pyrolysis oil is assumed to substitute varying crude oil-based oil fractions and accounted accordingly. The substitution is most frequently assumed to be mass-based without consideration to compositional differences to applicable product qualities (e.g. naphtha for steam cracking) despite significant potential impacts on process performance, product yield and composition [107–110]. Only few investigations [76, 80, 81] consider upgrading in general and only one study includes detailed composition-based balancing [83]. Gasification is mostly assessed in context with subsequent processes for production of substitutable products (process chains). Few investigations [39, 74] consider syngas as a product with the H_2-CO ratio as the only quality criteria without consideration of other syngas components (e.g. CO_2, CH_4, N_2, H_2S) that impact downstream processing and applicability.

2.5. Prospective technology assessment

Conventionally, LCA is applied for the evaluation of impacts of mature and established technologies with known process characteristics (*retrospective LCA*). On the other hand, the deployment of LCA for emerging or developing technologies can be helpful to evaluate the future environmental impact to determine promising technologies and identify focus points for further development. The concept is considered as *prospective LCA* (also *anticipatory* or *ex-ante* LCA) [111–113]. Therefore, process data of technologies at lower development stages are adapted and applied. The main issues for conducting prospective LCA include general process data availability, compatibility, projected scaling of technologies at lower development stages and integration of uncertainty [112, 114]. For quantification of the technology development status, the *technology readiness level (TRL)* is commonly applied. For waste gasification and pyrolysis, no mature and widely implemented technologies are available, but a number of technologies are under advanced development or early implementation with TRL ranging from 6 to 9 [13]. For both process types, lower TRL primarily concerns the conversion technology itself, as processing and utilization processes are broadly technologically mature from developments in coal gasification and crude oil processing with experiences from bio-oil upgrading [115–118]. Buyle at al. [111] further expand on the TRL concept by emphasizing further technology development after commercial implementation due to large-scale technology learning and diffusion, indicated by TRL 9+. They propose a concept to assess emerging technologies in three time horizons that are reflected in the foreground system (including the technology in focus) and the background system: the current situation, the situation when the technology is mature for market implementation, and the situation when the technology is fully developed. The concept is especially relevant for gasification technologies, that benefit from technology scaling to high capacities (due to high temperature and pressure and feedstock input stabilization) and are expected to show significant development after initial large-scale implementation based on experiences with coal gasification technologies [103, 119].

Process data availability for validation and inventory modelling is generally worst at high TRL before commercialization, since costs for implementation rise from experimental work to pilot and demonstration facilities [112]. Different methods for inventory upscaling are proposed in literature depending on the TRL. For scaling from pilot (TRL around 7) to commercial applications, process modelling is considered the preferable option if data on process steps and conditions are accessible [111, 120]. Data compatibility refers to both foreground and background processes. In comparative assessments, applied processes inventories should reflect similar development stages. Background processes (e.g. for energy supply) should reflect the expected implementation time frame of the developed technology [121].

Consideration of uncertainty is a matter of both foreground (i.e. gasification and pyrolysis process characteristics) and background processes (e.g. relevant energy supply mix for implementation). Methods to incorporate uncertainty in LCA are sensitivity analysis (single parameter variation), scenario analysis (variation of parameter sets) and Monte Carlo analysis (stochastic simultaneous parameter variation with probability distribution) [112, 122]. In previous LCA investigations on feedstock recycling, various assessment parameters are addressed for uncertainty analysis, including material process parameter (conversion or product yield), process energy demand, product substitution and background energy supply. However, analysis is consistently performed by direct variation of abstract process indicators (e.g. product yield, cumulated energy demand). No reviewed investigation addresses variation of process-specific characteristics (e.g. process temperature) or consider their impact on the process balance (elementary and energy balance) to maintain consistency during variation, potentially leading to false assessment results (compare 2.4).

2.6. Conclusions for the applied methodology

In order to holistically evaluate the environmental impact of the application of feedstock recycling, two methodological approaches are applied. First, the impact of technology development and the background energy supply is addressed in a non-comparative attributional prospective LCA. The focus is placed on the gasification and pyrolysis process and the respective subsequent processing pathway individually, to enhance the understanding of environmental hotspots, the impact of technological shortcomings and benefits of technology enhancement under die condition of a continuously developing energy production system.

The second LCA study follows three objectives:

(1) Comparatively assess feedstock recycling in various syngas and pyrolysis oil application pathways in relation to conventional waste treatment and chemical production,

(2) Compare chemical recycling pathways to other developing chemical production processes for integration of renewable energy for emission reduction,

(3) Demonstrate the potential quantitative environmental impact on a large production system.

To approach these objectives, system expansion from the isolated feedstock recycling pathway is necessary. A systemic inventory model is applied that integrates relevant processes of waste treatment and base chemical production. Thereby, the multifunctionality of feedstock recycling can be met without a shift in perspective. To consider quantitative interdependencies between various produced base chemicals and available quantities of applicable waste fractions, the functional unit is extended from an incremental quantity (e.g. treatment of one kg of waste) to a cumulative quantity (e.g. treatment of total amount of waste fraction and production of total amount of base chemicals) for reference quantities of the annual production or treatment in Germany. The expansion approach further enhances the understanding of the total potential impact of feedstock recycling, which can be especially relevant for legislative decision-making to adapt policy to enhance the implementation of the most efficient technology for emission reduction.

The approach is not considered a consequential LCA due to two reasons. First, it does not describe the immediate consequences of a decision (e.g. the implementation of a single industrial facility), but the potential large-scale consequences of a systemic shift to a maximum extent. Second, market effects are intentionally not included. Feedstock recycling application does not immediately influence the supply or demand of reference products like arising waste streams for treatment or produced base chemicals. Markets for intermediate products like RDF or pyrolysis oil are highly dependent on applied political measures, e.g. the recognition of feedstock recycling as recycling processes, certification of feedstock recycling products or taxation of CO_2 emissions from incineration. To provide a process-based perspective with minimal influence of political frameworks, market integration is spared. Further, prospective technology parameter variation is not applied, since discrete developing timeframes of gasification, pyrolysis and other developing technologies are not addressed. Therefore, comparability in various development stages is not warranted. Instead, the methodology is considered as a *systemic potential LCA* under the assumption of complete technology development and maximum quantitative application.

Neither detailed and consistent process data of for gasification and pyrolysis processes at varying configurations is available, nor process data of conventional chemical production processes to enable the generation of conclusive and comparable process balances that are necessary for a systemic evaluation. Therefore, necessary inventories are generated by process modelling, which is described in the next chapter.

Chapter 3

Process description and modelling

In this chapter, relevant processes and technologies for the contextual evaluation of feedstock recycling are addressed. The applied depth of description and modelling is oriented on the objective to generate a range of representative process balances for life cycle inventory. Figure 6 displays an overview of involved the process pathways. Table 2 gives an overview of the individual processes described in the following. The addressed processes are considered mature processes with a large number of current industrial applications, with the exceptions of gasification, pyrolysis, pyrolysis oil hydroprocessing, methanol-based BTX aromatic synthesis (MTA), CO_2-based methanol synthesis and electric heating of steam cracking, catalytic reforming and steam reforming.

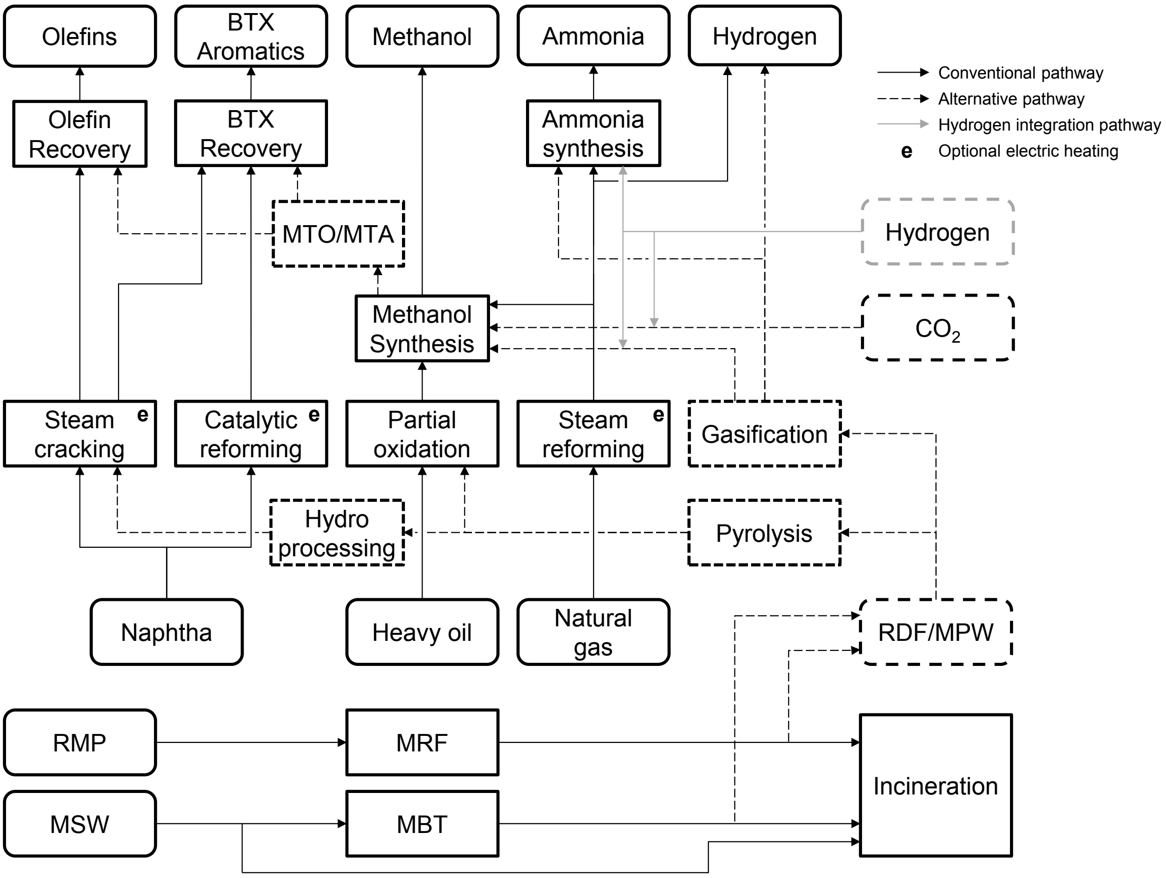

Figure 6: Visualization of processes and pathways for the contextual assessment of feedstock recycling

Table 2: Overview of applied chemical process models

Process	Feedstock	Main products
Steam cracking	Naphtha, LPG	Cracker gas (olefin-rich)
Olefin recovery	Olefin-rich gas	Ethylene, propylene, gasoline (BTX-rich), C4 olefins, Hydrogen, fuel oil, LPG, naphtha, fuel gas
Aromatic recovery	BTX-rich stream	BTX aromatics, Raffinate (paraffin-rich)
Steam reforming	Natural gas	Raw syngas
Partial oxidation	Fuel oil, pyrolysis oil	Raw gas
Quench & scrubber	Raw gas	Raw syngas
CO shift	Raw syngas	Converted syngas
Acid gas removal (physical)	Converted syngas	Syngas, Claus gas, CO_2
Acid gas removal (chemical)	Converted syngas	Syngas, CO_2
Carbon capture (chemical)	Flue gas	CO_2
Sulfur recovery (Claus)	Claus gas	Sulfur
Sulfur recovery (liq. ph.)	Off gas (H_2S-rich)	Sulfur
Methanol synthesis	Syngas (CO, CO_2, H_2)	Methanol
Ammonia synthesis	Syngas (N_2, H_2)	Ammonia
Catalytic reforming	Naphtha	Reformate (BTX-rich), Hydrogen, LPG, fuel gas
Methanol-to-Olefins (MTO)	Methanol	Product gas (olefin-rich)
Methanol-to-Aromatics (MTA)	Methanol	Reformate (BTX-rich), Hydrogen, fuel gas
Gasification	RDF, MPW	Raw gas
Pyrolysis	RDF, MPW	Pyrolysis oil, pyrolysis residue
Hydroprocessing	Pyrolysis oil	Naphtha / gasoline (BTX-rich), LPG, Hydrogen, fuel gas

The applied modelling approach of chemical reactors varies depending on the practically applied reactor type, the chemical reaction system, available reference models and the expected impact on the cumulated pathway balance. Reactor modelling is performed by the reproduction of validation data with the highest possible scale of industrial implementation, with the objective of closing data gaps (e.g. determination of energy balance, side product formation) and characterization of changing process conditions (if possible and necessary). Applied modelling approaches range from kinetic reaction models, equilibrium-based models to stoichiometric models. Equilibrium-based modelling was most frequently applied due to its versatility to reproduce industrial chemical reactor performance with limited detail data requirements (black box modelling), especially for catalytic and high-temperature reactors. If reproduction of product compositions is possible without or with limited equilibrium adjustment by approach temperature application (e.g. methanol and ammonia synthesis, methane steam reforming), the model can be applied to predict process characteristics with changing conditions (i.e. temperature, pressure, feed composition). If higher approach temperatures are necessary to fit validation data (e.g. MTO and MTA synthesis), the model is considered stiff and is applied for stationary reactor balancing with only minimal changes in reaction conditions, not for predictive model variation. If equilibrium-based modelling is not applicable (e.g. pyrolysis oil hydrotreating, catalytic reforming), the reaction system is approximated by fitting of individual reaction stoichiometry and conversions to balance the process mass and energy. Kinetic process models are applied for the steam cracking and hydrocracking processes. Applied Aspen Plus property models are shown in table S1. Detailed information on the applied equilibrium, kinetic and stoichiometric reaction systems is supplied in table S6 and following.

3.1. Feedstock recycling technologies

3.1.1. Gasification

Gasification describes the thermochemical process of converting solid carbonaceous feedstock into gas with a usable heating value, for chemical application preferably with significant contents in hydrogen and carbon monoxide [123]. The cumulated process consists of multiple conversion steps (drying, devolatilization, partial oxidation and combustion) that occur consecutively or simultaneously in a gasification reactor. The chemical process comprises a complex system of numerous chemical reactions, but the essential conversion of carbon to the major product gas components can described by the following reactions:

Carbon oxidation	$C + O_2 \rightarrow CO_2$	$\Delta H_R = -406$ kJ/mol	(1)
Boudouard reaction	$C + CO_2 \rightleftarrows 2\ CO$	$\Delta H_R = +160$ kJ/mol	(2)
Heterogeneous water-gas reaction	$C + H_2O \rightleftarrows CO + H_2$	$\Delta H_R = +119$ kJ/mol	(3)
Heterogeneous methanation	$C + 2\ H_2 \rightleftarrows CH_4$	$\Delta H_R = -88$ kJ/mol	(4)

The practical process implementation of gasification is diverse, mainly differentiated by the applicable feedstock and required pre-treatment, the regime of solid-gas contacting (fixed bed, fluidized bed or entrained flow), gasification agents (oxygen, carbon dioxide and/or steam), process heat supply (allothermal or autothermal), configuration of gasification and gas refining stages and process conditions (temperature and pressure).

For syngas generation from RDF, fixed-bed gasification with liquid slag discharge (BGL type) is considered in this investigation, due to its applicability with a wide range of waste-based feedstock with manageable demand on preprocessing, including low-calorific RDF generated from municipal solid waste, and advantageous gasification performance characteristics, including high syngas yield, feasibility of high gasification pressure up to 40 bar and recovery of inert feedstock components in a glassy, non-leachable slag. The technology was developed for coal gasification and initially applied on industrial scale at SVZ Schwarze Pumpe for the production of methanol from a mixture of RDF, plastic waste, wood, tar, sludge and coal [103, 124–126]. The technology is further developed and demonstrated at IEC as FlexiSlag technology with the main objectives to enable the application of unblended waste-based feedstock, increase process reliability and improve syngas quality (tar-free and low methane content) [127].

For the presented investigation, a generic waste gasification process based on the BGL technology with a downstream secondary gasification stage is assumed. The concept is visualized in figure 7. Gasification feedstock is entered at the reactor top and contacted with the gasification agent counter-currently, which is introduced near the bottom of the bed via tuyère nozzles. The gasification reaction is a non-catalytic, autothermal reaction with the reaction heat being generated by partial oxidation of the gasification feedstock. Mineral and residual metal components exit the reactor vessel at the bottom, heated and melted with a ring burner and discharged via a slag quencher. The reactor shell includes a steam jacket to recover process heat in form of steam. Primary raw gas exits the primary gasifier at the top and enters a secondary reaction stage with gasification agent injection in a downdraft reactor, similar to a gas-based POX reactor. By increasing the reaction temperature via partial oxidation, the product gas quality is improved (lower methane content, higher syngas yield and H_2-CO ratio) [123, 128]. To be applicable for fixed-bed gasification, waste feedstock requires compacting or pelletization to maintain a suitable energy density for the feeding and pressurization system. For downstream ammonia production, air is partially applied as gasification agent in the secondary stage for stoichiometric nitrogen supply.

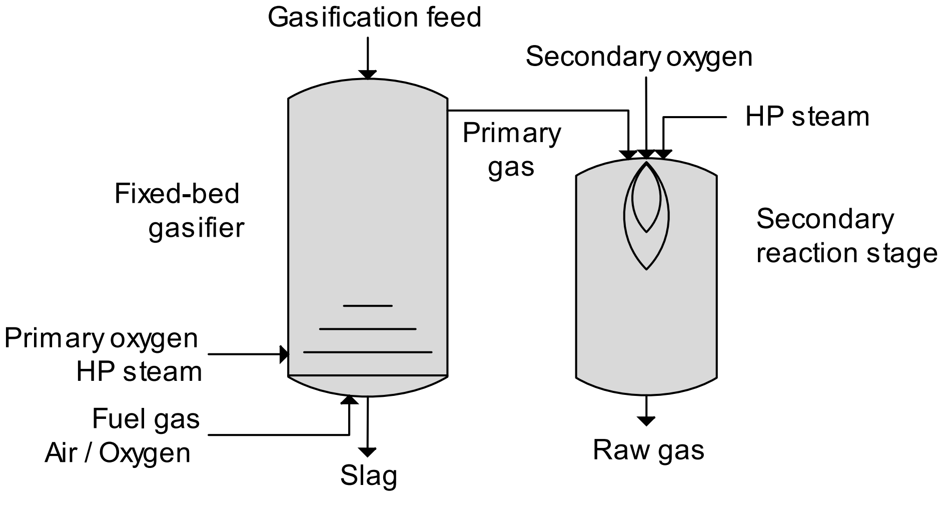

Figure 7: Visualization of the generic BGL waste gasification process

Table 3: Modelling assumptions for waste gasification [103, 129, 130]

Reaction modelling approach	3 stage adapted equilibrium
Temperatures	
Raw gas primary stage exit	750 °C
Raw gas secondary stage exit	1100 °C
Pressure	40 bar
Oxygen purity	99.5 vol.-%
Steam-oxygen ratio	0.9 kg / m^3 (STP)
Burner fuel gas	2.6 m^3 (STP) / t feed
Flushing gas input (CO_2)	16 m^3 (STP) / t feed
Dust formation in primary raw gas	20 g / m^3 (raw gas, STP, wf) 82 wt.-% carbon
Tar formation in primary raw gas	10 g / m^3 (raw gas, STP, wf)
Conversion in secondary reactor	100% (tar) / 99% (carbon in dust)
Residual carbon content in slag	1.0 wt.-%
Heat loss	1.5 % of LHV input 50% in secondary reactor (to surrounding air) 35% to primary reactor steam jacket 15% to primary reactor nozzle cooling (cooling water)
Pelletization electricity demand	77 kWh / t feed [131]

Prospective performance variation

To evaluate the impact of the applied technology development level for the gasification process, possible performance shortcomings are discussed and adapted for modelling and balancing implementation. A number of technology issues for waste gasification technologies are discussed in [103, 132]. For BGL gasification applications, these include raw gas outlet blocking by condensing volatiles, tuyère nozzle blacking and slag outlet solidification, which can lead to decreased running time or immediate shutdown of the gasifier operation overall. While this compromises the temporal availability of the facility (i.e. the profitability of the system), it does not impact the stationary input-output balance of the gasifier operation. Other occurring, quantifiable criteria for process performance level include the specific heat loss, carbon conversion and syngas yield.

The specific heat loss is defined as the total heat loss of the gasifier system specific to the introduced enthalpy of the gasification feedstock on lower heating value (LHV) basis (see equation (5)). For a built gasifier, the total heat loss depends on the process temperature and the outer heat transfer surface. Since both variables do not significantly change during operation, so does the total heat loss. However, the introduced enthalpy rate of the waste feedstock can be limited by the achievable feeding rate and low waste density, especially for high plastic contents, thereby leading to an increasing specific heat loss. A higher specific heat loss can also be expected for smaller reactors due to a higher ratio of reactor surface to volume. Therefore, the specific heat loss is applied as a cumulated parameter for a number of gasification reactor sizing and performance aspects with no further impact on the input-output balance of the process.

Specific heat loss $$Q_{loss,spec}=\frac{\dot{Q}_{loss,total}}{\dot{m}_{Feed}\cdot LHV_{Feed}} \quad (5)$$

Other gasification performance parameters include the conditions of the secondary gasification stage and the carbon residue in the bottom slag. A secondary gasification stage was so far not demonstrated for BGL gasification, therefore its characterization is hypothetical at this point. Under the assumption that the residence time is sufficient to approach a thermodynamic equilibrium, a gas outlet temperature of 1050 °C is enough to achieve a residual content of methane below 1 vol.-% in the product gas for a design pressure of 40 bar. For a practical application, higher process temperatures are likely necessary to overcome kinetic limitations of methane conversion, but have not been investigated until now. Further, nearly complete conversion of carbon in raw gas fly ash is assumed. An important aspect to consider in high-temperature gasification is the agglomeration and melting of ash components in solid particles, which can lead to fouling and clogging within the reactor [103]. To avoid this, limitation of the secondary gasification temperature can be necessary, which leads to a higher gas methane content and incomplete fly ash carbon conversion. In any case, the application of a secondary gasification stage is assumed to lead to complete conversion of higher hydrocarbons in form of tar/oil that are present in the primary raw gas. Secondly, carbon conversion of BGL gasification is limited by unconverted carbon residues in the bottom slag, which can be impacted by slagging burner performance.

For overview purposes, technology level scenarios are defined, differentiated between material efficiency (high efficiency M; low efficiency m) and energy efficiency (high efficiency E; low efficiency e) (see table 4). The defined basic case reflects the gasification technology in a development status at lower capacity and without a secondary reactor stage.

Table 4: Modelling assumptions and process characteristics for BGL gasification for varying implementation case, based on [103, 126, 129, 130, 133]

		Gasif (basic)	Gasif (E-M)	Gasif (e-M)	Gasif (E-m)	Gasif (e-m)
Material efficiency		basic	high	high	low	low
Energy efficiency		low	high	low	high	low
Modelling assumptions						
Specific heat loss (LHV-based)		5.0%	1.5%	5.0%	1.5%	5.0%
Slag carbon content [weight fraction]		1.0%	1.0%	1.0%	4.0%	4.0%
Fly ash carbon conversion		-	99%	99%	50%	50%
Temperature of secondary gasification [°C]		-	1100	1100	950	950
Gasification agent						
Oxygen	[m^3 (STP) / kg (waf)]	0.29	0.49	0.54	0.39	0.44
Steam	[kg / kg (waf)]	0.26	0.43	0.48	0.36	0.39
Results						
Gas exit temperature	[°C]	750	1100	1100	950	950
Carbon conversion		96.4%	99.5%	99.5%	96.5%	96.5%
Syngas yield	[m^3 (STP) / kg (waf)]	0.90	1.76	1.68	1.44	1.43
Cold gas efficiency		80.2%	79.8%	75.8%	81.1%	77.1%
CH_4 content	[vol.-%, wf, N_2-free]	19.9	0.8	0.6	7.9	6.5

Restrictions on applicable waste feedstock

A technological limitation for feedstock applicability in BGL gasification is the solidification of the slag bath due to a lack of combustible components reaching the bottom of the gasifier. This is especially critical for plastic-rich waste fractions with a low content of fixed carbon [134]. A correlation of applicability to the waste fixed carbon content is expected, but the effect has not been investigated quantitatively. Therefore, an estimation is performed based on the described equilibrium-based gasification model. In addition to the framework shown in table 3, modelling assumptions include flux addition to maintain a feedstock mix ash content of 30 wt.-% and oxygen supply to the slag bath at an equivalence ratio of 1.6. It is assumed that fixed carbon is only converted in the oxidation zone at the gasifier bottom. Based on the described modelling assumptions, a combustion zone temperature can be calculated, which is targeted to be above 1800 °C, i.e. at least 300 K above the highest assumed melting temperature of mineral contents at 1500 °C [133]. A binary mixture of the applied waste fractions RDF and MPW (see table 28) is investigated. A combustion zone temperature for 100% RDF is calculated to be 2690 °C and 1360 °C for 100% MPW. For a mix of 75 wt.-% MPW and 25 wt.-% RDF, an oxidation zone temperature of 1850 °C is calculated. Based on that, 75 wt.-% is considered the maximum MPW content in an RDF-MPW mixture in this investigation.

3.1.2. Syngas conditioning and purification

Raw gas from gasification, partial oxidation or reforming processes is not directly applicable for chemical synthesis, but requires conditioning and purification. The respective processing steps depend on the composition and contamination of raw gas, as well as the requirements of the subsequent synthesis process. An overview of typical syngas qualities for typical syngas-based processes is given in table 5. Raw gas conditioning and purification generally comprises the following main process steps: raw gas quench and water scrubbing, CO shift, acid gas removal and sulfur recovery. Modelling assumptions and literature sources for process design and validation are shown table 6.

Table 5: Typical syngas quality requirements [135]

Components	Methanol synthesis	Fischer-Tropsch synthesis	SNG synthesis	Ammonia synthesis
CO	30 -32 vol.-%	30 -32 vol.-%	25 vol.-%	< 5 ppm
H_2	64 - 68 vol.-%	64 - 68 vol.-%	75 vol.-%	75 vol.-%
CO_2	compatible	compatible	compatible	< 10 ppm
CH_4+Ar	< 4 vol.-% (incl. N_2)	< 5 vol.-% (incl. N_2)	< 2 - 3 vol.-% (excl. CH_4)	< 0.4 vol.-%
H_2O	inert	-	-	< 0.1 ppm
Sulfur components	< 0.1 mg/m³ (STP)	< 0.1 ppm	< 0.4 mg/m³ (STP)	<< 1 mg/m³ (STP)
Alkali metals	< 0.2 mg/m³ (STP)	< 10 ppb	< 1 mg/m³ (STP)	-
Dust	< 0.2 mg/m³ (STP)	0 mg/m³ (STP)	< 0.5 mg/m³ (STP)	-

Raw gas cooling and cleaning

Gasification and partial oxidation processes require initial gas cooling and removal of solid particles (fly ash), tar/oil loads and water-soluble gas components (especially HCl, NH_3) before further gas processing. Various process configurations can be applied within or subsequent to the gasification reactor, depending on the conversion process (especially the gas temperature), the carried contaminants and the intended gas utilization, including dry processes (including radiant and convective gas cooler; gas filter and cyclones) and wet processes (including water quench and scrubber) [103, 136, 137]. In the present investigation, a configuration based on spray quench and gas scrubber is assumed.

The primary water quench in practical applications is integrated in in the bottom of POX or secondary gasification reactors. In case of gasification without a secondary reaction stage, the quench is realized as a separate quench vessel in form of a wash cooler. After the quench, raw gas is introduced in a staged countercurrent water scrubber with a separate recycle. Wash water is recirculated over both steps. Fresh water is introduced in the scrubber to maximize syngas purity. Purged water from the scrubber cycle (grey water) is applied as quench water.

Bottom water from the quench (black water) is cooled and solved gas fractions, tar/oil and solid residues are recovered by decompression and multi-stage phase separation. The recycle water pH value is adjusted by caustic addition. Chloride loading in the water cycle is limited by waste water extraction.

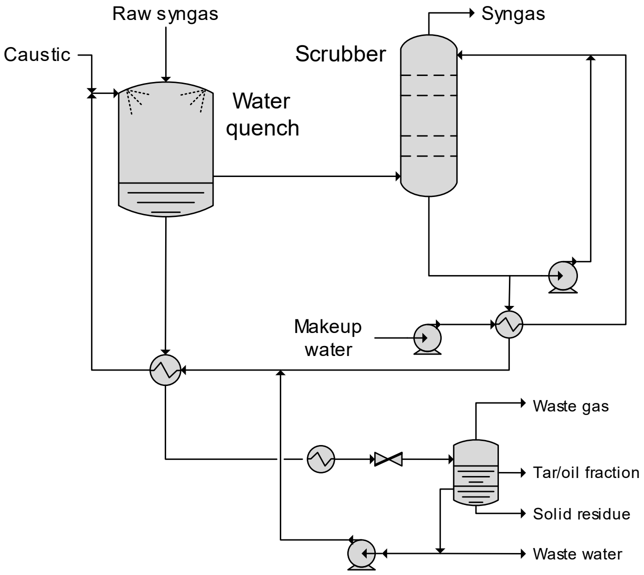

Figure 8: Visualization of the water quench and scrubber process

CO shift

The H_2-CO ratio of syngas is adapted by application of the homogeneous water-gas shift reaction shown in equation (6). The process is performed by application of catalytic adiabatic reactors, but its implementation in terms of the number of applied reactors, catalyst type and material and energy integration (especially reactor bypass and steam balancing) depends on the composition of the applied raw gas and the intended syngas utilization. Generally, the process configuration can be differentiated between a sweet shift type, which applies mixed oxide-based catalysts with high activity but low sulfur tolerance to enable low residual CO content below 0.5 vol.-%, and a sour shift type, that applies low-activity but sulfur-resistant sulfide-based catalysts with CO residuals between 2 and 4 vol.-% [124, 135, 138]. Due to recent technology developments, configurations with sulfur-tolerant catalysts with high activity are industrially available e.g. for coal-to-hydrogen applications [139, 140]. Secondary aspects of CO shift application include the removal of traces of COS and HCN by hydrolysis to avoid downstream syngas poisoning (see equations (7) and (8)), either as co-occuring reactions or in a separate reactor [124].

Homogeneous water-gas reaction $CO + H_2O \rightleftarrows CO_2 + H_2$ $\Delta H_R = -41$ kJ/mol (6)

COS hydrolysis $COS + H_2O \rightleftarrows CO_2 + H_2S$ $\Delta H_R = -34$ kJ/mol (7)

HCN hydrolysis $HCN + H_2O \rightleftarrows CO + NH_3$ $\Delta H_R = -51$ kJ/mol (8)

The applied process model shown in figure 9 includes two-staged catalytic conversion in adiabatic fixed bed reactors applying a sulfur-tolerant catalyst with high CO conversion. The resulting H_2-CO ratio is adjusted by a bypass stream around the catalytic converters, the extend depends on the raw gas composition and the type of synthesis gas utilization. COS and HCN hydrolysis are assumed to occur in-situ with the shift reactors and in a separate reactor in the bypass stream. The CO shift unit significantly impacts the syngas-based plants energy balance, as steam is consumed (HP steam for syngas saturation) and produced (HP steam in intercooling between shift stages, LP steam in shifted syngas cooling) at considerable margins.

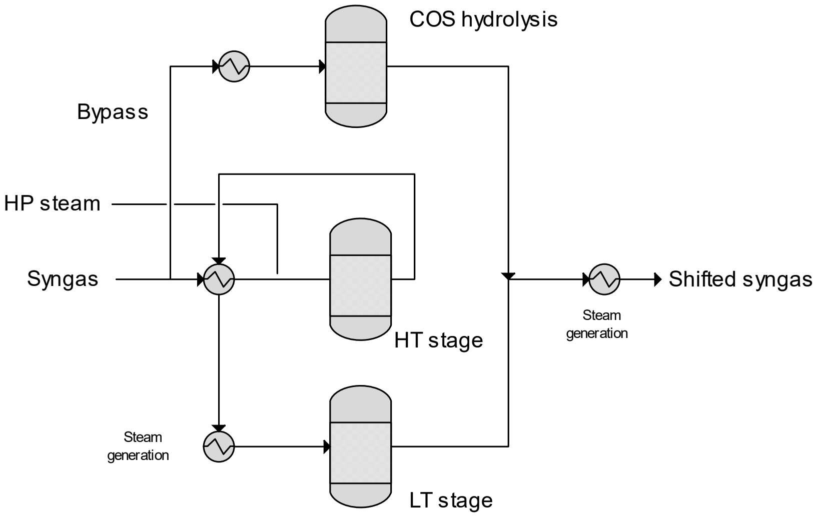

Figure 9: Visualization of the CO shift process

Acid gas removal

Sour gases (especially CO_2 and H_2S) must be removed before syngas utilization. Absorption processes are most widely applied for syngas purification, with a wide range of possible technologies that vary in absorption mechanism (chemical, physical or mixed), the absorbent substance and the process configuration [116]. For large-scale industrial applications with syngas with significant H_2S content and high pressure (especially in coal gasification applications), selective physical absorption with cryogenic methanol (Rectisol-type process) is most widely applied. The process provides a high-purity syngas free of trace components including NH_3, COS, HCN and higher hydrocarbons and enables the H_2S recovery in a separate stream at high concentration (Claus gas) for efficient downstream sulfur recovery. CO_2 is recovered in high purity (below 5 ppm sulfur content, further referred to as concentrated CO_2) and can be applied as flushing or feeding gas or as feedstock in PTX applications. The main drawback of the Rectisol process is a significant electricity demand for cryogenic cooling of methanol absorbent [141–143]. For small-scale gasification applications and low-sulfur feedstocks, but also for CO_2 capture from flue gases, chemical scrubbing agents like amine solutions are commonly applied with downstream residual gas desulfurization for the off-gas. Various types of amines can be utilized depending on the gas composition and the application type with differences in absorption rate, heat of reaction, H_2S absorption selectivity and suitability for COS removal. The process is less complex than the Rectisol process, but requires significant amounts of low-temperature heat for thermal amine regeneration [116, 144, 145]. The applied process concepts are visualized in figures 10 and 11.

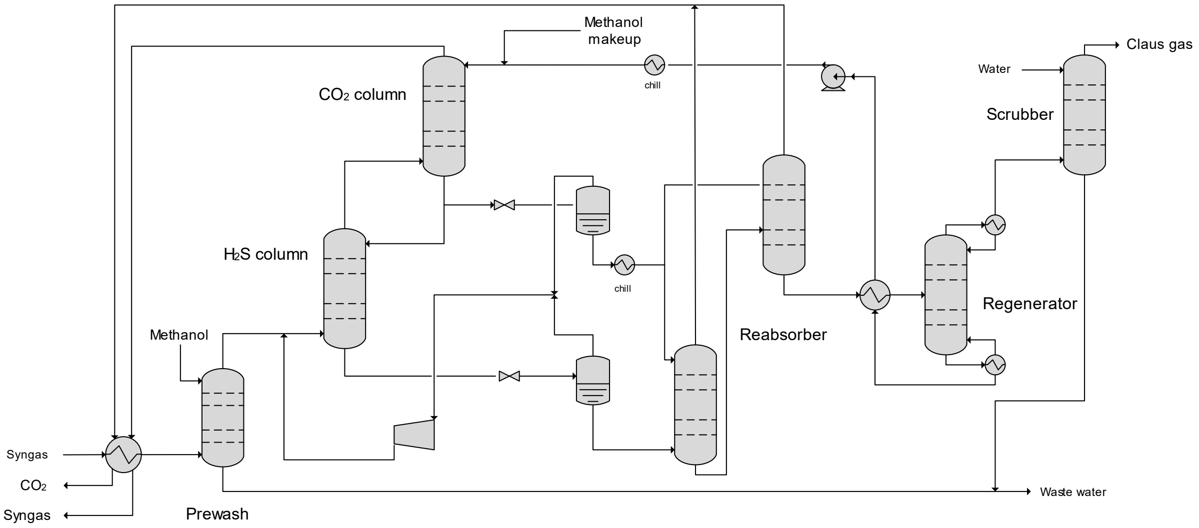

Figure 10: Visualization of the physical absorption process (based on [146])

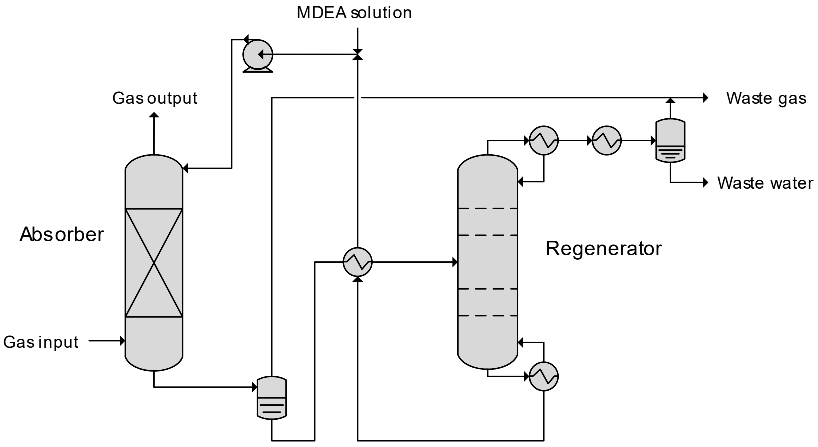

Figure 11: Visualization of the chemical absorption process (based on [147])

Sulfur recovery

Sulfuric compounds in syngas need to be recovered to avoid their emissions in accordance with pollutant emission legislation [148]. For H_2S separated from syngas at a concentration of at least 5 vol.-%, it can be converted to elemental sulfur via a Claus process and can further be used as a raw material in the chemical industry. The conversion takes place in a thermal stage (equations (9) and (10)) and at least two adiabatic catalytic stages (equation (11)) for sulfur production with intermittent cooling and sulfur condensation.

$$H_2S + 1.5\ O_2 \rightleftarrows SO_2 + H_2O \qquad \Delta H_R = -518\ \text{kJ/mol} \qquad (9)$$

$$H_2S + 0.5\ O_2 \rightleftarrows 0.125\ S_8 + H_2O \qquad \Delta H_R = -209\ \text{kJ/mol} \qquad (10)$$

$$2\ H_2S + SO_2 \rightleftarrows 0.375\ S_8 + 2\ H_2O \qquad \Delta H_R = -109\ \text{kJ/mol} \qquad (11)$$

The Claus process can be applied in various configurations depending on the feed gas H_2S content and the desired tail gas integration. If the H_2S content is above 50 vol.-%, the process is carried out as a full-flow process, with the entire feed gas stream being converted in the thermal stage via partial oxidation. Below 50 vol.-%, a partial bypass flow around the thermal process stage and stoichiometric oxidation is applied to achieve the necessary temperature in the furnace. Below 25 vol.-%, partial oxygen application instead of air is required. Further, tail gas treatment after the second catalytic reaction stage is necessary to achieve a sufficient sulfur recovery (above 99.5 %). In the considered process configuration (shown in figure 12), a third catalytic stage is applied that is operated below the sulfur dew point on a sulfur-resistant catalyst. Therefore, the practical operation requires frequent catalyst regeneration, which is not considered in the simulation [116, 135, 149].

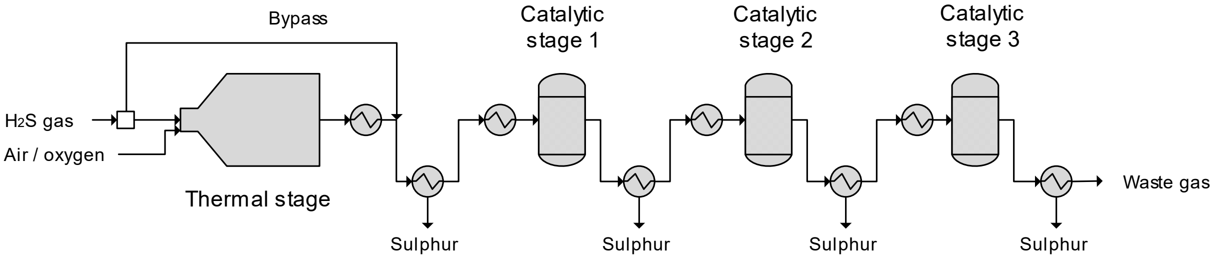

Figure 12: Visualization of the Claus process

For low-sulfur off-gas desulfurization, liquid-phase redox processes for the direct conversion of H_2S to elementary sulfur are preferable. In the present investigation, an iron chelate-based redox process is assumed as reference [116, 149, 150]. Due to the significant modelling complexity and limited impact on the overall process balance, the process is not modelled in detail but considered by KPIs.

Table 6: Modelling assumptions and literature sources for syngas cleaning and conditioning

Water quench and scrubber [124, 135]		
Temperature		
Quench water preheating	150 °C	
Syngas after scrubber	200 °C	
Pressure	Depending on raw syngas	
Maximum chloride content in water cycle	2000 ppmw	
Minimum pH value in quench water	5.0	
Maximum solid loading in quench water	3 wt.-%	
Scrubber stage number	4	
Scrubber water cycle purge	10 %	
CO shift [135]		
Reaction modelling approach	Adapted thermodynamic equilibrium	
Steam/dry gas ratio (molar)	1.5	
Entry temperature HT/LT stage	280 / 180 °C	
Physical absorption (Rectisol) [146]		
Methanol solvent feed temperature	- 60 °C	
Columns stage number: Prewash / H_2S column / CO_2 column	5 / 12 / 18	
Reabsorber pressure stages	3.5 / 1.3 bar	
Regenerator head temperature	30 °C	
Regenerator pressure	3.0 bar	
Chemical absorption [116, 147]		
MDEA solvent feed temperature	30 °C	
MDEA concentration	30 wt.-%	
Regenerator reboiler temperature	120 °C	
Regenerator pressure	1.75 bar	
Regenerator solvent loading ratio	3.0	
Column stage number absorber/ regenerator	20 / 20	
Claus process [116]		
Reaction modelling approach	Thermodynamic equilibrium	
Temperature thermal stage	1200 °C	
Excess air ratio full / partial stream configuration	0.33 / 1	
Input temperature catalytic stages	300 / 250 / 140 °C	
Sulfur recovery	99.5 %	
Selective sulfur liquid phase oxidation process [116]		
Electricity	3.7	kWh / kg H_2S
Process water	11.3	kg / kg H_2S
Sulfur recovery	99.5 %	

3.1.3. Pyrolysis

Pyrolysis describes the thermochemical process of decomposition of carbonaceous feedstock by application of heat without a chemical reaction agent. Products include gaseous, liquid and solid fractions with varying yield and composition depending on the feedstock and the reaction conditions including temperature, pressure, residence time and catalyst application [151, 152]. In the context of chemical recycling, pyrolysis is primarily applied for plastic-rich waste fractions to generate pyrolysis oil as a chemical feedstock. A number of pyrolysis technologies are currently under development or in early industrial implementation stage with technological differences in operation mode (continuous or batch operation), reactor type and heat supply, waste feeding and the catalyst application. Most developments focus on the conversion of primarily polyolefinic mixed waste fractions with limited contents of other plastic types (especially PET and PCV) or non-plastic fractions, which leads to reduced process complications in terms of reactor corrosion and fouling and the production of high-quality product oil, but restricts the availability of suitable feedstock and demands high effort for mechanical waste pretreatment [13, 153–155].

In the present investigation, the Carboliq technology [156, 157] is applied as reference pyrolysis technology, due to the availability of reference process data for RDF and mixed plastic feedstock. The technology is based on the KDV technology [158] and is one of few pyrolysis processes with demonstrated applicability of RDF at demonstration plant scale or above [13]. The catalytic liquefaction process applies low pressure and temperature, as process energy is introduced by means of a slurry turbine, generating heat by friction. The feedstock is preconditioned and introduced in circulating oil with dispersed catalyst. Product oil is extracted from the circulating oil as vapor, heavy and solid components are extracted by sedimentation. The process scheme is shown in figure 13.

Waste pyrolysis is experimentally examined in numerous investigations [159–162]. Process characteristics (i.e. energy demand, product yield and composition) vary significantly, especially depending on the applied feedstock and reactor and reaction type (i.e. catalytic/non-catalytic; process heating regime). Applicable simulation investigations in terms of feedstock and product composition addressed in this investigation are not available. Therefore, predictive modelling of pyrolysis processes of RDF for liquid production is considered not possible. The pyrolysis process inventory generation is thus based on process balancing with validation data of an existing pyrolysis facility.

Process balancing ist performed for steady state operation and consistency of mass, main elements (C, H, O, N, Cl, S and inerts) and energy under the following assumptions:

- Constant oil composition and variable oil yield;
- Constant waste gas composition and yield;
- Constant catalyst and limestone input;
- Adjusted water yield to satisfy elementary balance;
- Calculated yield and composition of solid residue;
- Adjusted electricity input for heat demand (electricity to heat efficiency of 1assumed);
- Calculated pyrolysis reaction enthalpy.

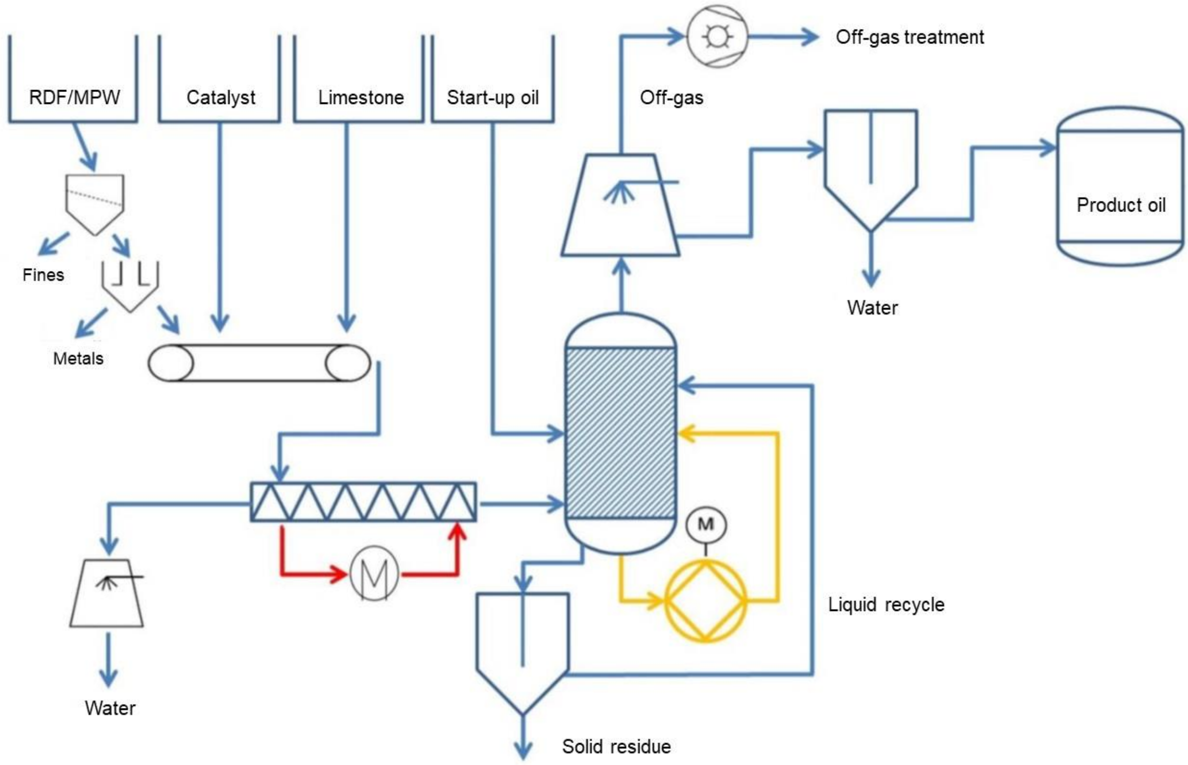

Figure 13: Visualization of the Carboliq process (adjusted from [163])

Table 7: Balancing assumptions and results for pyrolysis of RDF and MPW [164, 165]

			RDF	MPW
Inlet temperature	°C	Reported	150	150
Outlet temperature	°C	Reported	350	350
Input				
Catalyst	kg / t feed	Reported	20	20
Limestone	kg / t feed	Reported	5	5
Electricity	kWh / t feed	Adjusted	310	422
Steam	MJ / t feed	Calculated	345	345
Output				
Pyrolysis oil	kg / t feed	Adjusted	500	750
Solid residue	kg / t feed	Calculated	281	125
Waste gas	kg / t feed	Reported	50	70
Waste water	kg / t feed	Adjusted	114	30
Metals & fines	kg / t feed	Reported	30	0
Residue composition		Calculated		
Carbon	wt.-%		23.56	40.05
Hydrogen	wt.-%		2.66	16.21
Nitrogen	wt.-%		1.13	10.60
Oxygen	wt.-%		37.01	12.53
Chlorine	wt.-%		2.07	0.37
Sulfur	wt.-%		0.57	0.23
Ash	wt.-%		33.00	20.00
Sum	wt.-%		100.00	100.00
Lower heating value	MJ/kg		9.54	26.76

Prospective performance variation

To evaluate the impact of process inefficiencies, two relevant process variables in RDF pyrolysis are varied in liquid product yield and process energy demand, based on the balancing assumptions described prior. Process consistency requirements for mass, elements and energy are maintained during variation. Liquid yield of the KDV process of a similar feedstock is reported to be 0.35 [158], which is significantly lower than reported yields of the Carboliq process. Instead of direct variation of electricity input, the reaction temperature is varied to 450 °C in order to ensure realistic parameter variation. The calculated pyrolysis reaction enthalpy is maintained during variation. Calculation results are shown in table 8. Similar to gasification, technology level scenarios are applied.

Table 8: Calculation results of parameter variation of RDF pyrolysis process

Case		Pyr (E-M)	Pyr (E-m)	Pyr (e-M)	Pyr (e-m)
Material efficiency		high	low	high	low
Energy efficiency		high	high	low	low
Mass liquid yield	kg / t feed	500	350	500	350
Temperature	°C	350	350	450	450
Electricity demand	kWh / t feed	310	234	370	291
Residue composition					
Carbon	wt.-%	23.56	40.32	23.56	40.32
Hydrogen	wt.-%	2.66	6.77	2.66	6.77
Nitrogen	wt.-%	1.13	0.71	1.13	0.71
Oxygen	wt.-%	37.01	31.27	37.01	31.27
Chlorine	wt.-%	2.07	1.24	2.07	1.24
Sulfur	wt.-%	0.57	0.37	0.57	0.37
Ash	wt.-%	33.00	19.33	33.00	19.33
Sum	wt.-%	100.00	100.00	100.00	100.00
Lower heating value	MJ/kg	9.54	17.10	9.54	17.10

3.1.4. Pyrolysis oil hydroprocessing

Primary product oil from liquefaction processes varies widely in its properties. This affects its applicability and upgrading demand. Characteristics include:

- High contents of unsaturated hydrocarbons (especially mono and polycyclic aromatics, olefins, naphthenes),
- Wide boiling range (up to approximately 400 °C),
- Low hydrogen-carbon ratio,
- High contents of hetero atoms (especially oxygen, nitrogen, sulfur, chlorine, metals) depending on applied feedstock and pretreatment,
- Low heating value (compared to saturated hydrocarbons).

In view of naphtha quality requirements (compare table 32), primary pyrolysis oil is generally not applicable directly as steam cracker feedstock. Objectives for oil upgrading are the removal of hetero atoms, hydrocarbon saturation and ring opening and boiling range adjustment to achieve steam cracker specifications [107–110, 166]. Literature sources concerning experimental, modelling or large-scale applications of hydrotreating of aromatic-rich oils to naphtha-equivalent products is scarce [109]. Compared to conventional oil upgrading applications for fuel production from conventional heavy residue or bio crude, upgrading to steam cracker feed requires significant aromatic saturation and hydrocracking of middle distillate fractions. Nevertheless, process technologies are commercially available (e.g.

PureStep technology by Haldor Topsoe, Rewind Mix by Axens [167–169]). Alternatively, hydrotreated pyrolysis oil is applicable for BTX recovery. Already rich in aromatic compounds, it is possible to selectively convert olefinic and polyaromatic compounds and increase the BTX yield by means of hydrotreating catalyst selection [170, 171].

The considered process configuration comprises four process steps [172, 173], visualized in figure 14. Commercial process units for oxygen-rich oils (e.g. bio oils) include an initial catalytic hydrodeoxygenation reactor (HDO) for oxygen compound removal [118, 174, 175]. Feed oil is further catalytically hydrotreated (HTR) in hydrogen atmosphere for saturation and hydrogenation of hetero atoms. Aromatic saturation is highly exothermic and associated with significant hydrogen demand. Therefore, staged hydrotreating with intermittent cooling is necessary. The intercooling temperature level is high enough to be applicable for reboiler heating of the fractionation column. In the applied process model, hydrotreating is not modelled in detail, but as a cumulated stoichiometric reaction set. Formed waste gas components and CO_2 are removed from the gas fraction by amine scrubbing. Naphtha and LPG are separated in a fractionation step. Heavier oil fractions are recycled to a catalytic hydrocracking step (HCR). By kinetic modelling of the hydrocracking reactions the resulting product fraction ratio (Fuel gas, LPG, naphtha) depending on the feed composition and reaction conditions is considered. Table 10 shows the calculated hydrogen consumption for the processing of the assessed pyrolysis oils from RDF and MPW (compare table 32) to naphtha equivalent. The specific hydrogen demand for RDF-based pyrolysis oil is nearly twice as high due to a higher oxygen and aromatic content, but MPW-based pyrolysis oil displays a higher hydrogen demand for hydrocracking due to the higher fraction of heavy components.

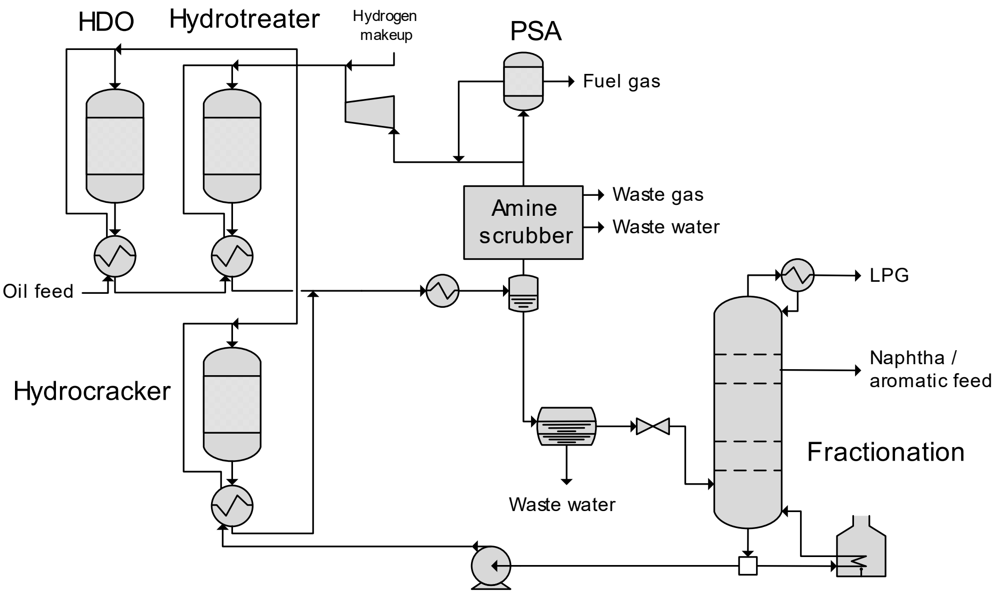

Figure 14: Visualization of pyrolysis oil hydroprocessing

Table 9: Modelling assumptions and literature sources for pyrolysis oil hydroprocessing

	Hydrotreater	**Hydrocracker**
Reaction modelling approach	Stoichiometric reactions with adapted conversion	Kinetic model [176, 177]
Reactor heat regime	adiabatic	adiabatic
H_2 - feed ratio	200 m^3/m^3 liquid	1000 m^3/m^3 liquid
Reactor inlet temperature	320 °C	360 °C
Reactor inlet pressure	75 bar	75 bar
Sources	[171, 172]	[117, 178, 179]
Pyrolysis oil product fractionation		
Stage number	25	
Bottom temperature	270 °C	
Naphtha exit temperature	180 °C	

Table 10: Specific hydrogen consumption for hydroprocessing of pyrolysis oil to naphtha

Pyrolysis feedstock		Total	HDO	HTR	HCR
RDF	[kg H_2 / t pyrolysis oil]	36.9	6.7	24.8	5.4
	Fraction	100%	18%	67%	15%
MPW	[kg H_2 / t pyrolysis oil]	22.1	5.4	7.7	9.0
	Fraction	100%	24%	35%	41%

3.2. Chemical production technologies

The chemical industry is subdivided into base chemical production and fine and pharmaceutical production. While fine chemicals are diverse and the main driver for financial valorization, a small number of organic base chemical production processes are associated with the major impact in terms of energy demand and greenhouse gas emissions [11, 180, 181]. Characterizing the main products (lower olefins, BTX aromatics, methanol, ammonia and hydrogen) and their main production processes (steam cracking, catalytic reforming, steam reforming and partial oxidation) is therefore essential in order to evaluate possible alternatives with significant impact. An overview of major petrochemical products and their production pathways is shown in figure 15.

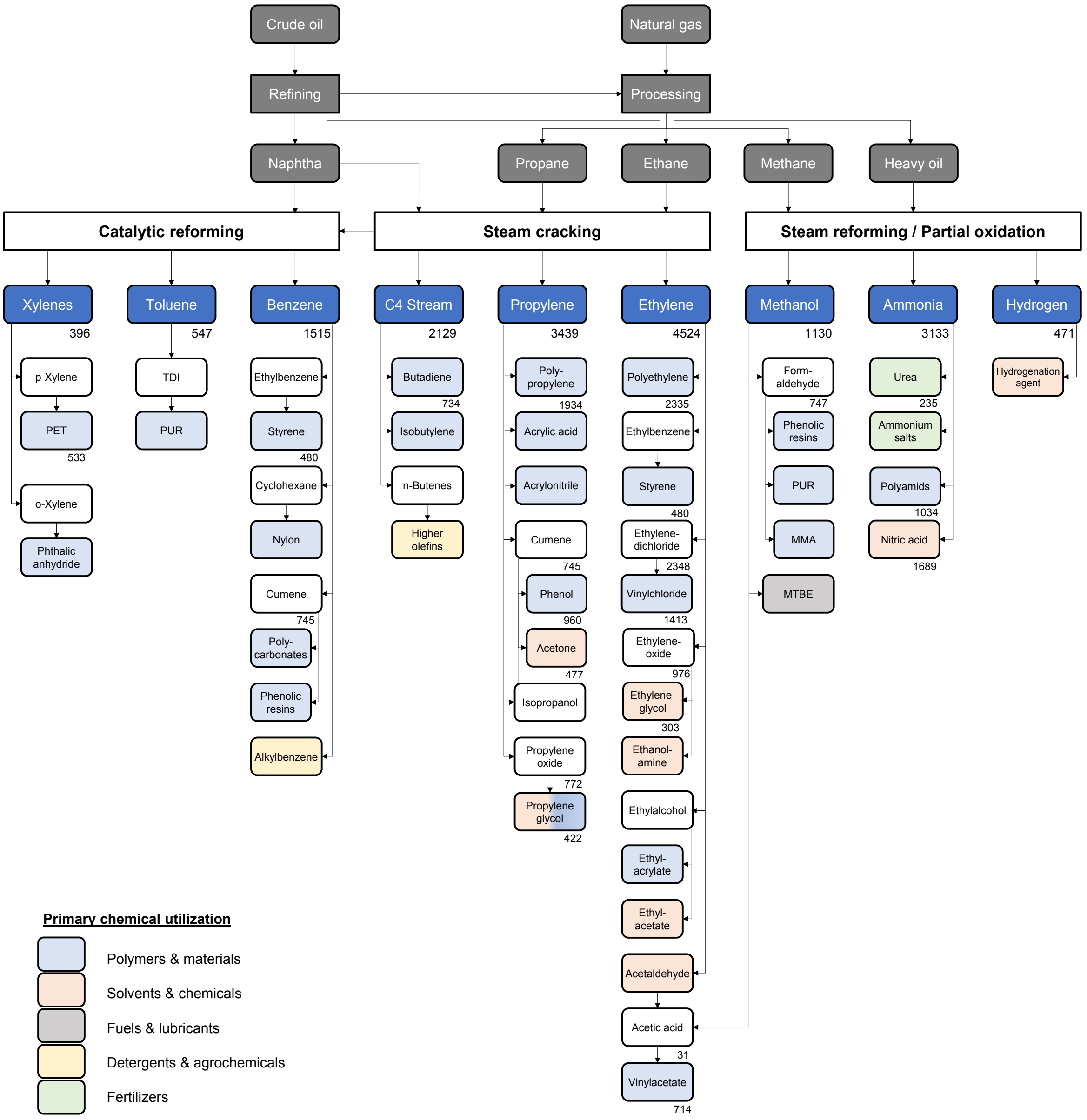

Figure 15: Simplified flowchart of organic chemical production and selected annual quantities for Germany (in kt) [182–185]

3.2.1. Steam cracking

Steam cracking is a non-catalytic high-temperature pyrolysis process of vaporized hydrocarbon feedstock. The endothermic steam cracking process is performed in a tubular reactor that is heated by firing of natural gas or fuel gas from subsequent product fractionation. A steam atmosphere is applied for process moderation and reduction of coking, but reforming reactions are avoided due to the applied process conditions and low residence time. The reactor is partitioned in a convection zone for feedstock preheating and a radiant reaction zone. After exiting the reaction zone, product gas is rapidly cooled in a transfer line exchanger to avoid secondary reactions under formation of high-pressure steam. The quantitatively most relevant feedstock in Europe is naphtha, but the range of industrially applied feedstock range from liquefied gases (from ethane), LPG to heavy oils (atmospheric gas oil, hydrocracking residues). The product gas composition varies widely depending on the applied feedstock and reaction conditions, including light gases, lower olefins, lower aromatics and higher aromatics [186, 187]. Formation of undesired higher aromatics (pyrolysis fuel oil) and reactor coking correlates with feedstock aromatic content [109]. Coking in radiant coils progressively impacts heat transfer and leads to increasing fuel demand. Coils are decoked by off-burning with an oxygen/steam mixture, but need to be taken off-stream for the process. Therefore, highly aromatic feedstocks compromise the unit's operation availability. Further, steam cracking feedstock require a high purity level, as contaminants lead to various process complications in the cracker unit and downstream processes [107, 109, 166].

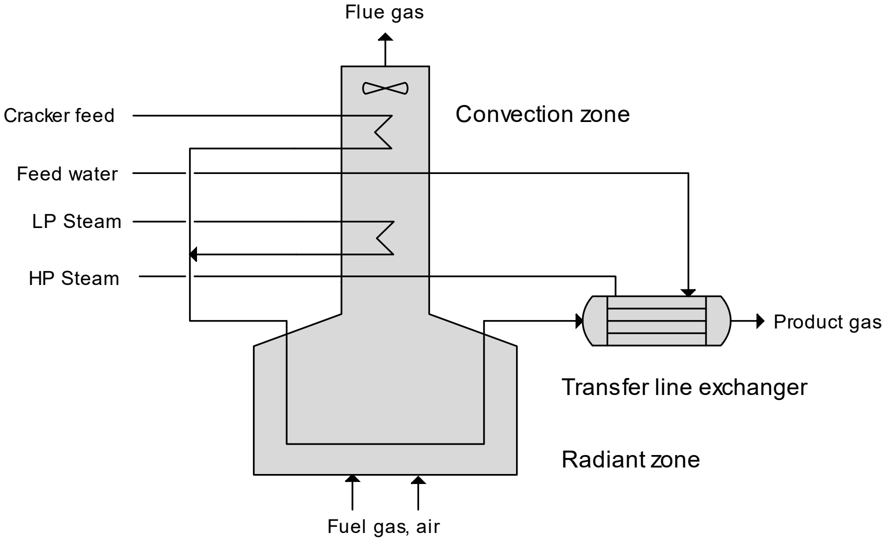

Figure 16: Visualization of the steam cracking process (based on [188])

Table 11: Modelling assumptions of steam cracking [186, 189]

Conversion modelling approach	Kinetic model [190]
Temperatures	
Entry radiant zone for naphtha/LPG feed	600/650 °C
Exit transfer line exchanger for naphtha/LPG feed	450/230 °C
Flue gas exit radiant zone / convection zone	1000/200 °C
Burner excess air ratio	1.1
Burner wall heat loss	1.5 % of LHV fuel input
Coil outlet pressure	2.0 bar
Steam content naphtha/LPG feed	(0.45/0.3) kg / kg feed
Reactor coil diameter/length	50 mm / 50 m
Reactor residence time	0.35 s
Coil outlet characteristic	
Naphtha feed: propylene/ethylene ratio	0.55
LPG feed: ethane conversion	0.70

3.2.2. Catalytic reforming

Catalytic reforming is a standard process in conventional petroleum processing for upgrading of naphtha fractions to gasoline, but is also applied for BTX production [191, 192]. The reforming reaction is an endothermic catalytic reaction, performed in a three-staged moving bed reactor in hydrogen atmosphere with intermediate gas heating in a fired furnace. Formed coke on the catalyst is continuously burned off. Hydrogen atmosphere is maintained by partial recycling of the formed gas fraction [117].

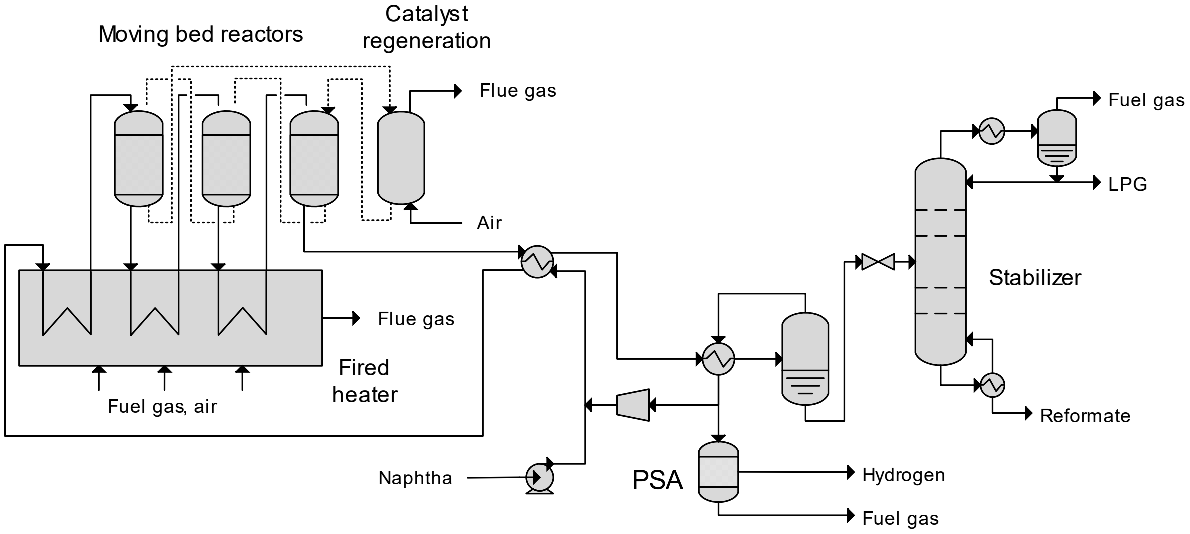

Figure 17: Visualization of the catalytic reforming process (based on [117])

Table 12: Modelling assumptions of naphtha catalytic reforming [117, 193, 194]

Reaction modelling approach	Stoichiometric reaction system
Reactor inlet temperature	500 °C
Reactor pressure	40 bar
Flue gas exit temperature Reactant preheating / heat recovery	700/200 °C
Hydrogen/hydrocarbon ratio	4
Recycle gas hydrogen content	90 mol.-%
Coke formation	2.5 g / t Naphtha
Yield Reformate / Aromatics (weight-based)	0.88 / 0.72
Stabilizer tower stage number	50
Stabilizer pressure	8 bar

3.2.3. Olefin and BTX recovery

Both steam cracking and catalytic reforming as well as alternative processes for olefin and BTX-aromatic production generate a product mix of a range of hydrocarbons, that require separation and purification. The olefin processing unit of a naphtha cracker consists of a two-stage quenching section (oil quench and water quench), liquid separation section, product gas compression, caustic scrubbing for removal of remaining sour gases (primarily CO_2), and a multi-stage product gas fractionation section for the supply of high-purity olefin product gases [186]. Depending on production technology and product gas composition, different plant components are required (see table 13). The energy balance for olefin recovery is primarily determined by gas compression and electricity demand for cryogenic separation of light product fractions (hydrogen, fuel gas, ethylene/ethane separation). In industrial applications, produced fuel gas is applied for steam cracker heating. Depending on the side infrastructure and requirements, hydrogen is recovered or left as fuel gas component. Formed BTX aromatics are recovered in the pyrolysis gasoline (pygas) fraction, which can be applied as gasoline component or for chemical BTX recovery [192].

The objective of the aromatic processing unit is the separation of non-aromatic compounds, BTX product yield adjustment and BTX purification. An overview of integrated process steps is presented in figure 19 and table 12. Non-aromatic compounds in pyrolysis gasoline or reformate feed are extracted from the integrated aromatic processing unit by extractive distillation and can be recycled to primary production units (raffinate). Benzene, p-xylene and o-xylene are the aromatic compounds with the highest demand as chemical feedstock. Significant other yields in BTX feedstock are toluene, m-xylene, ethylbenzene and higher aromatic compounds. Yields in desired products are increased by integrated catalytic transalkylation and isomerization units. The energy demand of a BTX plant is significantly determined by xylene separation due to high purity demand and close boiling points [117, 193, 195].

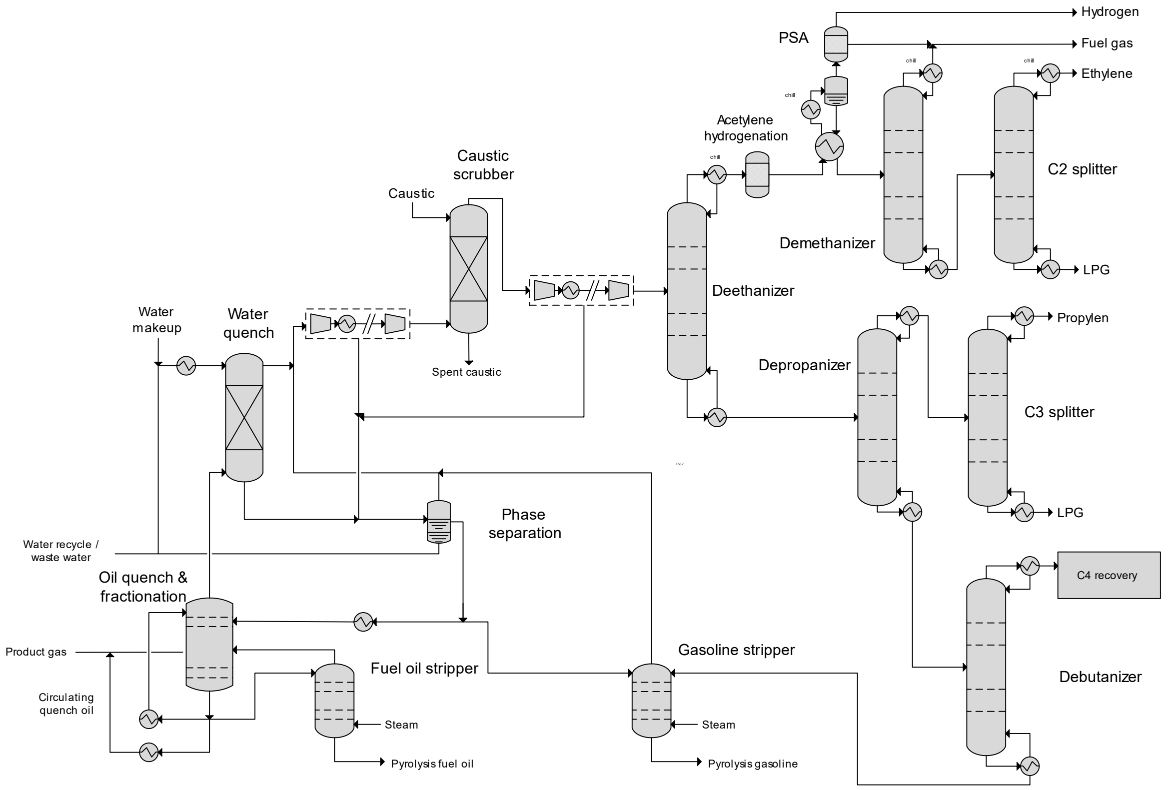

Figure 18: Visualization of the olefin recovery process (based on [186])

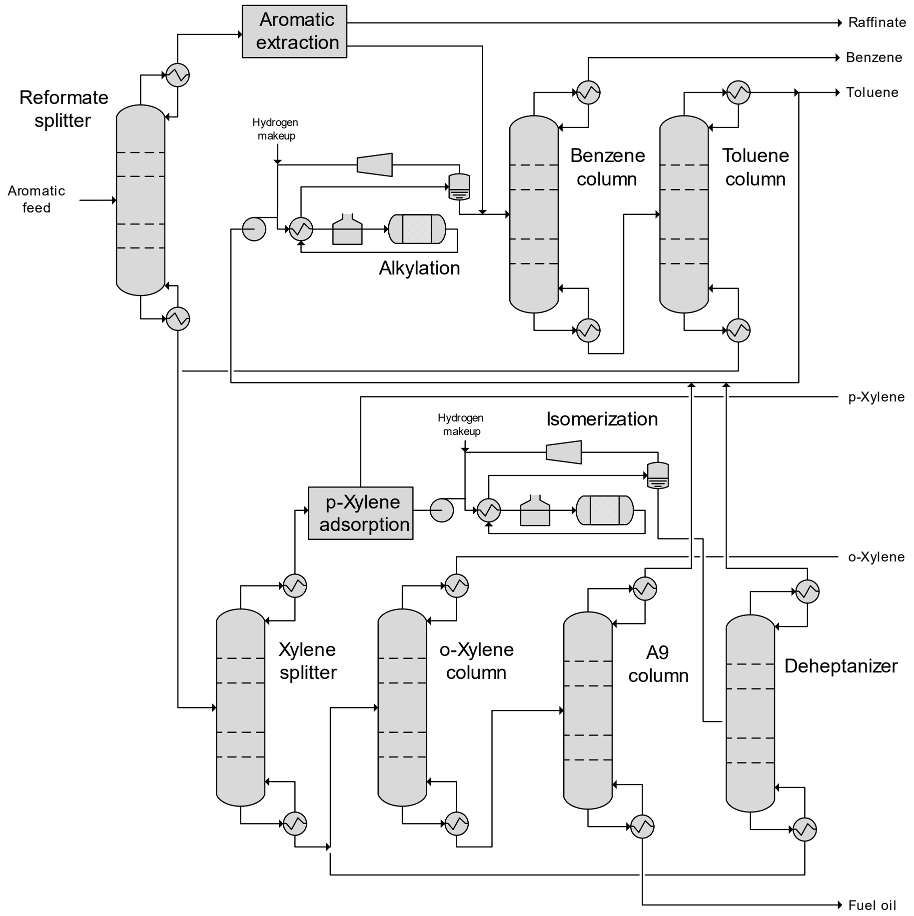

Figure 19: Visualization of BTX aromatic recovery process (based on [117])

Table 13: Process configuration by feed for the olefin recovery process

Primary production technology	Steamcracking		MTO
	Naphtha	LPG	
Oil quench	x		
Water scrubber	x	x	x
Phase separation	x	x	
Acid gas removal	x	x	x
Deethanizer, Demethanizer	x	x	x
Hydrogen recovery	x	x	
C2-Splitter, Depropanizer / C3 Splitter, Debutanizer/ C4 Recovery	x	x	x

Table 14: Overview of BTX aromatic recovery process steps [117]

Process	Extractive distillation	Transalkylation	p-xylene adsorption	Isomerization
Feed	Reformate, pyrolysis gasoline	Toluene, C10+ aromatics	Xylene mix	m-xylene, ethylbenzene
Product	Aromatic mix	Benzene, xylene	p-xylene	p-xylene, o-xylene
Modelling approach	KPI	Adapted equilibrium 430 °C, 35 bar (hydrogen atm.)	KPI	Reaction stoichiometry 390 °C, 17 bar (hydrogen atm.)

Table 15: Modelling assumptions of olefin and BTX recovery processes [186, 196, 197]

Oil quench/primary fractionation	
Oil to feed ratio	20
Head temperature	100 °C
Water quench head temperature	40 °C
Compressor exit pressure	30 bar
Column stage number: Deenthanizer / Demethanizer / Depropanizer / Debutanizer / C2 Splitter / C3 Splitter	30 / 30 / 50 / 50 / 70 / 150
Product purity ethylene/propylene	99.2 / 99.6 Mol.-%
Fractionation recovery ethylene / propylene	98 %
Column stage number: Reformate splitter / benzene column / toluene column / xylene splitter / o-Xylene column / deheptanizer / A9 column	30 / 30 / 30 / 150 / 120 / 40 / 30
Product purity: Benzene / Toluene / p-Xylene / o-Xylene	99.8 / 99.8 / 99.9 / 97.0 wt.-%

Table 16: Key process indicators for C4 olefin and BTX recovery processes

Butadiene extractive distillation [198, 199]		
Electricity	150	kWh / t butadiene
IP steam	1.7	t / t butadiene
Cooling water	150	t / t butadiene
Butadiene recovery	99 %	
Butene adsorption [117]		
Electricity	110	kWh / t butene
Fired heat	266	kJ / t butene
Cooling water	15.8	t / t butene
Butene recovery	99 %	
Aromatic extractive distillation [117]		
Electricity	7.16	kWh / t feed
HP steam	0.50	t / t Feed
Cooling water	5.03	t / t Feed
Aromatic recovery	98.5 %	
p-Xylene adsorption [117]		
Electricity	60.6	kWh / t p-Xylene
IP steam	0.25	t / t p-Xylene
p-Xylene recovery	97.0 %	

3.2.4. Conventional syngas production

Catalytic steam reforming of natural gas is the most common process worldwide for the large-scale production of synthesis gas and is primarily used for the production of hydrogen and ammonia [124]. For gas feedstock with contents in higher hydrocarbons, the feed is initially introduced to a catalytic adiabatic prereformer. After preheating, natural gas and steam are converted in catalyst-filled tubes in the primary reformer. The endothermic process is heated by firing of natural gas or alternative fuel gases (compare equation (12)). Depending on the addressed product, combined reforming is applied with a secondary reactor stage in form of an autothermal reformer with either oxygen (for methanol production) or air (for ammonia production) [124]. Process conditions for the respective configurations are summarized in table 17.

Steam reforming reaction $CH_4 + H_2O \rightleftarrows CO + 3\ H_2$ $\Delta H_R = +206$ kJ/mol (12)

Non-catalytic partial oxidation (POX) of heavy oil and liquid residues is an alternative process for synthesis gas production and the primary source for methanol production in Germany. The process is autothermal by application of oxygen and steam as reaction agents. Therefore, no external heat supply is necessary, but the H_2-CO ratio of the produced raw gas is lower compared to steam reforming. Due to the high reaction temperature and the non-catalytic operation, POX enables the conversion of a wide range of feedstock with potentially high contaminant levels, including petroleum-based heavy refinery residues, natural gas and alternative liquid hydrocarbon mixtures such as pyrolysis and bio oils [124, 200]. The produced raw gas contains soot, which is recovered in the subsequent quenching section (compare chapter 3.1.2) and recycled to the POX process.

$$C_mH_n + m/2\ O_2 \rightleftarrows m\ CO + n/2\ H_2 \quad (13)$$

$$C_mH_n + m\ H_2O \rightleftarrows m\ CO + (m + n/2)\ H_2 \quad (14)$$

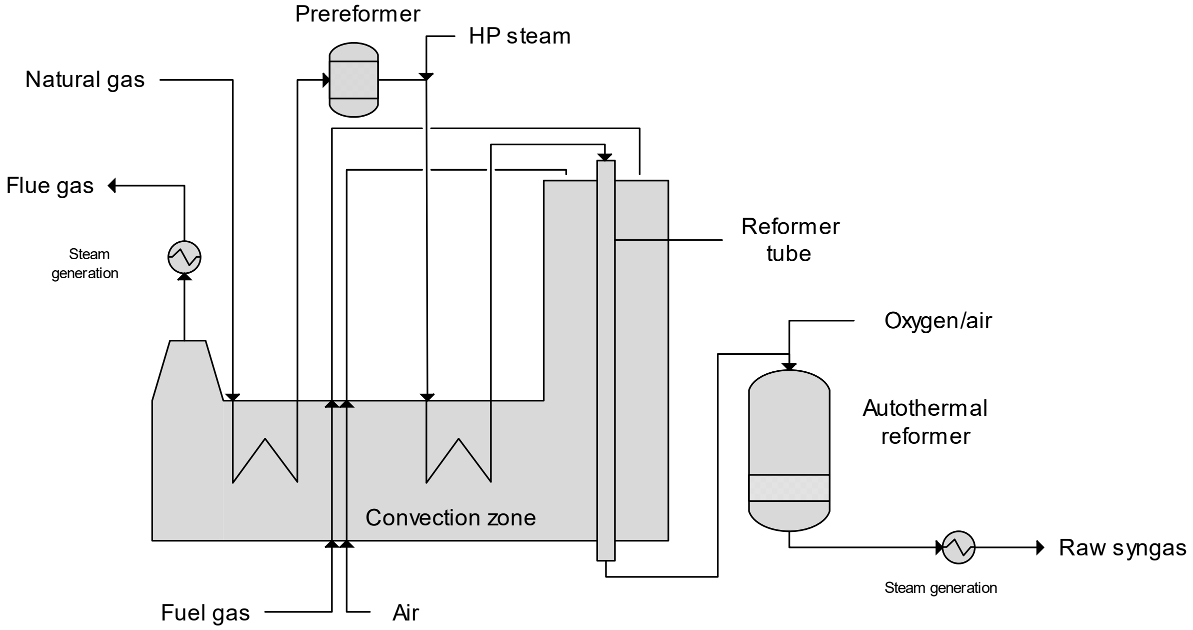

Figure 20: Visualization of the steam reforming process (based on [137])

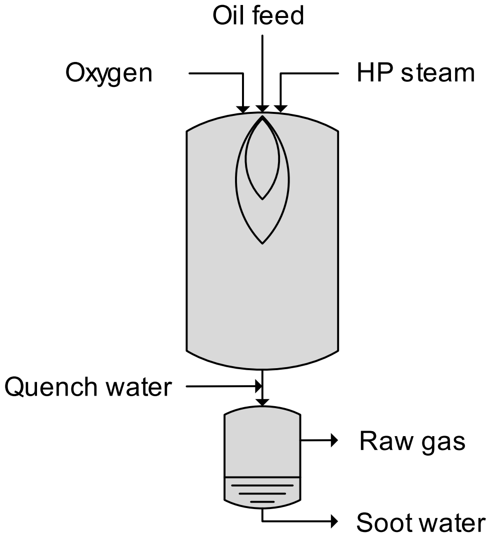

Figure 21: Visualization of the partial oxidation process (based on [201])

Table 17: Overview of process configuration depending product for steam reforming process [124, 137]

Product	Hydrogen	Methanol	Ammonia
Reformer pressure	25 bar	25 bar	35 bar
Reformer temperature	850 °C	750 °C	800 °C
Steam/carbon ratio (molar)	3.0	2.5	3.5
Secondary reformer agent	-	Oxygen	Air
Secondary reformer objective	-	$\frac{H_2 - CO_2}{CO + CO_2} = 2.05$	$\frac{H_2 + CO}{N_2} = 3.0$

Table 18: Modelling assumptions for steam reforming and POX process [137, 202]

Catalytic steam reforming	
Modelling approach for primary and secondary reformer	Thermodynamic equilibrium
Prereformer Input temperature	500 °C
Flue gas temperature: radiation zone / convection zone	1000/200 °C
Burner excess air ratio	1.1
Burner wall heat loss	1.5 % of LHV fuel input
Non-catalytic partial oxidation (POX)	
Reaction modelling approach	Adapted thermodynamic equilibrium
Exit temperature	1400 °C
Pressure	60 bar
Heat loss	0.5 % of LHV input
Steam-oxygen ratio	0.56 kg / m^3 (STP)
Soot formation	2.08 wt.-% of carbon input

3.2.5. Methanol and methanol-based synthesis

Methanol synthesis is an exothermic catalytic reaction based on the conversion of carbon monoxide and carbon dioxide with hydrogen. The applied syngas quality can be described by the syngas modulus SN.

Syngas modulus $$SN = \frac{H_2 - CO_2}{CO + CO_2} \quad (15)$$

CO-based methanol formation $CO + 2\ H_2 \rightleftarrows CH_3OH$ $\Delta H_R = -91$ kJ/mol (16)

CO_2-based methanol formation $CO_2 + 3\ H_2 \rightleftarrows CH_3OH + H_2O$ $\Delta H_R = -41$ kJ/mol (17)

In conventional gas-phase reactors, the single pass conversion is limited by the thermodynamic equilibrium, so the unconverted reactant gas is partially recycled. Recovered raw methanol is subsequently purified by staged distillation. Various technologies are commercially available with differences in the reactor unit size, the reactor type and catalyst, the number of reactor stages and the configuration for purge gas treatment and product purification [124, 203].

In the considered process configuration methanol synthesis is realized in an isothermal multi-tubular fixed-bed reactor with boiling water temperature control producing MP saturated steam (Lurgi conventional process design [124]). Hydrogen is recovered from purge gas by pressure swing adsorption (PSA). Methanol is purified in two stages, a primary light ends column for the removal of light side products and a secondary pure methanol column for the separation of methanol and water, which requires significant amounts of low-temperature heat. For subsequent MTO synthesis, the pure methanol column can be spared, as the required water content for moderation is lower than crude methanol water content (under 10 wt.-%).

Alternatively, methanol can be produced by direct hydrogenation of carbon dioxide. The process is in the industrial implementation stage, with the largest operational plant being a in 2022 commissioned 110,000 t/y facility by CRI in China, but a number of large-scale projects in development [204, 205]. Due to data availability, validation data from the RITE process are used which applies a similar process concept to the Lurgi process [206, 207]. Plant-related differences (esp. increased water tolerance of the catalyst) do not influence the process balancing in the applied modeling depth. Note that for subsequent MTO synthesis, partial water removal for crude methanol is required, as the crude water content is above 30 wt.-%.

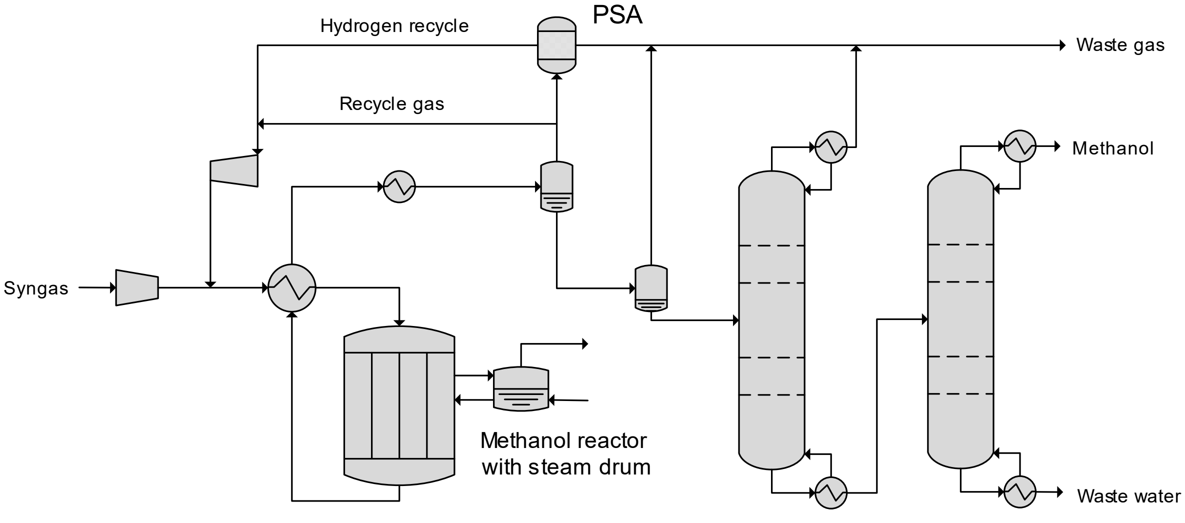

Figure 22: Visualization of the methanol synthesis process

Methanol can further be applied as an intermediate for the production of base chemicals that are conventionally produced from crude oil derivates. The MTO (methanol-to-olefin) process has a high technology maturity and is applied on large industrial scale in coal-based chemical production facilities in China [208, 209]. The oligomerization of methanol to olefins is a catalytic exothermic reaction, that is performed in a fluidized bed reactor with steam atmosphere for moderation, similar to conventional fluid catalytic cracking reactors [210]. Methanol is converted primarily to dimethyl ether and subsequently to a product gas mixture of mainly olefinic and paraffinic components up to C5. Compared to steam cracker-based olefin production, MTO shows a higher selectivity to ethylene and propylene and less fuel gas and hydrogen formation. The reaction temperature is regulated by steam generation. Due to a strong coking tendency on the reactive surface, the catalyst is continuously extracted and regenerated in a regeneration reactor by carbon burn-off with air.

Similar to MTO, the methanol-to-aromatic (MTA) technology was primarily developed in China in recent years for coal-based chemical production. The technology is considered to be in the demonstration stage, as the only documented industrial-scale facility is a 30 kt per year pilot plant in Yulin, China [211, 212]. The described process design is based on reported information of this plant. The aromatization process is a catalytic exothermic reaction, realized in a fluidized bed reactor with steam generation for temperature control, similar to the MTO reactor. The product gas is processed by phase separation, caustic scrubbing, fractionation and BTX recovery. Non-aromatic fractions (C3+ product gas fraction and raffinate from aromatic recovery) are recycled to a secondary reactor stage (LHTA) to increase BTX yield. The paraffin aromatization process is endothermic and is conducted adiabatically, therefore requiring preheating. The catalyst is applied in the LHTA stage before the MTA stage due to the higher coking tendency, and subsequently regenerated by carbon burn-off with air.

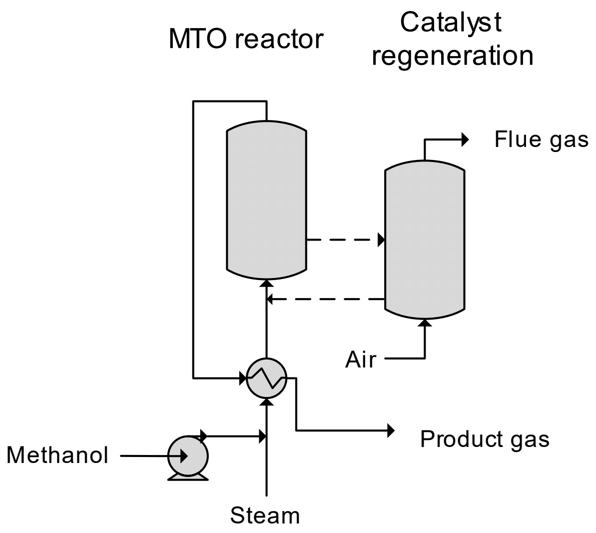

Figure 23: Visualization of the methanol-to-olefin process (based on [210])

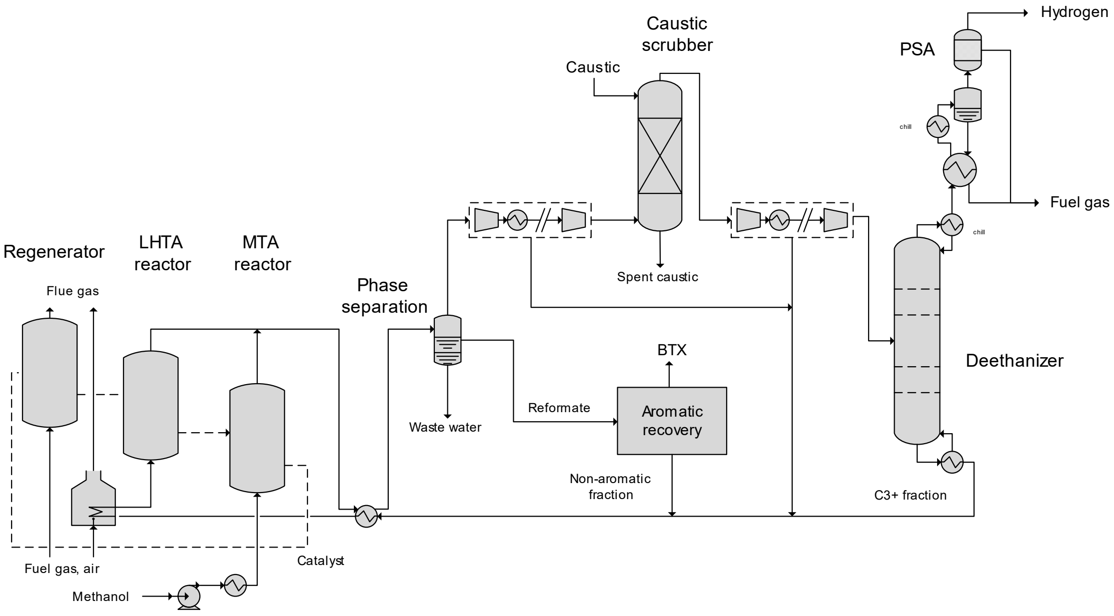

Figure 24: Visualization of the methanol-to-aromatics process (based on [211])

Table 19: Modelling assumptions for methanol and methanol-based synthesis

Methanol synthesis [124, 203, 206, 207]	
Reaction modelling approach	Adjusted thermodynamic equilibrium
Reactor temperature (CO / CO_2-based)	255 / 250 °C
Reactor pressure (CO / CO_2-based)	60 / 80 bar
Syngas module (CO-based)	2.05
H_2/CO_2-ratio (CO_2-based)	2.9
Recycle ratio (CO / CO_2-based)	3.5 / 4.0
Column stage number	70 / 90
Methanol purity	99.9 wt.-%
Methanol carbon recovery	> 95 %
Methanol-to-olefins (MTO) [210, 213–215]	
Reaction modelling approach	Adjusted thermodynamic equilibrium
Temperature reactor / regeneration	500 / 700 °C
Steam content	0.2 kg / kg Methanol
Process pressure	4.5 bar
Methanol conversion	99.5 %
C2 & C3 olefin selectivity	80 % of carbon input
Propylene / Ethylene ratio (mass-based)	1.1
Coke formation	2.5 % of carbon input
Methanol-to-aromatics (MTA) [211, 216, 217]	
Reaction modelling approach	Adjusted thermodynamic equilibrium
Temperature MTA Reactor / LHTA Reactor / regeneration	475 / 530 / 700 °C
Process pressure	4.5 bar
Methanol conversion	99.9 %
Coke formation	0.8 % of carbon input
Aromatic yield	75 % of methanol carbon input
Distribution aromatic formation MTA / LHTA	2:1
Product reformate aromatic content	90 wt.-%
Gas processing pressure	30 bar
Deethanizer stage number	30
General modelling assumptions [135, 206, 218]	
Pump/compressor efficiency (isentropic/mechanical)	0.85/0.998
PSA hydrogen recovery efficiency	80%
PSA off gas output pressure	1.6 bar

3.2.6. Ammonia synthesis

The Haber-Bosch process for ammonia production with from hydrogen and nitrogen is a exothermic catalytic reaction, that is characterized by an unfavorable thermodynamic equilibrium which leads to the requirement of high process pressure and limited single pass conversion. A gas cycle is applied, from which formed ammonia is separated by cryogenic cooling and condensation. Due to the process gas compression and cryogenic requirements, ammonia synthesis is characterized by a significant power demand. Ammonia catalysts are sensitive to oxygen-containing components (incl. carbon monoxide, carbon dioxide and water). Removal of residual loads after syngas shifting, acid gas removal and gas drying can be accomplished by various processes depending on the gas production process, including methanation, cryogenic separation, liquid nitrogen washing or PSA. A number of ammonia converter technologies are commercially available that are primarily differentiated by the ammonia converter design (number of reaction stages and heat integration configuration) and the plant configuration for hydrogen recovery from purge gas [219, 220].

Ammonia synthesis	$N_2 + 3\ H_2 \rightleftarrows 2\ NH_3$	$\Delta H_R = -92$ kJ/mol	(18)
CO methanation	$CO + 3\ H_2 \rightleftarrows CH_4 + H_2O$	$\Delta H_R = -206$ kJ/mol	(19)
CO_2 methanation	$CO_2 + 4\ H_2 \rightleftarrows CH_4 + 2\ H_2O$	$\Delta H_R = -165$ kJ/mol	(20)

The considered process configuration is based on the Haldor Topsoe advanced ammonia process [220], which applies a three stage adiabatic fixed-bed converter with intercooling by feed gas preheating for temperature control. Oxygen content removal is realized by an adiabatic methanation stage (compare equations (19) and (20)). Introduced methane cumulates in the gas cycle and is removed with a purge stream. Ammonia and hydrogen are recovered from the purge stream by water scrubbing and PSA, respectively.

Table 20: Modelling assumptions for ammonia production [220, 221]

Reaction modelling approach	Thermodynamic equilibrium
Temperatures output reactor stages	460 / 380 / 320 °C
Reactor pressure	190 bar
H_2/N_2-ratio syngas feed	3.0
Recycle methane content	< 5 vol.-%
Recycle chilling temperature	– 20 °C
Ammonia purity	99.8 mol.-%
Ammonia hydrogen recovery	> 90 %

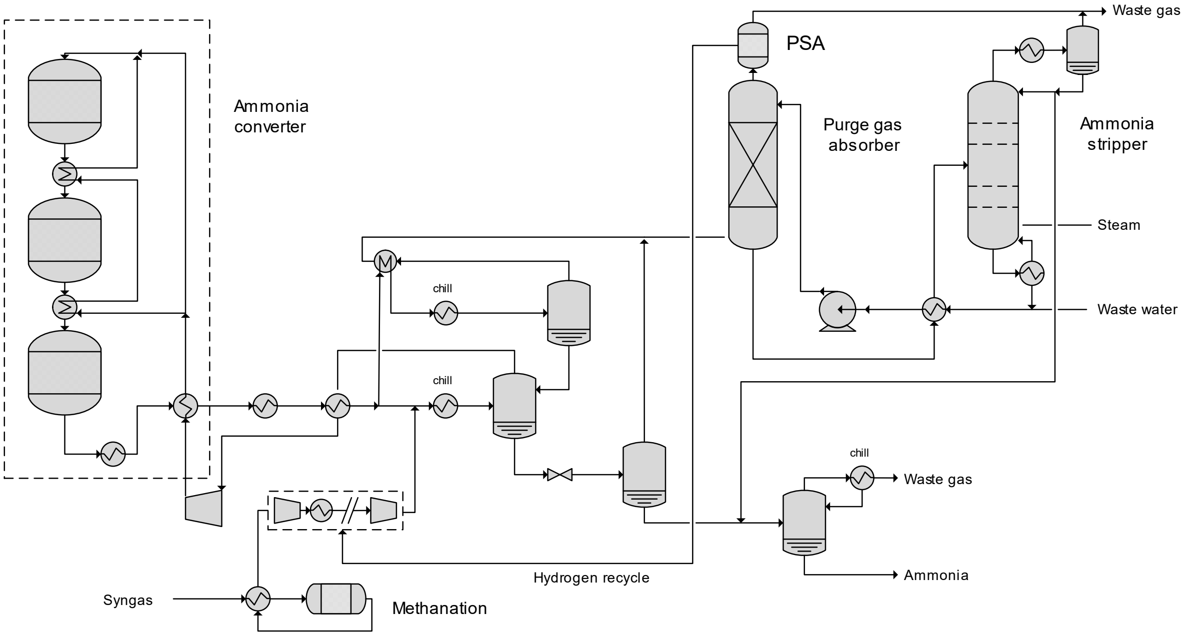

Figure 25: Visualization of the ammonia synthesis process (based on [221])

3.3. Electric power integration options

Integration of electric energy from renewable energy sources is widely considered a key factor for mitigation of greenhouse gas emissions and fossil resource demand of base chemical production processes [222–224]. Conceptional approaches for renewable energy integration can be divided into three groups: direct electric heating for substitution of firing in high-temperature processes (power-to-heat); hydrogen generation and application via water electrolysis (power-to-hydrogen); and application of alternative processes for direct electricity integration (power-to-commodities) [224].

Concerning power-to-heat technologies for chemical production, electric heating for steam cracking and natural gas reforming is a current focus point for industrial development. Haldor Topsoe recently commissioned a demonstration plant for electric steam reforming [225]. The technology applies resistive (ohmic) heat production in the catalyst-holding tube, potentially leading to significant improvements in heat transfer, process performance and reformer size reduction compared to conventional fired reformers [226]. A consortium of BASF, SABIC and Linde is currently in the process of building a demonstration unit for electrified steam cracking, while Shell and Dow are in the stage of lab-scale experimentation [227, 228]. Expected obstacles in technology development and implementation include the generation of a suitable reactor temperature profile and structural adaptation of process integration, especially for fuel gas utilization from steam cracking and substitution of steam from flue gas heat recovery [229, 230]. Documented efforts concerning other fired chemical and petrochemical processes, including naphtha catalytic reforming for BTX production, are not available. Generally, electric heating is considered less technologically demanding [231], as heating is applied for intermittent process gas reheating between reactor stages to temperatures of about 500 °C without significant requirements on the temperature profile.

Secondly, electric energy can be integrated in chemical production by means of hydrogen production (power-to-hydrogen). Besides production cost and durability, energy efficiency is the key criteria for electrolyzer development [232]. Efficiency benchmarks and development projections of the three main electrolysis technologies (alkali (AEC), proton exchange membrane (PEMEC) and high-temperature solid oxide electrolysis (SOEC)) are shown in figure 26. Note that steam generation energy demand for SOEC is not included in the graph.

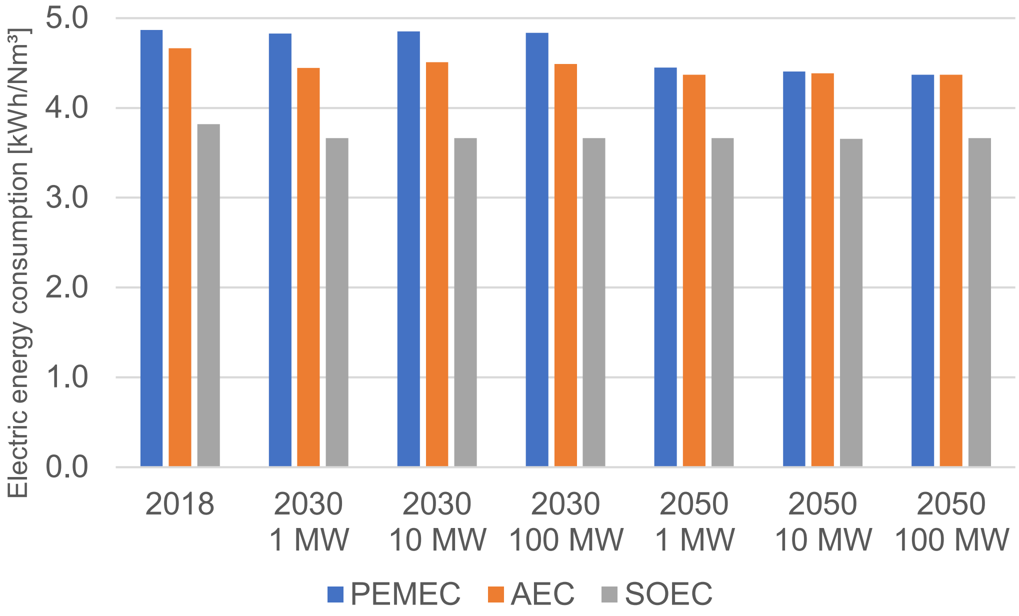

Figure 26: Development of electrolysis energy demand for hydrogen production (reproduced from [233])

For carbon capture and utilization (CCU) applications, CO_2 is applied as carbon feedstock. CO_2 is accessible in high purity from industrial sources including ethanol, ethylene oxide and ammonia production in limited quantities [234]. Increasing availability, CO_2 can be extracted from flue gas of combustion processes. Amine-based chemical absorption is the most prominent technological option with a high technological maturity. Their limited industrial implementation is significantly caused by financial restrictions, mostly determined by high capital cost [235, 236]. Other options for CO_2 recovery from flue gases include physical absorption, adsorption, membrane and cryogenic processes [237]. Further, CO_2 can be extracted directly from air (direct air capture), which is associated with a higher energy demand compared to the recovery from flue gas. Technologies based on chemical absorption and adsorption are currently in the stage of industrial implementation, albeit at small capacities [238].

For base chemical production, CO_2 and hydrogen can be directly converted to methanol (see chapter 3.2.5). Based on methanol as an intermediate, the PTX-based production of crude oil-based chemicals (especially via MTO) is conceptionally feasible without significant development demand. Similarly, ammonia can be produced with hydrogen based on conventional conversion technologies (see chapter 3.2.6). Nitrogen in the required purity can be provided from cryogenic air separation, either as side production from oxygen production or as primary product [239]. Other possible CO_2 conversion processes include syngas production via CO_2 electrolysis [240, 241], CO_2/H_2O co-electrolysis [242, 243] and high-temperature reverse water-gas shifting [244, 245]. Despite significant technological advancements in recent year, none of these processes have been demonstrated in industrial scale so far. Hydrogen can further be applied as a carbon-free fuel for steam cracker firing. Implementation demands adjustments in burner and furnace design due to the specific heat transfer profile and has not been applied yet [246].

Alternatives for direct electricity integration in base chemical production (power-to-commodities) include a wide range of processes, from which selected developments are highlighted. Coolbrook is developing a roto dynamic reactor (RDR) for the substitution of the fired radiant section in conventional steam crackers by an electric-motor driven turbo-reactor and aim a demonstration by 2024 in a collaboration with Braskem. A similar technology development is pursued by Technip and Siemens [247–249]. The direct decomposition of methane to produce hydrogen and solid coke as an alternative to conventional steam reforming is developed deploying various principles. Plasma-based methane pyrolysis is currently demonstrated by Monolith in Nebraska at a semi-industrial scale with 5 kt per year hydrogen production capacity [250, 251]. Process energy integration via thermal plasma is developed for various applications. Non-thermal plasma is primarily considered for direct conversion of CO_2 and/or methane to syngas or C1 and C2 chemicals, but is at a low technology development status [252, 253]. Thermal plasma is applied commerically in waste gasification for the treatment of hazardous and low-calorific waste, including medical waste, low level radioactive waste, waste incinerator residues, high-halogenic liquids and municipal solid waste. The application of of plasma in waste treatment brings two process advantages. First, plasma can be introduced close to the inert material discharge for residual carbon conversion and ash melting to produce a vitrified, non-leachable slag that is suitable for landfilling or material utilization, e.g. in construction. Second, plasma can be applied to raise the product gas temperature independently from oxygen supply to achieve a desirable syngas with a high H_2-CO ratio and low yields in methane, higher hydrocarbons and tar. While plasma gasification-based waste treatment with and without energy recovery is commercially applied in numerous facilities, it is currently not applied for chemical or fuel production at industrial scale [254–256].

In the present investigation, electric power integration is considered by electric heating for steam cracking, steam reforming and catalytic reforming (power-to-heat) and for the electrolysis-based hydrogen production (power-to-hydrogen) with subsequent N_2-based ammonia and CO_2-based methanol production (compare chapters 3.2.5 and 3.2.6). Due to missing applicable validation data, electric process heating is modelled by maintaining the reactor performance characteristics (i.e. temperature profile, product yield) and adjusting the thermal integration of the cracking/reforming reactor with subsequent process steps. Significant indirect impacts include the decrease of heat generation from flue gas heat recovery and the surplus of fuel gas generation that is conventionally applied for reactor heating.

Additionally to N_2 and CO_2-based conversion, hydrogen is further integrated in gasification-based production of carbonaceous products to improve the process performance [16, 257, 258]. As H_2-CO ratio after gasification is generally too low, syngas is conventionally shifted under formation of CO_2 (compare equation (3)). Further, CO_2 formed in both gasification and shift needs to be removed to achieve required syngas characteristics, e.i. the syngas modulus for methanol synthesis (see equation (15)). With increasing hydrogen integration, process efficiency indicators can be improved by two mechanisms. First, the CO shift bypass is increased until complete avoidance of the shift unit. Second, the CO_2 content in syngas can be increased by selective removal or by recompression and reintroduction of separated CO_2 from the AGR unit. The change of key indicators of gasification-based methanol production with increasing hydrogen input is exemplarily shown in figure 27 for the gasification of RDF with a lower heating value of 22.0 MJ/kg (compare table 31) under the conditions summarized in table 3. With increasing hydrogen input, carbon recovery into methanol increases from 50% to 95%. At 0.115 kg hydrogen per kg RDF feedstock, syngas-based hydrogen integration is maximized. Remaining CO_2 emissions at maximum hydrogen input are associated with the incineration of off-gases and cannot be avoided directly by hydrogen integration. Based on the applied equilibrium-based modelling of CO shift and methanol synthesis, process characteristics change linearly with hydrogen input, independently of the adaption mechanism. Therefore, partial hydrogen integration can be approximated by linear combination of the case without and with complete hydrogen integration.

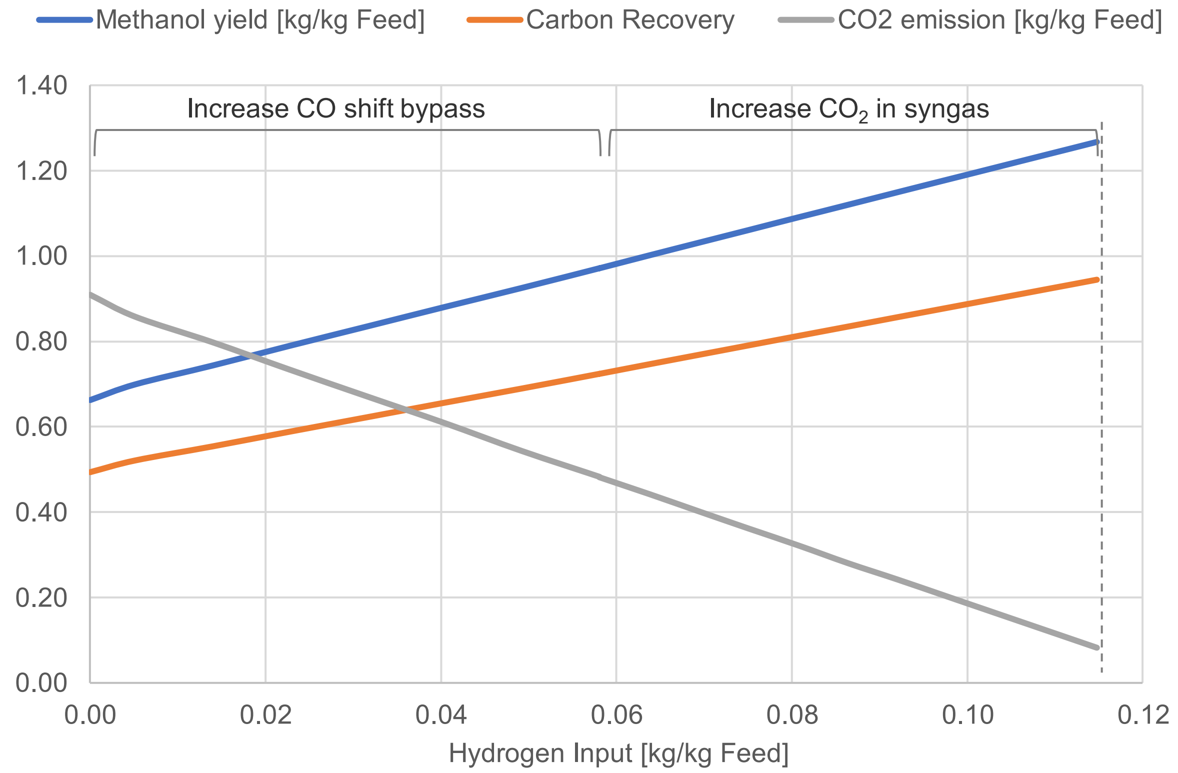

Figure 27: Key indicator development of RDF gasification-based methanol production with increasing hydrogen integration

3.4. Conventional waste treatment processes

Waste treatment of carbonaceous waste in Germany is generally more diverse compared to base chemical production. This is due to a number of reasons, including:

1. The composition of waste fractions for treatment is highly diverse due to the variety in waste origins, collection systems and regional particularities [259–261].
2. The primary function is the safe treatment of waste and the avoidance of direct waste emission to the environment, and only secondarily its utilization for secondary products or energy. Revenues are rather derived from disposal charges than from derived products [84, 262].
3. Waste treatment is a more regional and communal affair compared to chemical production, with a large number of facilities with low individual capacity and restrictions due to waste transportation costs [7, 263].
4. The general prioritization of waste treatment measures is defined in the Closed Substance Cycle Waste Management Act ((Kreislaufwirtschafts- und Abfallgesetz, KrW-/AbfG) [264]). In practice, the fate of individual waste streams is determined by the local market conditions and the availability of treatment capacities [86, 265].

The result is a highly diverse system of waste treatment processes with varying configuration and technology level [7, 266] with individual waste input compositions. Hence, the present investigation exemplarily demonstrates the impact of feedstock recycling application in the context of the German production system. Only light weight packaging waste (LWP) and residual municipal solid waste (MSW) as two major source-separated waste fractions in Germany are considered, which comprise the destination of most post-consumer plastics [267, 268]. Their primary treatment processes in Germany are direct incineration and mechanical-biological treatment (MBT) for MSW and material recovery (MRF) for LWP [7, 268]. The processes are assessed for an average waste input composition and for a representative process configuration at best available technique (BAT) development level. Neither MSW nor LWP are generally directly applicable feedstock for recycling processes. Balancing of waste pretreatment processes is essential for feedstock recycling evaluation, since they determine the feedstock composition, required pretreatment efforts and the quantitative availability.

Mechanical sorting processes involved in MBT and MRF cannot be balanced by thermodynamic modelling to generate required process data. Instead, balancing is based on mass flow modelling of representative material components in EASETECH [269], in order to consider the input waste composition and generate composition and yield of the output fractions while maintaining mass and enthalpy balance. Associated energy consumptions and direct emissions are considered by KPI application (see table 22). Further, waste incineration is modelled thermodynamically in Aspen Plus to determine the energy recovery efficiency for various waste materials. The applied compositions for light weight packaging waste (LWP) and municipal solid waste (MSW) are reproduced based on exemplary material compositions from literature sources.

3.4.1. Mechanical biological treatment and material recovery

Mechanical biological treatment (MBT) includes a range of process configurations for pretreatment of municipal waste and other waste fractions [266, 270]. The primary target is the generation of a high-calorific fraction by mechanical sorting. The biological treatment of the remaining organic-rich fraction by anaerobic digestion enables the generation of biogas, which can be used thermally to generate electricity and heat in a combined heat and power unit (CHP) or the production of substitute natural gas (SNG). Alternatively, the organic fraction can be composted for biological drying and conversion of biogenic carbon, in order to generate a residue that is suitable for landfilling [84]. For the present investigation, a representative MBT process is assumed without the generation of a residual fraction for landfilling. In the applied configuration (figure 29), thermal energy from biogas CHP is used for drying of RDF and biogenic residue, in order to decrease the mass flow and increase the heating value of both streams for thermal utilization [271]. The input waste composition is based on an average MSW composition of Germany [259]. Process design and parameters are adapted from Voss et al. [84].

Material recovery (MR) is the primary treatment option for light weight packaging and other plastic-rich waste fractions in Germany. The primary target of the process is the recovery of plastic and non-plastic materials with high purity for direct recycling as secondary materials. Material sorting units are composed of a range of single sorting and processing steps, including sieving, density separation, optical separation by near-infrared sensoring and manual sorting and quality control. The plastic fractions recovery rate and quality vary depending on the applied process configuration and the number of sorting steps [263, 272]. Non-recoverable fractions are collected in mixed plastic waste (MPW) and sorting residue fractions, which are conventionally processed by thermal treatment or as substitute fuels in cement kilns. The applied process model (see figure 28) is based on an average unit configuration for a plant in Germany [263, 273, 274]. Calculated mass-based yields for mixed plastic waste and sorting residues at 14% and 26% (compare table S22) are in accordance with average values achieved in German facilities [275].

Both calculated RDF fractions from MBT and MRF, as well as the RDF composition applied for pyrolysis balancing (compare tables 21 and 31) show good agreement in terms of heating value and carbon content, despite significant differences in terms of ash and oxygen content. Calculated material compositions of the input and output fractions, the applied transfer coefficients and total process balances of MBT and MRF are shown in tables S2 to S5 and table S22.

Table 21: Calculated elemental composition and heating value of input and output fractions of MBT and MRF

		MBT of MSW			MRF of LWP		
		MSW	RDF	Residue	LWP	MPW	RDF
Moisture	wt.-%	37.92	5.00	5.00	5.00	5.00	5.00
Ash	wt.-% (wf)	32.51	15.20	50.13	25.80	7.99	25.62
Carbon	wt.-% (wf)	40.45	52.87	31.32	52.32	69.02	50.49
Hydrogen	wt.-% (wf)	4.90	7.09	2.69	7.19	9.14	6.77
Nitrogen	wt.-% (wf)	1.42	1.68	1.61	0.51	0.48	0.78
Chlorine	wt.-% (wf)	0.28	0.20	0.40	0.90	3.51	0.96
Sulfur	wt.-% (wf)	0.10	0.13	0.10	0.05	0.05	0.07
Oxygen	wt.-% (wf)	20.34	22.83	13.74	13.24	9.80	15.31
Sum	wt.-% (wf)	100.00	100.00	100.00	100.00	100.00	100.00
LHV	kJ/kg (wf)	16,203	22,351	11,687	24,705	35,012	23,117
HHV	kJ/kg (wf)	17,200	23,794	12,233	26,165	36,869	24,493

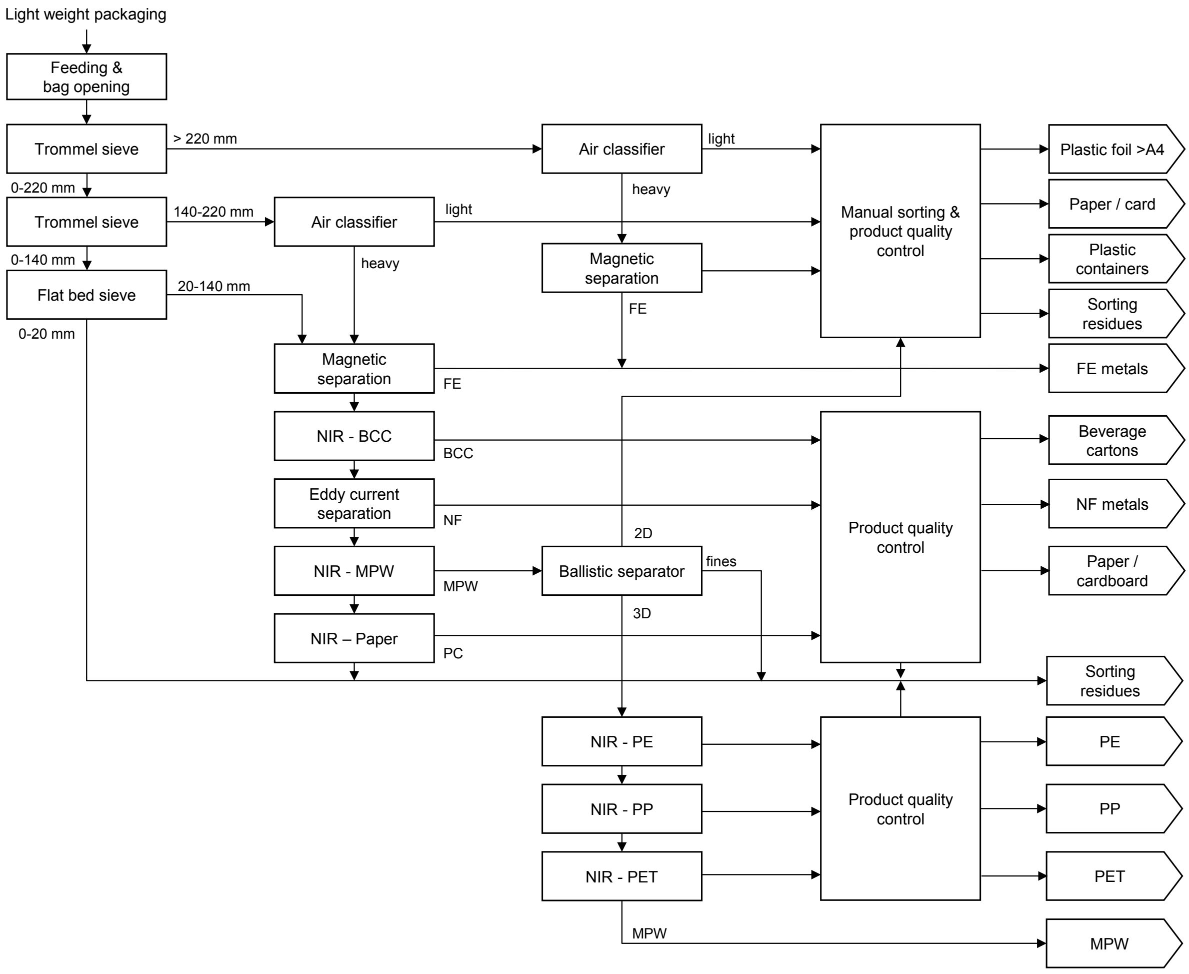

Figure 28: Visualization of the material sorting process (adapted from [273, 274])

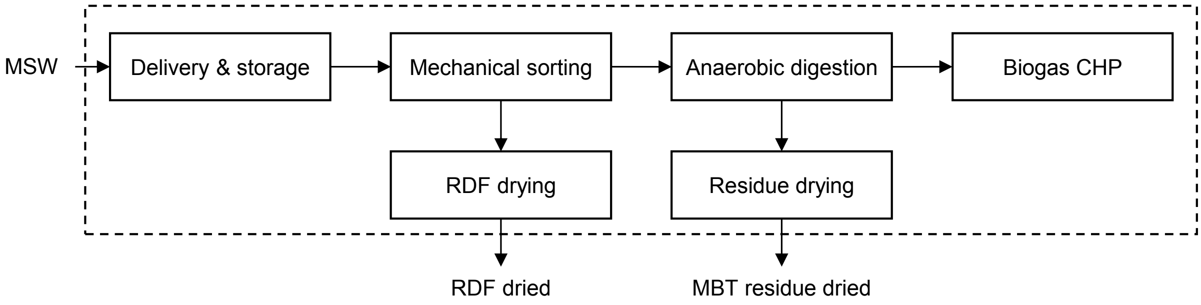

Figure 29: Visualization of the mechanical biological treatment (adapted from [84])

Table 22: Inventory modeling assumptions for the MBT and MR plant

MBT total plant input [276, 277]	
Fresh waster	963 l/t input
Natural gas	45 kWh/t input
MBT mechanical sorting [266]	
Electricity consumption	20 kWh/t input
RDF & MBT residue drying [266]	
Residual moisture content	5 wt.-%
Electricity consumption	60 kWh/t moisture
Heat consumption	850 kWh/t moisture
Anaerobic digestion [278]	
Diesel	0.9 l/t input
Heat consumption	30.6 kWh/t input
CH_4 yield from biochemical methane potential	70%
CH_4 fraction in biogas	63 vol.-%
Biogas leakage	2.7%
CHP engine [266, 279, 280]	
Heat / electricity efficiency	50% / 42%
CHP engine flue gas emissions	mg/m^3(STP)
NO_X	48
CO	65
NMVOC	10
CH_4	358
Material recovery [273]	
Diesel	2.2 l/t input
Electricity	90 kWh/t input

3.4.2. Waste incineration

Waste incineration facilities in Germany apply mature technology with high reliability and availability for waste conversion and flue gas cleaning [7, 106]. However, the energy efficiency can vary significantly depending on applied equipment, process configuration and feedstock [106]. The combustion process and energy recovery are modelled in Aspen Plus to determine direct correlations between configuration, feedstock and efficiency. Flue gas cleaning is modelled by KPI-based calculation. The modelled incineration process includes combustion chamber, 3-stage heat recovery (economizer, evaporator, superheater), 2-stage steam turbine (back pressure turbine and condensation turbine) and flue gas cleaning (dust removal, dry-sorbent acid gas removal, deNO$_X$ system). Process variations that impact the energy recovery efficiency include the applied steam cycle parameters and applied measures for energy integration (air and condensate preheating, intermediate steam reheating and flue gas recirculation). The process model is set up in two configurations (see table 23), which are both applied for CHP and electricity production. The basic level configuration reflects the current average efficiency level in Germany [7]. The advanced level configuration is adapted to increase the energy recovery to a level that is in accordance with best available technique requirements for newly built plants [106]. General modelling assumptions and the calculated energy efficiency for each concept are shown in tables 24 and 25.

Table 23: Applied technology configurations for basic and advanced waste incineration [106, 281]

		Technology level	
		Basic	Advanced
LP turbine outlet pressure	mbar	120	60
Air preheating temperature (via intermediate steam extraction)	°C	-	150
Flue gas outlet temperature (for condensate preheating)	°C	-	140
Intermediate steam reheating	°C	-	400
HP steam pressure	bar	40	130
HP steam temperature	°C	400	440
Flue gas recirculation		0%	20%

Table 24: Calculation results for incineration with varying feedstock and technology configuration in terms of net electrical efficiency / thermal output efficiency

	Basic		Advanced	
	CHP (σ=0.35)	Electricity only	CHP (σ=0.35)	Electricity only
MSW	MSW1 0.12 / 0.34	MSW2 0.19 / 0.0	MSW3 0.15 / 0.42	MSW4 0.26 / 0.0
RDF	RDF1 0.15 / 0.43	RDF2 0.24 / 0.0	RDF3 0.18 / 0.51	RDF4 0.31 / 0.0

Table 25: Modelling assumptions for waste incineration process [106, 282–286]

Incineration modelling approach	Thermodynamic equilibrium
Radiation heat loss	3.0 % of LHV input
Unconverted carbon	1.5 %
Combustion fly ash formation	3000 mg / m^3 (STP)
Combustion NOx formation	350 mg / m^3 (STP)
Air excess ratio	1.8
Light fuel oil input	2.5 l / t waste input
Flue gas temperature after economizer	180 °C
Isentropic efficiency of HP / LP turbine	92 % / 90 %
Plant electricity demand	4 % of LHV input
Heat export condition	5 bar saturated steam
CHP electric-thermal output ratio (σ)	0.35
Dry-gas acid gas removal with slaked lime	
Ca-(SO_2 + HCl) ratio (molar)	2.0
Activated carbon input	5 wt.-% of lime input
DeNOx ammonia-NOx ratio (molar)	1.1
Emissions to air (BAT average)	mg / m^3 (STP)
Dust	3.5
HCl	4
HF	1
SO_2	17.5
NO_X	85
CO	30
NH_3	6
CH_4	6.5

3.5. Utility processes and process chain balancing

The individual process models are applied and balanced in combination to generate coherent mass and energy balances for the respective chemical process chain. The applied process steps for each chemical production pathway are summarized in tables 29 and 30. Applied solid and liquid feedstock compositions are shown in tables 31 and 32. The following auxiliary process steps are applied. Cumulated process inventories are shown in table S13 and following.

Waste gas incineration

Occurring waste gases cannot be directly emitted but must be thermally treated. Flue gas heat is recovered for steam generation. Resulting emissions of CO_2 and SO_2 can be balanced directly from the gas composition. Other ecologically relevant flue gas component yields cannot be balanced directly and are therefore approximated by industrial emission values. These values are further applied for fired heating processes.

Table 26: Modelling assumptions of the waste gas incineration process

Flue gas temperature after energy recovery	200 °C
Burner excess air ratio	1.2
Non-fuel specific emission values	[287]
Reference state	Flue gas dry, 3 vol.-% oxygen
CO	40 mg / m³ (STP)
Particles	0.5 mg / m³ (STP)
NO_X	100 mg / m³ (STP)

Waste water treatment

Wastewater treatment is balanced according to a performance indicator-based life cycle inventory model for waste water treatment in the chemical sector [288]. Waste water compositions from Aspen Plus are converted into defined pollutant parameters shown in table 27. Calculated processing steps include nanofiltration, wet-air oxidation, mechanical-biological treatment and sludge incineration. The WWT process configuration is adjusted depending on waste water composition to fulfil emission limits, given in [288].

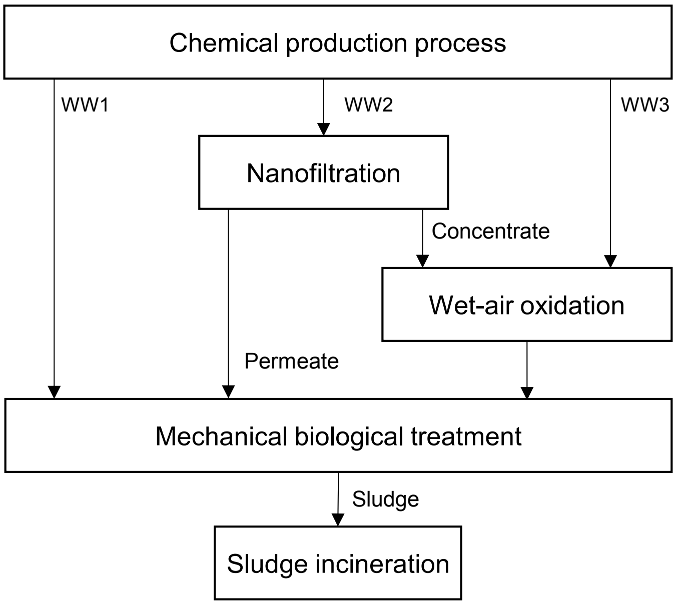

Figure 30: Process scheme of waste water treatment

Table 27: Overview waste water treatment balancing components

Water pollutant parameter	TOC ($TOC_{degradable}$, $TOC_{non\text{-}degradable}$), N_{total}, NH_4^+-N, Cl^-, SO_4^{2-}
Balanced utilities	Steam, electricity, deionized water, process water, natural gas, caustic soda, sulfuric acid
Balanced emissions to water	Chemical oxygen demand (COD), chloride, sulfate
Balanced emissions to air	CO_2, CO, NO_X, SO_2, Dust

Cryogenic cooling cycle

Multiple processes require cryogenic cooling at varying temperature levels. In practical applications, this is usually supplied by the integration of produced gases in compression/release cycles (e.g. ammonia, lower olefins). In this investigation, a representative three-stage refrigeration cycle is assumed and modelled, which associates the refrigeration demand at three temperature levels with the specific electricity and cooling water demand. Propylene, ethylene and methane are applied as refrigerants to supply cooling at – 25 °C, – 75 °C and – 135 °C, respectively [196].

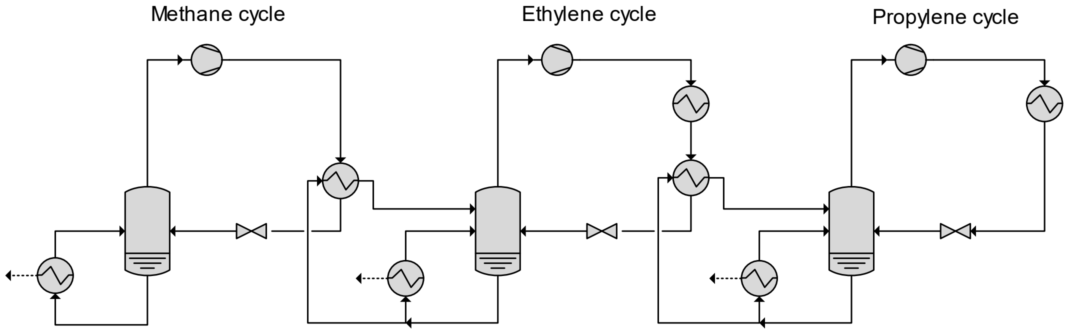

Figure 31: Visualization of the cooling cycle process

Utility balancing

Utilities are applied during process modelling to simplify uniform balancing of a large number of integrated process chains. Utilities are balanced in conclusion over all included process steps. Applied utilities are shown in table 28. Cumulated process utilities are calculated under the following assumptions:

- Produced fuel gas combustion is applied for direct heating and supply of HP and IP steam,
- excess HP and IP steam is thermally integrated for electricity production,
- cooling water is applied in a closed cycle with water loss of 2 % due to evaporation [289],
- boiler feed water (BFW) is prepared by membrane separation processes with utility demands of 1.175 t fresh water and 0.66 kWh electricity per t BFW [290].

Table 28: Overview of balanced process utilities for process chain balancing

Utility	Lower bound	Upper bound
HP steam	90 °C; 45 bar	275 °C; 45 bar
IP steam	90 °C; 15 bar	210 °C; 15 bar
LP steam	90 °C; 5 bar	160 °C; 5 bar
Cooling water	20 °C; 1 bar	30 °C; 1 bar

Table 29: Nomenclature of chemical production pathways

NSC	Naphtha steam cracking for olefin and aromatic production
NR	Naphtha catalytic reforming for aromatic production
LSC	LPG steam cracking for olefin production
NGR-MOH	Natural gas reforming for methanol production
NGR-NH3	Natural gas reforming for ammonia production
NGR-H2	Natural gas reforming for hydrogen production
(e)	Additional variation with electric heating instead of fired heating
FPOX	Heavy fuel oil partial oxidation for methanol production
G-MOH	Gasification for methanol production
G-MTO	Gasification for methanol-based olefin production
G-MTA	Gasification for methanol-based aromatic production
(h)	Additional variation with hydrogen integration in syngas (maximum extend)
G-NH3	Gasification for ammonia production
G-H2	Gasification for hydrogen production
P-fHTR	Pyrolysis with full hydrotreating for naphtha production
P-pHTR	Pyrolysis with partial hydrotreating for naphtha and aromatic production
P-POX	Pyrolysis and pyrolysis oil partial oxidation for methanol production
PTX-MOH	CO_2 and H_2-based methanol production
PTX-MTO	CO_2 and H_2-based olefin production (methanol intermediate)
PTX-MTA	CO_2 and H_2-based aromatic production (methanol intermediate)
PTX-NH3	N_2 and H_2-based ammonia production

Table 30: Overview of applied processes in base chemical production pathways

Process group	Conventional							Feedstock recycling								PTX			
Process	NSC (e)	NR (e)	LSC (e)	NGR-MOH (e)	NGR-NH3 (e)	NGR-H2 (e)	FPOX	G-MOH (h)	G-MTO (h)	G-MTA (h)	G-NH3	G-H2	P-fHTR	P-pHTR	P-POX	PTX-MOH	PTX-MTO	PTX-MTA	PTX-NH3
Feedstock	Naphtha		LPG	Natural gas			Heavy fuel oil	RDF / MPW								CO_2			N_2
Steam cracking	X		X																
Catalytic reforming		X																	
Steam reforming				X	X	X													
Partial oxidation							X								X				
Gasification								X	X	X	X	X							
Pyrolysis													X	X	X				
Oil hydroprocessing													X	X					
Olefin recovery	X		X						X								X		
Aromatic recovery	X	X								X				X				X	
Water quench							X	X	X	X	X	X			X				
CO Shift				X	X	X	X	(X)	(X)	(X)	X	X			X				
AGR (phys.)							X	X	X	X	X	X			X				
AGR (chem.)					X								X	X					
Sulfur recovery								X	X	X	X	X							
Hydrogen input								(X)	(X)	(X)			X	X		X	X	X	X
Methanol synthesis				X			X	X	X	X					X	X	X	X	
Ammonia synthesis					X						X								X
MTO synthesis									X								X		
MTA synthesis										X								X	
Main products																			
Olefins	X		X						X								X		
Aromatics	X	X								X				X				X	
Methanol				X			X	X							X	X			
Ammonia					X						X								X
Hydrogen						X						X							
Naphtha													X	X					

Table 31: Composition of waste feedstock

		RDF	MPW
Proximate analysis			
Moisture	wt.-%	4.88	5.00
Fixed carbon	wt.-% (wf)	13.86	3.67
Volatiles	wt.-% (wf)	75.84	89.27
Ash	wt.-% (wf)	10.30	7.06
Sum	wt.-% (wf)	100.00	100.00
Ultimate analysis			
Ash	wt.-% (wf)	10.30	7.06
Carbon	wt.-% (wf)	52.7	76.13
Hydrogen	wt.-% (wf)	8.12	11.45
Nitrogen	wt.-% (wf)	1.02	0.34
Chlorine	wt.-% (wf)	0.66	2.21
Sulfur	wt.-% (wf)	0.23	0.25
Oxygen	wt.-% (wf)	26.97	2.56
Sum	wt.-% (wf)	100.00	100.00
Heating value			
Lower heating value	kJ/kg (wf)	23,129	38,484
Higher heating value	kJ/kg (wf)	24,901	40,810
Source		[165]	[291]

Table 32: Composition of liquid flows

		Naphtha	RDF pyrolysis oil	MPW pyrolysis oil	Cracker fuel oil
Chemical composition					
Paraffins	wt.-%	72.7	40.3	49.5	13.1
Olefins/Naphthenes	wt.-%	21.3	18.6	35.1	15.3
Aromatics	wt.-%	6.0	41.1	15.4	71.6
Sum	wt.-%	100.0	100.0	100.0	100.0
Elementary composition					
Carbon	wt.-%	84.80	84.94	84.75	90.90
Hydrogen	wt.-%	15.17	13.05	13.42	7.20
Oxygen	wt.-%	0.00	1.63	1.30	1.80
Nitrogen	wt.-%	0.00	0.17	0.50	0.10
Chlorine	wt.-%	0.00	0.09	0.00	0.00
Sulfur	wt.-%	0.01	0.12	0.03	0.00
Sum	wt.-%	100.00	100.00	100.00	100.00
Lower heating value	MJ / kg	44.2	40.0	44.5	39.6
Boiling Curve					
10 vol.-%	°C	53	147	130	221
50 vol.-%	°C	77	279	290	323
90 vol.-%	°C	138	383	425	403
Source		[186]	[165]	[164]	[292]

3.6. Electricity and heat supply modelling

A focus point of differentiation between attributional and consequential LCA is the applied background data (compare chapter 2.3). In contrast to average processes applied in attributional LCA, marginal processes reflect the projected development in production that is caused by a change in the investigated foreground system. Especially energy and heat supply assumptions were shown to be critical in waste treatment and chemical production LCA [101, 293, 294]. The question is, how will the energy production system react to the increasing or decreasing energy demand that is caused by the application of the investigated process. The resulting marginal energy mix is impacted by the flexibility in production of the energy production sources, where they can either be able to react to changes (unconstrained) or not (constrained). Depending on the time frame, the flexibility can be restricted by the process technology, the energy source supply or the political framework.

To determine the marginal process or process mix, Weidema [96] proposed a procedure that includes the evaluation of the time horizon, the affected processes and markets, market trends and the flexibility of addressed technologies. However, Mathiesen et al. [101, 295] showed that the application is flawed for the prediction of energy system development and the associated determination of marginal processes. They recommend to include long-term perspectives on developments and sensitivity analysis of scenarios. Vandepaer et al. [296] proposed an approach based on existing energy trend scenarios, where the marginal energy mix is determined from the incremental shares of all unconstrained electricity producing technologies with a growing production in the respective time frame. The approach is applicable to energy system predictions without detailed insights into energy systems and is the basis of marginal energy processes mixes in the Ecoinvent database. The approach was exemplarily applied for generation of the long-term marginal electricity supply mix in Denmark [297]. In this case, renewable energy production (wind, solar, biomass) is considered unconstrained due to political targets in place to increase its production.

The approach is applied in this thesis for the development of electricity and district heating supply mixes. Development scenario investigations on the German electricity system are available in academic [298–300] and non-academic literature [301–304]. Projections of district heating development are addressed less frequently [305]. The report by BCG and Prognos [304] is applied due to its relative actuality, the consideration of German emission reduction targets and the inclusion of electricity and district heating development. Three pathways for energy system transformation are presented, the middle way (80% pathway) is used for this thesis going forward. The reconstructed production compositions for average and marginal electricity and heat supply are presented in figures 32 to 35, including the calculated CO_2 footprint based on GaBi process inventories for individual energy sources.

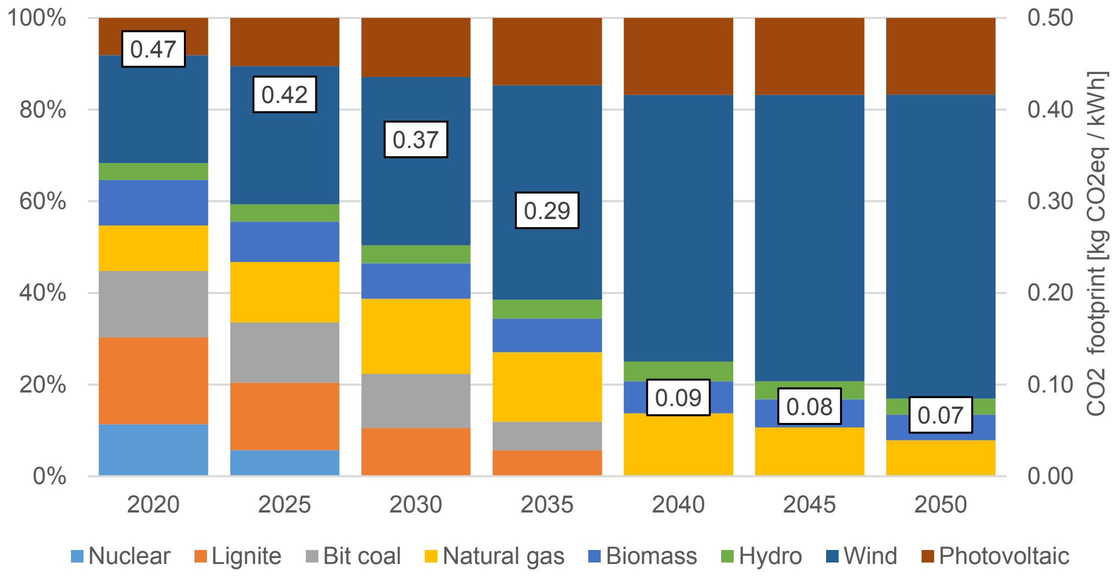

Figure 32: Composition and CO_2 footprint of projected average electricity mix

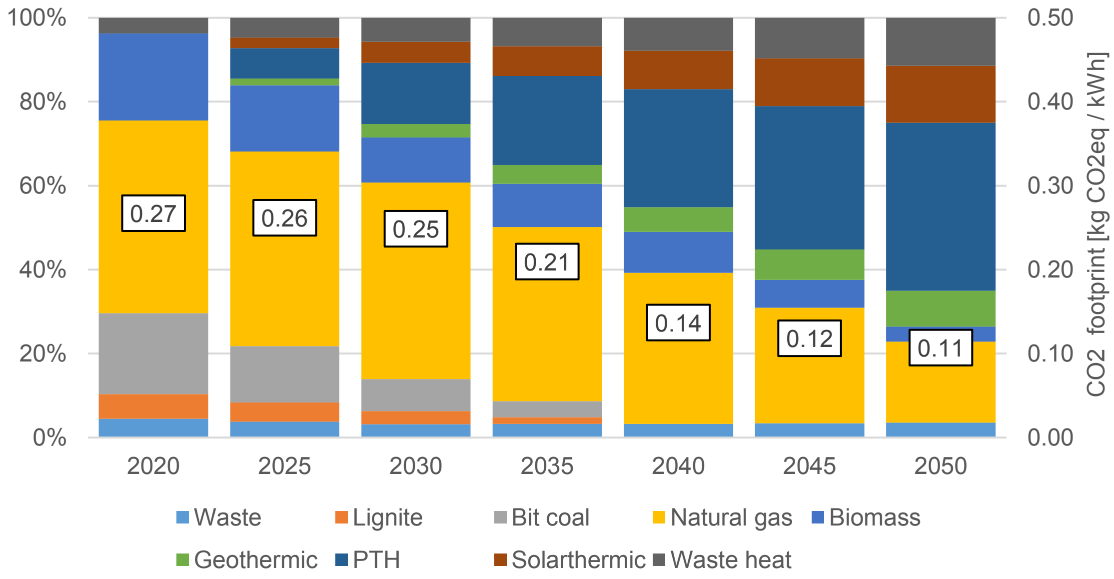

Figure 33: Composition and CO_2 footprint of projected average district heat mix

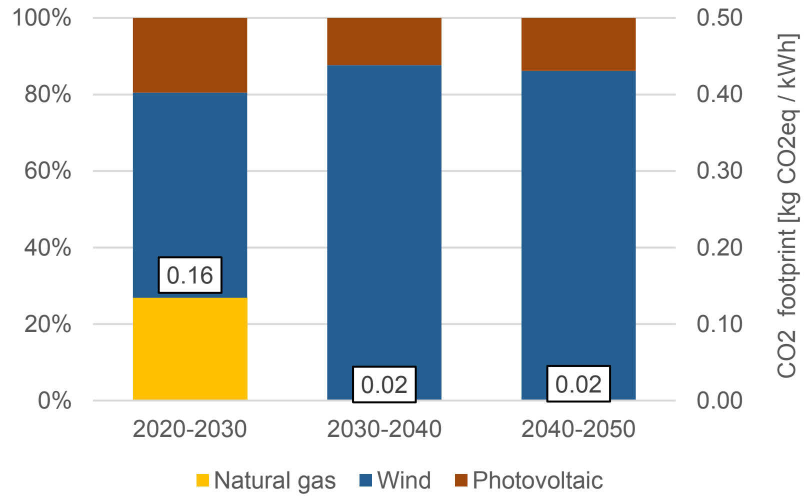

Figure 34: Composition and CO_2 footprint of projected marginal electricity mix

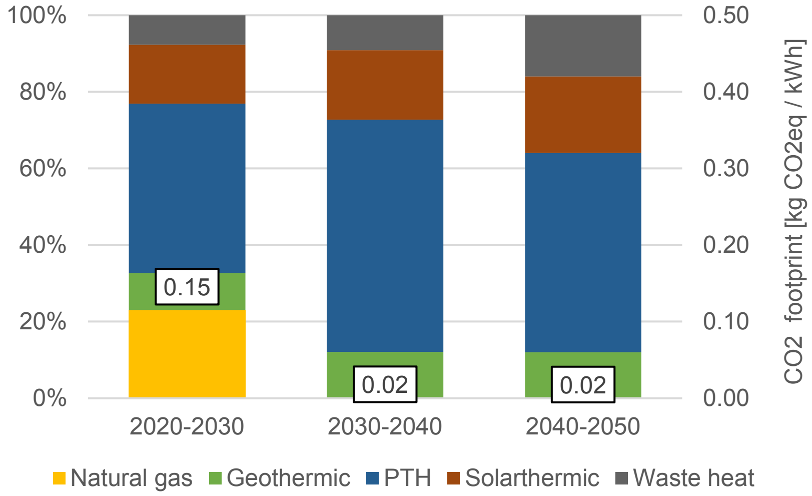

Figure 35: Composition and CO_2 footprint of projected marginal district heat mix

Chapter 4

Individual assessment of feedstock recycling processes

As feedstock recycling processes are not industrially deployed on a large scale and the technology development and demonstration is ongoing, the expectable process characteristics and the associated environmental impacts are unclear. Thus, the following chapter assesses exemplary waste gasification and pyrolysis pathways to quantify how much their environmental performance is impacted when non-optimal process technology is applied during process implementation or if the expected optimal process performance is not achievable.

4.1. Goal and scope definition

The objective of this investigation is the evaluation of three end-of-life treatment option for a commercial RDF under the condition of varying technology development levels and changes of the energy system in Germany in an attributional LCA. Various impact categories of the Product Environmental Footprint (PEF) methodology are assessed to rule out the occurrence of contradictory effects between the treatment processes or technology implementation levels. Further, the assessment is used to identify environmental hotspots and possible focus points of further development. Gasification, pyrolysis and incineration are assessed individually. A direct comparison of these treatment options is not subject of this assessment, as this is performed in a systemic context in the following chapter.

The applied RDF composition is shown in table 31. The functional unit is defined as the treatment of 1 kg of RDF. A zero-burden-approach is applied, meaning that waste generation is not considered as a supply chain (compare chapter 2.2). Further, waste collection, processing and upgrading of waste fractions to RDF are considered uniform between all treatment options and are therefore neglected.

4.2. Life cycle inventory

The investigated inventory systems are shown in figures 36 to 38. The foreground system (including all processes that are directly impacted by changes in the system) is marked by the grey area. Inventories are varied in two perspectives. First, the applied technology level in terms of material efficiency (high efficiency M; low efficiency m) and energy efficiency (high efficiency E; low efficiency e) for the gasification and pyrolysis processes is varied. Gasification assessment further includes the basic configuration, i.e. without application of a secondary gasification stage. The respective parameters and configurations are derived in chapter 3.1.1 (gasification) and chapter 3.1.3 (pyrolysis). For RDF incineration, the technology level concerning the energy efficiency is varied (compare chapter 3.4.2). Secondly, electricity and district heat reference years are varied between 2025, 2035 and 2045 to consider the impact of a long-term energy system transition (compare chapter 3.6).

Allocated products and utilities are summarized in table 33. This includes aggregated GaBi datasets for the end-of-life treatment of solid residues from incineration and gasification, which are direct landfilling of bottom ash and slag and advanced treatment of fly ash (including incineration, macro encapsulation, vitrification, transport and landfilling). The inventory system is expanded to include variable or non-available dataset, i.e. incineration with energy recovery for carbonaceous pyrolysis residues (compare chapter 3.4.2), oxygen supply for gasification by cryogenic air separation (compare table 36) and catalyst supply. The applied pyrolysis catalyst is reported to be a zeolitic material [18]. Applicable inventories for catalyst production are not available in GaBi databases, but can be reproduced from the GREET catalyst module [306]. The generated input materials are presented in table S25. The resulting calculated CO_2 footprint at 9.5 kg CO_2eq / kg is in reasonable alignment with the reported footprint by GREET (7.7 kg CO_2eq / kg [307]). However, the uncertainty of the catalyst production footprint is high, as other researchers report a significantly lower impact of 1.8 kg CO_2eq / kg for the production of a zeolitic catalyst [308].

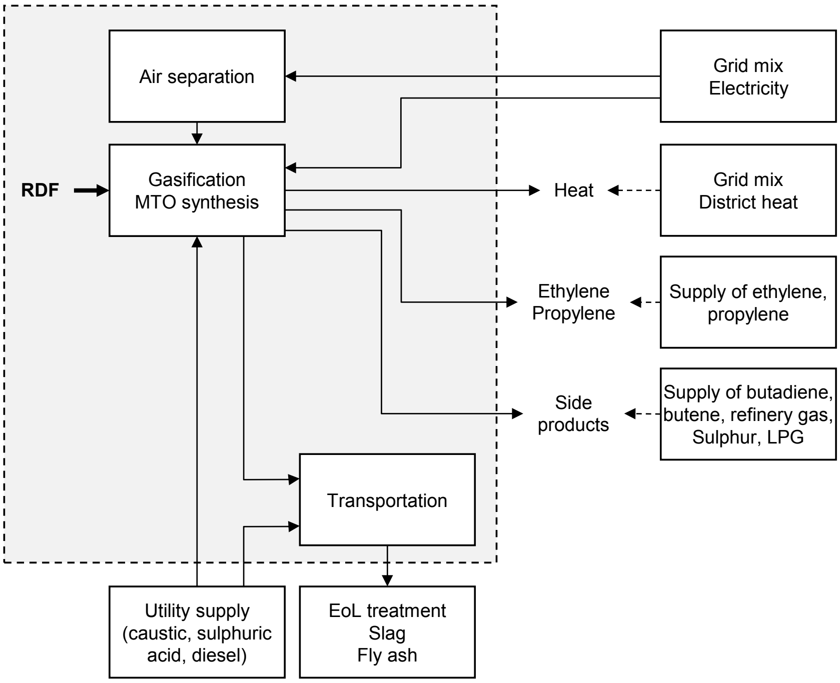

Figure 36: Visualization of life cycle inventory for RDF gasification process

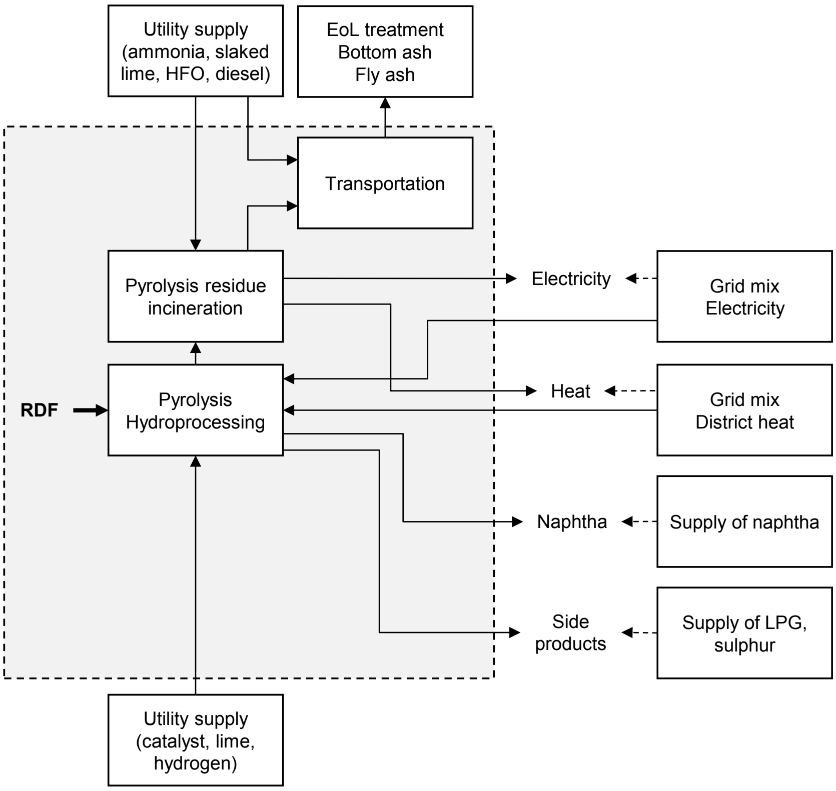

Figure 37: Visualization of life cycle inventory for RDF pyrolysis process

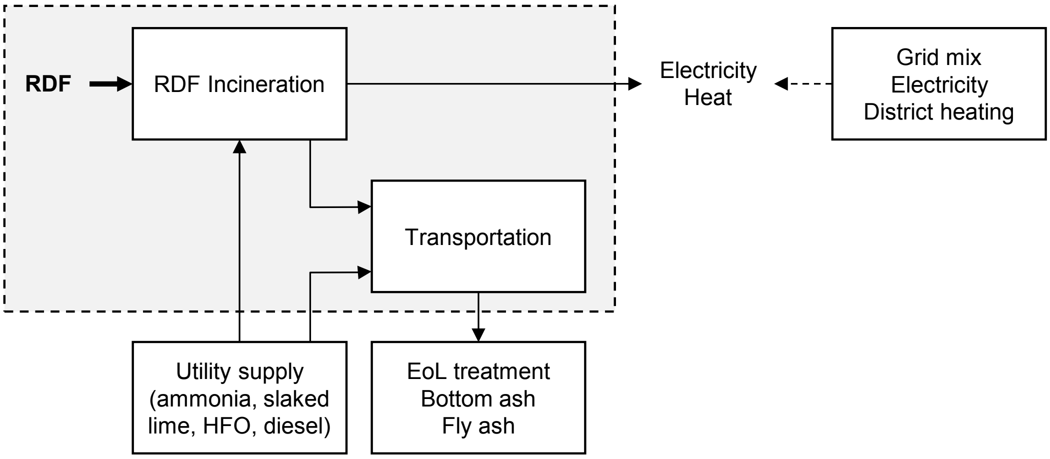

Figure 38: Visualization of life cycle inventory for RDF incineration process

Table 33: Overview of allocated products and processes

Allocated products / processes	Allocation	GaBI data set / source
Main products		
Naphtha	Mass	DE: Naphtha at refinery
Ethylene	Mass	DE: Ethene (ethylene)
Propylene	Mass	DE: Propene (propylene)
Side products		
Butadiene	Mass	DE: 1,3-Butadiene
C4 Mix	Mass	DE: Butane at refinery
LPG	Mass	DE: Liquefied Petroleum Gas (LPG)
Fuel gas	Energy	DE: Refinery gas at refinery
Sulfur	Mass	DE: Sulfur (elemental) at refinery
Utilities		
Ammonia	Mass	DE: Ammonia (NH_3) without CO_2 recovery
Slaked lime	Mass	DE: Calcium hydroxide ($Ca(OH)_2$; dry; slaked lime)
Diesel	Mass	DE: Diesel mix at refinery
Heavy fuel oil	Mass	DE: Heavy fuel oil at refinery
Caustic	Mass	DE: Sodium hydroxide (caustic soda) mix (100%)
Sulfuric acid	Mass	DE: Sulfuric acid mix (96%)
Lime	Mass	DE: Lime (CaO; quicklime lumpy)
Activated carbon	Mass	DE: Activated carbon
Catalyst	Mass	See table S25
Ash/slag end of life treatment		
Fly ash treatment	Mass	DE: Hazardous waste (statistic average) (C rich, worst case scenario incl. landfill)
Bottom ash / slag treatment	Mass	DE: Inert matter (Construction waste) to landfill
Energy		
Electricity	Energy	Average electricity production mix
Heat	Energy	Average district heating mix

4.3. Impact assessment

The environmental impacts of various impact categories are initially scanned to determine the critical aspects. Therefore, the total environmental impacts of the reference cases are normalized according to the Environmental Footprint normalization factors to determine the impact categories that are most significantly affected. Please note that normalization does not weight the different impact categories against each other in general significance, but puts the individual impact of the specific case in relation to the total category impact of the European Union divided by the total population number [309]. Normalized impacts are presented in person equivalents (PE). Results for major impact categories are presented in figure 39. It is apparent that significant impacts primarily concern global warming (GW) and depletion of fossil resources (FRD). Other impact categories in water scarcity (WSC), acidification (AC), eutrophication (EUT) and photochemical ozone formation (POF) show significantly lower normalized impacts. Consequently, the subsequent discussion focuses on global warming and fossil resource depletion. Please note that the application of normalized impacts is only significant for a generalized scouting, as criticality of aspects can vary for the process application in specific situations, e.g. process water consumption in water-deprived areas.

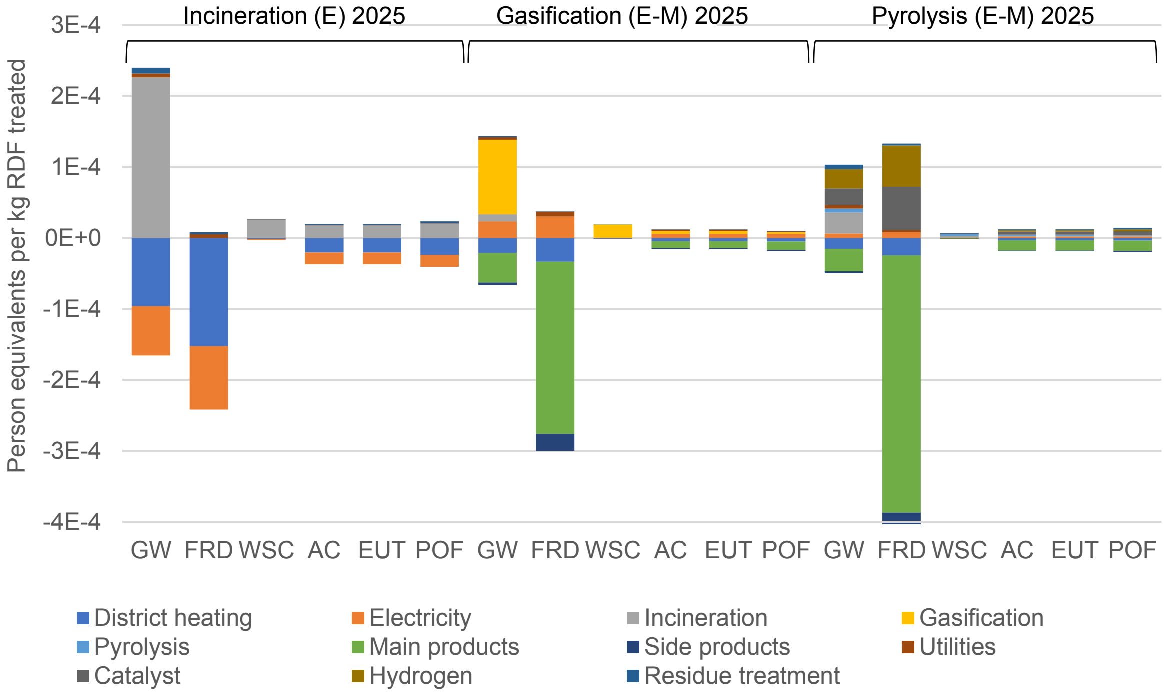

Figure 39: Normalized impact results of reference cases for major impact categories of PEF

Incineration

The impact assessment results of the incineration for global warming impact (GWI) and fossil resource depletion impact (FRDI) are shown in figures 40 and 41. It is shown that the net GWI is above zero for all applied cases, meaning that thermal waste treatment is associated with a climate burden. Due to the applied zero burden approach, thermal waste treatment is associated with fossil resource savings. Direct incineration emissions and the substituted electricity and district heat show the biggest impacts in GW and FRD while applied utilities and treatment of bottom ash and fly ash are shown to be insignificant. Direct incineration CO_2 emissions are only related to the feedstock carbon content and are therefore independent of the applied technology level or energy footprints.

Applying BAT level technology compared to the average level of energy recovery from waste, the substitutable energy (CHP electricity and heat at constant ratio) increases by 18 percent, leading to decreased GWI of 25 percent and an increase in FRDI savings by 19 percent. A steep increase in net GWI and reduction of FRDI savings with evolving energy supply is shown. The relative impact of technology level improvement is decreasing for GW to about 5% for 2045 energy mix. Consequently, the incentive for high level technology installation and further technology development in energy efficiency is decreasing with increasing renewable energy supply from an environmental perspective.

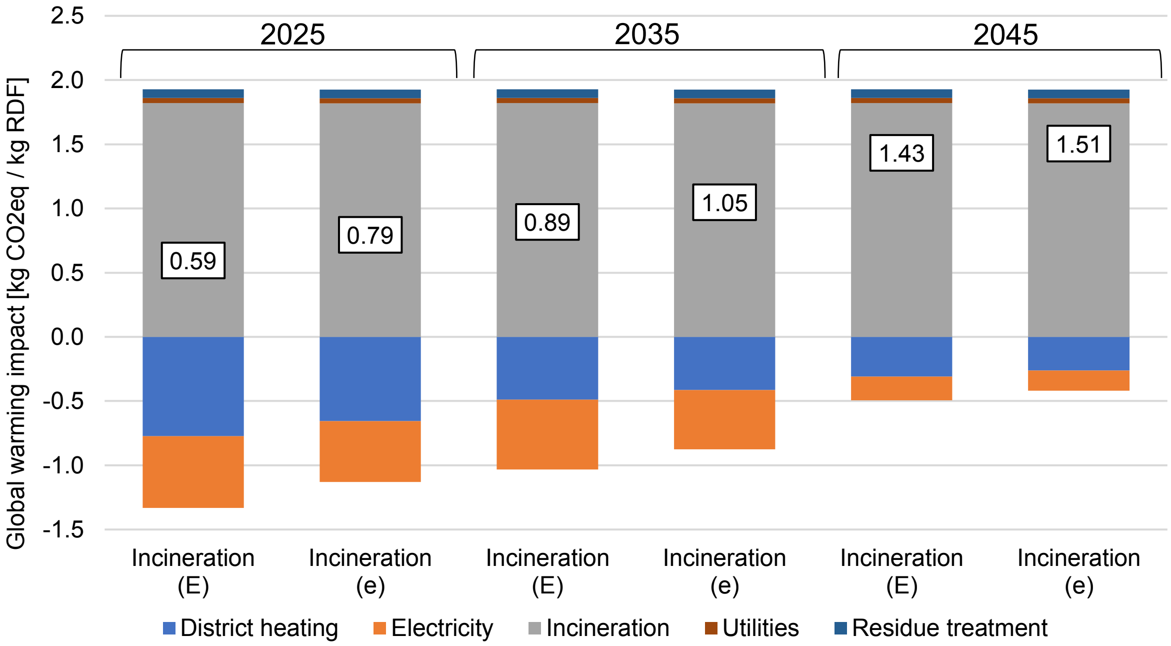

Figure 40: Global warming impact of RDF incineration with varying technology level and energy reference year

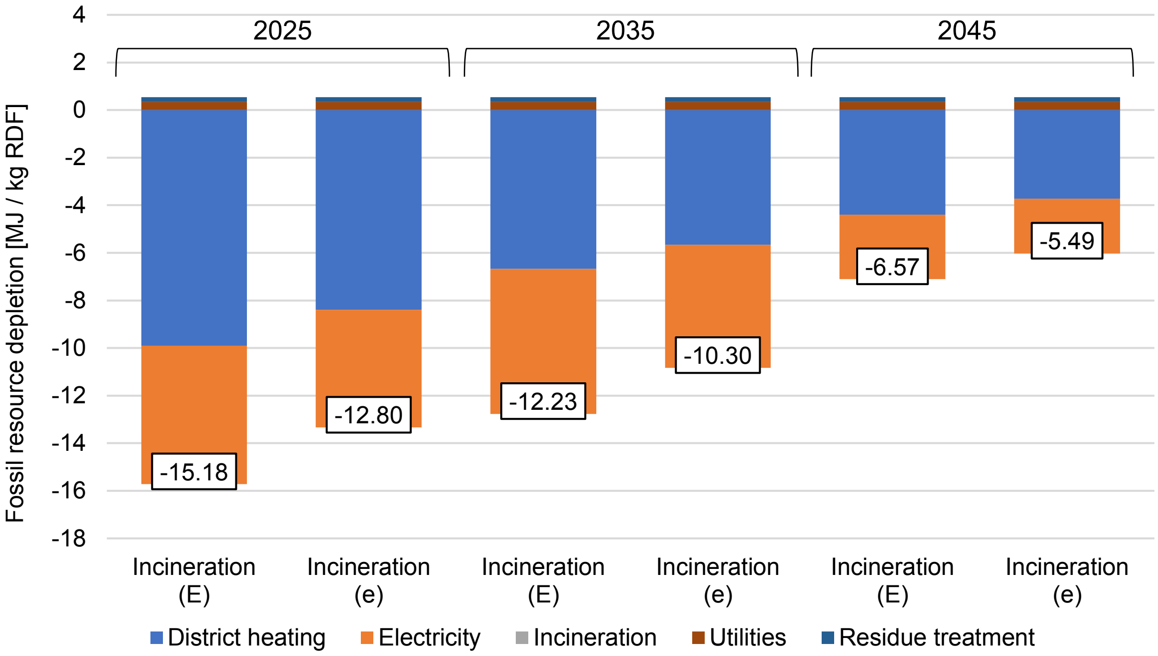

Figure 41: Resource depletion impact of RDF incineration with varying technology level and energy reference year

Gasification

The environmental impacts of gasification in the assessed cases are shown in figures 42 and 43. Net GWI burden and FRDI savings can be observed for all cases, similar to incineration. The main impacts include the direct process-based CO_2 emissions from syngas conditioning (concentrated CO_2 from acid gas removal), emissions from off-gas incineration, credits for main products and cumulated impacts of the electricity and heat balance. Impacts of side products, utilities and residue treatment are minor. The distribution of GW impacts between the main product fractions is shown in table 34. This distribution does not change significantly with technology level or applied background data. Expectedly, the targeted lower olefins in ethylene and propylene show the largest impact.

Assessing the impact of technology level requires a nuanced discussion due to the interconnection between material and energy outputs. In the visualizations of total GW and FRD impacts, cumulated electricity and heat impacts are shown despite including several sources that can contradict each other. Consequently, the impacts are illustrated in more detail in figures 44 and 45. Significant electricity demands leading to GWI are widely distributed over the gasification and syngas utilization process chain. Contributors include oxygen supply by air separation, RDF pelletizing, Rectisol scrubbing (primarily for cryogenic refrigeration), methanol synthesis (primarily for gas compression) and MTO synthesis (primarily for product gas compression and refrigeration for light product separation). Direct electricity-related GW benefits are generated by turbine decompression of excess HP steam. Further, substituted PTH due to district heat export contributes to a lower net electricity demand, especially in cases with low material efficiency. Heat sources along the gasification process chain include the CO shift reaction and consequent process steam condensation, methanol synthesis and off-gas incineration, while steam is consumed as process steam for gasification and for Rectisol scrubbing for solvent regeneration. The shown contributors summarize thermal balances of the units which can include several sources or demand that can vary in ratio (e.g. process steam and cooling jacket steam for the gasification unit; steam consumption and generation for CO shift unit).

In the following, the impact of technology level variation is discussed. In all configurations, energy efficiency reduction (E/e configuration, i.e. increase in specific heat loss) leads to a minor increase in GWI and decrease in FRDI benefit. Main contributors are the increased oxygen demand to achieve the desired gasification temperature, and the lowered syngas yield and subsequent product yield. The net impact of material efficiency reduction (M/m/basic configuration, i.e. decrease in carbon conversion and post-gasification temperature) depends on the underlying energy mix. Lower gasification temperature or lack of secondary gasification lead to a significant increase in syngas methane content, which is also visible by an increase in cold gas efficiency and decrease in syngas yield (compare table 4), which further leads to a lower overall product yield and higher process CO_2 emissions, but also lower electricity demand over the process chain. Methane contents are recovered into the methanol off-gas and thermally converted with energy recovery. Consequently, a lower material efficiency leads to a shift from material to energy production. All gasification configurations are net heat exporters, but the margin increases with decreasing material yield and the electricity balance switches from net import to export (see table S28). For high credits on energy production (i.e. under 2025 conditions) the low material efficiency configuration shows better GW and FRD performance than the high efficiency configuration. With decreasing energy credits, the trend is reversed and GW and FRD show better performance for configurations with high material efficiency. Configurations with high material efficiency display little sensitivity towards the applied energy framework due to the compensating impacts of net electricity and heat margins.

Table 34: Distribution of global warming impact benefits from main and side products

	Main products				Side products				
	Butadiene	Ethylene	Propylene	Naphtha	C4 Cut	LPG	Fuel gas	Sulfur	Sum
Gasif (E-M)	5.5%	42.1%	43.4%	0.0%	3.8%	3.4%	1.4%	0.4%	100.0%
Pyr (E-M)	0.0%	0.0%	0.0%	94.4%	0.0%	5.5%	0.0%	0.1%	100.0%

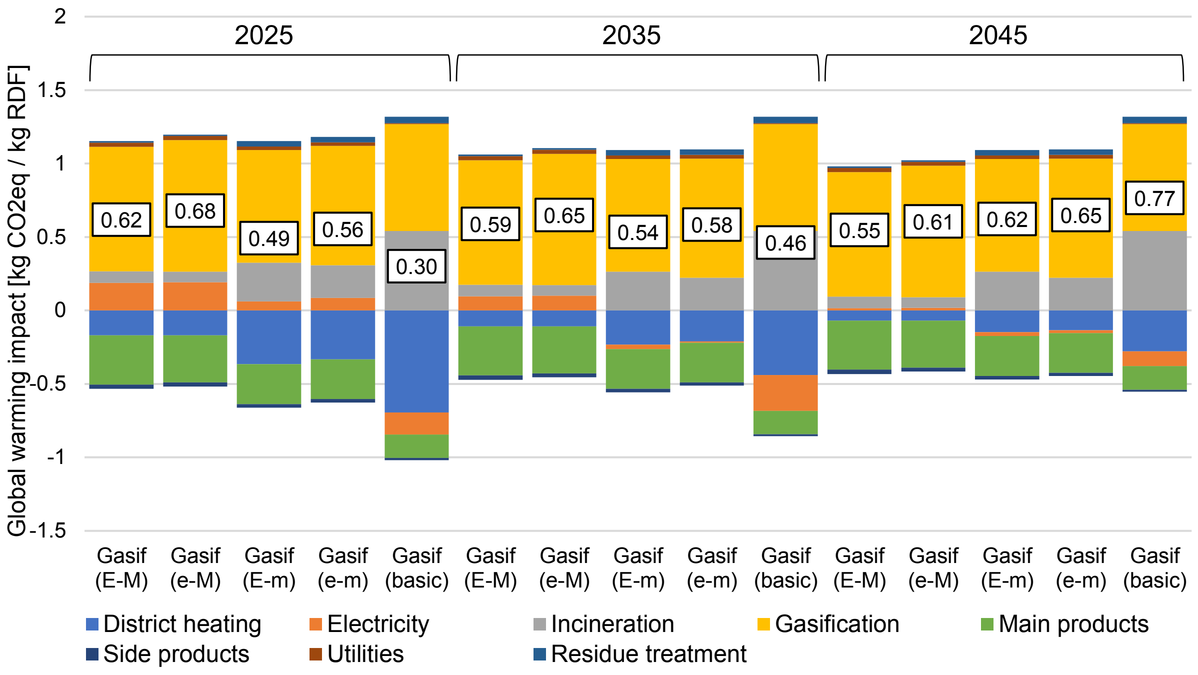

Figure 42: Global warming impact of RDF gasification with varying technology level and energy reference year

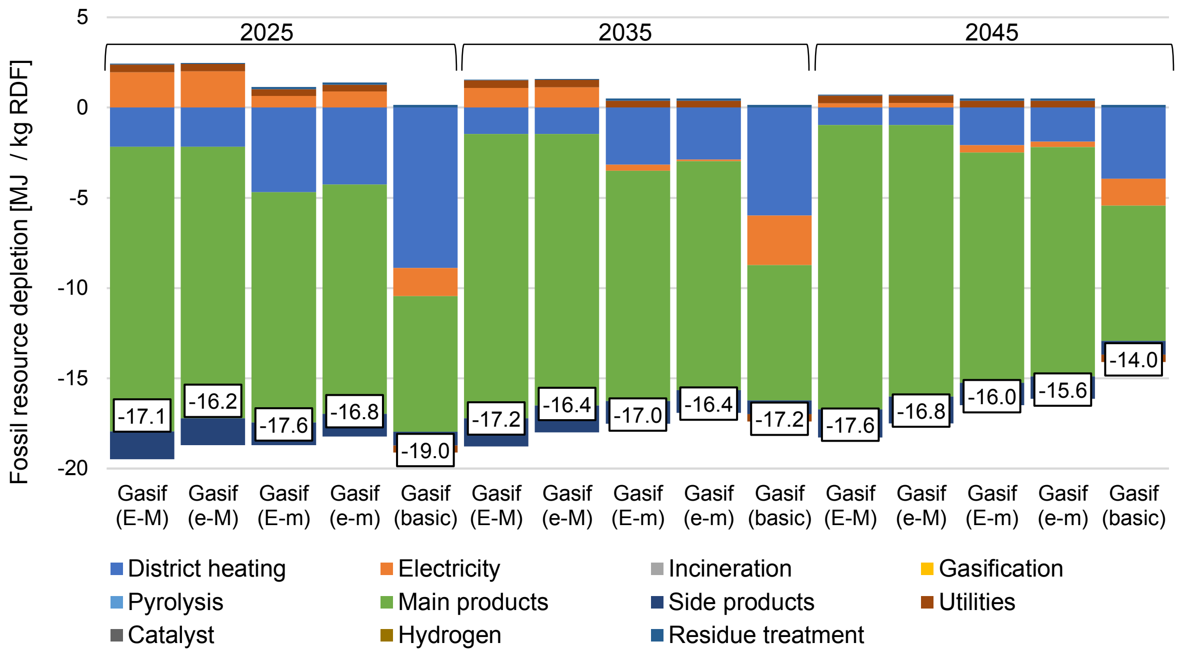

Figure 43: Resource depletion impact of RDF gasification with varying technology level and energy reference year

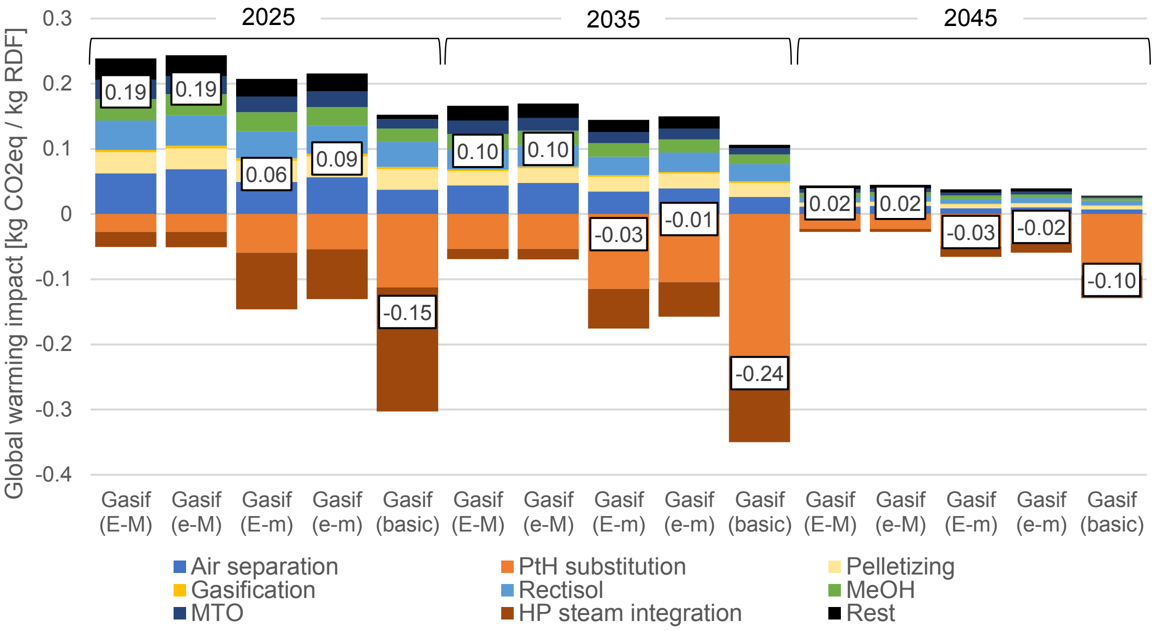

Figure 44: Distribution of electricity-related global warming impact of RDF gasification

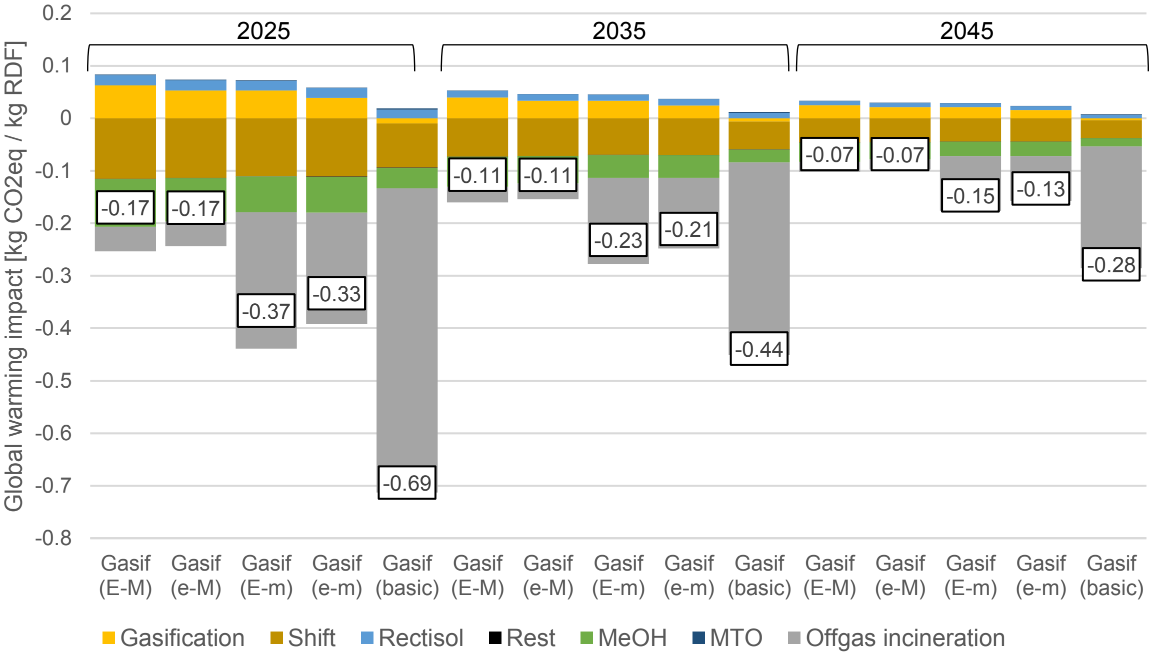

Figure 45: Distribution of heat-related global warming impact of RDF gasification

Pyrolysis

As for incineration and gasification, net GW burdens and FRD benefits are observed for all pyrolysis efficiency configurations and background energy mixes (see figures 46 and 47). Similar to gasification, main product credits (primarily naphtha, see table 34) and energy balances show a significant impact on GW and FRD. Further significant impacts include solid residue treatment by incineration, hydrogen demand for oil upgrading and catalyst supply. Direct emissions from pyrolysis and pyrolysis oil upgrading (i.e. incineration of pyrolysis gas and hydrotreating off-gas), consumed utilities and co-produced LPG lead to minor impacts.

Concerning the energy balance (figures 48 and 49), pyrolysis process electricity and heat demand show the largest contribution on the demand side. On the production site, electricity and heat supply are significantly determined by solid residue incineration, substitution of PTH-associated electricity and excess heat from oil upgrading. Note that fractionation of hydrotreated pyrolysis oil requires significant heating, which can be delivered by process integration with excess heat from hydrotreating and off-gas incineration, which is low in carbon emission due to its high hydrogen content (about 90 vol.-%). The impact of catalyst production is most significantly determined by heating (54% of GWI) and ammonia demand (22% of GWI, see table S25).

Energy efficiency variation (E/e configuration, i.e. increase in required pyrolysis temperature) leads to an increase of pyrolysis electricity demand of about 20%, but does not influence the total GWI or FRDI significantly. With decreasing material efficiency (M/m configuration, i.e. decrease in pyrolysis oil yield and increase in pyrolysis residue yield, carbon content and heating value) the GWI increase and FRDI benefits decrease. The system electricity balance shifts from net consumption to production, due to a lower pyrolysis process power demand and significant increase in energy generation from residue incineration. The hydrogen demand for oil hydroprocessing decreases as well. The benefits in energy production do not offset the additional GW burden from residue incineration and the decreasing credits from naphtha production. Similar to the effects observed for gasification, configurations with high material efficiency are not significantly impacted by the applied energy generation scenario due to partially compensation of GW impact margins of electricity and heat, while configurations with low material efficiency decrease in GW and FRD performance with increasing renewable energy yield.

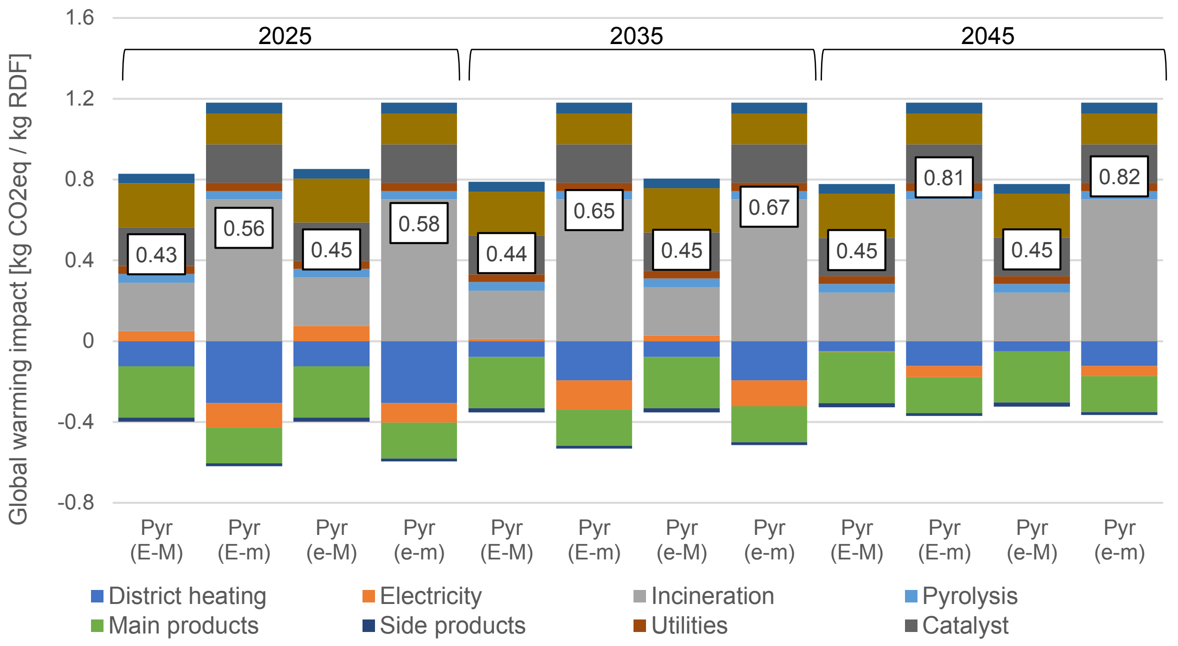

Figure 46: Global warming impact of RDF pyrolysis with varying technology level and energy reference year

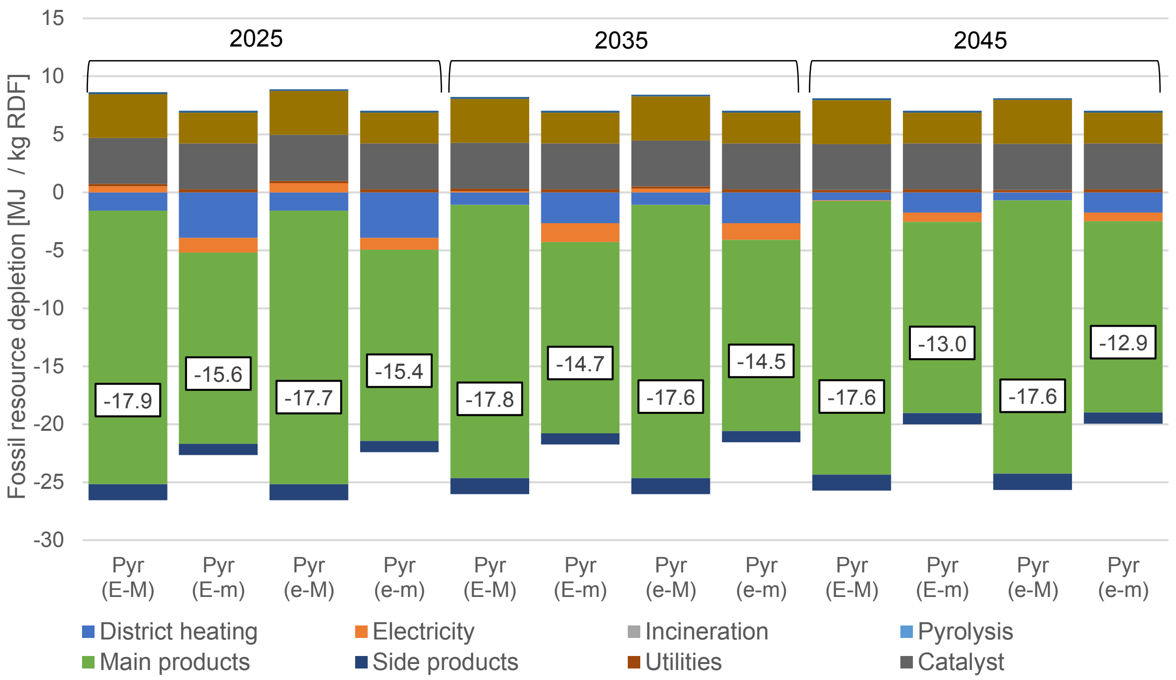

Figure 47: Resource depletion impact of RDF pyrolysis with varying technology level and energy reference year

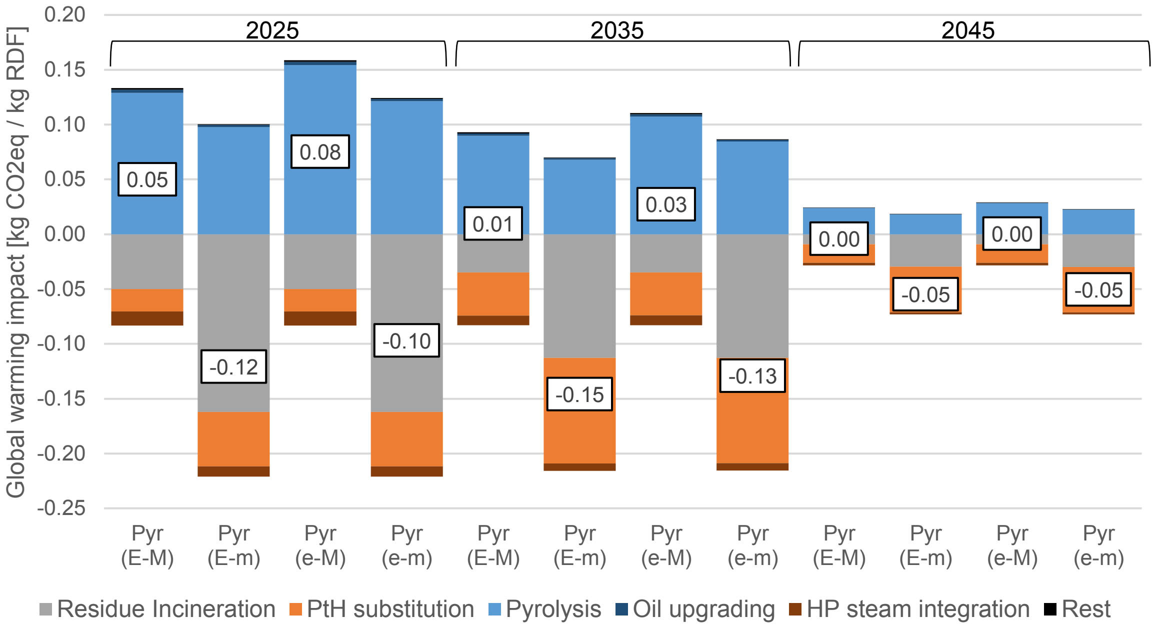

Figure 48: Distribution of electricity-related global warming impact of RDF pyrolysis

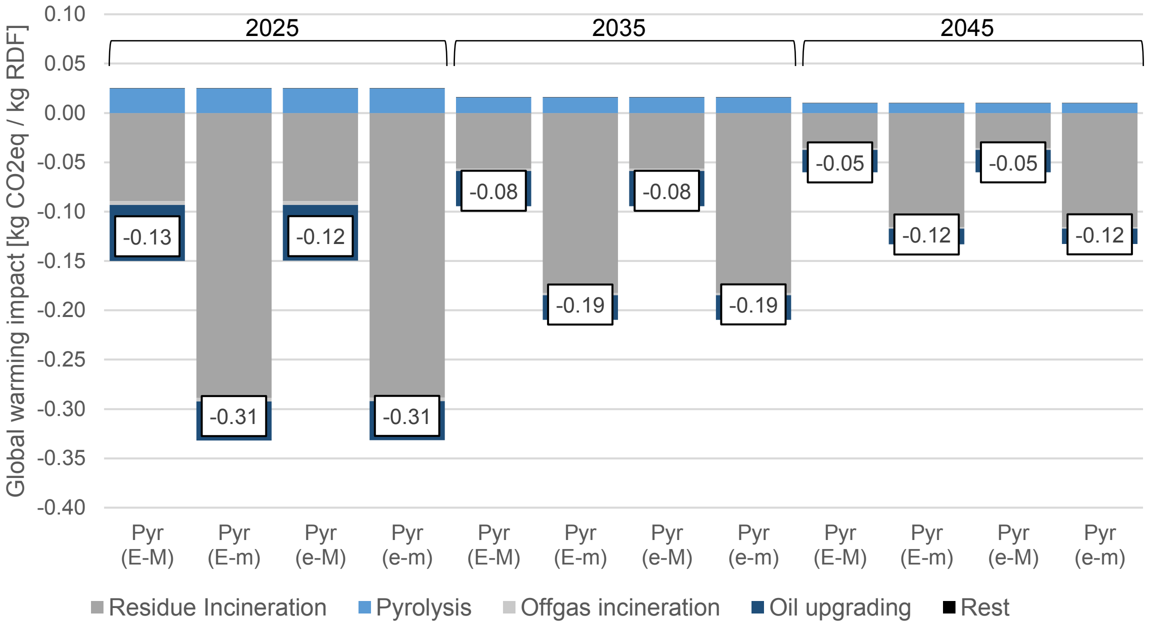

Figure 49: Distribution of heat-related global warming impact of RDF pyrolysis

4.4. Interpretation

For pyrolysis and gasification, the application of non-optimized process technology with a low material efficiency (meaning pyrolysis oil and syngas yield, respectively) leads to significant energy production from the thermal utilization of side streams and an associated high influence of grid electricity and district heating substitution. For gasification, the implementation of process technology on a lower level is not necessarily detrimental to the environmental performance in the short term if excess heat utilization can be facilitated, but high-level process technology application is shown to be necessary for environmental performance optimization under low credits from grid energy substitution. For pyrolysis, process technology with a high material efficiency is environmentally beneficial independently of the energy mix, but the margin compared to suboptimal technology increases with greener energy production footprints. For both processes, efficient excess heat utilization is essential for the environmental performance, especially for low material efficiency. For gasification, excess heat production is dissipated over several units in the process chain, leading to the preference of a facility location in a centralized setting with the possibility for industrial or district heat integration. For pyrolysis, heat integration is primarily relevant for centralized operation of oil upgrading and residue incineration, while the pyrolysis process can be operated in a decentralized site without significant impacts on environmental performance.

Process energy efficiency has a minor effect on the environmental impact. For gasification, this means that minimizing specific heat losses by avoiding partial load operation or increasing gasification pressure is not the decisive measure to optimize process sustainability. Similarly for pyrolysis, higher process temperature is acceptable from an environmental perspective if it contributes to higher oil yields. The environmental performance of incineration is significantly impacted by the underlying energy system. The margin of the environmental impact between high and low energy efficiency decreases with evolving energy generation, decreasing the incentive for technology development and high-level technology implementation for optimization of energy yields.

Limitations

Practically, a shift in product associated impacts would be expected in the discussed timeframe for the substituted chemical products (olefins and naphtha) due to shifts in production technologies and the underlying energy mix. Footprint development will presumably not be generated by process efficiency improvement of reference technologies (crude oil refining and steam cracking are highly mature technologies), but from technology shifting to alternative feedstocks and electricity-based production with an unclear pathway and significant uncertainty. Due to missing data, this effect is not considered in this assessment. Further focus points to increase robustness of the results would include more detailed sensitivity/uncertainty analysis on specific technology aspects instead of criteria grouping and the application of a concrete application setting with focus on the available local framework. In the impact assessment discussion, comparison of footprints between the addressed processes is avoided. Both issues are addressed in the next chapter.

Chapter 5

System-based assessment of feedstock recycling processes

The objective of the second LCA is the evaluation of the environmental impact of large-scale implementation of feedstock recycling pathways in relation to conventional chemical production and waste treatment as well as alternative processes for renewable energy integration to reduce environmental impacts. In a novel assessment approach, the multifunctionality of feedstock recycling processes is not addressed by shifting perspectives between waste and product (see chapter 2.2), but by integrating both production of major base chemicals and waste treatment for major post-consumer waste fractions in one common inventory system. By expanding the inventory foreground system to include all impacted processes system (i.e. processes of waste treatment and chemical production), the number of allocated products and processes is minimized to only maintain essential variables (background system, i.e. fossil feedstock and energy supply). Further, impact results are quantified in relation to the systemic framework, generating a general understanding on the application scope and the magnitude of total environmental impacts that can be expected from application of feedstock recycling or alternative technologies.

The system-based potential analysis applies framework principles of consequential LCA. This includes the system expansion of all affected processes and the application of a marginal mix for energy supply instead of an average mix. In the systemic context, no burden allocation to products is applied, instead environmental impacts are directly associated with the process of their origin. Still, the study should not be considered a consequential LCA, as the consideration of implementation pathways for alternative processes or products as the key defining element is missing, including the consideration market dynamics, regulatory framework or certification of products (compare chapter 2.3). Basically, consequential assessments describe possible transformation paths, while the introduced potential assessment addresses possible transformation results and their environmental impact regardless of the path.

5.1. Goal and scope definition

The assessment investigates the environmental impacts of feedstock recycling via the utilization of waste fractions from municipal solid waste (MSW), and recyclable materials rich in plastics (RMP) in a scenario-based case study of Germany. Basis for comparison is the assessment of the impact of: (1) feedstock recycling against conventional waste treatment processes (i.e. incineration) and fossil-based chemical production; (2) the comparison of various application pathways of feedstock recycling products (pyrolysis oil and syngas) and (3) feedstock recycling against alternative other developing technologies in PTX-based and electrically heated chemical production.

The system boundaries are chosen to reflect the direct effects associated with the application of feedstock recycling pathways without allocation. The environmental impacts of different feedstock recycling pathways can therefore be derived as the deviation in a uniform production system with and without their application. The impact is assessed on two scopes: (1) on an incremental application base to quantify specific environmental footprints of feedstock recycling pathways and (2) on a maximum application base to determine the total environmental impact potential under the defined system constraints. Note that the assessment does not provide absolute environmental footprints for individual products, processes or industry sectors.

System description & boundaries

The investigation is based on an exemplary system framework for Germany. Waste treatment and base chemical production are defined as one common system. In consequential LCA, the functional unit of a product system refers to the quantified description of the performance requirements that the product system fulfils [310]. Thus, the functional unit consists of the assumed quantities for waste treatment and major base chemical production (see table 35). Produced annual base chemical quantities are adopted from VCL statistics [185]. Applicable waste quantities are derived from the European Waste Classification System and from reported statistical data for waste treatment in Germany in 2018 [265, 268, 311]. MSW includes cumulated quantities of the waste code numbers EAV-20030101 (“Household waste, commercial waste similar to household waste collected together via public refuse collection”) and EAV-20030100 (“mixed municipal waste, non-differentiable”) that are directed to municipal solid waste incinerators and mechanical biological treatment plants. RMP includes the quantities of waste code numbers EAV-15010601 ("light weight packaging"), EAV-150102 (“plastic packaging”), EAV-15010600 (“mixed packaging, not differentiable”), EAV- 15010602 (“mixed valuable materials together with lightweight packaging”), EAV- 20019901 (“mixed valuable materials without lightweight packaging”) and EAV- 200139 (“plastics”). Quantities for produced base chemicals and treated waste are maintained consistent throughout the investigation.

Table 35: Assumptions for quantities for waste treatment and base chemical production

Waste treatment	[265, 268]
Residual municipal solid waste (MSW)	10.52 Mt
Recyclable materials rich in plastics (RMP)	3.93 Mt
Base chemical production	[185]
Lower olefins (C2 to C4)	9.37 Mt
BTX aromatics	2.59 Mt
Methanol	1.13 Mt
Ammonia	3.13 Mt
Hydrogen	0.47 Mt

The assessment is performed in two frameworks. The *Framework Status Quo* (FSQ, see figure 50) is based on a current production scenario for Germany. Conventional chemical production is based on fossil feedstock utilization (i.e. naphtha, natural gas). Conventional waste treatment of the investigated waste fractions considers thermal treatment of non-recyclables, associated with generation of electricity and steam for district heating. The system balance for electricity and heat (baseline energy) is determined by a reference scenario without application of feedstock recycling and is maintained through all scenarios in the framework. By feedstock recycling application, energy generation from waste is decreased. The offset in the system balance is substituted by energy integration (substitution/marginal energy). The marginal energy mix is derived from a projection of the development in the German energy system (see chapter 3.6).

The *Framework Energy Integration* (FEI, see figure 51) assumes a future renewable energy supply to the process industry to reduce GHG emissions via Power-to-Heat (PTH) applications, direct electric process heating and hydrogen integration. The scope of perspective additional electricity integration is unclear, since there is considerable uncertainty in renewable power projections. Germany's total renewable energy production in Germany in 2019 was 237 TWh, with 127 TWh being wind-based energy [312]. To achieve carbon neutrality, the German chemical industry projects an annual energy demand of 685 TWh [11], almost three times the current renewable energy production. In contrast, system scenarios assume that 8 to 116 TWh renewable energy would be required for PTX and PTH applications in order for Germany to achieve its carbon reduction targets [313]. In this study, an exemplary electricity input of 100 TWh is assumed. The quantity is chosen to reflect a significant potential for emission reduction by electricity integration, but not large enough for complete emission avoidance. Further, the required electric energy input to achieve net zero global warming impact of the defined system is determined for various application scenario. The assumption of constant waste treatment, base chemical production and energy balance are maintained.

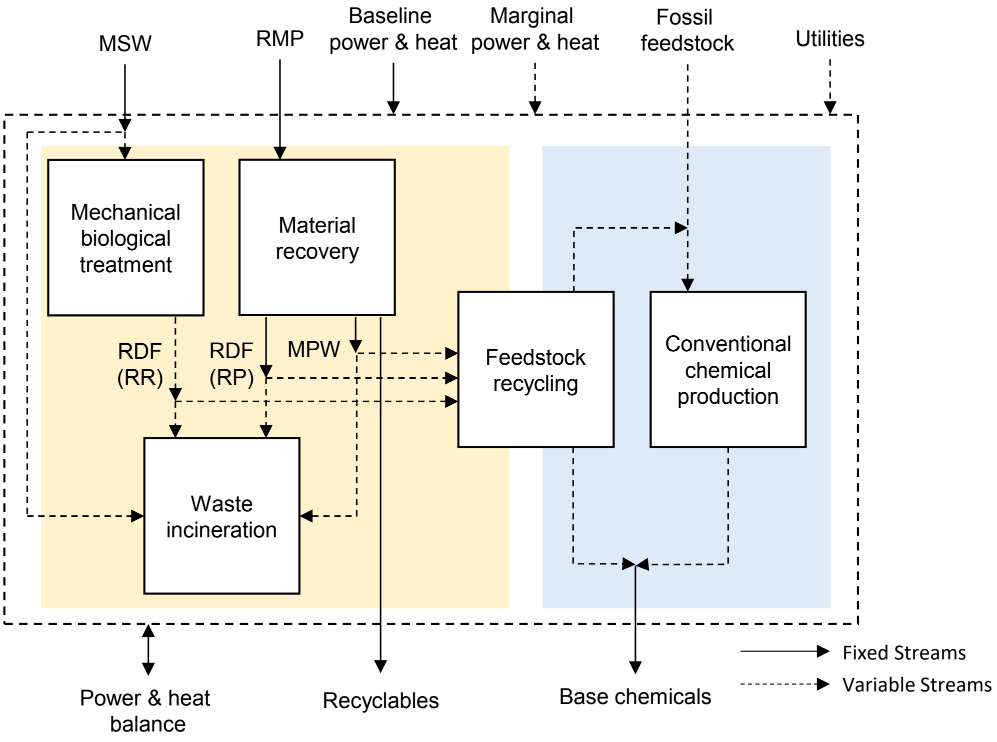

Figure 50: Visualization of inventory system in Framework Status Quo (FSQ)

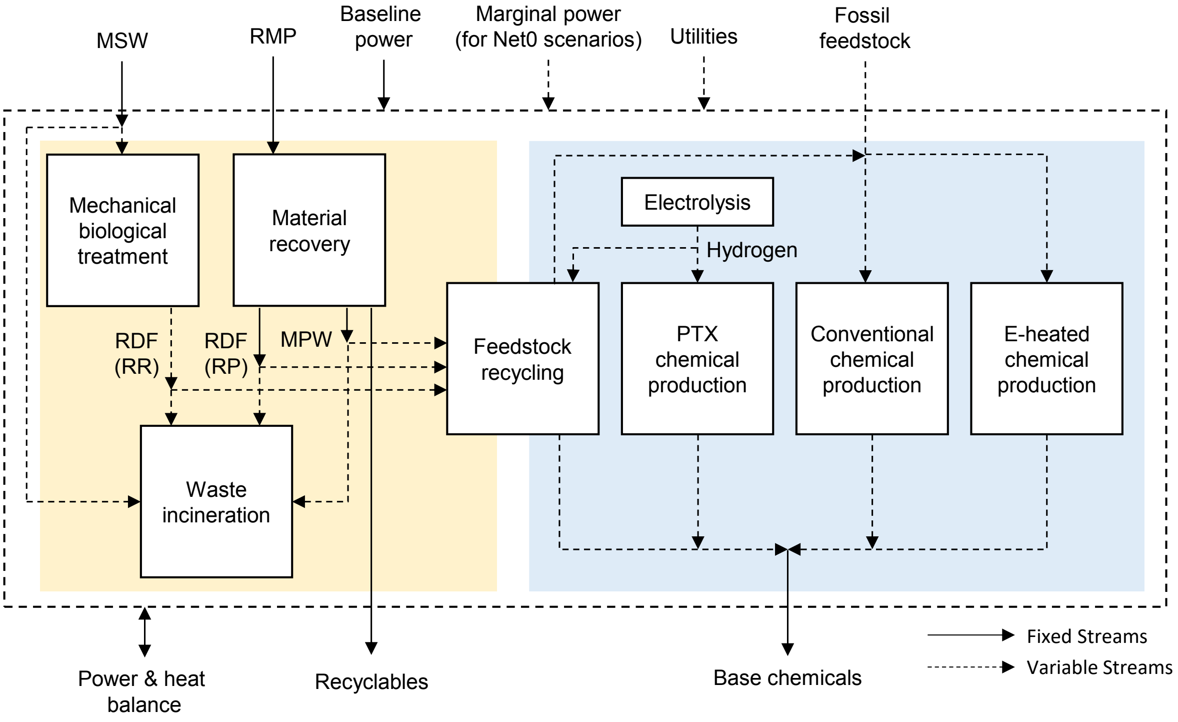

Figure 51: Visualization of inventory system in Framework Energy Integration (FEI)

5.2. Life cycle inventory

The life cycle inventory encompasses foreground system processes (i.e. waste treatment, chemical production, utility processes), background system processes and the applied assessment scenarios. Figure 52 provides an overview of the foreground system processes and the material streams in the inventory model. Modelling and inventory balancing of waste treatment and chemical processes is described in chapter 3. Applied process inventories are given in table S13 and following. Conventional reference production processes for the considered base chemicals (i.e. olefins, BTX aromatics, methanol, ammonia, hydrogen) include:

- steam cracking of naphtha and LPG,
- steam reforming of natural gas for the production of ammonia, methanol and hydrogen,
- partial oxidation of heavy fuel oil from naphtha steam cracking for methanol production,
- catalytic reforming of naphtha for the production of BTX aromatics.

For the treatment of LWP, material recovery is assumed to be the primary processing step in all scenarios as the investigation does not intend to assessment feedstock recycling against mechanical recycling. MSW is assessed for both direct incineration or mechanical biological treatment. Incineration of all applied waste fractions is uniformly performed at BAT level energy efficiency as prospective technology level variation is not subject of this chapter.

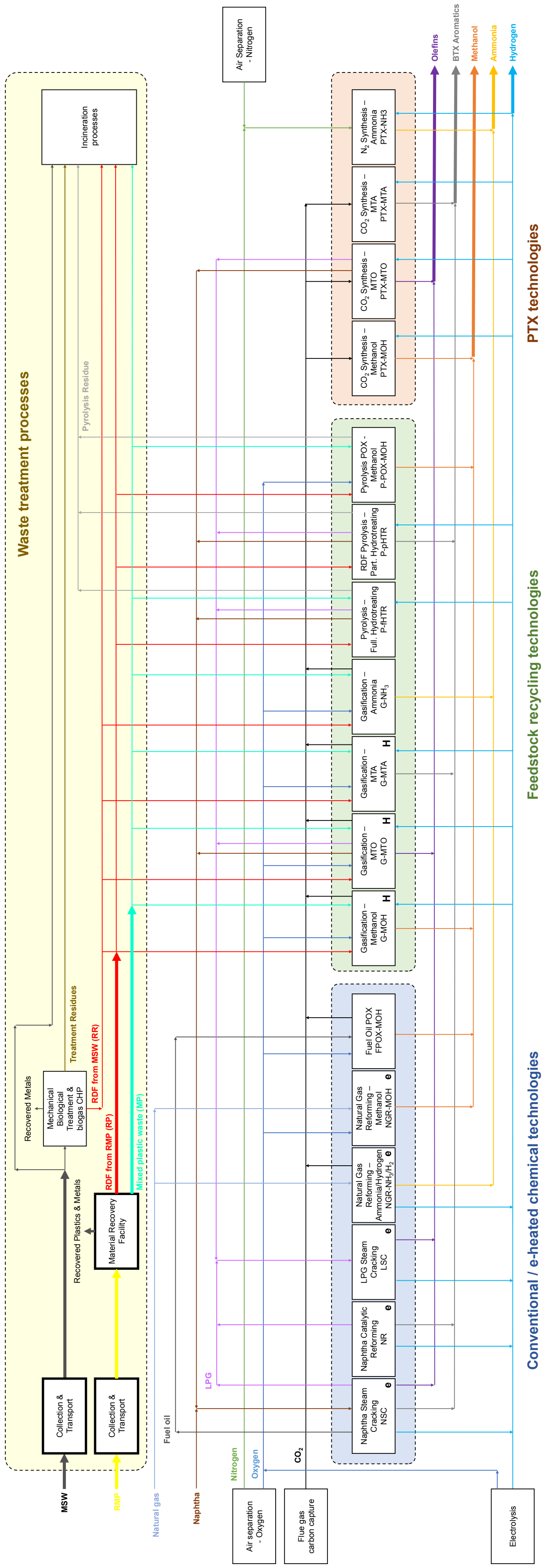

Figure 52: Visualization of processes and material streams of the inventory system

5.2.1. Utility, background system inventory and system integration

An overview of balancing assumptions for required utility processes is given in table 36. Applied background datasets are shown in table 37. System mass flow balancing, LCI integration and life cycle impact assessment is performed in GaBi 9.2.0. For both defined frameworks, a reference scenario without application of feedstock recycling pathways is defined. The impacts of feedstock recycling technologies are assessed based on scenarios with their application compared to respective reference scenario.

Table 36: Modelling assumptions of utility processes

Oxygen-ASU		
Oxygen purity	99.5 vol.-%	[314]
Electricity demand	0.245 kWh (el) / kg Oxygen	
High-purity nitrogen production	0.131 kg / kg Oxygen	
Nitrogen-ASU		
Electricity demand	0.2 kWh (el) / kg Nitrogen	[239]
Alkali electrolysis		
Electricity demand electrolysis	51.17 kWh (el) / kg Hydrogen	[233]
Electricity demand compression	0.63 kWh (el) / kg Hydrogen	[206]
Oxygen co-production	8.0 kg / kg Hydrogen	
Feed water supply for Power-to-Heat and electrolysis		
Feed water demand	1.175 t / t boiler feed water	[290]
Electricity demand	0.66 kWh / t boiler feed water	
Power-to-Heat efficiency for LP steam generation		
Electric boiler	0.99 MJ (th) / MJ (el)	[315]
High-temperature heat pump	2.50 MJ (th) / MJ (el)	[316]

Table 37: Overview of background processes

Process	Name in GaBi Database
Naphtha	DE: Naphtha at refinery, aggregated
Natural gas	DE: Natural gas mix, aggregated
Heavy fuel oil	DE: Heavy fuel oil at refinery, aggregated
Diesel	DE: Diesel mix at refinery, aggregated
Caustic soda	DE: Sodium hydroxide (caustic soda) mix, aggregated
Sulfuric acid	DE: Sulfuric acid mix (96%), aggregated
Limestone	DE: Limestone flour ($CaCO_3$, dried), aggregated
Slaked lime	DE: Calcium hydroxide ($Ca(OH)_2$; dry; slaked lime)
Activated carbon	DE: Activated carbon
Pyrolysis catalyst	See table S25

The following assumptions for general system integration are made:

- Electricity, LP steam and fuel gas are balanced on energy base, all other streams are balanced on mass base.
- Co-produced LPG is applied for steam cracking, external balancing is avoided.
- Co-produced fuel gas is balanced within the chemical production system, additional demand is met by natural gas supply.
- The external electricity and LP steam balance are benchmarked by the respective reference scenario and maintained constant in all scenarios within the framework.
- Pyrolysis residue and residue from mechanical biological treatment are treated by incineration.
- Pyrolysis fuel oil from naphtha cracking is applied as POX feedstock for methanol production in the scope of its production.

For the Framework Status Quo:

- The average 2025 electricity and district heating production mix (see chapter 3.6) is applied for baseline energy supply to give a quantitative reference for the determined marginal energy input, but is insignificant on evaluation results due to uniformity for all scenarios.
- For both marginal electricity and heat supply, the marginal mixes for Germany between 2020 and 2030 (long-term marginal mix) are applied.
- Oxygen is supplied by cryogenic air separation unit (Oxygen-ASU).

For the Framework Energy Integration:

- The average 2040 electricity production mix (see chapter 3.6) is applied for baseline electricity supply to give a quantitative reference for the determined marginal energy input, but is insignificant on evaluation results due to uniformity for all scenarios.
- Steam demand is balanced by application of Power-to-Heat.
- Concentrated CO_2 as feedstock is primarily provided by acid gas removal systems from syngas cleaning. Further demand is met by amine-based carbon capture from flue gas.
- High-purity nitrogen as feedstock is primarily provided as a side production from Oxygen-ASU. Further demand is met by air separation unit for nitrogen supply (Nitrogen-ASU).

The following products and processes are cut off due to:

- Uniformity for all investigated scenarios: recovered materials from material sorting
- Low expected significance on outcome (compare chapter 4.3): Sulfur production, ash, slag and fly ash treatment, recovered materials from mechanical biological treatment

5.2.2. Assessment scenario definition and parameter variation

The assessed scenarios are differentiated between the FSQ and the FEI framework. The impact of the application of individual process pathways is initially assessed in an incremental scope (INC) to quantify the specific impact of individual pathways without the variance of their quantitative application scope and to calculate pathway-specific footprints. In the FSQ framework, the incremental scope is reflected by the application of a relatively small amount of waste in the dimension of one large-scale facility with limited impact on the overall system and without restriction by the addressed product. An exemplary uniform limited scope of 300 kt treated waste per year as assumed, which is the magnitude of one industry-scale gasification facility. In the FEI framework, the incremental scope is reflected by the application of 1 TWh additional electricity input on the individual alternative technology pathways based on the reference scenario.

Larger-scale application is assessed for various scenarios. An overview of FSQ scenarios is given in table 38. The respective pathway configuration is applied to the maximum available scope, which can be restricted by the addressed waste quantity or target chemical. In the FEI framework, scenarios are assessed under two assumptions. FEI-100 scenarios assume a uniform input of 100 TWh of additional electric energy based on the reference scenario. FEI-Net0 scenarios describe system configurations with a calculated system global warming impact of zero (Net-Zero). Based on the applied technology pathways the resulting electricity input demand varies and is displayed in context with the impact assessment results. The investigated FEI scenarios are shown in table 39.

Further, sensitivity analysis is performed as parameter variation of key assessment parameters in the respective framework. In contrast to the prospective assessment of individual process in chapter 4, parameter variation is not applied for performance indicators of the investigated chemical processes, but auxiliary processes and assumptions of the system. For the FSQ framework, the impact of the marginal energy source is addressed. Contrasting the perspective (long-term) marginal energy supply mix, natural gas-based energy supply is applied as a short-term marginal energy source [98], representing energy market conditions in which renewable energy sources would not be able to react to an increase in energy demand from the described system. For the FEI framework, two key technology assumptions are addressed. Electrolysis efficiency varies depending on the assumed electrolysis development status (compare chapter 3.5) [232, 233]. The efficiency of substitution heat production from electricity (Power-to-Heat) varies depending on the application of electric boilers or high-temperature heat pumps [316].

Table 38: Overview of assessed scenarios in the Framework Status Quo

FSQ	**Chem. production**	**Waste treatment**	**Objective**
Ref	Conventional	MSW/RP/MP – Incineration	Reference
Ref-MBT	Conventional	MBT of MSW to RR RR/RP/MP – Incineration	Impact of MBT
G-RP/MP-MTO	MTO	RP/MP – Gasification MSW - Incineration	Gasification for olefin production with impact of MSW integration
G-MTO	MTO	MBT of MSW to RR RR/RP/MP – Gasification	
G-RP/MP-NH3	Gasification-based ammonia	RP/MP – Gasification MSW - Incineration	Impact of NH_3 production instead of MTO
G-NH3	Gasification-based ammonia	MBT of MSW to RR RR/RP/MP – Gasification	
P-fHTR	Conventional	RP/MP – Pyrolysis, full hydrotreating MSW - Incineration	Maximum impact of pyrolysis
P-MP-fHTR	Conventional	MP – Pyrolysis, full hydrotreating MSW/RP - Incineration	Impact of only MP pyrolysis
P-fHTR-G-RR-MTO	MTO	MBT of MSW to RR RP/MP – Pyrolysis, full hydrotreating RR - Gasification	Combination of pyrolysis and gasification
G-RP-MOH	Gasification-based methanol	RP – Gasification MSW/MP - Incineration	Impact of methanol substitution
G-RP/MP-MTA	MTO	RP/MP – Gasification MSW - Incineration	Impact of catalytic reforming substitution
P-RP-pHTR	Conventional	RP – Pyrolysis, partial hydrotreating MSW/MP - Incineration	Impact of BTX recovery from pyrolysis oil

Table 39: Overview of assessed scenarios in the framework Energy Integration

FEI	Chemical production/ electricity application	Waste treatment	Objective
Ref-0	Conventional	MSW/RP/MP – Incineration	Reference
100 TWh electricity integration			
100-PTX-MTO	PTX-based MTO	MSW/RP/MP – Incineration	100 TWh PTX reference
100-PTX-NH3/H2/MOH	PTX NH_3, H_2, MeOH; Rest for PTX-MTO	MSW/RP/MP – Incineration	Impact of substitution of reforming by PTX
100-eChem-NSC/LSC/NR	E-heating NSC, LSC, NR; Rest for PTX-MTO	MSW/RP/MP – Incineration	Impact of e-heating of olefin and aromatic production
100-eChem-NH3/H2/MOH	E-heating reforming processes; Rest for PTX-MTO	MSW/RP/MP – Incineration	Impact of e-heating of reforming process
100-eChem-all	E-heating processes; Rest for PTX-MTO	MSW/RP/MP – Incineration	Maximum impact of e-heating
100-G-MTO	MTOh; Rest for PTX-MTO	MBT of MSW to RR RR/RP/MP – Gasification	Maximum gasification-based olefin substitution
100-P-MP/RP-fHTR	PTX-based MTO	RP/MP – Pyrolysis, full hydrotreating MSW - Incineration	Maximum impact of pyrolysis
100-P-MP/RP-fHTR-G-RR-MTOh	G-MTOh; Rest for PTX-MTO	MBT of MSW to RR RP/MP – Pyrolysis, full hydrotreating RR - Gasification	Combination of pyrolysis and gasification
100-eChem-all-G-MTOh	G-MTOh; E-heating processes; Rest for PTX-MTO	MBT of MSW to RR RR/RP/MP – Gasification	Combination of e-heated processes with Maximum gasification-based olefin substitution
Electricity integration for net zero GW impact (Net-Zero)			
Net0-PTX-MTO/MTA	PTX-based MTO and MTA	MSW/RP/MP – Incineration	Substitution of olefins and aromatics by PTX
Net0-PTX-Mix	PTX NH_3, H_2, MeOH; Rest for PTX-MTO	MSW/RP/MP – Incineration	Impact of substitution of reforming by PTX
Net0-eChem-all-PTX-Mix	E-heating processes; Rest for PTX mix	MSW/RP/MP – Incineration	Net-Zero by electric heating and PTX
Net0-G-MTO-PTX-Mix	G-MTOh; Rest for PTX mix	MBT of MSW to RR RR/RP/MP – Gasification	Net-Zero by PTX and feedstock recycling
Net0-eChem-all-G-MTO-PTX-Mix	G-MTOh; E-heating processes; Rest for PTX mix	MBT of MSW to RR RR/RP/MP – Gasification	Net-Zero by electric heating and feedstock recycling

5.3. Impact assessment

5.3.1. Framework Status Quo (FSQ)

Similar to the attributional investigation, the environmental impacts of various impact categories are initially scanned by normalization to determine critical environmental categories (compare chapter 4.3). The normalized impacts of the FSQ reference scenario are visualized in figure 53. Similar to results in chapter 4, fossil resource depletion (FRD) and global warming (GW) are the impact categories with the highest normalized impact by the described system, while the system shows significantly lower impacts in other categories in water scarcity (WSC), acidification (AC), eutrophication (EUT) and photochemical ozone formation (POF) show. Therefore, the following impact assessment will focus on these two impact categories.

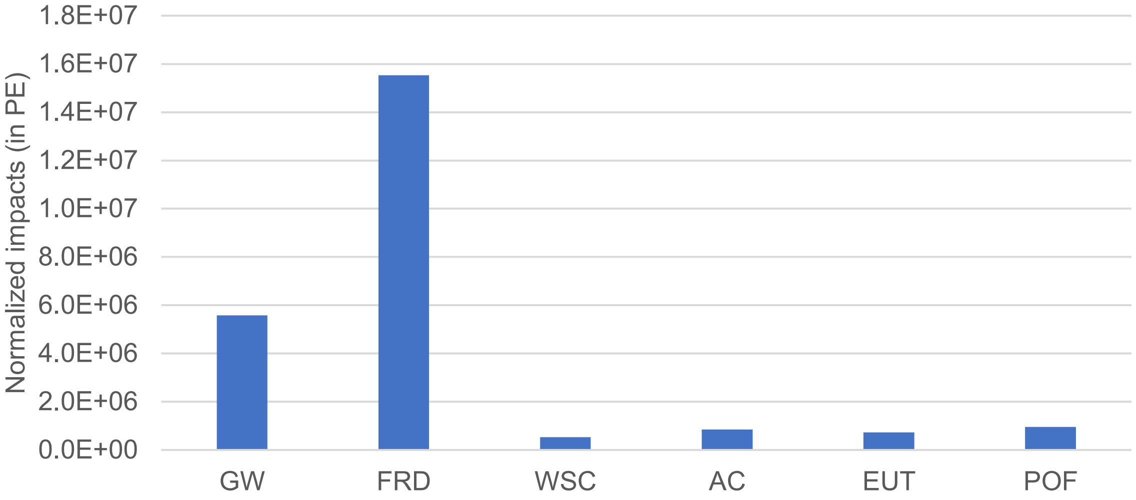

Figure 53: Normalized impacts of the FSQ reference scenario

Initially, the incremental application of individual feedstock recycling pathways compared to the reference scenario is discussed (results shown in table 40). All assessed pathways show a positive specific impact in terms on the systems GW and FRD impact. Impacts range from 0.30 to 1.33 kg CO_2eq saved ($GWI_{spec,mass}$) and 2.83 to 19.37 MJ saved ($FRDI_{spec,mass}$) per kg waste feedstock applied. Process pathways with the highest impact are pyrolysis with full pyrolysis oil hydroprocessing to naphtha (P-fHTR) and the syngas-based production of methanol and ammonia (G-MOH, G-NH3). For syngas-based pathways, MTO application is less beneficial compared to methanol and ammonia production, while MTA applications drop off significantly and show the lowest GW and FRD benefits of all assessed pathways. Among pyrolysis-based pathways, POX-based methanol production (P-POX) and partial oil hydroprocessing with BTX recovery (P-pHTR) are shown to be least effective. As a generalization, less complex processing pathways with fewer processing steps lead to better specific environmental impacts, i.e. substitution of syngas-based products via gasification and substitution of cracker feedstock via pyrolysis. Further, the application of high-calorific feedstock (i.e. high plastic content) is associated with a better environmental performance. As this tendency is similarly shown for a mass-based ($GWI_{spec,mass}$; $FRD_{spec,mass}$) as for heating value-based normalization ($GWI_{spec,LHV}$; $FRD_{spec,LHV}$), it can be concluded that its primarily cause is the increase in feedstock recycling process performance instead of the increased scope of incineration avoidance.

Process-specific impact
(mass-based normalization)

$$GWI_{spec,mass} = \frac{GWI_{abs,inc} - GWI_{abs,ref}}{m_{Waste}} \tag{21}$$

Process-specific impact
(LHV-based normalization)

$$GWI_{spec,LHV} = \frac{GWI_{spec,mass}}{LHV_{Waste}} \tag{22}$$

Table 40: Specific impact assessment results of the application of feedstock recycling pathways in the FSQ framework

Primary process	Scenario	Global warming impact		Fossil resource depletion impact	
		$GWI_{spec,mass}$ [kg CO_2eq / kg waste]	$GWI_{spec,LHV}$ [kg CO_2eq / GJ LHV waste]	$FRDI_{spec,mass}$ [MJ / kg waste]	$FRDI_{spec,LHV}$ [MJ / GJ LHV waste]
Gasification of RDF from mech.-biological treatment of MSW	G-RR-MTO	-0.70	-30	-8.56	-372
	G-RR-MTA	-0.31	-13	-3.28	-143
	G-RR-MOH	-0.81	-35	-13.03	-567
	G-RR-NH3	-0.77	-33	-12.54	-545
Gasification of RDF from mech. recovery sorting residues	G-RP-MTO	-0.68	-30	-8.12	-353
	G-RP-MTA	-0.30	-13	-2.83	-123
	G-RP-MOH	-0.79	-34	-12.60	-548
	G-RP-NH3	-0.75	-33	-12.11	-527
Gasification of MPW/RDF mix	G-MP/RP-MTO	-1.06	-33	-12.58	-393
	G-MP/RP-MTA	-0.50	-16	-5.05	-158
	G-MP/RP-MOH	-1.23	-38	-19.29	-603
	G-MP/RP-NH3	-1.23	-38	-19.37	-605
Pyrolysis of RDF from mech. recovery sorting residues	P-RP-pHTR	-0.57	-25	-8.99	-391
	P-RP-fHTR	-0.79	-34	-11.77	-512
	P-RP-POX	-0.40	-17	-11.30	-491
Pyrolysis of MPW from mech. recovery	P-MP-fHTR	-1.33	-38	-15.44	-441
	P-MP-POX	-0.87	-25	-15.86	-453

Following, full-scope scenarios are assessed to incorporate possible quantitative restrictions in the assessment. A scenario overview is given in table 38, table 41 shows the calculated available waste quantities for feedstock recycling application in the defined system. RDF from MBT of MSW (RR) displays the highest quantitative potential with about four times the available amount compared to mixed plastics from RMP sorting (MP). Figure 54 shows the total GWI of the system in the assessed scenarios and the distribution by emission sources.

Cumulated inventory results are shown in tables S30 and S31, while detailed impact assessment results can be found in table S32.

Focusing on the reference scenario, it is shown that the described system is associated with a total GWI of 45 Mt CO_2eq. As a reference, Germanys total GWI in 2019 was reported at 810 Mt CO_2eq [12]. It is shown that the GWI is not dominated by a single contributor, but dissipated over a range of processes, with the largest impacts caused by MSW incineration, naphtha steam cracking, naphtha supply and natural gas reforming for ammonia and hydrogen production. Calculated fossil demand includes 14.7 Mt of naphtha as feedstock and 5.6 Mt of natural gas, of which 52% is applied as reforming feedstock and 48% as process fuel gas. As reference, VCI [10] quantifies the demand of material feedstock at 15.3 Mt naphtha and other crude oil derivates and 2.3 Mt natural gas. The reference system requires a total electricity input of 3.5 TWh and generates a surplus of 36.6 TWh of heat as low-pressure steam, which forms the electricity and heat baseline that is maintained in all scenarios. Base chemical production is dissipated over several processes. 88.4% of olefins are produced from naphtha steam cracking and 11.6% by cracking of co-produced LPG. 88.1% of BTX are side products from naphtha steam cracking, the remaining 11.9% are produced by catalytic reforming. 49.4% of produced methanol comes from by partial oxidation of fuel oil from steam cracking, 50.6% from natural gas reforming. 76.3% of hydrogen are produced from natural gas reforming, with the rest being side products of steam cracking and catalytic reforming.

Table 41: Available waste quantities for feedstock recycling applications

Waste feedstock type	MPW from RMP (MP)	RDF from RMP (RP)	RDF from MSW (RR)	Sum
Source process	Mechanical recovery		Mechanical-biological treatment	
Available [kt]	554	1020	2375	3949
Applicable quantity for gasification [kt]	554 [1]	1020	2375	3949
Applicable quantity for pyrolysis [kt]	554	1020	0 [2]	1574

[1] for gasification, only considered applicable in mixture (see chapter 3.1.1)

[2] not considered applicable for pyrolysis (see chapter 3.1.3)

As shown by the total impact of the Ref-MBT scenario, upgrading of MSW to RDF for thermal utilization does not have a significant impact on the total GWI, only a shift of emissions from MSW incineration to RDF incineration with minimal subsequent effects by the energy balance. Compared to the reference scenario, all feedstock recycling scenarios exhibit a reduction of total GWI with the largest being 3.4 Mt CO_2eq (i.e. 7.5 % of the total impact). This relative insensitivity in the overall system is determined by the limited availability of waste feedstock in comparison to fossil feedstock input, but also the resulting systemic compensation between chemical production, waste treatment and energy generation.

By applying full quantities of both waste fraction from material sorting (MP and RP) for gasification-based MTO synthesis (G-RP/MP-MTO), 5.5% of conventional olefin production can be replaced, associated with a GW impact reduction of 1.35 Mt CO_2eq. By including RDF from MSW processing, olefin substitution can be increased to 12.3% with an associated GWI reduction of 3.01 Mt CO_2eq. If the same waste quantities are applied for gasification-based ammonia production, 43.4% and 96.2% of conventional ammonia production are substituted in the respective scenarios. Similar to the incremental results, GWI reduction by ammonia substitution is slightly higher compared to MTO application with 1.54 and 3.37 Mt CO_2eq, respectively. For the pyrolysis-based production of naphtha equivalent, the application of solely mixed plastic waste (P-MP-fHTR) leads to a substitution of only 2.6% of the total naphtha demand. Due to this quantitative restriction, the GW impact reduction potential is limited to 0.74 Mt CO_2eq, despite the highest specific GW impact (compare table 40). By including pyrolysis of RDF from material sorting (P-fHTR), naphtha substitution is increased to 6.5% and GW reduction rises to 1.54 Mt CO_2eq. By combining pyrolysis of all suitable waste fractions with the gasification of RDF from MSW (P-fHTR-RR-G-MTO), the total GW impaction reduction potential is 0.21 Mt CO_2eq higher compared to gasification of all fractions (G-MTO).

Methanol and BTX substitution potential are limited by total chemical demand and side production from other processes. For substitution of natural gas-based methanol via gasification, 83.2% of RDF from material sorting need to be applied (G-RP-MOH). Substitution of naphtha-based BTX production from catalytic reforming via MTA (G-RP/MP-MTA) requires 100% of RDF and 47% of mixed plastics from material sorting. The limited application scope also limits the GWI reduction potential in these scenarios. Lastly, by RDF pyrolysis and partial hydroprocessing with BTX recovery, 2.5% of naphtha demand and 37.0% of BTX from catalytic reforming can be replaced (P-RP-pHTR). Despite the associated lower hydrogen demand, the GW impact reduction is lower compared to full hydroprocessing, determined by the lower naphtha yield.

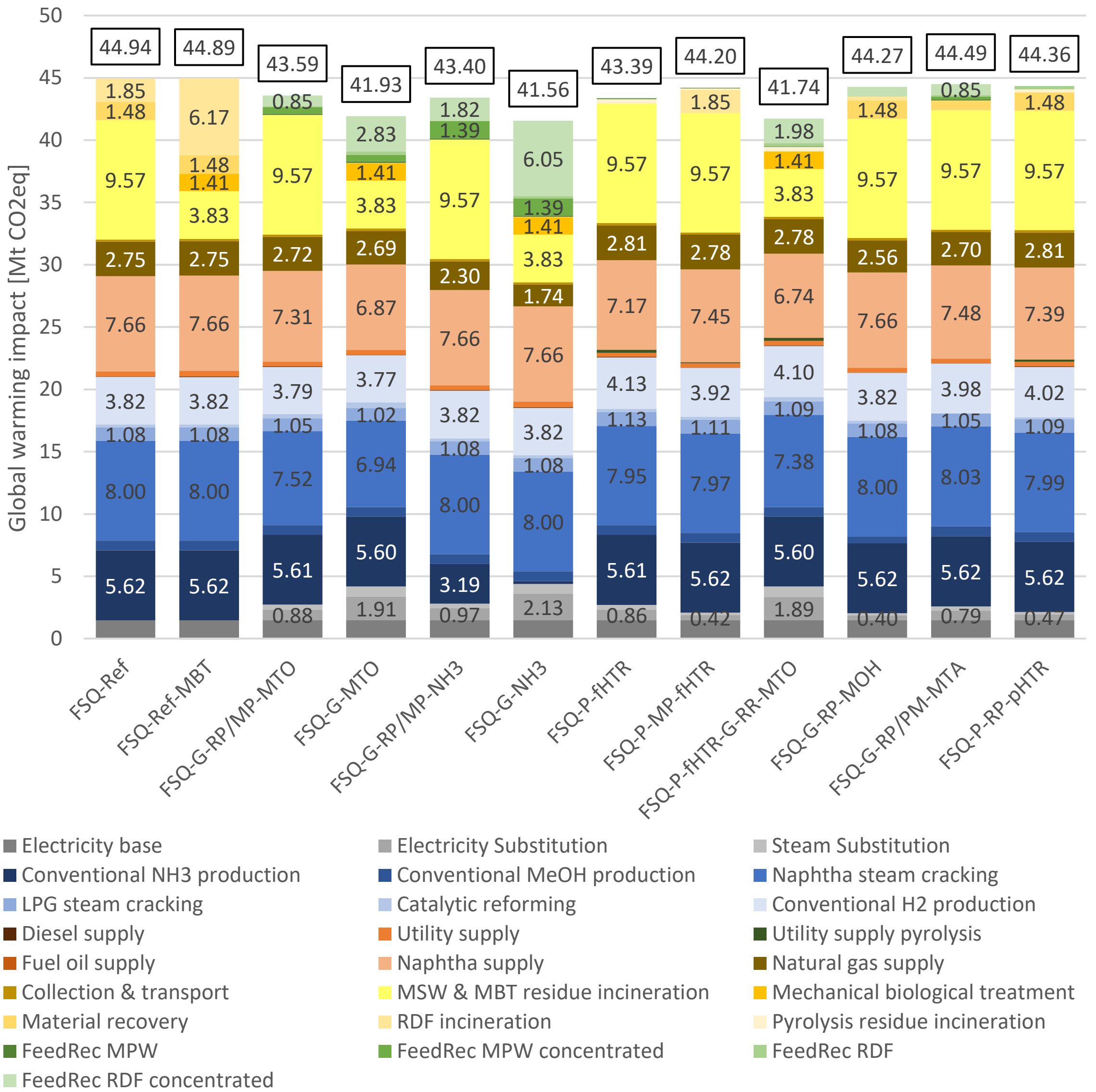

Figure 54: Global warming impact of FSQ scenarios

The corresponding FRD impact results are shown in figure 55. Similar to GW impact results, the maximum FRD reduction is limited to 5.3% of the total system impact. FRD is dominantly determined by naphtha and natural gas supply. Also mirroring GW results, the largest FRDI reduction is observed for gasification-based ammonia production, determined by the largest reduction in natural gas demand. In terms of total FRD impact, gasification-based MTO production and pyrolysis show similar impacts. While pyrolysis leads to a higher reduction in naphtha demand, gasification leads to a lowered natural gas demand by reduction of steam cracking and the associated fuel gas demand.

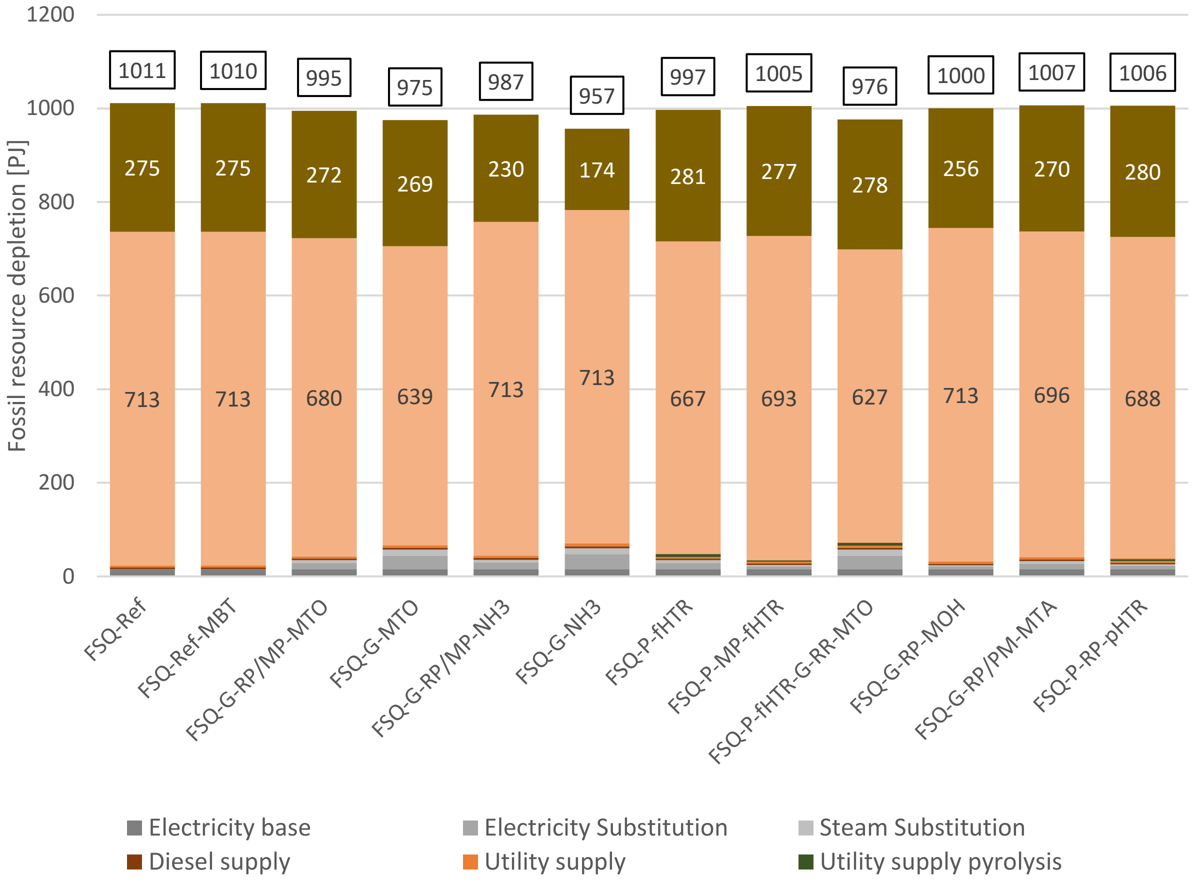

Figure 55: Fossil resource depletion impact of FSQ scenarios

Marginal energy variation

Table 42 shows the specific impact results of incremental application of all assessed feedstock recycling pathways under the assumption that natural gas-based electricity and heat are applied as substitution (marginal) energy sources. Compared to the application of the marginal energy mix (compare table 40), GW and FRD impacts of all pathways are significantly increased. Only pyrolysis with full hydroprocessing (P-fHTR) and gasification-based methanol production (G-MOH) still show GW and FRD benefits for all applicable feedstock. Especially the application of gasification-based MTA (G-MTA) and pyrolysis-based POX (G-POX) display significant burdens.

Table 42: Specific impact assessment results of the application of feedstock recycling pathways in the FSQ framework with natural gas-based marginal energy

Primary process	Scenario	Global warming impact	Fossil resource depletion impact
		$GWI_{spec, mass}$ [kg CO_2eq / kg waste]	$FRDI_{spec, mass}$ MJ / kg waste]
Gasification of RDF from mech.-biological treatment of MSW	G-RR-MTO	-0.03	2.23
	G-RR-MTA	0.50	9.96
	G-RR-MOH	-0.11	-1.77
	G-RR-NH3	0.01	0.18
Gasification of RDF from mech. recovery sorting residues	G-RP-MTO	0.04	3.48
	G-RP-MTA	0.57	11.22
	G-RP-MOH	-0.05	-0.53
	G-RP-NH3	0.08	1.43
Gasification of MPW/RDF mix	G-MP/RP-MTO	-0.03	4.10
	G-MP/RP-MTA	0.72	14.75
	G-MP/RP-MOH	-0.17	-2.17
	G-MP/RP-NH3	-0.05	-0.24
Pyrolysis of RDF from mech. recovery sorting residues	P-RP-pHTR	0.13	2.36
	P-RP-fHTR	-0.12	-1.00
	P-RP-POX	0.39	1.56
Pyrolysis of MPW from mech. recovery	P-MP-fHTR	-0.19	3.17
	P-MP-POX	0.46	5.75

5.3.2. Framework Energy Integration (FEI)

Initially, the incremental impacts of all considered hydrogen-based (PTX), electrical process heating (eChem) and feedstock recycling pathways are assessed. Table 43 shows the specific impact ($GWI_{spec,E}$; $FRDI_{spec,E}$) of the utilization of individual alternative technology pathways for integration of 1 TWh additional electricity input, based on the reference scenario without excess electricity integration. The achievable benefits from additional electricity integration range from 0.12 to 0.31 kg CO_2eq per kWh for GW and 0.37 to 1.32 kWh per kWh for FRD. Pyrolysis-based feedstock recycling stands out with the highest GW impact reduction. On the other side, MTA-based pathways show the lowest reduction potential. All other pathways vary within a close range of 0.09 kg CO_2eq per kWh. To evaluate the impact of feedstock recycling technologies specifically, pathways are compared to PTX ($GWI_{diff,PTX}$) and eChem pathways ($GWI_{diff,eChem}$) with the corresponding main product and normalized to the applied waste feedstock quantity. All feedstock recycling pathways show a significant reduction in GW and FRD impact compared to the corresponding PTX pathway up to 1.0 kg CO_2eq (GW) and 4.0 kWh (FRD) per kg waste input. Compared to eChem applications, feedstock recycling still displays a reduction in GW impact, but at a lower range and with the exception of gasification-based MTA. With the exceptions of RDF pyrolysis and gasification-based methanol production, FRD impact reduction of feedstock recycling pathways are lower compared to eChem processes. When comparing gasification feedstock for MTO synthesis, mixed plastic waste shows higher GWI and FRDI reduction compared to RDF, similar to the application in the FSQ framework.

Process-specific impact
(electricity input normalization)

$$GWI_{spec,E} = \frac{GWI_{abs,inc} - GWI_{abs,ref}}{E_{inc}} \tag{23}$$

Impact difference of FR compared to PTX
(mass-based normalization)

$$GWI_{diff,PTX} = \frac{GWI_{abs,inc,FR} - GWI_{abs,inc,PTX}}{m_{waste,FR}} \tag{24}$$

Impact difference of FR compared to eChem
(mass-based normalization)

$$GWI_{diff,eChem} = \frac{GWI_{abs,inc,FR} - GWI_{abs,inc,cChem}}{m_{waste,FR}} \tag{25}$$

Table 43: Specific impact assessment results of incremental application of process pathways in the FEI framework

	Global warming impact			Fossil resource depletion impact		
	$GWI_{spec,E}$	$GWI_{diff,PTX}$	$GWI_{diff,eChem}$	$FRDI_{spec,E}$	$FRDI_{diff,PTX}$	$FRDI_{diff,eChem}$
	[kg CO_2eq / kWh]	[kg CO_2eq / kg waste]		[MJ / kWh]	[MJ / kg waste]	
PTX-H2	-0.231			-3.73		
PTX-MTO	-0.180			-2.44		
PTX-MTA	-0.119			-1.33		
PTX-MOH	-0.194			-3.05		
PTX-NH3	-0.237			-3.83		
NSCe	-0.238			-4.59		
LSCe	-0.210			-4.05		
NRe	-0.226			-3.88		
NGR-H2e	-0.173			-2.58		
NGR-NH3e	-0.225			-3.72		
NGR-MOHe	-0.231			-3.82		
P-MP-HTR	-0.307	-1.039	-0.566	-4.19	-14.3	3.3
P-RP-HTR	-0.308	-0.643	-0.351	-4.76	-11.7	-0.9
G-RP-MTOh	-0.239	-0.563	-0.012	-3.33	-8.5	12.0
G-RP-MTAh	-0.157	-0.401	0.744	-2.21	-9.4	17.8
G-RP-MOHh	-0.263	-0.658	-0.305	-4.28	-11.8	-4.4
G-MP/RP-MTOh	-0.261	-0.999	-0.281	-3.48	-12.9	13.8
G-RR-MTOh	-0.244	-0.591	-0.053	-3.41	-9.0	11.0

Further, scenarios with a uniform electricity integration of 100 TWh are assessed (FEI-100, summarized in table 39, detailed inventory and impact assessment results given in table S33 and following). Impact assessment results for the GW impact are shown in figure 56. The reference scenario (Ref-0, without excess electricity integration) is added for comparison in the visualization. In all energy integration scenarios, the PTX-MTO pathway is applied as default for surplus electricity utilization due to the highest possible application scope of the production of olefins. By complete electricity application for PTX-MTO (100-PTX-MTO), 37.4% of the olefin demand can be covered, associated with GWI reduction of 15.1 Mt CO_2eq compared to the Ref-0 scenario. In order to substitute all natural gas-based chemicals by PTX (hydrogen, ammonia, methanol), 64.8% of accessible hydrogen from electrolysis needs to be applied (FEI-100-PTX-NH3/H2/MOH). Remaining hydrogen supply applied for PTX-MTO still leads to the substitution of 16.6% of olefin demand. Compared to PTX-MTO, natural gas-based chemical substitution leads to GWI reduction of 2.97 Mt CO_2eq, due to the higher specific GWI (compare table 43) and reduced energy demand for carbon capture for CO_2 supply, which decreases the electricity demand for heat generation via PTH and a higher total hydrogen supply.

Continuing, the impact of electric heating for high-temperature chemical processes is discussed. Electric heating of both olefin and BTX production processes (steam cracking and catalytic reforming in FEI-100-eChem-NSC/LSC/NR) consumes 32.0% of available electric energy, while electric heating for natural gas reforming processes requires 13.2% (FEI-100-eChem-NH3/H2/MOH). Corresponding, the PTX-MTO-based olefin substitution with surplus electricity decreases with increasing electricity demand for heating, from 32.7% if natural gas reforming is heated electrically, to 24.7% for heating of steam cracking and catalytic reforming, to 19.4% in the case that all chemical processes are heated electrically (FEI-100-eChem-all). Up to 4.74 Mt CO_2eq can be saved by electric process heating compared to the PTX-MTO scenario and up to 1.77 Mt CO_2eq compared to the most effective PTX scenario.

For gasification-based feedstock recycling pathways in this framework, MTO synthesis with hydrogen integration (G-MTOh) is applied for syngas utilization to limit the variance in scenarios. When all available waste feedstock is applied for gasification (FEI-100-G-MTO), 18.8% of the available electric energy is required to offset energy production from incineration. In this scenario, 30.9% of the produced hydrogen from electrolysis with excess electricity can be utilized for gasification-based syngas upgrading. Its application leads to an olefin production of 22.9% of the total demand. The remaining 69.1% of accessible hydrogen are applied for PTX-based olefin production, which yields a similar quantity of 23.2% of the total olefin demand. In this case, the application of waste gasification leads to a GWI reduction of 4.01 Mt CO_2eq compared to the PTX-MTO scenario and 1.05 Mt CO_2eq compared to the most effective PTX scenario, which is lower than the achievable reduction from electric heating.

Even more than gasification, the application scope of pyrolysis-based feedstock recycling (FEI-100-P-fHTR) is restricted by the applicable waste quantity (compare table 41). The resulting

GWI reduction of 1.59 Mt CO_2eq is similar to the corresponding case in the FSQ framework, as the considered pyrolysis-based pathway does not provide a principle for efficiency improvement via electricity or hydrogen integration. The combination of pyrolysis of all applicable waste quantities with gasification of the remaining RDF from MSW (FEI-100-P-fHTR-G-RR-MTO) yields a similar GWI reduction compared to gasification of all waste fractions, indicating a similar environmental performance for both pathways under this framework and only a slightly lower total impact reduction potential compared to electric process heating (FEI-100-eChem-all).

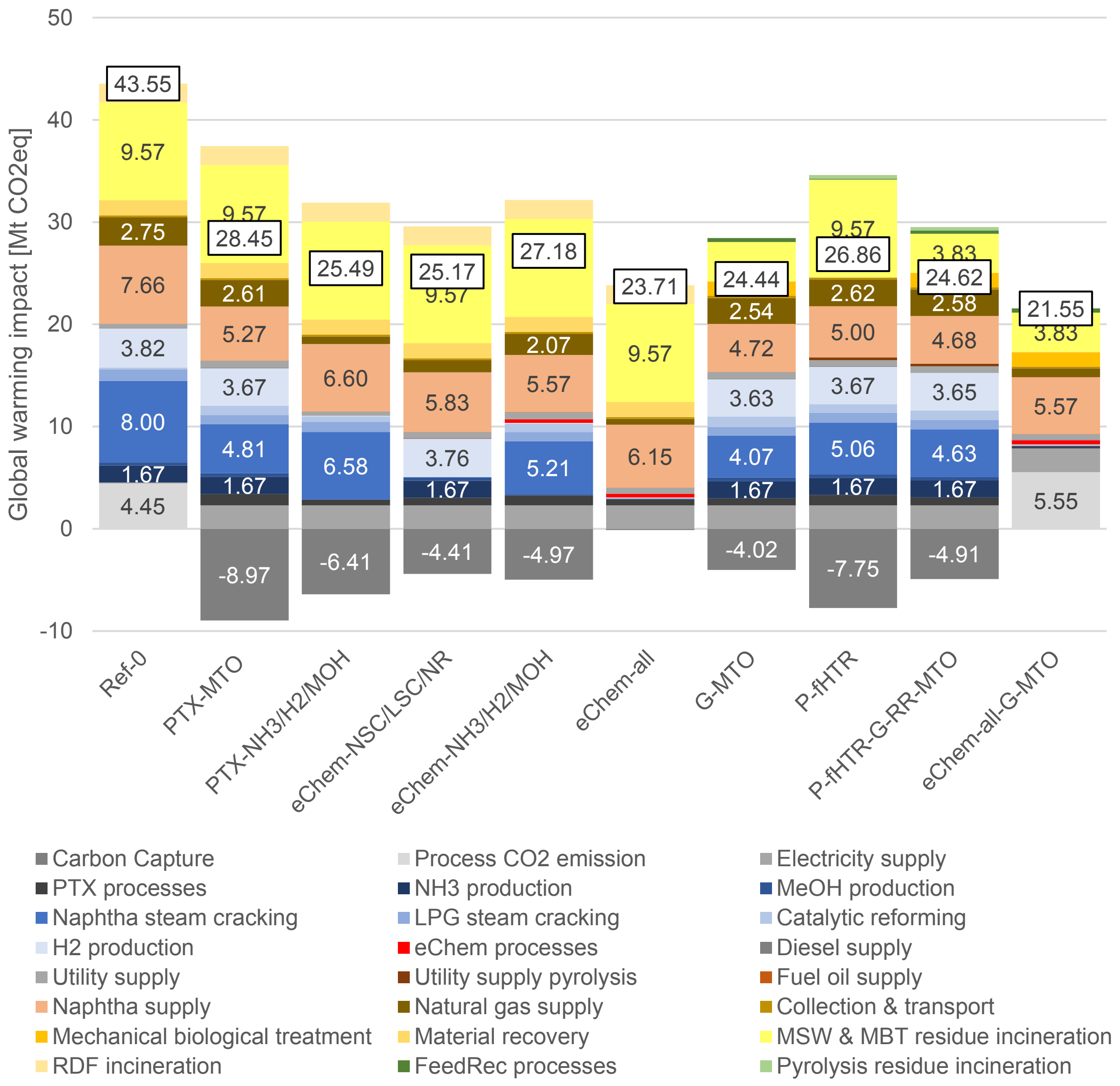

Figure 56: Global warming impact of FEI-100 scenarios

Further, the restriction of the feedstock recycling application by the available waste quantity enables its combination with electrical process heating applications within the scope of the 100 TWh framework, to further deduct from the low efficiency electricity via PTX application. If the maximum gasification scope is applied in combination with electric heating of all conventional processes (FEI-100-eChem-all-G-MTO), low residual electricity utilization only yields 7.7% olefins via PTX-MTO. The total GWI reduction is increase to 6.90 Mt CO_2eq, which is the most effective system configuration by a margin of 2.16 Mt CO_2eq and decreases total GWI by 24% compared to the PTX-MTO scenario and by 50.5% compared to the Ref-0 scenario without surplus energy integration. In comparison to the most effective PTX scenario, GWI savings of 3.93 Mt CO_2eq can be achieved.

Finally, selected Net-Zero scenarios are examined, indicating GHG emission neutrality for the defined system (FEI-Net0, summarized in table 39, detailed inventory and impact assessment results given in table S36 and following). The scope of necessary electric energy varies depending on the applied process pathway and functions as the key indicator under this framework. No single process pathway enables a sufficient impact reduction potential to achieve Net-Zero, hence the PTX-MTO pathway is applied in addition at the required scope. Results are visualized in figure 57, including the FEI-Ref0 scenario as reference.

In all assessed scenarios, the demand of CO_2 from carbon capture exceeds the available flue gas-based emissions, meaning that the availability of external flue gas point sources for carbon capture is an assumption of the concepts. As complete olefin substitution by PTX-MTO is not sufficient to achieve Net-Zero, an application ratio between MTO and MTA of 0.75 is assumed in the first scenario (FEI-Net0-PTX-MTO/MTA). Net-Zero is achieved at an electricity input of 327 TWh and a cumulated substitution of olefins and BTX of 81.4%, which equals 58.4% of all base chemicals produced (mass-based). By prioritizing the substitution of natural gas-based chemicals (FEI-Net0-PTX-Mix), Net-Zero is achieved at 284 TWh and a total chemical substitution of 66.2%, indicating a significantly higher efficiency for GWI reduction by minimization of the substitution of cracker-based chemicals. By application of electric heating for all conventional processes (FEI-Net0-eChem-all-PTX-Mix), the required electricity input is further lowered by 12 TWh to achieve Net-Zero. A similar reduction in electricity demand can be achieved by application of waste gasification instead of electrical heating (FEI-Net0-G-MTO-PTX-Mix), mirroring the similar efficiency and GWI reduction scope that was shown in the FEI-100 scenarios. By combined application of e-heating and gasification, the electricity demand to reach GHG neutrality is decreased to 255 TWh (FEI-Net0-eChem-all-G-MTO-PTX-Mix), meaning a reduction of electricity demand of 10% compared to the best PTX scenario and 22% compared to the cracker substitution scenario. In this case, 35% and 14% of the total mass-based base chemical demand are met by feedstock recycling and e-heated processes respectively, while 51% need to be produced via PTX pathways. Direct emissions from all chemical production processes are reduced by 85% compared to the reference Ref-0 scenario, but significant GWI compensation for associated processes is required, including from renewable energy production, residual waste fraction incineration and fossil feedstock supply of naphtha and natural gas.

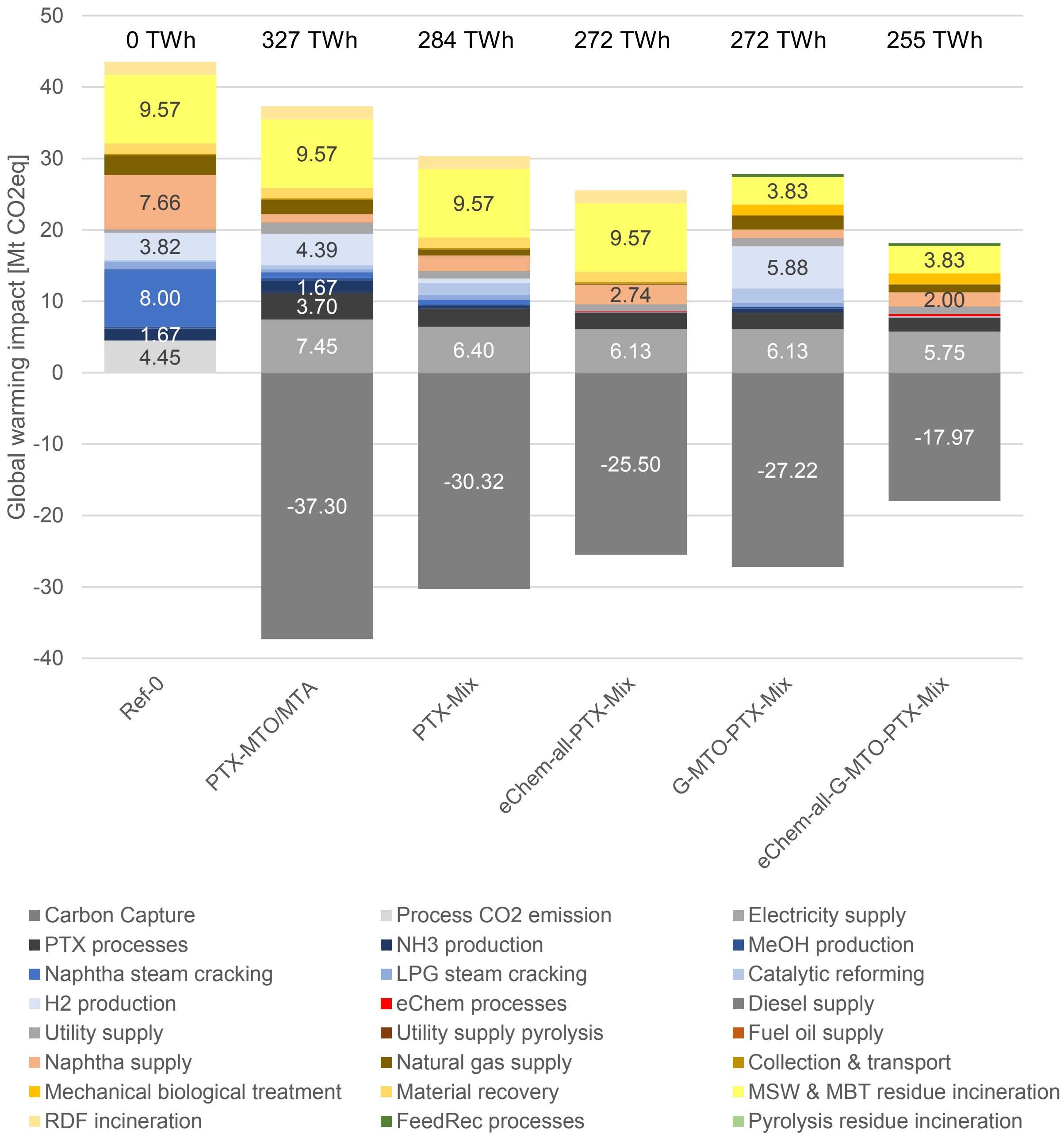

Figure 57: Global warming impact of FEI-Net0 scenarios

The corresponding results for the FRD impact of FEI-100 scenarios are shown in figure 58. Key qualitative tendencies mirror the results shown in the GWI assessment, including the impact reduction by substitution of natural gas-based chemical production instead of methanol-based pathways for PTX applications and the highest impact reduction potential via electrical process heating and the combination of feedstock recycling and e-heating. Due to the missing negative impact effect of carbon capture in terms of FRD, the relative impact reduction potential is smaller with up to 35% reduction compared to the reference Ref-0 scenario in FEI-100 scenarios (up to 51% for GWI). Hence, reaching impact neutrality in terms of fossil resource demand, meaning complete avoidance of fossil resource consumption, is not achievable by means of the investigated processes in this framework.

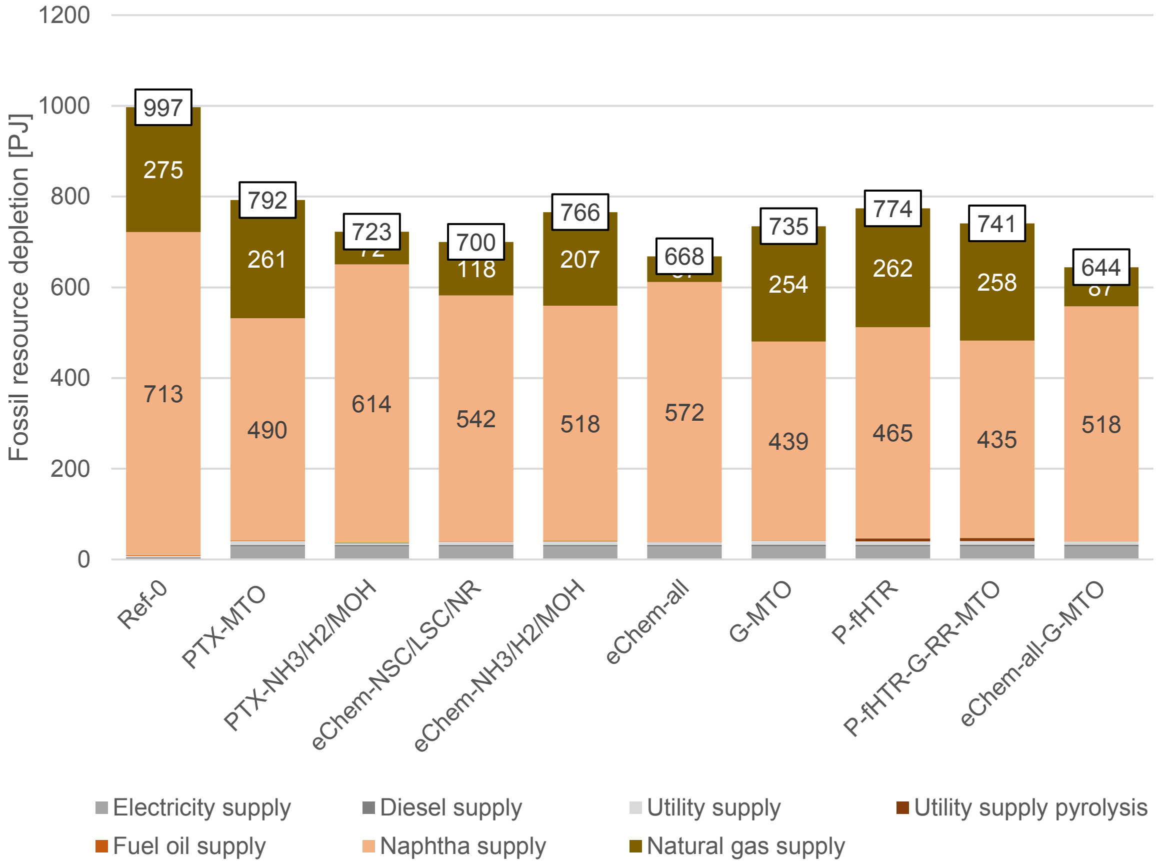

Figure 58: Fossil resource depletion impact of FEI-100 scenarios

Peripheral process variation

The efficiency of key peripheral processes is expected to have a significant effect on the environmental performance of various pathways within the defined system in the FEI framework. The impact is quantified by parameter variation for the efficiency of electrolysis and heat production from electricity to compensate deficits in LP steam production. Tendentially, the highest impact can be expected for the concepts with the highest respective application scope of hydrogen and power-to-heat. Parameter variation results are shown in table 44 in exemplary scenarios for the application of PTX (PTX-MTO), feedstock recycling (G-MTO) and electric process heating (eChem-all, see table 39). Electrolysis efficiency increase shows the highest benefit on GWI of PTX application and the lowest for the eChem scenario, associated with the scope of electrolysis-based hydrogen production in the respective framework. Higher efficiency in electricity-based heat production by high-temperature heat pump application shows the largest benefits for feedstock recycling scenarios, associated with the substitution of heat from waste incineration. PTX and eChem scenarios display a similar range of GWI benefit from higher PtH efficiency, primarily associated with heat supply for carbon capture (for PTX) and substitution of surplus heat that is recovered from flue gas conventional chemical processes (for eChem). Taking the variation of the two addressed system parameters into consideration, feedstock recycling application leads to a GWI reduction potential in the range of 0.81 to 2.14 Mt CO_2eq compared to PTX and -1.29 to 0.80 Mt CO_2eq compared to electric process heating.

Table 44: GWI for process variable variation in FEI-100 framework

		PTX-MTO	**G-MTO**	**eChem-all**
Scenario results at base conditions[1]				
Total GWI [Mt CO_2eq]		28.45	24.44	23.71
Electrolysis hydrogen production [Mt]		1.72	1.54	0.89
PtH LP steam production [TWh]		15.4	19.7	17.0
Parameter variation	Value	Absolute global warming impact [Mt CO_2eq]		
Electrolysis electricity demand [MJ / kg H_2]	160	-1.72	-1.48	-0.83
	200	+1.44	+1.24	+0.68
PtH efficiency (HT heat pump) [MJ(th) / MJ(el)]	2.50	-1.75	-2.64	-1.76

[1] Electrolysis electricity demand: 180 MJ / kg H_2; PtH efficiency: 0.99 MJ(th) / MJ(el) (electric boiler)

5.4. Interpretation

In a systemic context, the application of feedstock recycling processes leads to an increase in energy demand from external sources to substitute energy production from waste incineration. Consequently, the resulting environmental impact is determined by the considered burden for additional energy generation. Hence, all assessed feedstock recycling pathways show the potential to contribute to a more sustainable production system in terms of global warming and resource demand impact if the additional energy demand can be met by an energy production mix that reflects the projected energy system transformation for Germany. In case the application of feedstock recycling leads to energy substitution from fossil sources (natural gas), the impact ranges from a slight benefit to a significant burden depending on the applied technology pathway. Comparing applicable waste feedstock, mixed plastic waste shows a better specific environmental impact compared to refuse-derived fuel, associated with its high heating value, which is beneficial for gasification process performance, and high oil yield with low hydrogen demand for the upgrading of pyrolysis oils to naphtha equivalent.

Comparing feedstock recycling pathways, the highest specific impact reduction is shown for pyrolysis with full hydroprocessing for naphtha production and for gasification-based substitution of natural gas-based base chemicals, i.e. ammonia and methanol. These pathways also project to have to lowest infrastructural and development hurdles, as mixed plastic fractions are the primarily considered feedstock in most chemical recycling applications and ammonia and methanol synthesis are already applied in chemical production in Germany (in contrast to methanol-based substitution of steam cracker products). Therefore, they project to be best suited for a primary implementation. MTA applications show the least favorable environmental impact among feedstock recycling pathways by a considerable margin, and BTX recovery from pyrolysis oil decreases the environmental performance for pyrolysis oil utilization. Hence, BTX production by feedstock recycling is not preferential from an environmental perspective. Generally, more direct feedstock recycling product integration via short process chains leads to more favorable environmental impacts.

The application scope of feedstock recycling is restricted by waste availability in the descripted framework. Gasification-based olefin and ammonia production show the largest total GWI reduction potential with over 3 Mt CO_2eq, which is under 10% of the total system emissions. Pyrolysis-based feedstock recycling is restricted to a GWI reduction potential of 1.5 Mt CO_2eq, and 0.7 Mt for mixed plastic waste application.

For an assumed future production system that relies on the integration of renewable energy, PTX pathways display a low efficiency for GHG emission reduction due to high specific hydrogen demands and energy demand for carbon dioxide supply. Alternatively, both electrical heating of conventional chemical processes and gasification-based feedstock recycling with hydrogen integration are shown to be more efficient, but are limited in their application scope (avoidance of process emissions for eChem; waste quantity for feedstock recycling). Hence, both process groups have the individual potential to reduce the total system GWI and the electricity demand to achieve Net-Zero by a margin of only 4 to 7 % compared to the most efficient PTX scenario. As the quantitative application restrictions are not associated, the simultaneous application of both eChem and feedstock recycling yields a total reduction potential of 4.0 Mt CO_2eq or 29 TWh electricity demand, equaling a respective relative reduction of 15% and 10% based on the PTX benchmark.

Limitations

The introduced methodology and the applied case study encompass a number of simplifications that impact the generated results. First, only two specified waste fractions are considered. While residual solid waste and spurce-separated plastic-rich fractions present major post-consumer waste streams, it does not reflect the full quantitative potential of feedstock recycling. Second, interactions of chemical production with refinery operation are not considered, which is significant in mainly two aspects. In industrial facilities, aromatic crude utilization from steam cracking and catalytic naphtha reforming are often interconnected for production of BTX aromatics and gasoline. Further, methanol is primarily produced by partial oxidation of heavy oil fractions as refinery residues in Germany [317]. Also due to the assumed restriction of a complete integration in the applied inventory system, POX is instead applied for the conversion of residual pyrolysis fuel oil from naphtha steam cracking, which is not a practically applied association. The closed system also prevents compensational effects from international trading of waste, energy or chemicals, which are to be expected in a practical system. Lastly, infrastructural specifics and restrictions (e.g. chemical plant specifics, local restrictions for waste fraction availability) are not considered and the assessment does not include developments and projections for waste generation quantity, waste composition and base chemical demand, which are to be expected in the addressed time frame.

Chapter 6

Summary and conclusion

The major target of the presented thesis is the environmental assessment of waste gasification and pyrolysis as feedstock recycling technologies. The impact of following focus points is addressed:

- Variation of process performance of gasification and pyrolysis,
- Transformation of the energy production system,
- Variation of feedstock recycling integration in an existing production system,
- Comparison of feedstock recycling to emerging technologies for energy integration.

Process inventories are generated based on detailed process modelling in Aspen Plus and waste process balancing in EASETECH. Balanced processes include:

- Fixed-bed gasification with subsequent processing steps for the production of base chemicals, including process variations with hydrogen integration,
- Catalytic pyrolysis with pyrolysis oil hydroprocessing and oil partial oxidation,
- Conventional chemical processes (steam cracking, steam reforming, catalytic reforming, partial oxidation) and process variations with electric heating,
- Hydrogen and carbon dioxide-based base chemical production processes,
- Waste incineration, mechanical biological treatment and material sorting.

Based on the process balancing results, two LCA studies are conducted. In an attributional assessment for the treatment of refuse derived fuel, the global warming and resource depletion impacts of gasification, pyrolysis and incineration are determined with varying material and energy efficiency under the projected transformation of electricity and district heat generation in Germany between 2025 and 2045. In a novel system-based potential assessment, an integrated inventory system for Germany is applied for the treatment of municipal solid waste and plastic-rich waste and the production of major base chemicals in olefins, BTX aromatics, methanol, ammonia and hydrogen. Feedstock recycling pathways are integrated and assessed in the system for a near future situation, and a long-term outlook with excess electricity supply with alternative integration via hydrogen and electric process heating.

6.1. Results

It is shown that the individual global warming impacts of gasification (0.30 to 0.77 kg CO_2eq per kg RDF), pyrolysis (0.43 to 0.82 kg CO_2eq per kg RDF) and incineration (0.59 to 1.51 kg CO_2eq per kg RDF) generally rise with increasing renewable energy production, since all three treatment pathways show a net export of electricity and heat or only minor imports. For gasification-based pathways, deficits in process efficiency of syngas production lead to a prevalence in energy production by incineration of off-gases and decreased energy demand for syngas processing. Therefore, low-efficiency gasification displays the lowest global warming impact for carbon-intensive energy production but increases significantly with a shift to renewable energy supply. High-efficiency gasification shows only minor sensitivity to the energy system, where direct process emissions are lower and product credits are primarily determined by syngas-based chemicals. A similar trend is demonstrated for pyrolysis-based pathways, in which a decrease in oil yield leads to a higher yield and heating value of pyrolysis residues and higher energy production from subsequent incineration. Both pyrolysis and gasification show only minor impacts by non-optimal process energy efficiency, as the direct process energy demand does not show a decisive environmental influence for either process.

Assessed in a systemic context, all feedstock recycling pathways show specific global warming impact reductions in the range of 0.30 to 1.33 kg CO_2eq per kg waste feedstock compared to conventional waste incineration and chemical production, if the projected German energy system transformation trajectory is maintained. If natural gas-based energy needs to be applied to compensate energy offsets, the specific impact changes to a range between reduction of 0.19 kg CO_2eq per kg and a burden of 0.72 kg CO_2eq per kg waste feedstock. Generally, more direct feedstock recycling product integration via short process chains leads to more favorable environmental impacts. Specifically, the highest specific reduction is observed for mixed plastics-based pyrolysis for naphtha production and gasification-based pathways for the substitution of natural gas-based base chemicals, while gasification-based BTX substitution and pyrolysis oil-based partial oxidation are shown to be least effective. Despite consideration of major fractions of carbonaceous waste in the German waste treatment system, feedstock availability limits the application range and environmental impact of feedstock recycling pathways. Feedstock recycling shows a maximum global warming impact reduction for mixed plastics of 739 kt CO_2eq (1.6% of total system emissions), 803 kt CO_2eq (1.8%) for sorting residues from material sorting and 1657 kt CO_2eq (3.7%) for refuse-derived fuel from municipal solid waste.

Finally, feedstock recycling pathways are assessed in comparison to perspective technology alternatives to reduce greenhouse gas emissions by energy integration. It is shown that feedstock recycling reduces the global warming impact at constant electricity input compared to power-to-X technologies in a range from 0.56 to 1.04 kg CO_2eq per kg waste feedstock and compared to electric process heating in a range from 0.01 to 0.57 kg CO_2eq per kg waste feedstock. Considering the limited availability of applicable waste streams, feedstock recycling can lead to an impact reduction up to 1.0 Mt CO_2eq compared to the most favorable PTX pathway. The impact scope of electric heating is limited to the avoidance of chemical process emissions, resulting in a reduction potential of 1.8 Mt CO_2eq. By combining feedstock recycling and electric heating, up to 4.0 Mt CO_2eq can potentially be saved. A similar tendency is shown for the determination of the required electricity input to achieve Net-Zero global warming impact of the defined system. While 284 TWh are required by sole PTX application, up to 12 TWh can be saved by either feedstock recycling or electric heating and up to 29 TWh by their combined application.

These results indicate that a future sustainable production system including waste management and chemical production at the current scale will require significant quantities of carbon dioxide and hydrogen-based products to generate negative emissions to compensate diverse greenhouse gas sources. However, the effective utilization of limited quantities of low-carbon electricity is favored by processes that enable the initial avoidance of carbon emissions. Both feedstock recycling and process electrification show similar effectiveness and quantitative potential, making their implementation similarly attractive from an environmental perspective.

6.2. Recommendations and outlook

The presented investigation demonstrates the conceptional validity of feedstock recycling processes as an option to contribute to increased sustainability in waste treatment and chemical production. Further, a number of key aspects for the future development of feedstock recycling technologies can be derived.

For gasification, large-scale demonstration is required to address existing technology issues that limit plant availability. From an environmental perspective, small industrial units or suboptimal process performance in terms syngas and product yield are not problematic in the short-term, as long as co-produced heat can be credited to a locally available communal or industrial district heating system. Substitution of natural gas-based steam reforming is advantageous for initial implementation due to the presented environmental performance and the commercially available process technologies or even existing syngas processing infrastructure.

Long-term, scaling of gasification facilities to substitute conventional chemical processes is potentially restricted by the availability of applicable waste fractions. Therefore, the development of flexible processes with a wide feedstock range should be prioritized going forward. The possibility of staged hydrogen integration for emission reduction and production yield improvement while still being able to maintain constant gasification operation if renewable energy supply is limited is potentially a significant structural advantage compared to PTX and electric process heating, if the flexibility is considered during scaling of downstream processes. Other technology options for direct integration of electric energy integration in primary or secondary gasification, especially via plasma, are to be considered going forward as potentially more efficient compared to electrolysis application.

For pyrolysis processes, unit scaling and centralization is less critical due to the moderate process conditions and the smaller environmental incentive for heat integration in a district heating system, as long as oil hydroprocessing and residue incineration are conducted centrally. The application of mixed plastics, that is the focus of the majority of recent pyrolysis development efforts, is shown to perform well environmentally. However, the low quantitative availability of the feedstock limits the total impact potential. Therefore, the focus on technologies that enable the application of less specific feedstock is similarly critical as for gasification.

The presented thesis exemplarily evaluates conceptional and process aspects of feedstock recycling processes and indicates the environmental potential in a systemic context. However, further analysis is necessary to broaden the understanding of the technology variety and development on the environmental impact and to refine the methodological approach in terms of the considered reference processes and the feedstock recycling process implementation in a commercial market situation. Hence, specific focus aspects include the discussion of case studies that incorporate process characteristics of individual feedstock recycling technologies and waste feedstock in specific infrastructural circumstances (energy, utility and product integration), the economic viability of plant construction and operation, and varying regulatory frameworks (including recognition as recycling, emission crediting and product certification), to determine if practical implementation is feasible and what conditions are necessary for feedstock recycling to contribute to a sustainable production system in a substantial manner.

The presented system-based assessment methodology is shown to enable the quantification of both specific process footprints as well as their environmental impact potential on a national scale under a uniform and transparent framework for a range of processes with varying feedstock and products, which would not be practicable in a conventional attributional framework. When uniformly applied, the methodology can reduce the uncertainty associated with varying framework definitions in life cycle assessments and therefore improve confidence and transparency, especially for communicational and regulatory applications.

References

[1] M. Crippa, B. de Wilde, R. Koopmans, J. Leyssens, J. Muncke, Ritschkoff A-C., K. van Doorsselaer, C. Velis, M. Wagner, *A circular economy for plastics: Insights from research and innovation to inform policy and funding decisions*, Brussels 2019.

[2] R. Demets, K. van Kets, S. Huysveld, J. Dewulf, S. de Meester, K. Ragaert, *Resources, Conservation and Recycling* 2021, *174*, 105826. DOI: https://doi.org/10.1016/j.resconrec.2021.105826

[3] R. Pomberger, *Österreichische Wasser- und Abfallwirtschaft* 2021, *73 (1-2)*, 24 – 35. DOI: https://doi.org/10.1007/s00506-020-00721-5

[4] M. K. Eriksen, A. Damgaard, A. Boldrin, T. F. Astrup, *Journal of Industrial Ecology* 2019, *23 (1)*, 156 – 168. DOI: https://doi.org/10.1111/jiec.12822

[5] M. T. Brouwer, E. U. van Thoden Velzen, K. Ragaert, R. ten Klooster, *Sustainability* 2020, *12 (23)*, 10021. DOI: https://doi.org/10.3390/su122310021

[6] Conversio, *Stoffstrombild Kunststoffe in Deutschland 2019*.

[7] S. Flamme, J. Hanewinkel, P. Quicker, K. Weber, *Energieerzeugung aus Abfällen: Stand und Potenziale in Deutschland bis 2030*, Umweltbundesamt, Dessau-Roßlau 2018.

[8] European Commission, *Directive 2008/98/EC of the European Parliament and of the Council of 19 November 2008 on waste and repealing certain Directives: Waste Framework Directive* 2018.

[9] ECHA, *Chemical Recycling of Polymeric Materials from Waste in the Circular Economy* 2021.

[10] VCI, *Rohstoffbasis der chemischen Industrie: Daten und Fakten*, Frankfurt am Main 2018.

[11] R. Geres, A. Kohn, S. Lenz, F. Ausfelder, A. M. Bazzanella, A. Möller, *Roadmap Chemie 2050: Auf dem Weg zu einer treibhausgasneutralen chemischen Industrie in Deutschland* 2019.

[12] Umweltbundesamt, *Berichterstattung unter der Klimarahmenkonvention der Vereinten Nationen und dem Kyoto-Protokoll 2021: Nationaler Inventarbericht zum Deutschen Treibhausgasinventar 1990 – 2019*, Dessau-Roßlau 2021.

[13] L. G. Seidl, *Overview of Pyrolysis and Gasification Technologies for Chemical Recycling of Mixed Plastic and other Waste*, Chemical Recycling – Beyond Thermal Use of Plastic and other Waste, Dresden 2021.

[14] K. Ragaert, L. Delva, K. van Geem, *Waste Management* 2017, *69*, 24 – 58. DOI: https://doi.org/10.1016/j.wasman.2017.07.044

[15] I. Vollmer, M. J. F. Jenks, M. C. P. Roelands, R. J. White, T. van Harmelen, P. de Wild, G. P. van der Laan, F. Meirer, J. T. F. Keurentjes, B. M. Weckhuysen, *Angewandte Chemie (International ed. in English)* 2020, *59 (36)*, 15402 – 15423. DOI: https://doi.org/10.1002/anie.201915651

[16] L. G. Seidl, W.-R. Poganietz, F. Keller, R. P. Lee, A. Grunwald, B. Meyer, *Chemie Ingenieur Technik* 2020, *244 (1)*, 118629. DOI: https://doi.org/10.1002/cite.202000102

[17] F. Keller, R. Voss, R. P. Lee, *Overcoming Challenges of Life Cycle Assessment (LCA) & Techno-Economic Assessment (TEA) for Chemical Recycling: Recommendations for Increasing Transparency, Comprehensiveness and Comparability of LCA & TEA for Chemical Recycling Technologies* 2022.

[18] P. Quicker, F. Neuerburg, Y. Noël, A. Huras, *Sachstand zu den alternativen Verfahren für die thermische Entsorgung von Abfällen*, Dessau-Roßlau 2017.

[19] P. Quicker, M. Seitz, J. Vogel, *Waste management & research the journal of the International Solid Wastes and Public Cleansing Association, ISWA* 2022, *40 (10)*, 1494 – 1504. DOI: https://doi.org/10.1177/0734242X221084044

[20] H. Friege, B. Kummer, K. G. Steinhäuser, J. Wuttke, B. Zeschmar-Lahl, *Environmental Sciences Europe* 2019, *31 (1)*, 90. DOI: https://doi.org/10.1186/s12302-019-0236-7

[21] Eunomia, *A Comparative Assessment of Standards and Certification Schemes for Verifying Recycled Content in Plastic Products* 2021.

[22] ECHA, *Chemical Recycling of Polymeric Materials from Waste in the Circular Economy* 2021.

[23] DIN EN ISO 14044:2006, *Environmental management – Life cycle assessment – Requirements and guidelines (ISO 14044:2006)* 2006.

[24] DIN EN ISO 14040:2006, *Environmental management – Life cycle assessment – Principles and framework (ISO 14040:2006); German and English version EN ISO 14040:2006* 2006.

[25] M. Z. Hauschild, R. K. Rosenbaum, S. I. Olsen, *Life Cycle Assessment*, Springer International Publishing, Cham 2018.

[26] G. Myhre, D. Shindell, F.-M. Bréon, W. Collins, J. Fuglestvedt, J. Huang, D. Koch, J.-F. Lamarque, D. Lee, B. Mendoza, T. Nakajima, A. Robock, G. Stephens, Takemura T., H. Zhang, *Climate Change 2013: The Physical Science Basis*, Cambridge University Press, Cambridge 2014.

[27] M. Z. Hauschild, M. Goedkoop, J. Guinée, R. Heijungs, M. Huijbregts, O. Jolliet, M. Margni, A. de Schryver, S. Humbert, A. Laurent, S. Sala, R. Pant, *The International Journal of Life Cycle Assessment* 2013, *18 (3)*, 683 – 697. DOI: https://doi.org/10.1007/s11367-012-0489-5

[28] B. Weidema, *Journal of Industrial Ecology* 2014, *18 (3)*, 324 – 326. DOI: https://doi.org/10.1111/jiec.12139

[29] European Commission, *International Reference Life Cycle Data System (ILCD) handbook: Review schemes for Life Cycle Assessment*, EUR 24710 EN, Publications Office of the European Union, Luxembourg 2010.

[30] G. Sonnemann, B. Vigon, *Global Guidance Principles for Life Cycle Assessment Databases: A Basis for Greener Processes and Products*, United Nations Environment Programme, Nairobi 2011.

[31] S. Manfredi, R. Pant, *Supporting Environmentally Sound Decisions for Waste Management: A technical guide to Life Cycle Thinking (LCT) and Life Cycle Assessment (LCA) for waste experts and LCA practitioners*, Publications Office of the European Union, Luxembourg 2011.

[32] A. Laurent, J. Clavreul, A. Bernstad, I. Bakas, M. Niero, E. Gentil, T. H. Christensen, M. Z. Hauschild, *Waste Management* 2014, *34 (3)*, 589 – 606. DOI: https://doi.org/10.1016/j.wasman.2013.12.004

[33] S. Nessi, T. Sinkko, C. Bulgheroni, P. Garcia-Gutierrez, J. Giuntoli, A. Konti, E. Sanye-Mengual, D. Tonini, R. Pant, L. Marelli, F. Ardente, *Life Cycle Assessment (LCA) of alternative feedstocks for plastics production: Part 1: the Plastics LCA method*, JRC125046, Publications Office of the European Union, Luxembourg, 2021.

[34] T. F. Astrup, D. Tonini, R. Turconi, A. Boldrin, *Waste Management* 2015, *37*, 104 – 115. DOI: https://doi.org/10.1016/j.wasman.2014.06.011

[35] U. Arena, F. Ardolino, F. Di Gregorio, *Waste Management* 2015, *41*, 60 – 74. DOI: https://doi.org/10.1016/j.wasman.2015.03.041

[36] J. Dong, Y. Tang, A. Nzihou, Y. Chi, E. Weiss-Hortala, M. Ni, Z. Zhou, *Journal of Cleaner Production* 2018, *203*, 287 – 300. DOI: https://doi.org/10.1016/j.jclepro.2018.08.139

[37] A. U. Zaman, *International Journal of Environmental Science and Technology* 2013, *10 (5)*, 1029 – 1038. DOI: https://doi.org/10.1007/s13762-013-0230-3

[38] A. Ramos, C. A. Teixeira, A. Rouboa, *Energies* 2019, *12 (1)*, 137. DOI: https://doi.org/10.3390/en12010137

[39] A. E. Schwarz, T. N. Ligthart, D. Godoi Bizarro, P. de Wild, B. Vreugdenhil, T. van Harmelen, *Waste Management* 2021, *121*, 331 – 342. DOI: https://doi.org/10.1016/j.wasman.2020.12.020

[40] R. Meys, F. Frick, S. Westhues, A. Sternberg, J. Klankermayer, A. Bardow, *Resources, Conservation and Recycling* 2020, *162*, 105010. DOI: https://doi.org/10.1016/j.resconrec.2020.105010

[41] M. Yang, X. Tian, F. You, *Industrial & Engineering Chemistry Research* 2017, *57 (17)*, 5980 – 5998. DOI: https://doi.org/10.1021/acs.iecr.7b03731

[42] F. Keller, R. P. Lee, B. Meyer, *Journal of Cleaner Production* 2020, *250*, 119484. DOI: https://doi.org/10.1016/j.jclepro.2019.119484

[43] I. D. Posen, W. M. Griffin, H. S. Matthews, I. L. Azevedo, *Environmental science & technology* 2015, *49 (1)*, 93 – 102. DOI: https://doi.org/10.1021/es503521r

[44] C. Liptow, A.-M. Tillman, M. Janssen, *The International Journal of Life Cycle Assessment* 2015, *20 (5)*, 632 – 644. DOI: https://doi.org/10.1007/s11367-015-0855-1

[45] M. Rosental, T. Fröhlich, A. Liebich, *Frontiers in Climate* 2020, *2*, 71. DOI: https://doi.org/10.3389/fclim.2020.586199

[46] M. Ghanta, D. Fahey, B. Subramaniam, *Applied Petrochemical Research* 2014, *4 (2)*, 167 – 179. DOI: https://doi.org/10.1007/s13203-013-0029-7

[47] C. Liptow, A.-M. Tillman, *Journal of Industrial Ecology* 2012, *16 (3)*, 420 – 435. DOI: https://doi.org/10.1111/j.1530-9290.2011.00405.x

[48] B. Winter, R. Meys, A. Bardow, *Journal of Cleaner Production* 2021, *290 (11)*, 125818. DOI: https://doi.org/10.1016/j.jclepro.2021.125818

[49] W. Hoppe, N. Thonemann, S. Bringezu, *Journal of Industrial Ecology* 2018, *22 (2)*, 327 – 340. DOI: https://doi.org/10.1111/jiec.12583

[50] A. Sternberg, C. M. Jens, A. Bardow, *Green Chemistry* 2017, *19 (9)*, 2244 – 2259. DOI: https://doi.org/10.1039/C6GC02852G

[51] M. Pérez-Fortes, J. C. Schöneberger, A. Boulamanti, E. Tzimas, *Applied Energy* 2016, *161*, 718 – 732. DOI: https://doi.org/10.1016/j.apenergy.2015.07.067

[52] L. Eggemann, N. Escobar, R. Peters, P. Burauel, D. Stolten, *Journal of Cleaner Production* 2020, *271*, 122476. DOI: https://doi.org/10.1016/j.jclepro.2020.122476

[53] E. Delikonstantis, E. Igos, S.-A. Theofanidis, E. Benetto, G. B. Marin, K. van Geem, G. D. Stefanidis, *Green Chem.* 2021, *23 (18)*, 7243 – 7258. DOI: https://doi.org/10.1039/D1GC01730F

[54] K. M. Holmgren, E. Andersson, T. Berntsson, T. Rydberg, *Energy* 2014, *69 (1)*, 622 – 637. DOI: https://doi.org/10.1016/j.energy.2014.03.058

[55] J. Tallaksen, F. Bauer, C. Hulteberg, M. Reese, S. Ahlgren, *Journal of Cleaner Production* 2015, *107*, 626 – 635. DOI: https://doi.org/10.1016/j.jclepro.2015.05.130

[56] S. C. D’Angelo, S. Cobo, V. Tulus, A. Nabera, A. J. Martín, J. Pérez-Ramírez, G. Guillén-Gosálbez, *ACS Sustainable Chemistry & Engineering* 2021, *9 (29)*, 9740 – 9749. DOI: https://doi.org/10.1021/acssuschemeng.1c01915

[57] S. Ghavam, C. M. Taylor, P. Styring, *Journal of Cleaner Production* 2021, *320*, 128776. DOI: https://doi.org/10.1016/j.jclepro.2021.128776

[58] Y. Bicer, I. Dincer, G. Vezina, F. Raso, *Environmental management* 2017, *59 (5)*, 842 – 855. DOI: https://doi.org/10.1007/s00267-017-0831-6

[59] G. Reiter, J. Lindorfer, *The International Journal of Life Cycle Assessment* 2015, *20 (4)*, 477 – 489. DOI: https://doi.org/10.1007/s11367-015-0848-0

[60] O. Machhammer, A. Bode, W. Hormuth, *Chemie Ingenieur Technik* 2015, *87 (4)*, 409 – 418. DOI: https://doi.org/10.1002/cite.201400151

[61] J. Dufour, D. P. Serrano, J. L. Gálvez, A. González, E. Soria, J. L.G. Fierro, *International Journal of Hydrogen Energy* 2012, *37 (2)*, 1173 – 1183. DOI: https://doi.org/10.1016/j.ijhydene.2011.09.135

[62] A. Mehmeti, A. Angelis-Dimakis, G. Arampatzis, S. McPhail, S. Ulgiati, *Environments* 2018, *5 (2)*, 24. DOI: https://doi.org/10.3390/environments5020024

[63] W. Jenseit, H. Stahl, V. Wollny, R. Wittlinger, *Recovery options for plastic parts from end-of-life vehicles: an eco-efficiency assessment* 2003.

[64] F. Perugini, M. L. Mastellone, U. Arena, *Environmental Progress* 2005, *24 (2)*, 137 – 154. DOI: https://doi.org/10.1002/ep.10078

[65] P. Shonfield, *LCA of Management Options for Mixed Waste Plastics* 2008.

[66] P. Nuss, K. H. Gardner, S. Bringezu, *Journal of Industrial Ecology* 2013, *17 (6)*, 912 – 925. DOI: https://doi.org/10.1111/jiec.12066

[67] S. M. Al-Salem, S. Evangelisti, P. Lettieri, *Chemical Engineering Journal* 2014, *244*, 391 – 402. DOI: https://doi.org/10.1016/j.cej.2014.01.066

[68] P. N. Pressley, T. N. Aziz, J. F. DeCarolis, M. A. Barlaz, F. He, F. Li, A. Damgaard, *Journal of Cleaner Production* 2014, *70 (12)*, 145 – 153. DOI: https://doi.org/10.1016/j.jclepro.2014.02.041

[69] H. Wang, L. Wang, A. Shahbazi, *Journal of Cleaner Production* 2015, *87 (5)*, 511 – 519. DOI: https://doi.org/10.1016/j.jclepro.2014.09.011

[70] P. T. Benavides, P. Sun, J. Han, J. B. Dunn, M. Wang, *Fuel* 2017, *203*, 11 – 22. DOI: https://doi.org/10.1016/j.fuel.2017.04.070

[71] M. Gear, J. Sadhukhan, R. Thorpe, R. Clift, J. Seville, M. Keast, *Journal of Cleaner Production* 2018, *180 (80)*, 735 – 747. DOI: https://doi.org/10.1016/j.jclepro.2018.01.015

[72] H. H. Khoo, *Waste Management* 2009, *29 (6)*, 1892 – 1900. DOI: https://doi.org/10.1016/j.wasman.2008.12.020

[73] G. Faraca, V. Martinez-Sanchez, T. F. Astrup, *Resources, Conservation and Recycling* 2019, *143 (5)*, 299 – 309. DOI: https://doi.org/10.1016/j.resconrec.2019.01.014

[74] M. Broeren, E. R. Lindgreen, G. Bergsma, *Exploration chemical recycling: What is the potential contribution of chemical recycling to Dutch climate policy?*, Delft 2019.

[75] M. Russ, M. Gonzalez, M. Horlacher, *Evaluation of pyrolysis with LCA – 3 case studies* 2020.

[76] H. Jeswani, C. Krüger, M. Russ, M. Horlacher, F. Antony, S. Hann, A. Azapagic, *The Science of the total environment* 2021, *769*, 144483. DOI: https://doi.org/10.1016/j.scitotenv.2020.144483

[77] Quantis, *Life cycle assessment of Plastic Energy technology for the chemical recycling of mixed plastic waste* 2020.

[78] F. Keller, R. P. Lee, B. Meyer, *Journal of Cleaner Production* 2020, *250*, 119484. DOI: https://doi.org/10.1016/j.jclepro.2019.119484

[79] P. Ramesohl, R. Meys, L. Vetter, S. Steger, *Chemical plastics recycling - potentials and development prospects: A contribution to defossiling the chemical and plastics processing industry in NRW* 2020.

[80] D. Civancik-Uslu, T. T. Nhu, B. van Gorp, U. Kresovic, M. Larrain, P. Billen, K. Ragaert, S. de Meester, J. Dewulf, S. Huysveld, *Resources, Conservation and Recycling* 2021, *171*, 105633. DOI: https://doi.org/10.1016/j.resconrec.2021.105633

[81] R. Volk, C. Stallkamp, J. J. Steins, S. P. Yogish, R. C. Müller, D. Stapf, F. Schultmann, *Journal of Industrial Ecology* 2021, *25 (5)*, 1318 – 1337. DOI: https://doi.org/10.1111/jiec.13145

[82] M. Sardarmehni, J. W. Levis, *Resources, Conservation and Recycling* 2021, *169*, 105503. DOI: https://doi.org/10.1016/j.resconrec.2021.105503

[83] X. Zhao, F. You, *ACS Sustainable Chemistry & Engineering* 2021, *9 (36)*, 12167 – 12184. DOI: https://doi.org/10.1021/acssuschemeng.1c03587

[84] R. Voss, R. P. Lee, L. Seidl, F. Keller, M. Fröhling, *Waste Management* 2021, *134*, 206 – 219. DOI: https://doi.org/10.1016/j.wasman.2021.07.040

[85] Sabic, *Life Cycle Assessment of certified circular polymers* 2021.

[86] R. Voss, R. P. Lee, M. Fröhling, *Journal of Industrial Ecology* 2022, 421. DOI: https://doi.org/10.1111/jiec.13303

[87] A. Rolfe, Y. Huang, N. Hewitt, *Waste and Biomass Valorization* 2022, *13 (9)*, 3801 – 3819. DOI: https://doi.org/10.1007/s12649-022-01757-2

[88] U. Arena, F. Ardolino, *Resources, Conservation and Recycling* 2022, *183 (12)*, 106379. DOI: https://doi.org/10.1016/j.resconrec.2022.106379

[89] C. Gomez-Camacho, S. Cecconi, R. Hischier, B. Ruggeri, *From refuse-derived fuel (RDF) to NH3: Key pathway for the sustainability and security of the food production chain*, Sustainable Energy and Environmental Protection conference SEEP 2022, London 2022.

[90] S. Huysveld, K. Ragaert, R. Demets, T. T. Nhu, D. Civancik-Uslu, M. Kusenberg, K. M. van Geem, S. de Meester, J. Dewulf, *Waste Management* 2022, *152*, 69 – 79. DOI: https://doi.org/10.1016/j.wasman.2022.08.006

[91] F. Keller, R. L. Voss, R. P. Lee, B. Meyer, *Resources, Conservation and Recycling* 2022, *179 (1)*, 106106. DOI: https://doi.org/10.1016/j.resconrec.2021.106106

[92] A. Laurent, I. Bakas, J. Clavreul, A. Bernstad, M. Niero, E. Gentil, M. Z. Hauschild, T. H. Christensen, *Waste Management* 2014, *34 (3)*, 573 – 588. DOI: https://doi.org/10.1016/j.wasman.2013.10.045

[93] S. Taelman, D. Sanjuan-Delmás, D. Tonini, J. Dewulf, *Resources, Conservation and Recycling* 2020, *162 (1)*, 104964. DOI: https://doi.org/10.1016/j.resconrec.2020.104964

[94] V. Bisinella, R. Götze, K. Conradsen, A. Damgaard, T. H. Christensen, T. F. Astrup, *Journal of Cleaner Production* 2017, *164*, 1180 – 1191. DOI: https://doi.org/10.1016/j.jclepro.2017.07.013

[95] B. P. Weidema, *Market information in life cycle assessment*, Copenhagen 2003.

[96] T. Ekvall, B. P. Weidema, *The International Journal of Life Cycle Assessment* 2004, *9 (3)*, 161 – 171. DOI: https://doi.org/10.1007/BF02994190

[97] M. Brandão, M. Martin, A. Cowie, L. Hamelin, A. Zamagni, in *Encyclopedia of Sustainable Technologies*, Elsevier 2017.

[98] T. Ekvall, in *Sustainability Assessment at the 21st century* (Eds: M. José Bastante-Ceca et al.), IntechOpen 2020.

[99] Ellen MacArthur Foundation, *Enabling a circular economy for chemicals with the mass balance approach* 2019.

[100] C. Krüger, A. Kicherer, C. Kormann, N. Raupp, in *Designing Sustainable Technologies, Products and Policies* (Eds: E. Benetto, K. Gericke, M. Guiton), Springer International Publishing. Cham 2018.

[101] J. Kleinekorte, L. Fleitmann, M. Bachmann, A. Kätelhön, A. Barbosa-Póvoa, N. von der Assen, A. Bardow, *Annual review of chemical and biomolecular engineering* 2020, *11*, 203 – 233. DOI: https://doi.org/10.1146/annurev-chembioeng-011520-075844

[102] U. Arena, in *Fluidized Bed Technologies for Near-Zero Emission Combustion and Gasification*, Vol. 87, Elsevier 2013.

[103] M. Gräbner, *Industrial coal gasification technologies covering baseline and high-ash coal*, Wiley-VCH, Weinheim, Germany 2015.

[104] D. Chen, L. Yin, H. Wang, P. He, *Waste Management* 2014, *34 (12)*, 2466 – 2486. DOI: https://doi.org/10.1016/j.wasman.2014.08.004

[105] S. M. Al-Salem, A. Antelava, A. Constantinou, G. Manos, A. Dutta, *Journal of Environmental Management* 2017, *197*, 177 – 198. DOI: https://doi.org/10.1016/j.jenvman.2017.03.084

[106] Frederik Neuwahl, Gianluca Cusano, Jorge Gómez Benavides, Simon Holbrook, Serge Roudier, European IPPC Bureau, JRC Directorate B – Growth and Innovation, European Commission, *Best Available Techniques (BAT) Reference Document for Waste Incineration*.

[107] K. M. Sundaram, *How much is too much?: Feed Contaminants and their Consequences*, AIChE 2018 Spring National Meeting, Orlando 2018.

[108] S&P Global, *Specifications Guide: Europe And Africa Refined Oil Products*.

[109] M. Kusenberg, A. Eschenbacher, M. R. Djokic, A. Zayoud, K. Ragaert, S. de Meester, Van Geem, Kevin M., *Waste Management* 2021, *138*, 83 – 115. DOI: https://doi.org/10.1016/j.wasman.2021.11.009

[110] M. Kusenberg, M. Roosen, A. Zayoud, M. R. Djokic, H. Dao Thi, S. de Meester, K. Ragaert, U. Kresovic, Van Geem, Kevin M., *Waste Management* 2022, *141*, 104 – 114. DOI: https://doi.org/10.1016/j.wasman.2022.01.033

[111] Buyle, Audenaert, Billen, Boonen, van Passel, *Sustainability* 2019, *11 (19)*, 5456. DOI: https://doi.org/10.3390/su11195456

[112] N. Thonemann, A. Schulte, D. Maga, *Sustainability* 2020, *12 (3)*, 1192. DOI: https://doi.org/10.3390/su12031192

[113] S. Cucurachi, C. van der Giesen, J. Guinée, *Procedia CIRP* 2018, *69*, 463 – 468. DOI: https://doi.org/10.1016/j.procir.2017.11.005

[114] S. M. Moni, R. Mahmud, K. High, M. Carbajales-Dale, *Journal of Industrial Ecology* 2020, *24 (1)*, 52 – 63. DOI: https://doi.org/10.1111/jiec.12965

[115] W. Boll, G. Hochgesand, C. Higman, E. Supp, P. Kalteier, W.-D. Müller, M. Kriebel, H. Schlichting, H. Tanz, in *Ullmann's Encyclopedia of Industrial Chemistry*, Vol. 70, Wiley-VCH Verlag GmbH & Co. KGaA. Weinheim, Germany 2000.

[116] *Gas Purification*, 5th ed. (Eds: A. L. Kohl, R. B. Nielsen), Elsevier 1997.

[117] *Handbook of petroleum refining processes* (Eds: R. A. Meyers), McGraw-Hill Education, New York, Chicago, San Francisco 2016.

[118] A. H. Zacher, M. V. Olarte, D. M. Santosa, D. C. Elliott, S. B. Jones, *Green Chem* 2014, *16 (2)*, 491 – 515. DOI: https://doi.org/10.1039/C3GC41382A

[119] *Die Veredlung und Umwandlung von Kohle: Technologien und Projekte 1970 bis 2000 in Deutschland* (Eds: J. Schmalfeld), DGMK, Hamburg 2008.

[120] N. Tsoy, B. Steubing, C. van der Giesen, J. Guinée, *The International Journal of Life Cycle Assessment* 2020, *25 (9)*, 1680 – 1692. DOI: https://doi.org/10.1007/s11367-020-01796-8

[121] R. Arvidsson, A.-M. Tillman, B. A. Sandén, M. Janssen, A. Nordelöf, D. Kushnir, S. Molander, *Journal of Industrial Ecology* 2018, *22 (6)*, 1286 – 1294. DOI: https://doi.org/10.1111/jiec.12690

[122] V. Bisinella, K. Conradsen, T. H. Christensen, T. F. Astrup, *The International Journal of Life Cycle Assessment* 2016, *21 (3)*, 378 – 394. DOI: https://doi.org/10.1007/s11367-015-1014-4

[123] C. Higman, M. van der Burgt, *Gasification*, Elsevier 2008.

[124] M. Bertau, H. Offermanns, L. Plass, F. Schmidt, H.-J. Wernicke, *Methanol: The basic chemical and energy feedstock of the future*, Springer, Berlin, Heidelberg 2014.

[125] A. Tukker, H. de Groot, L. Simons, S. Wiegersma, *Chemical Recycling of Plastics Waste (PVC and other resins)*, Delft 1999.

[126] C. Greil, H. Hirschfelder, O. Turna, T. Obermeier, *Operational results from gasification of waste material and biomass in fixed bed and circulating fluidized bed gasifiers*, Conference on gasification: the clean choice for carbon management, Noordwijk 2002.

[127] Prof. Dr.-Ing. Bernd Meyer (IEC), *Development of FlexiSlag gasification technology*, Personal communication 2022.

[128] M. Gräbner, B. Meyer, *Fuel* 2014, *116*, 910 – 920.
DOI: https://doi.org/10.1016/j.fuel.2013.02.045

[129] B. Meyer, O. Schulze, D. Küttner, D. Klinger, D. Scheithauer, M. Nguyen, K. Boblenz, F. Compart, P.-H. Rathsack, A. Laugwitz, *Weiterentwicklung der BGL-Vergasung zu einem IGCC- und Polygeneration-Vergasungsverfahren*, Freiberg 2019.

[130] S. Guhl, *Thermodynamische Modellierung des Mineralstoffverhaltens im BGL-Vergasungsprozess*, Dissertation, TU Bergakademie Freiberg 2011.

[131] F. Sabery, *Modell zur Vorkalkulation von mechanisch-biologischen Restabfallbehandlungsanlagen zur Herstellung von Ersatzbrennstoffen*, Dissertation, Technische Universität Berlin 2004.

[132] R. P. Lee, L. G. Seidl, Q.-l. Huang, B. Meyer, *Journal of Fuel Chemistry and Technology* 2021, *49 (8)*, 1057 – 1076. DOI: https://doi.org/10.1016/S1872-5813(21)60093-2

[133] Dr.-Ing. Stefan Guhl (IEC), *Slag bath conditions and residual carbon in BGL gasification*, Personal communication 2022.

[134] R. P. Lee, B. Meyer, Q. Huang, R. Voss, *Clean Energy* 2020, *4 (3)*, 169 – 201.
DOI: https://doi.org/10.1093/ce/zkaa013

[135] R. Pardemann, *Stoff-Kraft-Kopplung in kohlebasierten Polygenerationkonzepten*, Dissertation, TU Bergakademie Freiberg 2013.

[136] C. Higman, S. Tam, *Chemical reviews* 2014, *114 (3)*, 1673 – 1708.
DOI: https://doi.org/10.1021/cr400202m

[137] R. Reimert, F. Marschner, H.-J. Renner, W. Boll, E. Supp, M. Brejc, W. Liebner, G. Schaub, in *Ullmann's Encyclopedia of Industrial Chemistry*, Vol. 214, Wiley-VCH Verlag GmbH & Co. KGaA. Weinheim, Germany 2000.

[138] C. Ratnasamy, J. P. Wagner, *Catalysis Reviews* 2009, *51 (3)*, 325 – 440. DOI: https://doi.org/10.1080/01614940903048661

[139] Clariant, *Clariant ShiftMax 820S presulfided Sour Gas Shift catalyst Successful commercial launch in China* 2015.

[140] Clariant, *Catalysts And Adsorbents For Syngas* 2017.

[141] I. Y. Mohammed, M. Samah, G. Sabina, A. Mohamed, *International Journal of Engineering Research* 2014, *3 (12)*, 742 – 744. DOI: https://doi.org/10.17950/ijer/v3s12/1207

[142] Air Liquide, *Lurgi Rectisol: The world's leading synthesis gas purification process*.

[143] B. Munder, S. Grob, P. M. Fritz, *Selection of Wash Systems for Sour Gas Removal*, International Freiberg Conference on IGCC & XtL Technologies, Dresden 2010.

[144] S. Moioli, L. A. Pellegrini, M. C. Romano, A. Giuffrida, *Energy Procedia* 2017, *114*, 2136 – 2145. DOI: https://doi.org/10.1016/j.egypro.2017.03.1349

[145] D. Chiche, C. Diverchy, A.-C. Lucquin, F. Porcheron, F. Defoort, *Oil & Gas Science and Technology – Revue d'IFP Energies nouvelles* 2013, *68 (4)*, 707 – 723. DOI: https://doi.org/10.2516/ogst/2013175

[146] M. Rieger, *Advanced modeling and simulation of integrated gasification combined cycle power plants with CO2-capture*, Dissertation, TU Bergakademie Freiberg 2014.

[147] S. Kureti, T. Kuchling, C. Schmidt, *CO2-Wandlung durch dynamische Methanol-Synthese (CODY)*, Freiberg 2018.

[148] Bundesministerium für Umwelt, Naturschutz und nukleare Sicherheit, *Neufassung der Ersten Allgemeinen Verwaltungsvorschrift zum Bundes-Immissionsschutzgesetz: Technische Anleitung zur Reinhaltung der Luft – TA Luft* 2021.

[149] Linde, *Linde Sulfur Process Technology* 2015.

[150] H. G. Sönmez, *Techno-economic evaluation of a liquid redox process employing amino acid salts for sour natural gas treatment*, Dissertation, TU Berlin 2017.

[151] *Thermochemical Process Engineering*, Advances in Chemical Engineering (Eds: Kevin M. Van Geem), Elsevier 2016.

[152] D. Reichel, *Rohstoffliche und verfahrenstechnische Einflussfaktoren der Pyrolyse biogener Rohstoffe*, Dissertation, TU Bergakademie Freiberg 2017.

[153] Nova Institute, *Chemical Recycling – Status, Trends and Challenges: Technologies, Sustainability. Policy and Key Players* 2020.

[154] H. Punkkinen, A. Oasmaa, J. Laatikainen-Luntama, M. Nieminen, J. Laine-Ylijoki, *Thermal conversion of plastic-containing waste: A review*, VTT Research Report 2017.

[155] P. Mamani-Soliz, L. G. Seidl, F. Keller, R. P. Lee, B. Meyer, in *Recycling und Sekundärrohstoffe, Band 13*, Recycling und Rohstoffe, Vol. 13 (Eds: E. Thomé-Kozmiensky, O. Holm, B. Friedrich, D. Goldmann), Thomé-Kozmiensky Verlag GmbH. Nietwerder 2020.

[156] C. Haupts, in *Recycling und Sekundärrohstoffe, Band 13*, Recycling und Rohstoffe, Vol. 13 (Eds: E. Thomé-Kozmiensky, O. Holm, B. Friedrich, D. Goldmann), Thomé-Kozmiensky Verlag GmbH. Nietwerder 2020.

[157] C. Haupts, *Status und Herausforderungen bei der Anwendung des CTC-Verfahrens am Beispiel der Pilotinstallation in Ennigerloh*, Pyrolysetag, Freiberg 2019.

[158] A. Gonzalez-Quiroga, M. R. Djokic, Van Geem, Kevin M., G. B. Marin, *Energy Fuels* 2016, *30 (10)*, 8292 – 8303. DOI: https://doi.org/10.1021/acs.energyfuels.6b01639

[159] D. Chen, L. Yin, H. Wang, P. He, *Waste Management* 2014, 2466 – 2486. DOI: https://doi.org/10.1016/j.wasman.2014.08.004

[160] S. D. Anuar Sharuddin, F. Abnisa, W. M. A. Wan Daud, M. K. Aroua, *Energy Conversion and Management* 2016, *115*, 308 – 326. DOI: https://doi.org/10.1016/j.enconman.2016.02.037

[161] S. M. Al-Salem, A. Antelava, A. Constantinou, G. Manos, A. Dutta, *Journal of Environmental Management* 2017, 177 – 198. DOI: https://doi.org/10.1016/j.jenvman.2017.03.084

[162] M. Kusenberg, A. Zayoud, M. Roosen, H. D. Thi, M. S. Abbas-Abadi, A. Eschenbacher, U. Kresovic, S. de Meester, Van Geem, Kevin M., *Fuel Processing Technology* 2022, *227 (20)*, 107090. DOI: https://doi.org/10.1016/j.fuproc.2021.107090

[163] Umweltbundesamt, *Evaluation neuer Entwicklungen bei alternativen thermischen Abfallbehandlungsanlagen mit dem Schwerpunkt Verölungsverfahren*, Dessau-Roßlau 2018.

[164] Carboliq, *Product Datasheet CLR Suedpack material* 2021.

[165] Carboliq, *Product Datasheet CLR Eco20* 2021.

[166] P. James, *Managing challenges in the production and use of pyrolysis oil*, Chemical Recycling – Beyond Thermal Use of Plastic and other Waste, Dresden 2021.

[167] https://blog.topsoe.com/partnership-between-dow-and-haldor-topsoe-will-turn-waste-plastics-into-circular-plastics (Accessed on October 15, 2022).

[168] https://www.topsoe.com/processes/renewables/waste-to-plastic (Accessed on August 01, 2022).

[169] https://www.axens.net/markets/plastic-recycling (Accessed on September 06, 2022).

[170] C. Vasile, M. A. Brebu, T. Karayildirim, J. Yanik, H. Darie, *Fuel* 2007, *86 (4)*, 477 – 485. DOI: https://doi.org/10.1016/j.fuel.2006.08.010

[171] P. Kokayeff, S. Zink, P. Roxas, in *Handbook of Petroleum Processing*, Vol. 11 (Eds: S. A. Treese, D. S. Jones, P. R. Pujado), Springer International Publishing. Cham 2015.

[172] S. Gust, *BioBoost project: Process concept on upgrading and utilization of catalytic pyrolysis oil at NESTE Oil refineries* 2015.

[173] S. Jones, P. Meyer, L. Snowden-Swan, A. Padmaperuma, E. Tan, A. Dutta, J. Jacobson, K. Cafferty, *Process Design and Economics for the Conversion of Lignocellulosic Biomass to Hydrocarbon Fuels: Fast Pyrolysis and Hydrotreating Bio-oil Pathway* 2013.

[174] A. P. Pinheiro Pires, J. Arauzo, I. Fonts, M. E. Domine, A. Fernández Arroyo, M. E. Garcia-Perez, J. Montoya, F. Chejne, P. Pfromm, M. Garcia-Perez, *Energy Fuels* 2019, *33 (6)*, 4683 – 4720. DOI: https://doi.org/10.1021/acs.energyfuels.9b00039

[175] D. C. Dayton, *Catalytic Upgrading of Thermochemical Intermediates to Hydrocarbons* 2017.

[176] L. Pellegrini, S. Bonomi, S. Gamba, V. Calemma, D. Molinari, *Chemical Engineering Science* 2007, *62 (18-20)*, 5013 – 5020. DOI: https://doi.org/10.1016/j.ces.2007.01.076

[177] S. Herrmann, *Modellierung einer Prozesskette zur Aufbereitung von Rohprodukten der Fischer-Tropsch-Synthese mit AspenPlus*, Diploma thesis, TU Bergakademie Freiberg 2019.

[178] L. Pellegrini, S. Locatelli, S. Rasella, S. Bonomi, V. Calemma, *Chemical Engineering Science* 2004, *59 (22-23)*, 4781 – 4787. DOI: https://doi.org/10.1016/j.ces.2004.08.027

[179] P. Leprince, *Petroleum Refining: Vol. 3 Conversion Processes*, Technip, Paris 2001.

[180] Statista, *Chemieindustrie: Statista-Dossier zum Thema Chemieindustrie* 2018.

[181] B. Gehrke, I. Weilage, V.-S. Gulden, K. Ingwersen, *Branchenanalyse Chemieindustrie: Der Chemiestandort Deutschland im Spannungsfeld globaler Verschiebungen von Nachfragestrukturen und Wertschöpfungsketten*, Nr. 395, Hans-Böckler-Stiftung, Düsseldorf 2018.

[182] Petrochemicals Europe, *Petrochemistry Flowchart* 2021.

[183] Destatis, *Produktion des Verarbeitenden Gewerbes sowie des Bergbaus und der Gewinnung von Steinen und Erden: Fachserie 4 Reihe 3.1* 2019.

[184] P. Lanzafame, G. Centi, S. Perathoner, *Chemical Society reviews* 2014, *43 (22)*, 7562 – 7580. DOI: https://doi.org/10.1039/c3cs60396b

[185] VCI, *Chemiewirtschaft in Zahlen*, Frankfurt am Main 2019.

[186] H. Zimmermann, R. Walzl, in *Ullmann's Encyclopedia of Industrial Chemistry*, Wiley-VCH Verlag GmbH & Co. KGaA. Weinheim, Germany 2012.

[187] T. Ren, M. Patel, K. Blok, *Energy* 2006, *31 (4)*, 425 – 451. DOI: https://doi.org/10.1016/j.energy.2005.04.001

[188] M. Alizadeh, S. M. Sadrameli, *Journal of Heat Transfer* 2016, *138 (4)*, 42801. DOI: https://doi.org/10.1115/1.4032171

[189] K. van Geem, D. Hudebine, M. F. Reyniers, F. Wahl, J. J. Verstraete, G. B. Marin, *Computers & Chemical Engineering* 2007, *31 (9)*, 1020 – 1034. DOI: https://doi.org/10.1016/j.compchemeng.2006.09.001

[190] P. Kumar, D. Kunzru, *Industrial & Engineering Chemistry Process Design and Development* 1985, *24 (3)*, 774 – 782. DOI: https://doi.org/10.1021/i200030a043

[191] PlasticsEurope, *Benzene, Toluene, and Xylenes (Aromatics, BTX)*, Eco-profiles and Environmental Product Declarations of the European Plastics Manufacturers 2013.

[192] M. Bender, in *New technologies and alternative feedstocks in petrochemistry and refining: October 9-11, 2013, Dresden, Germany*, Tagungsbericht / DGMK, 2013,2, Suppl (Eds: S. Ernst), DGMK. Hamburg 2012.

[193] H. O. Folkins, in *Ullmann's Encyclopedia of Industrial Chemistry*, Wiley-VCH Verlag GmbH & Co. KGaA. Weinheim, Germany 2012.

[194] J. Ancheyta-Juárez, E. Villafuerte-Macías, L. Díaz-García, E. González-Arredondo, *Energy Fuels* 2001, *15 (4)*, 887 – 893. DOI: https://doi.org/10.1021/ef000273f

[195] J. Fabri, U. Graeser, T. Simo, in *Ullmann's Encyclopedia of Industrial Chemistry*, Wiley-VCH Verlag GmbH & Co. KGaA. Weinheim, Germany 2012.

[196] M. Yang, F. You, *Industrial & Engineering Chemistry Research* 2017, *56 (14)*, 4038 – 4051. DOI: https://doi.org/10.1021/acs.iecr.7b00354

[197] T. Ren, M. Patel, K. Blok, *Energy* 2008, *33 (5)*, 817 – 833. DOI: https://doi.org/10.1016/j.energy.2008.01.002

[198] https://www.engineering-airliquide.com/butadiene-extraction (Accessed on November 24, 2020).

[199] M. Dahlmann, J. Grub, E. Löser, in *Ullmann's Encyclopedia of Industrial Chemistry*, Vol. 83, Wiley-VCH Verlag GmbH & Co. KGaA. Weinheim, Germany 2000.

[200] P. Rößger, L. G. Seidl, F. Compart, J. Hußler, M. Gräbner, A. Richter, *Journal of Cleaner Production* 2022, *358*, 132053. DOI: https://doi.org/10.1016/j.jclepro.2022.132053

[201] S. Walter, *The HP POX Pilot Plant - A door opener to a new era of natural gas valorisation*, International Freiberg Conference on IGCC & XtL Technologies, Freiberg 2005.

[202] A. Bader, M. Hartwich, A. Richter, B. Meyer, *Fuel Processing Technology* 2018, *169*, 58 – 70. DOI: https://doi.org/10.1016/j.fuproc.2017.09.003

[203] J. Ott, V. Gronemann, F. Pontzen, E. Fiedler, G. Grossmann, D. B. Kersebohm, G. Weiss, C. Witte, in *Ullmann's Encyclopedia of Industrial Chemistry*, Wiley-VCH Verlag GmbH & Co. KGaA. Weinheim, Germany 2012.

[204] S. Kang, F. Boshell, A. Goeppert, S. G. Prakash, I. Landälv, D. Saygin, *Innovation outlook: Renewable methanol*, International Renewable Energy Agency, Abu Dhabi 2021.

[205] https://www.carbonrecycling.is/news-media/worlds-largest-co2-to-methanol-plant-starts-production (Accessed on February 02, 2023).

[206] C. Wolfersdorf, *Elektroenergieeinkopplung bei der stofflichen Nutzung von Braunkohle und CO2*, Dissertation, TU Bergakademie Freiberg 2017.

[207] M. Saito, M. Takeuchi, et al., *Applied Organometallic Chemistry* 2000, *14*, 763 – 772. DOI: https://doi.org/10.1002/1099-0739(200012)14:12<763:AID-AOC98>3.0.CO;2-4

[208] M. Ye, P. Tian, Z. Liu, *Engineering* 2021, *7 (1)*, 17 – 21. DOI: https://doi.org/10.1016/j.eng.2020.12.001

[209] M. Gootz, C. Forman, *Konzeptuntersuchung zu Polygeneration-Annex-Anlagen auf Basis Braunkohle: Abschlussbericht*, Freiberg 2017.

[210] M. Ye, H. Li, Y. Zhao, T. Zhang, Z. Liu, in *Mesoscale Modeling in Chemical Engineering Part II*, Vol. 47, Advances in Chemical Engineering, Elsevier 2015.

[211] W. Qian, F. Wei, in *Multiphase reactor engineering for clean and low-carbon energy applications* (Eds: Y. Cheng, F. Wei, Y. Jin), Wiley. Hoboken, New Jersey 2017.

[212] T. Li, T. Shoinkhorova, J. Gascon, J. Ruiz-Martínez, *ACS Catalysis* 2021, *11 (13)*, 7780 – 7819. DOI: https://doi.org/10.1021/acscatal.1c01422

[213] B. V. Vora, T. L. Marker, P. T. Barger, H. R. Nilsen, S. Kvisle, T. Fuglerud, *Studies in Surface Science and Catalysis* 1997, *107*, 87 – 98. DOI: https://doi.org/10.1016/S0167-2991(97)80321-7

[214] I. Hannula, V. Arpiainen, *Biomass Conversion and Biorefinery* 2014, *31 (4)*, 425. DOI: https://doi.org/10.1007/s13399-014-0123-9

[215] Y. Wang, F. Wei, in *Multiphase reactor engineering for clean and low-carbon energy applications* (Eds: Y. Cheng, F. Wei, Y. Jin), Wiley. Hoboken, New Jersey 2017.

[216] A. M. Niziolek, O. Onel, Y. A. Guzman, C. A. Floudas, *Energy Fuels* 2016, *30 (6)*, 4970 – 4998. DOI: https://doi.org/10.1021/acs.energyfuels.6b00619

[217] T. Wang, X. Tang, X. Huang, W. Qian, Y. Cui, X. Hui, W. Yang, F. Wei, *Catalysis Today* 2014, *233*, 8 – 13. DOI: https://doi.org/10.1016/j.cattod.2014.02.007

[218] UOP, *50 Years of PSA Technology for H2 Purification* 2015.

[219] V. Pattabathula, in *Kirk-Othmer Encyclopedia of Chemical Technology* (Eds: J. W. & S. Inc), John Wiley & Sons, Inc. Hoboken, NJ, USA 2000.

[220] M. Appl, in *Ullmann's Encyclopedia of Industrial Chemistry*, Wiley-VCH Verlag GmbH & Co. KGaA. Weinheim, Germany 2012.

[221] N. K. Agnihotra, *Ammonia Production by Haldor Topsøe Advanced Process*, Process Economics Program Review 2017.

[222] R. Geres, A. Kohn, S. C. Lenz, F. Ausfelder, A. Bazzanella, A. Möller, *Roadmap Chemie 2050: Auf dem Weg zu einer treibhausgasneutralen chemischen Industrie in Deutschland eine Studie von DECHEMA und FutureCamp für den VCI*, DECHEMA Gesellschaft für Chemische Technik und Biotechnologie e.V, Frankfurt am Main 2019.

[223] Agora Energiewende, *Klimaneutrale Industrie: Schlüsseltechnologien und Politikoptionen für Stahl, Chemie und Zement* 2019.

[224] M. Bonheure, L. A. Vandewalle, G. B. Marin, K. van Geem, *CEP Magazine*, *2021*.

[225] https://www.process-worldwide.com/topsoes-demo-plant-begins-operations-for-sustainable-methanol-production-a-1066683/.

[226] S. T. Wismann, J. S. Engbæk, S. B. Vendelbo, F. B. Bendixen, W. L. Eriksen, K. Aasberg-Petersen, C. Frandsen, I. Chorkendorff, P. M. Mortensen, *Science* 2019, *364 (6442)*, 756 – 759. DOI: https://doi.org/10.1126/science.aaw8775

[227] https://www.basf.com/global/en/who-we-are/sustainability/whats-new/sustainability-news/2022/basf-sabic-and-linde-start-construction-of-the-worlds-first-demonstration-plant-for-large-scale-electrically-heated-steam-cracker-furnaces.html.

[228] https://www.shell.com/business-customers/chemicals/media-releases/2022-media-releases/shell-and-dow-start-up-e-cracking-furnace-experimental-unit.html (Accessed on October 15, 2022).

[229] C. Oliveira, T. van Dril, *Decarbonisation options for Large Volume Organic Chemicals production, SABIC Geleen* 2021.

[230] M. Bender, *Energy Efficiency – Key to Defossilizing the Chemical Industry*, K³/C³ - Defossilizing the chemical industry – technological approaches & engineering concepts, Dresden 2022.

[231] C. Oliveira, K. Schure, *Decarbonisation options for the Dutch refinery sector* 2020.

[232] O. Schmidt, A. Gambhir, I. Staffell, A. Hawkes, J. Nelson, S. Few, *International Journal of Hydrogen Energy* 2017, *42 (52)*, 30470 – 30492.
DOI: https://doi.org/10.1016/j.ijhydene.2017.10.045

[233] T. Smolinka, N. Wiebe, P. Sterchele, A. Palzer, F. Lehner, M. Jansen, S. Kiemel, R. Miehe, S. Wahren, F. Zimmermann, *Studie IndWEDe. Industrialisierung der Wasserelektrolyse in Deutschland: Chancen und Herausforderungen für nachhaltigen Wasserstoff für Verkehr, Strom und Wärme*, Berlin 2018.

[234] T. Fröhlich, S. Blömer, D. Münter, L.-A. Brischke, *CO2-Quellen für die PtX-Herstellung in Deutschland: Technologien, Umweltwirkung, Verfügbarkeit*, Heidelberg 2019.

[235] Z. Kapetaki, J. Scowcroft, *Energy Procedia* 2017, *114*, 6623 – 6630.
DOI: https://doi.org/10.1016/j.egypro.2017.03.1816

[236] M. Wang, A. Lawal, P. Stephenson, J. Sidders, C. Ramshaw, *Chemical Engineering Research and Design* 2011, *89 (9)*, 1609 – 1624.
DOI: https://doi.org/10.1016/j.cherd.2010.11.005

[237] X. Wang, C. Song, *Frontiers in Energy Research* 2020, *8*, 321.
DOI: https://doi.org/10.3389/fenrg.2020.560849

[238] N. McQueen, K. V. Gomes, C. McCormick, K. Blumanthal, M. Pisciotta, J. Wilcox, *Progress in Energy* 2021, *3 (3)*, 32001. DOI: https://doi.org/10.1088/2516-1083/abf1ce

[239] H.-W. Häring, *Industrial Gases Processing*, Wiley 2007.

[240] S. van Bavel, S. Verma, E. Negro, M. Bracht, *ACS Energy Letters* 2020, *5 (8)*, 2597 – 2601. DOI: https://doi.org/10.1021/acsenergylett.0c01418

[241] A. Hauch, R. Küngas, P. Blennow, A. B. Hansen, J. B. Hansen, B. V. Mathiesen, M. B. Mogensen, *Science* 2020, *370 (6513)*. DOI: https://doi.org/10.1126/science.aba6118

[242] Y. Zheng, J. Wang, B. Yu, W. Zhang, J. Chen, J. Qiao, J. Zhang, *Chemical Society reviews* 2017, *46 (5)*, 1427 – 1463. DOI: https://doi.org/10.1039/c6cs00403b

[243] https://www.sunfire.de/en/news/detail/breakthrough-for-power-to-x-sunfire-puts-first-co-electrolysis-into-operation-and-starts-scaling (Accessed on October 15, 2022).

[244] M. González-Castaño, B. Dorneanu, H. Arellano-García, *React. Chem. Eng.* 2021, *6 (6)*, 954 – 976. DOI: https://doi.org/10.1039/D0RE00478B

[245] S. Thor Wismann, K.-E. Larsen, P. Mølgaard Mortensen, *Angewandte Chemie (International ed. in English)* 2022, *61 (8)*, e202109696. DOI: https://doi.org/10.1002/anie.202109696

[246] H. Eerens, D. van Dam, *Decarbonisation options for Large Volume Organic Chemicals Production, DOW Terneuzen* 2022.

[247] https://www.process-worldwide.com/rotating-olefins-cracker-technology-to-advance-energy-transition-of-olefin-production-a-1062996/ (Accessed on October 15, 2022).

[248] https://coolbrook.com/news/2022/coolbrook-and-braskem-to-enter-into-decarbonisation-project-for-olefins-production-through-electrification/ (Accessed on February 15, 2023).

[249] D. Rubini, N. Karefyllidis, L. Xu, B. Rosic, H. Johannesdahl, *Journal of the Global Power and Propulsion Society* 2022, *6 (2)*, 135 – 150. DOI: https://doi.org/10.33737/jgpps/150550

[250] S. Timmerberg, M. Kaltschmitt, M. Finkbeiner, *Energy Conversion and Management: X* 2020, *7 (1)*, 100043. DOI: https://doi.org/10.1016/j.ecmx.2020.100043

[251] S. Schneider, S. Bajohr, F. Graf, T. Kolb, *Chemie Ingenieur Technik* 2020, *92 (8)*, 1023 – 1032. DOI: https://doi.org/10.1002/cite.202000021

[252] X. Chen, Y. Cheng, T. Li, Y. Cheng, *Current Opinion in Chemical Engineering* 2017, *17*, 68 – 77. DOI: https://doi.org/10.1016/j.coche.2017.07.001

[253] A. George, B. Shen, M. Craven, Y. Wang, D. Kang, C. Wu, X. Tu, *Renewable and Sustainable Energy Reviews* 2021, *135*, 109702. DOI: https://doi.org/10.1016/j.rser.2020.109702

[254] V. S. Sikarwar, M. Hrabovský, G. van Oost, M. Pohořelý, M. Jeremiáš, *Progress in Energy and Combustion Science* 2020, *81*, 100873. DOI: https://doi.org/10.1016/j.pecs.2020.100873

[255] M. Oliveira, A. Ramos, T. M. Ismail, E. Monteiro, A. Rouboa, *Energies* 2022, *15 (4)*, 1475. DOI: https://doi.org/10.3390/en15041475

[256] F. Fabry, C. Rehmet, V. Rohani, L. Fulcheri, *Waste and Biomass Valorization* 2013, *4 (3)*, 421 – 439. DOI: https://doi.org/10.1007/s12649-013-9201-7

[257] M. Ostadi, K. G. Paso, S. Rodriguez-Fabia, L. E. Øi, F. Manenti, M. Hillestad, *Energies* 2020, *13 (18)*, 4859. DOI: https://doi.org/10.3390/en13184859

[258] M. Hillestad, M. Ostadi, G.d. Alamo Serrano, E. Rytter, B. Austbø, J. G. Pharoah, O. S. Burheim, *Fuel* 2018, *234 (12)*, 1431 – 1451. DOI: https://doi.org/10.1016/j.fuel.2018.08.004

[259] Umweltbundesamt, *Vergleichende Analyse von Siedlungsrestabfällen aus repräsentativen Regionen in Deutschland zur Bestimmung des Anteils an Problemstoffen und verwertbaren Materialien*, Dessau-Roßlau 2020.

[260] R. Götze, A. Boldrin, C. Scheutz, T. F. Astrup, *Waste Management* 2016, *49*, 3 – 14. DOI: https://doi.org/10.1016/j.wasman.2016.01.008

[261] M. E. Edjabou, V. Takou, A. Boldrin, C. Petersen, T. F. Astrup, *Journal of Cleaner Production* 2021, *295 (4)*, 126439. DOI: https://doi.org/10.1016/j.jclepro.2021.126439

[262] C. Cimpan, A. Maul, H. Wenzel, T. Pretz, *Insight into economies of scale for waste packaging sorting plants*, 30th International Conference on Solid Waste Technology and Management 2015.

[263] C. Cimpan, A. Maul, M. Jansen, T. Pretz, H. Wenzel, *Journal of Environmental Management* 2015, *156*, 181 – 199. DOI: https://doi.org/10.1016/j.jenvman.2015.03.025

[264] Bundesministerium für Justiz, *Gesetz zur Förderung der Kreislaufwirtschaft und Sicherung der umweltverträglichen Bewirtschaftung von Abfällen: Kreislaufwirtschaftsgesetz - KrWG* 2021.

[265] Destatis, *Abfallentsorgung: Fachserie 19 Reihe 1* 2019.

[266] Umweltbundesamt, *Bewährte Verfahren zur kommunalen Abfallbewirtschaftung* 2018.

[267] C. Picuno, A. Alassali, Z. K. Chong, K. Kuchta, *Resources, Conservation and Recycling* 2021, *169 (1)*, 105515. DOI: https://doi.org/10.1016/j.resconrec.2021.105515

[268] Destatis, *Abfallbilanz: Abfallaufkommen/-verbleib, Abfallintensität, Abfallaufkommen nach Wirtschaftszweigen* 2020.

[269] C. Lodato, D. Tonini, A. Damgaard, T. Fruergaard Astrup, *The International Journal of Life Cycle Assessment* 2020, *25 (1)*, 73 – 88. DOI: https://doi.org/10.1007/s11367-019-01665-z

[270] S. Thiel, K. J. Thomé-Kozmiensky, *Mechanisch-biologische Abfallbehandlung: Verfahrenskonzepte, Technik, Probleme* 2011.

[271] J. Martens, R. Sieksmeyer, *Drei Konzepte zur Nassvergärung im Rahmen einer MBA* 2004.

[272] M. L. Mastellone, *The Science of the total environment* 2020, *718*, 137233. DOI: https://doi.org/10.1016/j.scitotenv.2020.137233

[273] C. Cimpan, A. Maul, H. Wenzel, T. Pretz, *Journal of Cleaner Production* 2016, *112*, 4387 – 4397. DOI: https://doi.org/10.1016/j.jclepro.2015.09.011

[274] K. Krell, *Erstellung eines Sachbilanzmodells für das werkstoffliche Kunststoffrecycling in EASETECH*, Studienarbeit, TU Bergakademie Freiberg 2021.

[275] J. Christiani, *Recycling und Recyclingfähigkeit bei Verpackungen: Das neue VerpackG in der Praxis*, Berlin 2017.

[276] M. Canova, A. Pinasseau, J. Roth, S. Roudier, B. Zerger, *Best available techniques (BAT) reference document for waste treatment: Industrial Emissions Directive 2010/75/EU (integrated pollution prevention and control)*, EUR 29362, Publications Office of the European Union, Luxembourg 2018.

[277] J. Rose, in *Refuse derived fuels - 2* (Eds: K. J. Thomé-Kozmiensky), TK-Verl. Neuruppin 2002.

[278] I. Naroznova, J. Møller, C. Scheutz, *Waste Management* 2016, *58*, 397 – 407. DOI: https://doi.org/10.1016/j.wasman.2016.08.020

[279] M. Münster, H. Lund, *Waste Management* 2010, *30 (7)*, 1251 – 1263. DOI: https://doi.org/10.1016/j.wasman.2009.07.001

[280] T. Brinkmann, H. Falcke, S. Holbrook, T. Sanalan, J. Roth, L. Delgado Sancho, A. López Carretero, I. Clenahan, S. Roudier, B. Zerger, *Best Available Techniques (BAT) Reference Document for the Production of Large Volume Organic Chemicals* 2017.

[281] M. J. Murer, H. Spliethoff, C. M. W. de Waal, S. Wilpshaar, B. Berkhout, M. A. J. van Berlo, O. Gohlke, J. J. E. Martin, *Waste management & research the journal of the International Solid Wastes and Public Cleansing Association, ISWA* 2011, *29 (10 Suppl)*, 20 – 29. DOI: https://doi.org/10.1177/0734242X11413334

[282] N. Tanner, in *Energie aus Abfall* (Eds: K. J. Thomé-Kozmiensky, M. Beckmann), TK Verl. Karl Thomé-Kozmiensky. Neuruppin 2011.

[283] W. Bogale, F. Viganò, *Energy Procedia* 2014, *45*, 1315 – 1324. DOI: https://doi.org/10.1016/j.egypro.2014.01.137

[284] US EPA, *Selective Catalytic Reduction*, Cost Reports and Guidance for Air Pollution Regulations 2019.

[285] US EPA, *Wet and Dry Scrubbers for Acid Gas Control*, Cost Reports and Guidance for Air Pollution Regulations 2021.

[286] M. Kranert, *Einführung in die Kreislaufwirtschaft*, Springer Fachmedien Wiesbaden, Wiesbaden 2017.

[287] B. Pascal, M. Chaugny, L. Delgado Sancho, S. Roudier, *Best available techniques (BAT) reference document for the refining of mineral oil and gas industrial emissions: Industrial Emissions Directive 2010/75/EU (integrated pollution prevention and control)*, EUR, Scientific and technical research series, Vol. 27140, Publications Office, Luxembourg 2015.

[288] A. Köhler, S. Hellweg, E. Recan, K. Hungerbühler, *Environmental science & technology* 2007, *41 (15)*, 5515 – 5522. DOI: https://doi.org/10.1021/es0617284

[289] U. Vengateson, *Cooling towers: Estimate evaporation loss and makeup water requirements* 2017.

[290] C. Ras, H. von Blottnitz, *Water SA* 2012, *38 (4)*. DOI: https://doi.org/10.4314/wsa.v38i4.10

[291] J. Lei, G. Yuan, P. Weerachanchai, S. W. Lee, K. Li, J.-Y. Wang, Y. Yang, *Journal of Material Cycles and Waste Management* 2018, *20 (1)*, 137 – 146. DOI: https://doi.org/10.1007/s10163-016-0555-3

[292] N. D. Ristic, M. R. Djokic, E. Delbeke, A. Gonzalez-Quiroga, C. V. Stevens, Van Geem, Kevin M., G. B. Marin, *Energy Fuels* 2018, *32 (2)*, 1276 – 1286. DOI: https://doi.org/10.1021/acs.energyfuels.7b03242

[293] M. Münster, G. Finnveden, H. Wenzel, *Waste Management* 2013, *33 (11)*, 2457 – 2464. DOI: https://doi.org/10.1016/j.wasman.2013.07.013

[294] T. Fruergaard, T. Astrup, T. Ekvall, *Waste management & research the journal of the International Solid Wastes and Public Cleansing Association, ISWA* 2009, *27 (8)*, 724 – 737. DOI: https://doi.org/10.1177/0734242X09345276

[295] B. V. Mathiesen, M. Münster, T. Fruergaard, *Journal of Cleaner Production* 2009, *17 (15)*, 1331 – 1338. DOI: https://doi.org/10.1016/j.jclepro.2009.04.009

[296] L. Vandepaer, K. Treyer, C. Mutel, C. Bauer, B. Amor, *The International Journal of Life Cycle Assessment* 2019, *24 (8)*, 1409 – 1428. DOI: https://doi.org/10.1007/s11367-018-1571-4

[297] I. Munoz, B. Weidema, *Example – marginal electricity in Denmark* 2021.

[298] N. Baumgärtner, S. Deutz, C. Reinert, N. Nolzen, L. E. Kuepper, M. Hennen, D. E. Hollermann, A. Bardow, *Frontiers in Energy Research* 2021, *9*, 886. DOI: https://doi.org/10.3389/fenrg.2021.621502

[299] M. L. Parisi, S. Maranghi, R. Basosi, A. Sinicropi, *Data in Brief* 2020, *30*, 105499. DOI: https://doi.org/10.1016/j.dib.2020.105499

[300] S. Misconel, R. Leisen, J. Mikurda, F. Zimmermann, C. Fraunholz, W. Fichtner, D. Möst, C. Weber, *Renewable and Sustainable Energy Reviews* 2022, *153*, 111785. DOI: https://doi.org/10.1016/j.rser.2021.111785

[301] European Commission, *EU Reference Scenario 2020: Energy, transport and GHG emissions - Trends to 2050* 2021.

[302] M. Schlesinger, D. Lindenberger, C. Lutz, *Entwicklung der Energiemärkte - Energiereferenzprognose* 2014.

[303] J. Brandes, M. Haun, C. Senkpiel, C. Kost, A. Bett, H.-M. Henning, *Wege zu einem klimaneutralen Energiesystem: Die deutsche Energiewende im Kontext gesellschaftlicher Verhaltensweisen* 2021.

[304] P. Gerbert, P. Herhold, J. Burchardt, S. Schönberger, *Klimapfade für Deutschland* 2018.

[305] J. Pelda, S. Holler, U. Persson, *Energy* 2021, *233 (9)*, 121018. DOI: https://doi.org/10.1016/j.energy.2021.121018

[306] Z. Wang, P. T. Benavides, J. B. Dunn, D. C. Cronauer, *Development of the GREET Catalyst Module* 2015.

[307] P. T. Benavides, P. Sun, J. Han, J. B. Dunn, M. Wang, *Fuel* 2017, *203*, 11 – 22. DOI: https://doi.org/10.1016/j.fuel.2017.04.070

[308] F. Grimaldi, H. Ramirez, C. Lutz, P. Lettieri, *Journal of Industrial Ecology* 2021, *25 (6)*, 1617 – 1630. DOI: https://doi.org/10.1111/jiec.13180

[309] L. Benini, L. Mancini, S. Sala, S. Manfredi, E. Schau, R. Pant, *Normalisation method and data for Environmental Footprints*, Publications Office of the European Union 2014.

[310] Consequential-LCA.org, *Defining the functional unit* 2015.

[311] European Commission, *Commission Decision of 18th December 2014 amending Decision 2000/532/EC on the list of waste pursuant to Directive 2008/98/EC of the European Parliament and of the Council: 2014/955/EU* 2014.

[312] B. Burger, *Öffentliche Nettostromerzeugung in Deutschland im Jahr 2019* 2020.

[313] Fraunhofer IWES, *Wie hoch ist der Stromverbrauch in der Energiewende?: Energiepolitische Zielszenarien 2050 – Rückwirkungen auf den Ausbaubedarf von Windenergie und Photovoltaik*, Berlin 2015.

[314] D. Dave, M. Arné, *Air Separation Unit Update: PEP Review 2016-07* 2016.

[315] B. den Ouden, N. Lintmeijer, J. van Aken, *Electrification in the Dutch process industry: In-depth study of promising transition pathways and innovation opportunities for electrification in the Dutch process industry*, Utrecht 2017.

[316] D. Schuewer, C. Schneider, *Electrification of industrial process heat: Long-term applications, potentials and impacts* 2018.

[317] https://www.icis.com/explore/resources/news/2018/08/01/10245412/chemical-profile-europe-methanol (Accessed on 16.02.21).

[318] AspenTech, *Aspen Physical Property System: Physical Property Methods*, Bedford, MA 2019.

[319] C. Montejo, C. Costa, P. Ramos, Márquez, María del Carmen, *Applied Thermal Engineering* 2011, *31 (13)*, 2135 – 2140.
DOI: https://doi.org/10.1016/j.applthermaleng.2011.03.041

[320] C. Montejo, D. Tonini, Márquez, María del Carmen, T. F. Astrup, *Journal of Environmental Management* 2013, *128*, 661 – 673.
DOI: https://doi.org/10.1016/j.jenvman.2013.05.063

[321] Umweltbundesamt, *Planspiel zur Fortentwicklung der Verpackungsverordnung: Teilvorhaben 1: Bestimmung der Idealzusammensetzung der Wertstofftonne*, Dessau-Roßlau 2011.

Supplementary Material

A Process modelling assumptions and results

Table S 1: Overview of applied Property Methods in Aspen Plus modeling [318]

Steam Cracking	RK-SOAVE
Olefin recovery	
Quench section	NRTL-RK
Caustic scrubber	ENRTL-RK
Olefin separation	PR-BM
BTX aromatic recovery process	NRTL-RK
Steam reforming	RK-SOAVE
Partial oxidation	RK-SOAVE
Water quench and scrubber	ENRTL-RK
CO shift	RK-SOAVE
Physical absorption	PSRK
Chemical absorption	ENRTL-RK
Claus	PSRK
Methanol synthesis	SR-POLAR
Ammonia synthesis	RKS-BM
Catalytic reforming	GRAYSON
Methanol-to-olefins	RK-SOAVE
Methanol-to-aromatics	
MTA / LHTA section, gas processing	RK-SOAVE
Caustic scrubber	ENRTL-RK
Gasification	RK-SOAVE
Oil upgrading	SRK

Table S 2: Transfer coefficients of mechanical sorting during MBT based on [319, 320]

Notation	RDF (%)	Residue (%)	FE (%)	N-FE (%)
Brown glass	6	94	-	-
Clear glass	6	94	-	-
Compounds	77	23	-	-
FE	53	-	47	-
Fine fraction	10	90	-	-
Green glass	6	94	-	-
Hard plastics	96	3.6	-	-
Hygiene products	5	95	-	-
Inerts	10	90	-	-
N-FE	51	-	-	49
Non-recyclable glass	6	94	-	-
Organic waste	18	82	-	-
Other	10	90	-	-
Paper & cardboard	85	15	-	-
Problematic waste	10	90	-	-
Soft plastics	96	3.6	-	-
Textiles	90	10	-	-
Wood	68	32	-	-

Table S 3: Recovery ratios of waste components of material sorting steps (in percent) [274]

	other plastic	Rest	Plastic bottles	PET	PP	PS	PE	Aluminum	Tinplate	Liquid carton	Plastic containers	Paper	Plastic foil
Trommel sieve 1	1.0	1.0	30.0	1.0	1.0	1.0	1.0	1.0	1.0	5.0	50.0	5.0	99.0
Trommel sieve 2	0.5	5.0	30.0	95.0	70.0	60.0	100.0	2.0	2.0	66.7	90.0	70.0	99.0
Flat bed sieve	98.0	95.0	100.0	98.0	98.0	98.0	10.0	100.0	100.0	100.0	100.0	100.0	50.0
Air classifier 1	5.0	5.0	5.0	5.0	5.0	5.0	5.0	5.0	5.0	5.0	5.0	70.0	97.0
Air classifier 2	5.0	5.0	5.0	5.0	5.0	5.0	5.0	5.0	5.0	5.0	5.0	70.0	97.0
Magnetic separation 1	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0	85.0	1.0	1.0	1.0	1.0
Magnetic separation 2	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0	85.0	1.0	1.0	1.0	1.0
Magnetic separation 3	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0	85.0	1.0	1.0	1.0	1.0
NIR BCC 1	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5	90.0	0.5	0.5	0.5
NIR BCC 2	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5	90.0	0.5	0.5	0.5
Eddy current sep 1	0.5	0.5	0.5	0.5	0.5	0.5	0.5	75.0	0.5	0.5	0.5	0.5	0.5
Eddy current sep 2	0.5	0.5	0.5	0.5	0.5	0.5	0.5	75.0	0.5	0.5	0.5	0.5	0.5
NIR MPW 1	90.0	10.0	90.0	90.0	90.0	90.0	90.0	10.0	10.0	10.0	90.0	10.0	90.0
NIR MPW 2	90.0	10.0	90.0	90.0	90.0	90.0	90.0	10.0	10.0	10.0	90.0	10.0	90.0
NIR Paper	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5	80.0	0.5
Ballistic separator													
3D	80.0	48.0	98.0	98.0	98.0	98.0	98.0	95.0	95.0	80.0	10.0	5.0	2.0
2D	15.0	48.0	1.0	1.0	1.0	1.0	1.0	5.0	5.0	20.0	90.0	95.0	98.0
NIR PE	0.1	0.1	0.1	0.1	0.1	0.1	98.0	0.1	0.1	0.1	0.1	0.1	0.1
NIR PP	0.1	0.1	0.1	0.1	98.0	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1
NIR PET	0.1	0.1	0.1	98.0	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1
Manual sorting 1													
Foils	50.0	50.0	50.0	10.0	10.0	10.0	10.0	50.0	50.0	50.0	5.0	50.0	80.0
Plastic containers	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5	90.0	0.5	0.1
Manual sorting 2													
Plastic containers	0.1	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5	90.0	0.1	0.1
Paper	10.0	10.0	10.0	5.0	5.0	5.0	5.0	10.0	10.0	10.0	2.0	80.0	5.0
Manual sorting 3													
Plastic containers	0.1	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5	90.0	0.5	0.1
Paper	0.1	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5	0.5	80.0	0.5

Table S 4: Fractional composition of input and output fractions of municipal solid waste MBT

		MSW [259]	RDF	MBT residue
Compounds	wt.-%	4.3%	12.8%	2.2%
FE metals	wt.-%	1.0%	2.1%	0.0%
Paper/ cardboard	wt.-%	5.2%	15.9%	1.5%
Textiles	wt.-%	3.5%	13.8%	1.0%
Inerts	wt.-%	3.9%	1.8%	10.9%
Problematic waste	wt.-%	0.5%	0.2%	1.3%
Wood	wt.-%	1.3%	3.5%	1.0%
Hard plastic	wt.-%	3.4%	14.5%	0.4%
Soft plastic	wt.-%	3.4%	12.9%	0.3%
Hygiene products	wt.-%	13.5%	1.7%	19.9%
Fines	wt.-%	6.3%	2.9%	17.6%
Glass	wt.-%	4.6%	1.2%	12.4%
Rest	wt.-%	8.9%	2.4%	14.5%
NF metals	wt.-%	1.0%	1.9%	0.0%
Organic	wt.-%	39.3%	12.4%	16.9%
Sum	wt.-%	100.0%	100.0%	100.0%

Table S 5: Fractional composition of input and output fractions of plastic waste material sorting

		LWP [321]	MPW	RDF
Plastic foil	wt.-%	8.0%	0.0%	6.4%
Plastic containers	wt.-%	2.0%	0.6%	1.0%
Paper/ cardboard	wt.-%	8.0%	0.1%	5.2%
Tinplate	wt.-%	12.0%	1.1%	5.7%
Aluminum	wt.-%	5.0%	0.8%	4.3%
Liquid cartons	wt.-%	8.0%	0.4%	4.3%
Plastic bottles	wt.-%	2.0%	7.9%	2.7%
Packaging - PE	wt.-%	10.1%	1.1%	5.8%
Packaging - PS	wt.-%	1.5%	7.8%	0.8%
Packaging - PP	wt.-%	3.0%	0.3%	1.6%
Packaging - PET	wt.-%	7.4%	0.8%	4.3%
Other plastics	wt.-%	16.0%	75.7%	17.8%
Rest	wt.-%	17.0%	3.5%	40.0%
Sum	wt.-%	100.0%	100.0%	100.0%

Table S 6: Applied global approach temperatures

BGL secondary reactor	-50 K
Oil partial oxidation	-200 K
BTX transalkylation	150 K

Table S 7: Applied individual approach temperatures (part 1)

														T-App [K]
BGL primary reactor														
1	CH4	+	1	CO2				↔	2	CO	+	2	H2	107
1	C	+	1	H2O				↔	1	CO	+	1	H2	198
1	C	+	1	CO2				↔	2	CO	+			199
1	N2	+	3	H2				↔	2	NH3				0
1	H2	+	1	S				↔	1	H2S				0
1	COS	+	1	H2O				↔	1	H2S	+	1	CO2	0
2	CH4							↔	1	C2H6	+	1	H2	1593
3	CH4							↔	1	C3H8	+	2	H2	1630
1	N2	+	2	O2				↔	2	NO2				0
1	S	+	1	O2				↔	1	SO2				0
1	CL2	+	1	H2				↔	2	HCL				0
1	C	+	1	O2				↔	1	CO2				0
CO shift reactor														
1	H2O	+	1	CO				↔	1	CO2		1	H2	25
1	CHN	+	1	H2O				↔	1	CO		1	NH3	0
1	COS	+	1	H2O				↔	1	H2S		1	CO2	0
Methanol reactor – CO-based														
1	CO	+	2	H2				↔	1	MeOH				40
1	CO2	+	1	H2				↔	1	CO		1	H2O	0
1	CO2	+	4	H2				↔	1	CH4		2	H2O	1980
2	CO	+	5	H2				↔	1	C2H6		2	H2O	739
2	CO2	+	6	H2				↔	1	DME		3	H2O	235
1	CO2	+	3	H2	+	1	CO	↔	1	HCOOCH3		1	H2O	-25
1	CO	+	5	H2	+	1	CO2	↔	1	Ethanol		2	H2O	325
Methanol reactor – CO2-based														
1	CO2	+	3	H2				↔	1	MeOH		1	H2O	26
1	CO2	+	1	H2				↔	1	CO		1	H2O	-3
1	CO2	+	4	H2				↔	1	CH4		2	H2O	1980
2	CO	+	5	H2				↔	1	C2H6		2	H2O	739
2	CO2	+	6	H2				↔	1	DME		3	H2O	235
1	CO2	+	3	H2	+	1	CO	↔	1	HCOOCH3		1	H2O	-25
1	CO	+	5	H2	+	1	CO2	↔	1	Ethanol		2	H2O	325

Table S 8: Applied individual approach temperatures (part 2)

														T-App [K]
MTO reactor														
2	MeOH				↔	1	DME	+	1	H2O				0
1	DME				↔	1	C2H4	+	1	H2O				-374
1	DME	+	1	MeOH	↔	1	C3H6	+	2	H2O				45
2	DME				↔	1	C4H8	+	2	H2O				93
1	C4H8				↔	1	C4H6	+	1	H2				70
2	DME	+	1	MeOH	↔	1	C5H10	+	3	H2O				37
3	DME				↔	3	H2O	+	1	C6H12				30
1	H2	+	1	C6H12	↔	1	C6H14							40
1	CH3OH	+	1	H2	↔	1	CH4		1	H2O				682
1	C2H4	+	1	H2	↔	1	C2H6							367
1	C3H6	+	1	H2	↔	1	C3H8							140
1	C4H8	+	1	H2	↔	1	C4H10							200
1	C5H10	+	1	H2	↔	1	C5H12							200
1	CH4	+	1	H2O	↔	1	CO	+	3	H2				-261
1	CO	+	1	H2O	↔	1	CO2	+	1	H2				0
MTA – MTA reactor														
2	MeOH				↔	1	DME	+	1	H2O				0
1	DME				↔	1	C2H4	+	1	H2O				1600
1	DME	+	1	MeOH	↔	1	C3H6	+	2	H2O				229
2	DME				↔	1	C4H8	+	2	H2O				102
2	DME	+	1	MeOH	↔	1	C5H10	+	3	H2O				113
1	MeOH	+	1	H2	↔	1	CH4	+	1	H2O				667
1	C2H4	+	1	H2	↔	1	C2H6							342
1	C3H6	+	1	H2	↔	1	C3H8							0
1	C4H8	+	1	H2	↔	1	C4H10							36
1	C5H10	+	1	H2	↔	1	C5H12							-65
1	CH4	+	1	H2O	↔	1	CO	+	3	H2				-128
1	CO	+	1	H2O	↔	1	CO2	+	1	H2				0
2	C3H6				↔	1	Benzene	+	3	H2				-462
1	C3H6	+	1	C4H8	↔	1	Toluene	+	3	H2				-534
4	DME	+	1	MeOH	↔	1	C9H12	+	5	H2O	+	3	H2	515
2	C4H8				↔	1	m-Xylene	+	3	H2				-629
2	C4H8				↔	1	p-Xylene	+	3	H2				-621
2	C4H8				↔	1	o-Xylene	+	3	H2				-613
2	C4H8				↔	1	Ethylbenzene	+	3	H2				-562
MTA – LHTA reactor														
2	MeOH				↔	1	DME	+	1	H2O				0
1	DME				↔	1	C2H4	+	1	H2O				1600
1	DME	+	1	MeOH	↔	1	C3H6	+	2	H2O				229
2	DME				↔	1	C4H8	+	2	H2O				102
2	DME	+	1	MeOH	↔	1	C5H10	+	3	H2O				113
1	CH3OH	+	1	H2	↔	1	CH4	+	1	H2O				667
1	C2H4	+	1	H2	↔	1	C2H6							342
1	C3H6	+	1	H2	↔	1	C3H8							0
1	C4H8	+	1	H2	↔	1	C4H10							36
1	C5H10	+	1	H2	↔	1	C5H12							-65
1	CH4	+	1	H2O	↔	1	CO	+	3	H2				-128
1	CO	+	1	H2O	↔	1	CO2	+	1	H2				0
2	C4H8				↔	1	Ethylbenzene	+	3	H2				-562
2	C3H6				↔	1	Benzene	+	3	H2				-462
1	C3H6	+	1	C4H8	↔	1	Toluene	+	3	H2				-534
4	DME	+	1	MeOH	↔	1	C9H12	+	5	H2O	+	3	H2	515
2	C4H8				↔	1	m-Xylene	+	3	H2				-629
2	C4H8				↔	1	p-Xylene	+	3	H2				-621
2	C4H8				↔	1	o-Xylene	+	3	H2				-613

Table S 9: Applied steam cracking kinetic (part 1)

Stoichiometry	k	EA [MJ/kmol]
Initial decomposition		
C10H22 → 1.23 CH4 + 2 C2H4 + 0.1 C2H6 + 0.73 C3H6 + 0.02 C3H8 + 0.36 C4H6 + 0.21 C4H8 + 0.01 C4H10	6.565E+11	220
C7H16 → 0.85 CH4 + 1.25 C2H4 + 0.19 C2H6 + 0.48 C3H6 + 0.05 C3H8 + 0.1 C4H6 + 0.31 C4H8 + 0.01 C4H10	6.565E+11	220
C5H12 → 0.6 CH4 + 0.61 C2H4 + 0.42 C2H6 + 0.34 C3H6 + 0.04 C3H8 + 0.07 C4H6 + 0.22 C4H8 + 0.01 C4H10	6.565E+11	220
C6H14 → 0.72 CH4 + 0.91 C2H4 + 0.32 C2H6 + 0.42 C3H6 + 0.04 C3H8 + 0.09 C4H6 + 0.26 C4H8 + 0.01 C4H10	6.565E+11	220
C8H18 → 0.97 CH4 + 1.52 C2H4 + 0.12 C2H6 + 0.53 C3H6 + 0.08 C3H8 + 0.18 C4H6 + 0.29 C4H8 + 0.01 C4H10	6.565E+11	220
C6H12 → 0.2 CH4 + 1.24 C2H4 + 0.1 C2H6 + 0.51 C3H6 + 0.05 C3H8 + 0.35C4H6 + 0.01 C4H8 + 0 C4H10	6.565E+11	220
C7H14 → 0.3 CH4 + 1.5 C2H4 + 0.05 C2H6 + 0.61 C3H6 + 0.03 C3H8 + 0.38 C4H6 + 0.04 C4H8 + 0 C4H10	6.565E+11	220
C8H16 → 0.4 CH4 + 1.71 C2H4 + 0.03 C2H6 + 0.69 C3H6 + 0.03 C3H8 + 0.46 C4H6 + 0.03 C4H8 + 0 C4H10	6.565E+11	220
C5H10 → 0.15 CH4 + 1.06 C2H4 + 0.03 C2H6 + 0.42 C3H6 + 0.07 C3H8 + 0.25 C4H6 + 0.05 C4H8 + 0 C4H10	6.565E+11	220
C7H14 → 0.27 CH4 + 1.57 C2H4 + 0.03 C2H6 + 0.57 C3H6 + 0.06 C3H8 + 0.36 C4H6 + 0.05 C4H8 + 0 C4H10	6.565E+11	220
C6H12 → 0.18 CH4 + 1.32 C2H4 + 0.06 C2H6 + 0.52 C3H6 + 0.06 C3H8 + 0.3 C4H6 + 0.03 C4H8 + 0 C4H10	6.565E+11	220
C8H16 → 0.32 CH4 + 1.74 C2H4 + 0.05 C2H6 + 0.69 C3H6 + 0.05 C3H8 + 0.42 C4H6 + 0.05 C4H8 + 0 C4H10	6.565E+11	220
C5H10 → 0.15 CH4 + 1.06 C2H4 + 0.03 C2H6 + 0.42 C3H6 + 0.07 C3H8 + 0.25 C4H6 + 0.05 C4H8 + 0 C4H10	6.565E+11	220
C11H24 → 1.35 CH4 + 2.26 C2H4 + 0.04 C2H6 + 0.83 C3H6 + 0 C3H8 + 0.4 C4H6 + 0.23 C4H8 + 0.01 C4H10	6.565E+11	220
C9H20 → 1.1 CH4 + 1.85 C2H4 + 0.04 C2H6 + 0.63 C3H6 + 0.05 C3H8 + 0.2 C4H6 + 0.31 C4H8 + 0.01 C4H10	6.565E+11	220
Olefin formation		
C2H6 → C2H4 + H2	4.65E+13	273
C3H6 → C2H2 + CH4	7.28E+12	274
C2H2 + C2H4 → C4H6	1.03E+12	173
2 C2H6 → C3H8 + CH4	3.75E+12	273
C2H4 + C2H6 → C3H6 + CH4	7.08E+13	253
C3H8 → C3H6 + H2	5.89E+10	215
C3H8 → C2H4 + CH4	4.69E+10	212
C3H8 + C2H4 → C2H6 + C3H6	2.54E+13	247
2 C3H6 → 3 C2H4	7.39E+12	269
C3H6 + C2H6 → C4H8 + CH4	1.00E+14	251
C4H10 → C3H6 + CH4	7.00E+12	250
C4H10 → 2 C2H4 + H2	7.00E+14	296
C4H10 → C2H4 + C2H6	4.10E+12	257
C4H10 → C4H8 + H2	1.64E+12	261
C4H8 → H2 + C4H6	1.00E+10	209
C2H4 + H2 → C2H6	8.49E+08	137
C2H2 + CH4 → C3H6	3.81E+08	147
C3H6 + H2 → C3H8	9.03E+05	94
C4H8 + H2 → C4H10	1.78E+07	135

Table S 10: Applied steam cracking kinetic (part 2)

Stoichiometry	k	EA [MJ/kmol]
BTX formation		
C_2H_4 + C_4H_6 → C_6H_6 + 2 H_2	8.39E+08	128
C_3H_6 + C_4H_6 → C_7H_8 + 2 H_2	1.95E+09	137
C_4H_6 + C_4H_8 → EB-C_8H_{10} + 2 H_2	4.80E+14	243
2 C_4H_6 → C_8H_8 + 2 H_2	6.04E+08	116
2 C_4H_8 → M-C_8H_{10} + 3 H_2	1.57E+08	116
2 C_4H_8 → P-C_8H_{10} + 3 H_2	6.34E+07	116
2 C_4H_8 → O-C_8H_{10} + 3 H_2	7.85E+07	116
Coking		
C_6H_6 → 3 H_2 + 6 C	6.39E+11	212
C_7H_8 → 4 H_2 + 7 C	5.48E+11	212
EB-C_8H_{10} → 5 H_2 + 8 C	4.79E+11	212
C_8H_8 → 4 H_2 + 8 C	4.79E+11	212
M-C_8H_{10} → 5 H_2 + 8 C	4.79E+11	212
P-C_8H_{10} → 5 H_2 + 8 C	4.79E+11	212
O-C_8H_{10} → 5 H_2 + 8 C	4.79E+11	212
$C_{12}H_{12}$ → 10 C + 6 H_2	3.83E+13	212
$C_{10}H_8$ → 10 C + 4 H_2	3.83E+13	212
$C_{14}H_{14}$ → 14 C + 7 H_2	2.74E+13	212
$C_{14}H_{10}$ → 14 C + 5 H_2	2.74E+13	212
C + H_2O → H_2 + CO	5.09E+06	240

Table S 11: Stoichiometric reaction system of catalytic reforming

Stoichiometry											Frac. Conversion
C6-N			→		C6-A	+	3	H2			0.681
C7-N			→		C7-A	+	3	H2			0.783
C8-N			→		C8-A-o	+	3	H2			0.143
C8-N			→		C8-A-p	+	3	H2			0.116
C8-N			→		C8-A-m	+	3	H2			0.285
C8-N			→		C8-A-EB	+	3	H2			0.348
C9-N			→		C9-A	+	3	H2			0.948
C6-P			→		C6-A	+	4	H2			0.120
C7-P			→		C7-A	+	4	H2			0.604
C8-P			→		C8-A-o	+	4	H2			0.217
C8-P			→		C8-A-p	+	4	H2			0.178
C8-P			→		C8-A-m	+	4	H2			0.435
C8-P			→		C8-A-EB	+	4	H2			0.066
C9-P			→		C9-A	+	4	H2			0.090
C10-P	+	H2	→	2	C5H12						0.227
C10-P	+	H2	→		C6-P	+		C4-P			0.227
C10-P	+	H2	→		C7-P	+		C3-P			0.233
C9-P	+	H2	→		C4-P	+		C5-P			0.146
C9-P	+	H2	→		C6-P	+		C3-P			0.146
C9-P	+	2 H2	→		C3-P	+		C4-P	+	C2-P	0.150
C8-P	+	H2	→	2	C4-P						0.002
C8-P	+	H2	→		C3-P	+		C5-P			0.002
C8-P	+	3 H2	→	4	C2-P						0.002
C9-P	+	H2	→		C8-P	+		CH4			0.200

Table S 12: Stoichiometric reaction system of C8 aromatic isomerization

Stoichiometry						Frac. Conversion
2	C8-A-EB	→	C8-A-p	+	C8-A-o	0.240
2	C8-A-m	→	C8-A-p	+	C8-A-o	0.250
2	C8-A-m	→	C7-A	+	C9-A	0.030

Table S 13: Inventory results for conventional chemical processes

		NSC	NR	LSC	NGR-MOH	NGR-NH3	NGR-H2	FPOX
Inputs								
Naphtha	kg	10.000	10.000	0.000	0.000	0.000	0.000	0.000
Natural Gas	kg	0.000	0.000	0.000	10.000	10.000	10.000	0.000
LPG	kg	-0.966	-1.267	10.000	0.000	0.000	0.000	0.000
Oxygen	kg	0.000	0.000	0.000	5.593	0.000	0.000	11.716
Electricity	MJ	17.492	0.245	16.299	-3.977	33.215	6.819	6.852
Fresh Water	kg	36.998	28.368	60.097	88.285	126.604	65.679	84.455
Fuel gas	MJ	45.368	73.091	34.233	119.340	165.334	211.307	0.038
Caustic	kg	0.019	0.000	0.008	0.068	0.412	0.438	0.019
Sulfuric acid	kg	0.003	0.000	0.002	0.049	0.298	0.316	0.014
Outputs								
Ammonia	kg	0.000	0.000	0.000	0.000	19.762	0.000	0.000
Aromatics	kg	1.603	7.733	0.334	0.000	0.000	0.000	0.000
Hydrogen	kg	0.036	0.366	0.271	0.000	0.000	3.582	0.000
Methanol	kg	0.000	0.000	0.000	18.112	0.000	0.000	13.052
Olefins	kg	5.803	0.000	7.371	0.000	0.000	0.000	0.000
Fuel Oil	kg	0.269	0.000	0.000	0.000	0.000	0.000	10.000
Steam LP	kg	8.587	2.797	28.223	8.973	13.337	14.375	3.180
Emissions to air								
CO2 diffuse	kg	5.604	5.683	7.334	7.784	10.497	38.017	1.044
CO2 concentrated	kg	0.000	0.000	0.000	0.000	24.791	0.000	11.633
SO2	kg	9.39E-11	0.00E+00	1.08E-09	2.55E-08	9.02E-09	4.46E-07	2.15E-02
CO	kg	1.29E-03	1.34E-03	1.76E-03	1.65E-03	2.41E-03	4.11E-03	3.19E-04
Dust	kg	1.62E-05	1.67E-05	2.20E-05	2.07E-05	3.02E-05	5.13E-05	4.01E-06
NOX	kg	3.23E-03	3.35E-03	4.40E-03	4.13E-03	6.03E-03	1.03E-02	7.96E-04
Emissions to water								
COD	kg	4.03E-05	0.00E+00	4.62E-04	7.67E-04	2.30E-03	2.74E-08	3.17E-03
Chloride	kg	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00
Sulfate	kg	9.40E-04	0.00E+00	5.43E-04	1.54E-02	9.25E-02	9.83E-02	7.94E-03

Table S 14: Inventory results for conventional chemical processes with electric heating

		NSCe	NRe	LSCe	NGR-MOHe	NGR-NH3e	NGR-H2e
Inputs							
Naphtha	kg	10.000	10.000	0.000	0.000	0.000	0.000
Natural Gas	kg	0.000	0.000	0.000	10.000	10.000	10.000
LPG	kg	-0.995	-1.267	10.000	0.000	0.000	0.000
Oxygen	kg	0.000	0.000	0.000	5.593	0.000	0.000
Electricity	MJ	92.356	91.480	95.045	79.315	151.289	205.738
Steam LP	kg	0.000	0.000	-6.183	2.479	2.100	16.581
Fresh Water	kg	35.335	24.133	35.898	91.330	108.988	60.726
Caustic	kg	0.025	0.000	0.011	0.069	0.404	0.440
Sulfuric acid	kg	0.003	0.000	0.002	0.050	0.292	0.318
Outputs							
Ammonia	kg	0.000	0.000	0.000	0.000	19.813	0.000
Aromatics	kg	1.637	7.733	0.335	0.000	0.000	0.000
Hydrogen	kg	0.038	0.366	0.271	0.000	0.000	3.579
Methanol	kg	0.000	0.000	0.000	18.040	0.000	0.000
Olefins	kg	6.112	0.000	7.372	0.000	0.000	0.000
Fuel Oil	kg	0.327	0.000	0.000	0.000	0.000	0.000
Fuel gas	MJ	59.279	34.771	106.709	0.000	0.000	0.000
Emissions to air							
CO2 diffuse	kg	0.007	0.029	0.001	1.265	1.297	0.905
CO2 concentrated	kg	0.000	0.000	0.000	0.000	24.791	23.872
SO2	kg	1.15E-10	0.00E+00	8.89E-10	4.01E-08	9.00E-09	1.95E-09
CO	kg	1.89E-06	1.38E-05	1.01E-08	2.70E-04	4.71E-04	8.10E-04
Dust	kg	2.37E-08	1.73E-07	9.19E-10	3.41E-06	5.90E-06	1.01E-05
NOX	kg	4.71E-06	3.45E-05	0.00E+00	6.74E-04	1.18E-03	2.03E-03
Emissions to water							
COD	kg	1.70E-05	0.00E+00	1.32E-04	1.26E-03	2.25E-03	9.20E-08
Chloride	kg	2.90E-04	0.00E+00	1.53E-04	0.00E+00	0.00E+00	0.00E+00
Sulfate	kg	1.04E-03	0.00E+00	5.95E-04	1.56E-02	9.07E-02	9.88E-02

Table S 15: Inventory results for RDF gasification-based pathways

		GR-MOH	GR-MTO	GR-MTA	GR-NH3	GR-H2
Inputs						
RDF	kg	10.000	10.000	10.000	10.000	10.000
Oxygen	kg	5.744	5.744	5.744	4.395	5.744
Electricity	MJ	7.448	12.181	14.459	31.724	14.205
Fresh Water	kg	65.175	49.570	72.257	60.595	44.104
Fuel gas	MJ	0.983	-2.160	-32.467	0.943	0.325
Caustic	kg	0.083	0.219	0.087	0.457	0.356
Sulfuric acid	kg	0.009	0.106	0.012	0.279	0.206
Outputs						
Ammonia	kg	0.000	0.000	0.000	6.972	0.000
Aromatics	kg	0.000	0.000	2.056	0.000	0.000
Hydrogen	kg	0.000	0.000	0.000	0.000	1.139
Methanol	kg	6.723	0.000	0.000	-0.033	-0.001
Olefins	kg	0.000	2.681	0.000	0.000	0.000
Steam LP	kg	10.888	11.876	1.573	13.983	12.793
Sulfur	kg	0.021	0.021	0.021	0.020	0.020
Ash	kg	1.015	1.015	1.015	1.015	1.015
Naphtha	kg	0.000	0.048	0.000	0.000	0.000
LPG	kg	0.000	0.111	0.000	0.000	0.000
Emissions to air						
CO2 diffuse	kg	0.716	0.859	1.246	0.527	1.520
CO2 concentrated	kg	8.339	8.338	8.338	17.831	16.834
SO2	kg	1.26E-03	1.29E-03	1.26E-03	1.21E-03	1.30E-03
CO	kg	1.94E-04	3.54E-04	4.10E-04	2.21E-04	4.95E-04
Dust	kg	2.45E-06	4.44E-06	5.16E-06	2.77E-06	6.19E-06
NOX	kg	4.85E-04	8.85E-04	1.02E-03	5.53E-04	1.24E-03
Emissions to water						
COD	kg	3.07E-03	2.11E-03	9.24E-03	1.24E-03	2.91E-04
Chloride	kg	3.55E-02	2.68E-02	3.55E-02	3.06E-02	1.86E-02
Sulfate	kg	3.06E-03	3.31E-02	3.93E-03	8.70E-02	6.42E-02

Table S 16: Inventory results for MPW gasification-based pathways

		GM-MOH	GM-MTO	GM-MTA	GM-NH3	GM-H2
Inputs						
MPW	kg	10.000	10.000	10.000	10.000	10.000
Oxygen	kg	8.099	8.099	8.099	5.697	8.099
Electricity	MJ	5.738	14.517	16.266	44.539	-8.065
Fresh Water	kg	102.937	79.320	117.771	95.976	93.376
Fuel gas	MJ	1.009	-4.249	-54.978	0.944	0.231
Caustic	kg	0.255	0.480	0.261	0.770	0.526
Sulfuric acid	kg	0.014	0.173	0.018	0.386	0.210
Outputs						
Ammonia	kg	0.000	0.000	0.000	11.695	0.000
Aromatics	kg	0.000	0.000	3.388	0.000	0.000
Hydrogen	kg	0.000	0.000	0.000	0.000	1.326
Methanol	kg	11.075	0.000	0.000	-0.033	-0.023
Olefins	kg	0.000	4.426	0.000	0.000	0.000
Sulfur	kg	0.023	0.025	0.023	0.022	0.023
Steam LP	kg	22.586	22.257	8.654	27.477	57.106
Ash	kg	0.710	0.710	0.710	0.709	0.710
Naphtha	kg	0.000	0.080	0.000	0.000	0.000
LPG	kg	0.000	0.184	0.000	0.000	0.000
Emissions to air						
CO2 diffuse	kg	2.030	2.072	3.098	1.476	17.170
CO2 concentrated	kg	9.242	9.255	9.250	25.015	9.249
SO2	kg	1.15E-03	1.17E-03	1.11E-03	9.13E-04	1.09E-03
CO	kg	5.77E-04	7.65E-04	1.01E-03	5.72E-04	2.34E-03
Dust	kg	7.25E-06	9.58E-06	1.26E-05	7.15E-06	2.92E-05
NOX	kg	1.44E-03	1.91E-03	2.52E-03	1.43E-03	5.84E-03
Emissions to water						
COD	kg	2.80E-03	3.78E-03	1.37E-02	1.64E-03	5.15E-04
Chloride	kg	4.97E-02	9.87E-02	8.77E-02	1.01E-01	8.63E-02
Sulfate	kg	4.50E-03	5.44E-02	5.85E-03	1.20E-01	6.53E-02

Table S 17: Inventory results for gasification-based pathways with hydrogen integration

	GR-MOHh	GM-MOHh	GR-MTOh	GM-MTOh	GR-MTAh	GM-MTAh
Inputs						
RDF	10.000	0.000	10.000	0.000	10.000	0.000
MPW	0.000	10.000	0.000	10.000	0.000	10.000
Oxygen	5.744	8.099	5.744	8.099	5.744	8.099
Electricity	2.898	-0.652	12.445	13.490	18.960	38.634
Fresh Water	92.438	132.592	62.137	91.899	177.694	175.876
Fuel gas	1.020	1.051	-5.133	-7.336	-55.900	-86.338
Hydrogen	1.207	1.331	1.206	1.334	1.104	1.188
Caustic	0.109	0.271	0.353	0.619	0.118	0.277
Sulfuric acid	0.028	0.025	0.201	0.272	0.035	0.029
Outputs						
Ammonia	0.000	0.000	0.000	0.000	0.000	0.000
Aromatics	0.000	0.000	0.000	0.000	3.874	5.498
Hydrogen	0.000	0.000	0.000	0.000	0.000	0.000
Methanol	12.961	17.876	0.000	0.000	0.000	0.000
Olefins	0.000	0.000	5.172	7.020	0.000	0.000
Sulfur	0.021	0.022	0.021	0.024	0.021	0.023
Steam LP	16.357	26.280	15.674	26.940	-3.124	3.636
Ash	1.015	0.710	1.015	0.710	1.015	0.710
Naphtha	0.000	0.000	0.093	0.126	0.000	0.000
LPG	0.000	0.000	0.215	0.291	0.000	0.000
Emissions to air						
CO2 diffuse	0.871	2.089	0.913	1.868	2.475	3.624
CO2 concentrated	-0.314	-0.314	-0.314	-0.314	-0.314	-0.314
SO2	1.37E-03	1.61E-03	1.38E-03	1.68E-03	1.34E-03	1.52E-03
CO	2.38E-04	6.46E-04	3.99E-04	7.59E-04	5.67E-04	1.10E-03
Dust	3.01E-06	8.12E-06	5.00E-06	9.51E-06	7.21E-06	1.39E-05
NOX	5.93E-04	1.61E-03	9.96E-04	1.90E-03	1.41E-03	2.75E-03
Emissions to water						
COD	3.05E-03	3.29E-03	1.52E-03	2.72E-03	1.74E-02	2.12E-02
Chloride	2.32E-02	4.11E-02	1.30E-02	6.00E-02	3.04E-02	9.96E-02
Sulfate	8.82E-03	7.94E-03	6.26E-02	8.50E-02	1.10E-02	9.36E-03

Table S 18: Inventory results for pyrolysis-based pathways

	PR-HTR	PM-HTR	PR-BTX	PR-POX	PM-POX
Inputs					
RDF	10.000	0.000	10.000	10.000	0.000
MPW	0.000	10.000	0.000	0.000	10.000
Oxygen	0.000	0.000	0.000	5.468	8.745
Electricity	10.412	14.884	11.640	14.172	19.445
Fresh Water	7.472	12.277	21.103	54.693	77.022
Fuel gas	0.000	5.425	24.328	0.020	0.029
Hydrogen	0.201	0.195	0.143	0.000	0.000
Caustic	0.005	0.005	0.031	0.014	0.018
Sulfuric acid	0.003	0.004	0.023	0.009	0.013
Limestone	0.050	0.050	0.050	0.050	0.050
Catalyst	0.200	0.200	0.200	0.200	0.200
Outputs					
Ammonia	0.000	0.000	0.000	0.000	0.000
Aromatics	0.000	0.000	1.125	0.000	0.000
Methanol	0.000	0.000	0.000	6.567	10.142
Steam LP	2.059	2.163	-0.533	1.705	2.379
Sulfur	0.008	0.002	0.007	0.011	0.001
Metal residues	0.300	0.000	0.300	0.300	0.000
Naphtha	4.851	6.874	3.457	0.000	0.000
LPG	0.259	0.640	0.271	0.000	0.000
Emissions to air					
CO2 diffuse	0.430	0.969	2.118	1.388	2.301
CO2 concentrated	0.000	0.000	0.000	6.030	7.283
SO2	5.16E-04	1.84E-04	4.71E-04	4.33E-04	7.71E-04
CO	4.36E-05	1.46E-04	4.29E-01	4.29E-01	6.43E-01
Dust	5.47E-07	1.84E-06	4.07E-06	2.46E-06	3.29E-06
NOX	1.10E-04	3.68E-04	8.14E-04	4.90E-04	6.54E-04
Emissions to water					
COD	7.11E-11	2.91E-10	3.02E-10	5.95E-04	5.58E-04
Chloride	3.82E-03	5.80E-06	3.59E-03	1.39E-03	0.00E+00
Sulfate	1.03E-03	1.13E-03	7.07E-03	2.72E-03	4.23E-03

Table S 19: Inventory results for PTX-based pathways

	PTX-MOH	PTX-MTO	PTX-MTA	PTX-NH3	CC
Inputs					
Carbon Dioxide	10.000	10.000	10.000	0.000	-10.000
Nitrogen	0.000	0.000	0.000	10.000	0.000
Electricity	2.514	4.430	10.073	10.088	2.93E-03
Steam LP	4.129	0.000	10.418	-15.493	22.017
Fresh Water	14.940	27.397	25.463	34.384	1.226
Fuel gas	0.015	0.026	-34.308	0.000	0.000
Hydrogen	1.303	1.303	1.253	2.158	0.000
Caustic	0.071	0.184	0.296	0.003	1.14E-03
Sulfuric acid	0.051	0.131	0.108	0.002	8.97E-04
Outputs					
Ammonia	0.000	0.000	0.000	11.485	0.000
Aromatics	0.000	0.000	1.522	0.000	0.000
Methanol	6.758	0.000	0.000	0.000	0.000
Olefins	0.000	2.649	0.000	0.000	0.000
Naphtha	0.000	0.048	0.000	0.000	0.000
LPG	0.000	0.157	0.000	0.000	0.000
Emissions to air					
CO2 diffuse	0.270	0.832	1.080	0.000	0.000
CO2 concentrated	0.000	0.000	0.000	0.000	-10.000
SO2	8.15E-09	1.43E-08	1.18E-08	1.71E-11	0.000
CO	5.21E-05	2.39E-04	2.02E-04	2.52E-04	0.000
Dust	6.59E-07	3.00E-06	2.54E-06	3.16E-06	0.000
NOX	1.30E-04	5.97E-04	5.06E-04	6.31E-04	0.000
Emissions to water					
COD	2.75E-04	4.82E-04	3.98E-04	9.64E-07	4.73E-04
Chloride	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.000
Sulfate	1.59E-02	4.07E-02	3.37E-02	6.51E-04	2.80E-04

Table S 20: Inventory results for performance variation for gasification-based MTO pathways

		Gasif0-MTO	Gasif1-MTO	Gasif2-MTO	Gasif3-MTO	Gasif4-MTO
material efficiency		basic	high	high	low	low
energy efficiency		low	high	low	high	low
Input						
RDF	kg	10.000	10.000	10.000	10.000	10.000
Oxygen	kg	3.527	5.934	6.507	4.672	5.332
Electricity	MJ	-6.490	13.222	13.086	6.164	7.161
Fresh water	kg	64.871	49.663	50.901	55.480	54.326
Caustic	kg	0.082	0.219	0.212	0.191	0.191
Sulfuric Acid	kg	0.007	0.106	0.101	0.086	0.086
Output						
LPG	kg	0.052	0.111	0.106	0.090	0.089
Ethylene	kg	0.561	1.180	1.126	0.955	0.951
Propylene	kg	0.597	1.254	1.197	1.015	1.010
Butadiene	kg	0.079	0.164	0.157	0.133	0.133
Butene	kg	0.058	0.121	0.116	0.098	0.098
LP Steam	kg	40.254	9.847	9.870	21.244	19.337
Fuel oil	kg	0.131	0.000	0.000	0.000	0.000
Fuel gas	MJ	0.908	2.153	2.006	1.542	1.529
Sulfur	kg	0.020	0.021	0.021	0.021	0.021
Fly ash	kg	0.359	0.067	0.068	0.286	0.291
Slag	kg	0.947	0.949	0.948	0.979	0.978
Emission to air						
CO2 diffuse	kg	12.694	9.251	9.672	10.296	10.337
CO	kg	1.82E-03	3.19E-04	3.09E-04	9.31E-04	7.89E-04
Dust	kg	2.27E-05	4.00E-06	3.87E-06	1.16E-05	9.87E-06
NOX	kg	4.54E-03	7.98E-04	7.71E-04	2.33E-03	1.97E-03
SO2	kg	4.10E-04	1.36E-03	1.42E-03	1.29E-03	1.42E-03
Emission to water						
COD	kg	4.48E-03	2.26E-03	3.26E-03	4.05E-03	3.04E-03
Chloride	kg	1.55E-02	2.88E-02	5.01E-02	4.98E-02	2.79E-02
Sulfate	kg	2.52E-03	3.30E-02	3.17E-02	2.69E-02	2.68E-02

Table S 21: Inventory results for performance variation for pyrolysis-based pathways

		Pyr1-HTR	Pyr2-HTR	Pyr3-HTR	Pyr4-HTR
material efficiency		high	low	high	low
energy efficiency		high	high	low	low
Input					
RDF	kg	20.000	28.571	20.000	28.571
Hydrogen	kg	0.402	0.402	0.402	0.402
Catalyst	kg	0.400	0.571	0.400	0.571
Limestone	kg	0.100	0.143	0.100	0.143
Electricity	MJ	20.823	22.485	25.188	28.378
Fresh water	kg	14.944	15.528	16.765	17.972
Residue 10 MJ	kg	-5.627	0.000	-5.627	0.000
Residue 17 MJ	kg	0.000	-13.727	0.000	-13.727
Caustic	kg	0.009	0.011	0.009	0.011
Sulfuric Acid	kg	0.007	0.008	0.007	0.008
Output					
Naphtha	kg	9.703	9.703	9.703	9.703
LPG	kg	0.518	0.518	0.518	0.518
Residue (10 MJ)	kg	5.627	0.000	5.627	0.000
Residue (17 MJ)	kg	0.000	13.727	0.000	13.727
LP Steam	kg	4.119	3.070	4.119	3.070
Sulfur	kg	0.008	0.008	0.008	0.008
Metal residues	kg	0.600	0.857	0.600	0.857
Emission to air					
CO2 diffuse	kg	0.861	1.163	0.861	1.163
CO	kg	8.72E-05	1.02E-04	8.72E-05	1.02E-04
Dust	kg	1.09E-06	1.28E-06	1.09E-06	1.28E-06
NOX	kg	2.19E-04	2.56E-04	2.19E-04	2.56E-04
SO2	kg	1.03E-03	1.03E-03	1.03E-03	1.03E-03
Emission to water					
COD	kg	1.42E-10	1.42E-10	1.42E-10	1.42E-10
Chloride	kg	7.65E-03	7.64E-03	7.65E-03	7.64E-03
Sulfate	kg	2.07E-03	2.59E-03	2.07E-03	2.59E-03

Table S 22: Inventory results for mechanical biological treatment and material recovery

	Material recovery	Mechanical biological treatment
Input		
MSW	0.000	10.000
LWP	10.000	0.000
Diesel	0.038	0.009
Electricity	3.447	-0.943
Fresh water	0.000	9.630
Steam (LP)	1.089	-0.228
Output		
RDF	2.600	2.265
Mixed Plastic Waste	1.411	0.000
MBT Residues	0.000	3.382
Recovered Plastics	1.049	0.000
Iron Scrap	0.849	0.053
Aluminum Scrap	0.288	0.049
Emission to air		
Carbon dioxide	0.059	1.346
Carbon monoxide	2.13E-04	8.91E-05
Sulfur dioxide	4.53E-07	1.89E-07
Dust	3.02E-05	1.26E-05
Methane	3.99E-06	1.67E-06
NOX	5.88E-04	5.99E-04
Higher hydrocarbons	0.00E+00	7.40E-05

Table S 23: Inventory results for configuration variation of incineration of MSW and RDF

		MSW1	MSW2	MSW3	MSW4	RDF1	RDF2	RDF3	RDF4
Energy efficiency		low	low	high	high	low	low	high	high
Energy recovery		CHP	Electricity	CHP	Electricity	CHP	Electricity	CHP	Electricity
Input									
Activated carbon	kg	0.002	0.002	0.002	0.002	0.003	0.003	0.003	0.003
Ammonia	kg	0.018	0.018	0.018	0.018	0.020	0.020	0.020	0.020
Slaked lime	kg	0.187	0.187	0.187	0.187	0.363	0.363	0.363	0.363
Fresh water	kg	46.85	38.56	50.83	36.44	67.56	53.12	69.11	49.17
Fuel oil	kg	0.039	0.039	0.039	0.039	0.021	0.021	0.021	0.021
MSW	kg	18.5	18.5	18.5	18.5				
RDF	kg					10.0	10.0	10.0	10.0
Output									
Electricity	MJ	22.3	35.5	27.3	48.0	31.8	50.2	37.5	65.6
LP Steam	kg	26.7	0.0	32.7	0.0	38.0	0.0	44.8	0.0
Bottom Ash	kg	3.56	3.56	3.56	3.56	0.96	0.96	0.96	0.96
Fly ash	kg	0.47	0.47	0.47	0.47	0.52	0.52	0.52	0.52
Emission to air									
CO2 diffuse	kg	16.84	16.84	16.84	16.84	18.15	18.15	18.15	18.15
NH3	kg	4.88E-04	4.88E-04	4.88E-04	4.88E-04	5.62E-04	5.62E-04	5.62E-04	5.62E-04
CO	kg	2.44E-03	2.44E-03	2.44E-03	2.44E-03	2.81E-03	2.81E-03	2.81E-03	2.81E-03
PM	kg	2.84E-04	2.84E-04	2.84E-04	2.84E-04	3.28E-04	3.28E-04	3.28E-04	3.28E-04
CH4	kg	5.28E-04	5.28E-04	5.28E-04	5.28E-04	6.09E-04	6.09E-04	6.09E-04	6.09E-04
NOX	kg	6.91E-03	6.91E-03	6.91E-03	6.91E-03	7.97E-03	7.97E-03	7.97E-03	7.97E-03
SO2	kg	1.42E-03	1.42E-03	1.42E-03	1.42E-03	1.64E-03	1.64E-03	1.64E-03	1.64E-03

Table S 24: Inventory results for incineration of various waste fractions

Waste type		Pyrolysis residue	Pyrolysis residue	MPW	Pyrolysis residue	MBT Residue
Heating value	MJ/kg	9.5	17.1	36.6	26.8	11.1
Energy efficiency		high	high	high	high	high
Energy recovery		CHP	CHP	CHP	CHP	CHP
Input						
Waste input		10.0	10.0	10.0	10.0	20.0
Activated carbon	kg	0.010	0.006	0.008	0.002	0.003
Ammonia	kg	0.006	0.016	0.033	0.026	0.021
Slaked lime	kg	1.127	0.688	0.987	0.261	0.405
Fresh water	kg	28.38	52.84	116.00	84.02	68.14
Fuel oil	kg	0.021	0.021	0.021	0.021	0.043
Output						
Electricity	MJ	15.4	29.1	64.0	46.3	37.5
LP Steam	kg	18.4	34.9	76.5	55.2	44.8
Bottom Ash	kg	3.30	1.92	0.63	1.94	9.52
Fly ash	kg	1.35	0.88	1.29	0.43	0.57
Emission to air						
CO2 diffuse	kg	8.52	14.60	26.24	14.56	21.57
NH3	kg	1.70E-04	4.35E-04	9.08E-04	7.14E-04	5.86E-04
CO	kg	8.48E-04	2.17E-03	4.54E-03	3.57E-03	2.93E-03
PM	kg	9.90E-05	2.54E-04	5.29E-04	4.17E-04	3.42E-04
CH4	kg	1.84E-04	4.71E-04	9.83E-04	7.74E-04	6.35E-04
NOX	kg	2.40E-03	6.16E-03	1.29E-02	1.01E-02	8.31E-03
SO2	kg	4.95E-04	1.27E-03	2.65E-03	2.08E-03	1.71E-03

B Results of individual and system-based assessment

Table S 25: Inventory and impact assessment of the production of 1 kg ZSM-5 catalyst

	Inventory		GW impact		FRD impact	
	[per kg ZSM-5]		Total [kg CO_2eq / kg ZSM-5]	Distribution	Total [MJ / kg ZSM-5]	Distribution
Acetonitrile	0.16	kg	0.77	8.1%	19.5	9.8%
Ammonia	0.83	kg	2.13	22.3%	29.7	15.0%
Electricity	0.43	MJ	0.07	0.7%	0.9	0.4%
HCl	0.72	kg	0.18	1.8%	3.5	1.8%
Heat	68.44	MJ	5.16	54.1%	81.7	41.2%
SiO_2	0.94	kg	0.04	0.4%	0.6	0.3%
NaOH	0.05	kg	0.30	3.2%	4.0	2.0%
Toluene	0.18	kg	0.31	3.2%	11.1	5.6%
Propane	0.86	kg	0.51	5.4%	46.2	23.3%
γ-Al_2O_3	0.06	kg	0.07	0.7%	1.1	0.6%
Total			9.53	100.0%	198.1	100.0%

Table S 26: Fractional distribution of energy demand in gasification pathways

	Gasif (E-M)	Gasif (e-M)	Gasif (E-m)	Gasif (e-m)	Gasif (basic)
Electricity					
Air separation	0.29	0.31	0.41	0.41	-0.99
Pelletizing	0.15	0.15	0.27	0.23	-0.84
Gasifier	0.02	0.02	0.03	0.03	-0.09
Rectisol	0.21	0.21	0.34	0.31	-1.01
MeOH	0.15	0.15	0.24	0.21	-0.55
MTO	0.14	0.13	0.20	0.17	-0.37
Steam Integration	-0.11	-0.11	-0.72	-0.55	5.04
Rest	0.15	0.14	0.23	0.19	-0.19
Sum	1.00	1.00	1.00	1.00	1.00
Heat					
Gasifier	-0.37	-0.31	-0.14	-0.12	0.01
Shift	0.68	0.67	0.30	0.33	0.12
Rectisol	-0.12	-0.12	-0.05	-0.06	-0.02
Claus	0.00	0.00	0.00	0.00	0.00
MeOH	0.54	0.49	0.19	0.20	0.06
MTO	-0.01	-0.01	0.00	0.00	0.00
Incineration	0.27	0.28	0.71	0.64	0.84
Sum	1.00	1.00	1.00	1.00	1.00

Table S 27: Fractional distribution of energy demand in pyrolysis pathways

	Pyr (E-M)	Pyr (E-m)	Pyr (e-M)	Pyr (e-m)
Electricity				
Residue incineration	-0.71	2.28	-0.52	3.44
Pyrolysis	1.83	-1.38	1.61	-2.58
Oil upgrading	0.04	-0.03	0.03	-0.04
Steam Integration	-0.18	0.13	-0.13	0.20
Rest	0.02	-0.01	0.01	-0.02
Sum	1.00	1.00	1.00	1.00
Heat				
Residue incineration	0.72	0.94	0.72	0.94
Pyrolysis	-0.20	-0.08	-0.20	-0.08
Off-gas incineration	0.03	0.01	0.03	0.01
Oil upgrading	0.45	0.13	0.45	0.13
Rest	0.00	0.00	0.00	0.00
Sum	1.00	1.00	1.00	1.00

Table S 28: Background process inventory results in gasification and pyrolysis pathways

		2025					2035					2045				
		Gasif (E-M)	Gasif (e-M)	Gasif (E-m)	Gasif (e-m)	Gasif (basic)	Gasif (E-M)	Gasif (e-M)	Gasif (E-m)	Gasif (e-m)	Gasif (basic)	Gasif (E-M)	Gasif (e-M)	Gasif (E-m)	Gasif (e-m)	Gasif (basic)
Heat	MJ	-2.733	-2.739	-5.895	-5.366	-11.170	-2.733	-2.739	-5.895	-5.366	-11.170	-2.733	-2.739	-5.895	-5.366	-11.170
Electricity	MJ	1.627	1.665	0.531	0.737	-1.298	1.204	1.241	-0.382	-0.094	-3.028	0.781	0.817	-1.295	-0.925	-4.758
Butadiene	kg	-0.016	-0.016	-0.013	-0.013	-0.008	-0.016	-0.016	-0.013	-0.013	-0.008	-0.016	-0.016	-0.013	-0.013	-0.008
Ethylene	kg	-0.118	-0.113	-0.096	-0.095	-0.056	-0.118	-0.113	-0.096	-0.095	-0.056	-0.118	-0.113	-0.096	-0.095	-0.056
Propylene	kg	-0.125	-0.120	-0.102	-0.101	-0.060	-0.125	-0.120	-0.102	-0.101	-0.060	-0.125	-0.120	-0.102	-0.101	-0.060
Butane	kg	-0.012	-0.012	-0.010	-0.010	-0.006	-0.012	-0.012	-0.010	-0.010	-0.006	-0.012	-0.012	-0.010	-0.010	-0.006
LPG	kg	-0.011	-0.011	-0.009	-0.009	-0.005	-0.011	-0.011	-0.009	-0.009	-0.005	-0.011	-0.011	-0.009	-0.009	-0.005
Refinery gas	kg	-0.004	-0.004	-0.003	-0.003	-0.002	-0.004	-0.004	-0.003	-0.003	-0.002	-0.004	-0.004	-0.003	-0.003	-0.002
Sulfur	kg	-0.002	-0.002	-0.002	-0.002	-0.002	-0.002	-0.002	-0.002	-0.002	-0.002	-0.002	-0.002	-0.002	-0.002	-0.002
Heavy fuel oil	kg	0.000	0.000	0.000	0.000	-0.013	0.000	0.000	0.000	0.000	-0.013	0.000	0.000	0.000	0.000	-0.013
Caustic	kg	0.022	0.021	0.019	0.019	0.008	0.022	0.021	0.019	0.019	0.008	0.022	0.021	0.019	0.019	0.008
Sulph. Acid	kg	0.011	0.010	0.009	0.009	0.001	0.011	0.010	0.009	0.009	0.001	0.011	0.010	0.009	0.009	0.001

		2025				2035				2045			
		Pyr (E-M)	Pyr (E-m)	Pyr (e-M)	Pyr (e-m)	Pyr (E-M)	Pyr (E-m)	Pyr (e-M)	Pyr (e-m)	Pyr (E-M)	Pyr (E-m)	Pyr (e-M)	Pyr (e-m)
Catalyst	kg	0.020	0.020	0.020	0.020	0.020	0.020	0.020	0.020	0.020	0.020	0.020	0.020
Heat	MJ	0.175	0.000	0.175	0.430	0.486	0.000	0.486	1.196	0.797	0.000	0.797	1.962
Electricity	MJ	0.433	0.000	0.651	-0.837	0.122	0.000	0.340	-1.603	-0.190	0.000	0.029	-2.369
Hydrogen	kg	0.020	0.014	0.020	0.014	0.020	0.014	0.020	0.014	0.020	0.014	0.020	0.014
Naphtha	kg	-0.485	-0.340	-0.485	-0.340	-0.485	-0.340	-0.485	-0.340	-0.485	-0.340	-0.485	-0.340
LPG	kg	-0.026	-0.018	-0.026	-0.018	-0.026	-0.018	-0.026	-0.018	-0.026	-0.018	-0.026	-0.018
Slaked lime	kg	0.032	0.033	0.032	0.033	0.032	0.033	0.032	0.033	0.032	0.033	0.032	0.033
Heavy fuel oil	kg	0.001	0.001	0.001	0.001	0.001	0.001	0.001	0.001	0.001	0.001	0.001	0.001
Quicklime	kg	0.005	0.005	0.005	0.005	0.005	0.005	0.005	0.005	0.005	0.005	0.005	0.005

Table S 29: Global warming impact results of gasification and pyrolysis pathways (in kg CO_2eq / kg RDF)

	2025					2035					2045				
	Gasif (E-M)	Gasif (e-M)	Gasif (E-m)	Gasif (e-m)	Gasif (basic)	Gasif (E-M)	Gasif (e-M)	Gasif (E-m)	Gasif (e-m)	Gasif (basic)	Gasif (E-M)	Gasif (e-M)	Gasif (E-m)	Gasif (e-m)	Gasif (basic)
Heat	-0.17	-0.17	-0.37	-0.33	-0.69	-0.11	-0.11	-0.23	-0.21	-0.44	-0.07	-0.07	-0.15	-0.13	-0.28
Electricity	0.19	0.19	0.06	0.09	-0.15	0.10	0.10	-0.03	-0.01	-0.24	0.02	0.02	-0.03	-0.02	-0.10
Incineration	0.08	0.07	0.26	0.22	0.54	0.08	0.07	0.26	0.22	0.54	0.08	0.07	0.26	0.22	0.54
Gasification	0.85	0.90	0.77	0.81	0.73	0.85	0.90	0.77	0.81	0.73	0.85	0.90	0.77	0.81	0.73
Main products	-0.34	-0.32	-0.27	-0.27	-0.16	-0.34	-0.32	-0.27	-0.27	-0.16	-0.34	-0.32	-0.27	-0.27	-0.16
Side products	-0.03	-0.03	-0.02	-0.02	-0.01	-0.03	-0.03	-0.02	-0.02	-0.01	-0.03	-0.03	-0.02	-0.02	-0.01
Utilities	0.03	0.03	0.03	0.03	0.00	0.03	0.03	0.03	0.03	0.00	0.03	0.03	0.03	0.03	0.00
Residue treatment	0.01	0.01	0.04	0.04	0.05	0.01	0.01	0.04	0.04	0.05	0.01	0.01	0.04	0.04	0.05
Sum	0.62	0.68	0.49	0.56	0.30	0.59	0.65	0.54	0.58	0.46	0.55	0.61	0.62	0.65	0.77

	2025				2035				2045			
	Pyr (E-M)	Pyr (E-m)	Pyr (e-M)	Pyr (e-m)	Pyr (E-M)	Pyr (E-m)	Pyr (e-M)	Pyr (e-m)	Pyr (E-M)	Pyr (E-m)	Pyr (e-M)	Pyr (e-m)
Heat	-0.13	-0.31	-0.12	-0.31	-0.08	-0.19	-0.08	-0.19	-0.05	-0.12	-0.05	-0.12
Electricity	0.05	-0.12	0.08	-0.10	0.01	-0.15	0.03	-0.13	0.00	-0.05	0.00	-0.05
Incineration	0.24	0.70	0.24	0.70	0.24	0.70	0.24	0.70	0.24	0.70	0.24	0.70
Pyrolysis	0.04	0.04	0.04	0.04	0.04	0.04	0.04	0.04	0.04	0.04	0.04	0.04
Main products	-0.25	-0.18	-0.25	-0.18	-0.25	-0.18	-0.25	-0.18	-0.25	-0.18	-0.25	-0.18
Side products	-0.02	-0.01	-0.02	-0.01	-0.02	-0.01	-0.02	-0.01	-0.02	-0.01	-0.02	-0.01
Utilities	0.04	0.04	0.04	0.04	0.04	0.04	0.04	0.04	0.04	0.04	0.04	0.04
Catalyst	0.19	0.19	0.19	0.19	0.19	0.19	0.19	0.19	0.19	0.19	0.19	0.19
Hydrogen	0.22	0.15	0.22	0.15	0.22	0.15	0.22	0.15	0.22	0.15	0.22	0.15
Residue treatment	0.05	0.05	0.05	0.05	0.05	0.05	0.05	0.05	0.05	0.05	0.05	0.05
Sum	0.43	0.56	0.45	0.58	0.44	0.65	0.45	0.67	0.45	0.81	0.45	0.82

Table S 30: Cumulated life cycle inventory results of FSQ scenarios (part 1)

		Electricity	Steam	Fuel gas	Naphtha	Nat gas	LPG	Olefins	BTX	Methanol	Ammonia	Hydrogen	RDF/MPW
		[GWh]	[GWh]	[GWh]	[kt]	[kt]	[kt]	[kt]	[kt]	[kt]	[kt]	[kt]	[kt]
FSQ-Ref	Input/Output	-3512	36595	0	-14671	-5641	0	9368	2592	1130	3133	471	0
	Conv Chem	9315	-15826	34462	14671	2911	0	-9368	-2592	-1130	-3147	-471	0
	Incineration	-6350	-21098	0	0	0	0	0	0	0	14	0	1574
	Utilities	172	0	-34462	0	2729	0	0	0	0	0	0	0
	Feed Rec	0	0	0	0	0	0	0	0	0	0	0	0
FSQ-Ref-MBT	Input/Output	-3221	36808	0	-14671	-5639	0	9368	2592	1130	3133	471	0
	Conv Chem	9314	-15825	34458	14671	2911	0	-9368	-2592	-1130	-3145	-471	0
	Incineration	-6366	-21129	0	0	0	0	0	0	0	12	0	3949
	Utilities	172	0	-34458	0	2729	0	0	0	0	0	0	0
	Feed Rec	0	0	0	0	0	0	0	0	0	0	0	0
FSQ-G-RP/MP-MTO	Input/Output	-6051	31077	0	-13992	-5584	0	9368	2592	1130	3133	471	0
	Conv Chem	8878	-15216	33733	14003	2922	21	-8849	-2592	-1130	-3143	-471	0
	Incineration	-4304	-14306	0	0	0	0	0	0	0	10	0	0
	Utilities	533	0	-33606	0	2661	0	0	0	0	0	0	0
	Feed Rec	569	-1885	-127	-11	0	-21	-519	0	0	0	0	1574
FSQ-G-MTO	Input/Output	-8979	24507	0	-13162	-5513	0	9368	2592	1130	3133	471	0
	Conv Chem	8342	-14463	32836	13184	2935	45	-8213	-2592	-1130	-3137	-471	0
	Incineration	-1847	-6130	0	0	0	0	0	0	0	4	0	0
	Utilities	1010	0	-32564	0	2579	0	0	0	0	0	0	0
	Feed Rec	1374	-4060	-272	-23	0	-45	-1155	0	0	0	0	3949
FSQ-G-RP/MP-NH3	Input/Output	-6776	31368	0	-14671	-4706	0	9368	2592	1130	3133	471	0
	Conv Chem	8679	-15119	31303	14671	2224	0	-9368	-2592	-1135	-1784	-471	0
	Incineration	-4304	-14306	0	0	0	0	0	0	0	10	0	0
	Utilities	443	0	-31343	0	2482	0	0	0	0	0	0	0
	Feed Rec	1583	-2273	39	0	0	0	0	0	5	-1359	0	1574
FSQ-G-NH3	Input/Output	-10644	25073	0	-14671	-3569	0	9368	2592	1130	3133	471	0
	Conv Chem	7903	-14256	27454	14671	1387	0	-9368	-2592	-1142	-122	-471	0
	Incineration	-1847	-6130	0	0	0	0	0	0	0	4	0	0
	Utilities	814	0	-27553	0	2182	0	0	0	0	0	0	0
	Feed Rec	3675	-4832	99	0	0	0	0	0	12	-3015	0	3949

Table S 31: Cumulated life cycle inventory results of FSQ scenarios (part 2)

		Electricity	Steam	Fuel gas	Naphtha	Nat gas	LPG	Olefins	BTX	Methanol	Ammonia	Hydrogen	RDF/MPW
		[GWh]	[GWh]	[GWh]	[kt]	[kt]	[kt]	[kt]	[kt]	[kt]	[kt]	[kt]	[kt]
FSQ-P-fHTR	Input/Output	-5874	30930	0	-13730	-5767	0	9368	2592	1130	3133	471	0
	Conv Chem	9319	-15998	34938	14612	2994	64	-9368	-2592	-1130	-3144	-502	0
	Incineration	-4516	-15008	0	0	0	0	0	0	0	11	0	0
	Utilities	172	0	-35021	0	2773	0	0	0	0	0	0	0
	Feed Rec	524	-254	83	-882	0	-64	0	0	0	0	31	1574
FSQ-P-MP-fHTR	Input/Output	-4636	33787	0	-14258	-5688	0	9368	2592	1130	3133	471	0
	Conv Chem	9314	-15899	34623	14641	2940	33	-9368	-2592	-1130	-3145	-482	0
	Incineration	-5455	-18125	0	0	0	0	0	0	0	12	0	1020
	Utilities	172	0	-34706	0	2748	0	0	0	0	0	0	0
	Feed Rec	229	-92	83	-382	0	-33	0	0	0	0	11	554
FSQ-P-MP/RP-fHTR-G-RR-MTO	Input/Output	-8802	24360	0	-12900	-5697	0	9368	2592	1130	3133	471	0
	Conv Chem	8782	-15245	34041	13794	3006	88	-8731	-2592	-1130	-3137	-502	0
	Incineration	-2058	-6832	0	0	0	0	0	0	0	4	0	0
	Utilities	648	0	-33979	0	2691	0	0	0	0	0	0	0
	Feed Rec	1329	-2429	-62	-894	0	-88	-637	0	0	0	31	3949
FSQ-G-RP-MOH	Input/Output	-4732	34156	0	-14671	-5244	0	9368	2592	1130	3133	471	0
	Conv Chem	9349	-15607	33414	14671	2596	0	-9368	-2592	-560	-3145	-471	0
	Incineration	-5467	-18166	0	0	0	0	0	0	0	12	0	725
	Utilities	300	0	-33438	0	2648	0	0	0	0	0	0	0
	Feed Rec	174	-712	24	0	0	0	0	0	-570	0	0	849
FSQ-G-RP/PM-MTA	Input/Output	-5865	31722	0	-14331	-5535	0	9368	2592	1130	3133	471	0
	Conv Chem	9328	-15725	33929	14331	2953	0	-9368	-2293	-1130	-3144	-471	0
	Incineration	-4823	-16028	0	0	0	0	0	0	0	11	0	292
	Utilities	455	0	-32608	0	2582	0	0	0	0	0	0	0
	Feed Rec	529	-298	-1321	0	0	0	0	-299	0	0	0	1282
FSQ-P-RP-pHTR	Input/Output	-4787	33477	0	-14156	-5750	0	9368	2592	1130	3133	471	0
	Conv Chem	9322	-15868	34475	14513	2965	31	-9368	-2478	-1130	-3145	-485	0
	Incineration	-5411	-17981	0	0	0	0	0	0	0	12	0	554
	Utilities	172	0	-35164	0	2785	0	0	0	0	0	0	0
	Feed Rec	329	42	689	-357	0	-31	0	-114	0	0	14	1020

Table S 32: Global warming impact results for scenarios in FSQ framework (in Mt CO_2eq)

	Ref	Ref-MBT	G-RP/MP-MTO	G-MTO	G-RP/MP-NH3	G-NH3	P-fHTR	P-MP-fHTR	P-fHTR-G-RR-MTO	G-RP-MOH	G-RP/PM-MTA	P-RP-pHTR
Electricity base	1.46	1.46	1.46	1.46	1.46	1.46	1.46	1.46	1.46	1.46	1.46	1.46
Electricity Substitution	0.00	-0.07	0.88	1.91	0.97	2.13	0.86	0.42	1.89	0.40	0.79	0.47
Steam Substitution	0.00	-0.01	0.38	0.82	0.36	0.78	0.39	0.19	0.83	0.17	0.33	0.21
Conventional NH3 production	5.62	5.62	5.61	5.60	3.19	0.22	5.61	5.62	5.60	5.62	5.62	5.62
Conventional MeOH production	0.79	0.79	0.77	0.75	0.79	0.79	0.79	0.79	0.76	0.54	0.79	0.79
Naphtha steam cracking	8.00	8.00	7.52	6.94	8.00	8.00	7.95	7.97	7.38	8.00	8.03	7.99
LPG steam cracking	1.08	1.08	1.05	1.02	1.08	1.08	1.13	1.11	1.09	1.08	1.05	1.09
Catalytic reforming	0.23	0.23	0.33	0.45	0.23	0.23	0.24	0.23	0.36	0.23	0.00	0.14
Conventional H2 production	3.82	3.82	3.79	3.77	3.82	3.82	4.13	3.92	4.10	3.82	3.98	4.02
Diesel supply	0.04	0.05	0.04	0.05	0.04	0.05	0.04	0.04	0.05	0.04	0.04	0.04
Utility supply	0.38	0.43	0.36	0.39	0.38	0.44	0.33	0.33	0.37	0.36	0.35	0.39
Utility supply pyrolysis	0.00	0.00	0.00	0.00	0.00	0.00	0.24	0.09	0.24	0.00	0.00	0.16
Fuel oil supply	0.01	0.01	0.01	0.00	0.01	0.00	0.01	0.01	0.00	0.01	0.01	0.01
Naphtha supply	7.66	7.66	7.31	6.87	7.66	7.66	7.17	7.45	6.74	7.66	7.48	7.39
Natural gas supply	2.75	2.75	2.72	2.69	2.30	1.74	2.81	2.78	2.78	2.56	2.70	2.81
Collection & transport	0.19	0.19	0.19	0.19	0.19	0.19	0.19	0.19	0.19	0.19	0.19	0.19
Mechanical biological treatment	0.00	1.41	0.00	1.41	0.00	1.41	0.00	0.00	1.41	0.00	0.00	0.00
Material recovery	1.48	1.48	0.02	0.02	0.02	0.02	0.02	0.02	0.02	1.48	0.79	1.48
MSW & MBT residue incineration	9.57	3.83	9.57	3.83	9.57	3.83	9.57	9.57	3.83	9.57	9.57	9.57
FeedRec MPW	0.00	0.00	0.11	0.11	0.08	0.08	0.05	0.05	0.05	0.00	0.08	0.00
FeedRec MPW concentrated	0.00	0.00	0.51	0.51	1.39	1.39	0.00	0.00	0.00	0.00	0.24	0.00
FeedRec RDF	0.00	0.00	0.09	0.29	0.05	0.18	0.04	0.00	0.25	0.06	0.13	0.28
FeedRec RDF concentrated	0.00	0.00	0.85	2.83	1.82	6.05	0.00	0.00	1.98	0.71	0.85	0.00
RDF incineration	1.85	6.17	0.00	0.00	0.00	0.00	0.00	1.85	0.00	0.31	0.00	0.00
Pyrolysis residue incineration	0.00	0.00	0.00	0.00	0.00	0.00	0.35	0.10	0.35	0.00	0.00	0.24
Total impact	44.94	44.89	43.59	41.93	43.40	41.56	43.39	44.20	41.74	44.27	44.49	44.36
relative Impact to Ref		-0.04	-1.35	-3.01	-1.54	-3.37	-1.54	-0.74	-3.20	-0.67	-0.45	-0.58

Table S 33: Cumulated life cycle inventory results of FEI-100 scenarios (part 1)

		Electricity	Steam	Fuel gas	Naphtha	Nat gas	LPG	Olefins	Aromatics	Methanol	Ammonia	Hydrogen	RDF/MPW
		[GWh]	[GWh]	[GWh]	[kt]	[kt]	[kt]	[kt]	[kt]	[kt]	[kt]	[kt]	[kt]
FEI-Ref-0	Input/Output	-3512	36595	0	-14671	-5641	0	9368	2592	1130	3133	471	0
	Conv Chem	9315	-15826	34462	14671	2911	0	-9368	-2592	-1130	-3147	-471	0
	Incineration	-6350	-21098	0	0	0	0	0	0	0	14	0	1574
	Utilities	172	0	-34462	0	2729	0	0	0	0	0	0	0
	PTX	0	0	0	0	0	0	0	0	0	0	0	0
	eChem	0	0	0	0	0	0	0	0	0	0	0	0
	Feed Rec	0	0	0	0	0	0	0	0	0	0	0	0
FEI-100-PTX-MTO	Input/Output	-103512	36595	0	-10093	-5342	0	9368	2592	1130	3133	471	0
	Conv Chem	6378	-11721	29603	10157	2997	144	-5866	-2592	-1130	-3147	-471	0
	Incineration	-6350	-21098	0	0	0	0	0	0	0	14	0	1574
	Utilities	101483	-4416	-29613	0	2345	0	0	0	0	0	-1723	0
	PTX	1627	311	10	-63	0	-144	-3502	0	0	0	1723	0
	eChem	0	0	0	0	0	0	0	0	0	0	0	0
	Feed Rec	0	0	0	0	0	0	0	0	0	0	0	0
FEI-100-PTX-NH3/H2/MOH	Input/Output	-103512	36595	0	-12634	-1481	0	9368	2592	1130	3133	471	0
	Conv Chem	6414	-11055	18176	12662	41	64	-7809	-2592	-467	-38	-124	0
	Incineration	-6350	-21098	0	0	0	0	0	0	0	14	0	1574
	Utilities	101522	-1989	-18180	0	1440	0	0	0	0	0	-1826	0
	PTX	1551	-2782	5	-28	0	-64	-1559	0	-663	-3109	1479	0
	eChem	0	0	0	0	0	0	0	0	0	0	0	0
	Feed Rec	0	0	0	0	0	0	0	0	0	0	0	0

Table S 34: Cumulated life cycle inventory results of FEI-100 scenarios (part 2)

		Electricity	Steam	Fuel gas	Naphtha	Natl gas	LPG	Olefins	Aromatics	Methanol	Ammonia	Hydrogen	RDF/MPW
		[GWh]	[GWh]	[GWh]	[kt]	[kt]	[kt]	[kt]	[kt]	[kt]	[kt]	[kt]	[kt]
FEI-100-eChem-NSC/LSC/NR	Input/Output	-103512	36595	0	-11164	-2417	0	9368	2592	1130	3133	471	0
	Conv Chem	1675	-3081	14397	0	2968	0	0	0	-1130	-3147	-354	0
	Incineration	-6350	-21098	0	0	0	0	0	0	0	14	0	1574
	Utilities	74702	-12355	6967	0	-552	0	0	0	0	0	-1138	0
	PTX	1075	205	6	-42	0	-95	-2314	0	0	0	1138	0
	eChem	32035	-596	-21370	11206	0	95	-7054	-2592	0	0	-117	0
	Feed Rec	0	0	0	0	0	0	0	0	0	0	0	0
FEI-100-eChem-NH3/H2/MOH	Input/Output	-103512	36595	-1	-10671	-4236	0	9368	2592	1130	3133	471	0
	Conv Chem	5143	-9233	15805	10726	0	126	-6307	-2592	-364	0	-124	0
	Incineration	-6350	-21098	0	0	0	0	0	0	0	14	0	1574
	Utilities	89765	-8443	-15814	0	1252	0	0	0	0	0	-1505	0
	PTX	1422	272	8	-55	0	-126	-3061	0	0	0	1505	0
	eChem	13157	1579	1	0	2984	0	0	0	-766	-3147	-347	0
	Feed Rec	0	0	0	0	0	0	0	0	0	0	0	0
FEI-100-eChem-all	Input/Output	-103512	36595	-1	-11784	-1164	0	9368	2592	1130	3133	471	0
	Conv Chem	68	-87	0	0	0	0	0	0	-461	0	0	0
	Incineration	-6350	-21098	0	0	0	0	0	0	0	14	0	1574
	Utilities	61706	-16886	22588	0	-1789	0	0	0	0	0	-892	0
	PTX	843	161	5	-33	0	-75	-1814	0	0	0	892	0
	eChem	46871	986	-22592	11816	2953	75	-7554	-2592	-669	-3147	-471	0
	Feed Rec	0	0	0	0	0	0	0	0	0	0	0	0

Table S 35: Cumulated life cycle inventory results of FEI-100 scenarios (part 3)

		Electricity	Steam	Fuel gas	Naphtha	Natl gas	LPG	Olefins	Aromatics	Methanol	Ammonia	Hydrogen	RDF/MPW
		[GWh]	[GWh]	[GWh]	[kt]	[kt]	[kt]	[kt]	[kt]	[kt]	[kt]	[kt]	[kt]
FEI-100-G-MTO	Input/Output	-103512	36595	0	-9030	-5215	0	9368	2592	1130	3133	471	0
	Conv Chem	5689	-10753	28437	9109	3009	174	-5050	-2592	-1130	-3137	-470	0
	Incineration	-1847	-6130	0	0	0	0	0	0	0	4	0	0
	Utilities	97182	-14799	-27850	0	2205	0	0	0	0	0	-1549	0
	PTX	1010	193	6	-39	0	-89	-2173	0	0	0	1069	0
	eChem	0	0	0	0	0	0	0	0	0	0	0	0
	Feed Rec	1377	-5252	-593	-39	0	-85	-2144	0	0	0	479	3949
FEI-100-P-MP/RP-fHTR	Input/Output	-103512	36595	0	-9574	-5368	0	9368	2592	1130	3133	471	0
	Conv Chem	6635	-12174	30014	10514	2984	195	-6188	-2592	-1130	-3144	-471	0
	Incineration	-4516	-15008	0	0	0	0	0	0	0	11	0	0
	Utilities	99016	-9771	-30106	0	2384	0	0	0	0	0	-1595	0
	PTX	1477	282	9	-58	0	-131	-3180	0	0	0	1564	0
	eChem	0	0	0	0	0	0	0	0	0	0	0	0
	Feed Rec	524	-254	83	-882	0	-64	0	0	0	0	31	1574
FEI-100-P-MP/RP-fHTR-G-RR-MTOh	Input/Output	-103512	36595	0	-8963	-5297	0	9368	2592	1130	3133	471	0
	Conv Chem	6240	-11617	29349	9913	2992	211	-5720	-2592	-1130	-3137	-471	0
	Incineration	-2058	-6832	0	0	0	0	0	0	0	4	0	0
	Utilities	96764	-15383	-29102	0	2305	0	0	0	0	0	-1507	0
	PTX	1124	215	7	-44	0	-100	-2420	0	0	0	1190	0
	eChem	0	0	0	0	0	0	0	0	0	0	0	0
	Feed Rec	1342	-3123	-253	-906	0	-111	-1228	0	0	0	317	3949
FEI-100-eChem-all-G-MTOh	Input/Output	-103512	36595	-1	-10482	-1587	0	9368	2592	1130	3133	471	0
	Conv Chem	58	-74	0	0	0	0	0	0	-392	0	0	0
	Incineration	-1847	-6130	0	0	0	0	0	0	0	4	0	0
	Utilities	58733	-26676	20603	0	-1632	0	0	0	0	0	-748	0
	PTX	336	64	2	-13	0	-30	-724	0	0	0	356	0
	eChem	44755	1326	-20011	10534	3219	114	-6500	-2592	-738	-3137	-558	0
	Feed Rec	1377	-5252	-593	-39	0	-85	-2144	0	0	0	479	3949

Table S 36: Cumulated life cycle inventory results of FEI-Net0 scenarios (part 1)

		Electricity	Steam	Fuel gas	Naphtha	Nat gas	LPG	Olefins	Aromatics	Methanol	Ammonia	Hydrogen	RDF/MPW
		[GWh]	[GWh]	[GWh]	[kt]	[kt]	[kt]	[kt]	[kt]	[kt]	[kt]	[kt]	[kt]
FEI-Net0-PTX-MTO/MTA	Input/Output	-334712	36595	0	-2211	-4152	0	9368	2592	1130	3133	471	0
	Conv Chem	2579	-5768	20349	2358	3341	334	-1245	-974	-1130	-3147	-471	0
	Incineration	-6350	-21098	0	0	0	0	0	0	0	14	0	1574
	Utilities	331361	-19316	-10241	0	811	0	0	0	0	0	-5328	0
	PTX	6748	9257	-10108	-147	0	-334	-8123	-1618	0	0	5328	0
	eChem	0	0	0	0	0	0	0	0	0	0	0	0
	Feed Rec	0	0	0	0	0	0	0	0	0	0	0	0
FEI-Net0-PTX-Mix	Input/Output	-287798	36595	0	-4117	-1770	0	9368	2592	1130	3133	471	0
	Conv Chem	1284	-4035	12101	4263	810	332	-1293	-2592	-606	-690	-197	0
	Incineration	-6350	-21098	0	0	0	0	0	0	0	14	0	1574
	Utilities	288085	-10200	-12123	0	960	0	0	0	0	0	-4808	0
	PTX	4404	-1591	22	-146	0	-332	-8075	0	-524	-2457	4534	0
	eChem	0	0	0	0	0	0	0	0	0	0	0	0
	Feed Rec	0	0	0	0	0	0	0	0	0	0	0	0
FEI-Net0-eChem-all-PTX-Mix	Input/Output	-275542	36595	-1	-5250	-303	0	9368	2592	1130	3133	471	0
	Conv Chem	16	-21	0	0	0	0	0	0	-112	0	0	0
	Incineration	-6350	-21098	0	0	0	0	0	0	0	14	0	1574
	Utilities	257224	-14444	9667	0	-766	0	0	0	0	0	-4225	0
	PTX	3870	-1398	20	-129	0	-292	-7095	0	-460	-2159	3984	0
	eChem	20407	37	-9686	5378	1068	292	-2273	-2592	-558	-989	-230	0
	Feed Rec	0	0	0	0	0	0	0	0	0	0	0	0

Table S 37: Cumulated life cycle inventory results of FEI-Net0 scenarios (part 2)

		Electricity	Steam	Fuel gas	Naphtha	Nat gas	LPG	Olefins	Aromatics	Methanol	Ammonia	Hydrogen	RDF/MPW
		[GWh]	[GWh]	[GWh]	[kt]	[kt]	[kt]	[kt]	[kt]	[kt]	[kt]	[kt]	[kt]
FEI-Net0-G-MTO-PTX-Mix	Input/Output	-275642	36595	0	-2302	-3856	0	9368	2592	1130	3133	471	0
	Conv Chem	484	-4096	19051	2474	2393	386	97	-2592	-655	-909	-702	0
	Incineration	-1847	-6130	0	0	0	0	0	0	0	4	0	0
	Utilities	271534	-19821	-18478	0	1463	0	0	0	0	0	-4360	0
	PTX	3993	-1443	20	-133	0	-301	-7321	0	-475	-2227	4111	0
	eChem	0	0	0	0	0	0	0	0	0	0	0	0
	Feed Rec	1377	-5252	-593	-39	0	-85	-2144	0	0	0	479	3949
FEI-Net0-eChem-all-G-MTO-PTX-Mix	Input/Output	-258351	36595	-1	-3837	-2124	0	9368	2592	1130	3133	471	0
	Conv Chem	5	-7	0	0	0	0	0	0	-36	0	0	0
	Incineration	-1847	-6130	0	0	0	0	0	0	0	4	0	0
	Utilities	229873	-26084	7463	0	-591	0	0	0	0	0	-3629	0
	PTX	3324	-1201	17	-110	0	-251	-6095	0	-395	-1854	3422	0
	eChem	25517	1932	-6885	3987	2715	335	-1129	-2592	-698	-1282	-744	0
	Feed Rec	1377	-5252	-593	-39	0	-85	-2144	0	0	0	479	3949

Table S 38: Global warming impact results for FEI-100 scenarios (in MT CO_2eq)

	Ref-0	PTX-MTO	PTX-NH3/H2/MOH	eChem-NSC/LSC/NR	eChem-NH3/H2/MOH	eChem-all	G-MTO	P-fHTR	P-fHTR-G-RR-MTO	eChem-all-G-MTO
Carbon Capture	0.00	-8.97	-6.41	-4.41	-4.97	-0.12	-4.02	-7.75	-4.91	0.00
Process CO2 emission	4.45	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	5.55
Electricity supply	0.08	2.30	2.30	2.30	2.30	2.30	2.30	2.30	2.30	2.30
PTX processes	0.00	1.10	0.52	0.73	0.96	0.57	0.68	1.00	0.76	0.18
NH3 production	1.67	1.67	0.02	1.67	0.00	0.00	1.67	1.67	1.67	0.00
MeOH production	0.29	0.37	0.04	0.34	0.08	0.08	0.39	0.36	0.37	0.08
Naphtha steam cracking	8.00	4.81	6.58	0.01	5.21	0.01	4.07	5.06	4.63	0.01
LPG steam cracking	1.08	0.89	1.00	0.00	0.91	0.00	0.84	0.95	0.92	0.00
Catalytic reforming	0.23	0.90	0.52	0.00	0.81	0.00	1.05	0.84	0.93	0.00
H2 production	3.82	3.67	0.07	3.76	0.09	0.09	3.63	3.67	3.65	0.13
eChem processes	0.00	0.00	0.00	0.01	0.35	0.36	0.00	0.00	0.00	0.40
Diesel supply	0.04	0.04	0.04	0.04	0.04	0.04	0.05	0.04	0.05	0.05
Utility supply	0.38	0.70	0.39	0.60	0.66	0.55	0.65	0.62	0.62	0.54
Utility supply pyrolysis	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.24	0.24	0.00
Fuel oil supply	0.01	0.01	0.01	0.01	0.01	0.01	0.00	0.01	0.00	0.00
Naphtha supply	7.66	5.27	6.60	5.83	5.57	6.15	4.72	5.00	4.68	5.57
Natural gas supply	2.75	2.61	0.72	1.18	2.07	0.57	2.54	2.62	2.58	0.87
Collection & transport	0.19	0.19	0.19	0.19	0.19	0.19	0.19	0.19	0.19	0.19
Mechanical biological treatment	0.00	0.00	0.00	0.00	0.00	0.00	1.41	0.00	1.41	1.41
Material recovery	1.48	1.48	1.48	1.48	1.48	1.48	0.02	0.02	0.02	0.02
MSW & MBT residue incineration	9.57	9.57	9.57	9.57	9.57	9.57	3.83	9.57	3.83	3.83
RDF incineration	1.85	1.85	1.85	1.85	1.85	1.85	0.00	0.00	0.00	0.00
Pyrolysis residue incineration	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.35	0.35	0.00
FeedRec processes	0.00	0.00	0.00	0.00	0.00	0.00	0.41	0.10	0.31	0.41
Total impact	43.55	28.45	25.49	25.17	27.18	23.71	24.44	26.86	24.62	21.55
relative Impact to reference		15.10	18.06	18.38	16.37	19.84	19.11	16.69	18.93	22.00

Table S 39: Global warming impact results for FEI-Net0 scenarios (in Mt CO_2eq)

	PTX-MTO/MTA	PTX-Mix	eChem-all-PTX-Mix	G-MTO-PTX-Mix	eChem-all-G-MTO-PTX-Mix
Carbon Capture	-37.30	-30.32	-25.50	-27.22	-17.97
Process CO2 emission	0.00	0.00	0.00	0.00	0.00
Electricity supply	7.45	6.40	6.13	6.13	5.75
PTX processes	3.70	2.56	2.25	2.32	1.93
NH3 production	1.67	0.37	0.00	0.48	0.00
MeOH production	0.47	0.24	0.05	0.30	0.05
Naphtha steam cracking	0.78	0.65	0.00	0.00	0.00
LPG steam cracking	0.44	0.63	0.00	0.54	0.00
Catalytic reforming	0.55	1.77	0.01	2.04	0.01
H2 production	4.39	0.58	0.02	5.88	0.15
eChem processes	0.00	0.00	0.14	0.00	0.30
Diesel supply	0.04	0.04	0.04	0.05	0.05
Utility supply	1.54	1.00	0.93	1.10	1.01
Utility supply pyrolysis	0.00	0.00	0.00	0.00	0.00
Fuel oil supply	0.01	0.01	0.01	0.00	0.00
Naphtha supply	1.15	2.16	2.74	1.20	2.00
Natural gas supply	2.03	0.87	0.15	1.88	1.04
Collection & transport	0.19	0.19	0.19	0.19	0.19
Mechanical biological treatment	0.00	0.00	0.00	1.41	1.41
Material recovery	1.48	1.48	1.48	0.02	0.02
MSW & MBT residue incineration	9.57	9.57	9.57	3.83	3.83
RDF incineration	1.85	1.85	1.85	0.00	0.00
Pyrolysis residue incineration	0.00	0.00	0.00	0.00	0.00
FeedRec processes	0.00	0.00	0.00	0.41	0.41