



Entrained flow gasification-based biomass-to-X processes: An energetic and technical evaluation

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ABSTRACT

A large number of process routes is available for the production of sustainable energy carriers from biogenic residues. Benchmarking these routes usually suffers from a lack of comparable performance data. The present work addresses this through a comprehensive model-based comparison of various biomass-to-X routes. Herein, seven routes (methanol, synthetic natural gas, dimethyl ether, Fischer-Tropsch syncrude, ammonia, and hydrogen with and without carbon capture) are modelled in detailed Aspen Plus® simulations. The evaluation itself is based on various key performance indicators, which capture both energetic (i.e. energy yield and usable heat per feedstock) and material-based (i.e. carbon and hydrogen conversion efficiency, and CO₂ emissions) properties of the routes. The results show, that no simple correlations can be drawn between energetic and material-based indicators. In summary across all considered properties, the methanol route exhibits the best combined results, in particular with the highest carbon efficiency of 40 %. Fischer-Tropsch is more suitable for integration into existing industrial parks due to the lowest energy yield of 40 % with a lot of by-product formation and the highest amount of useable heat per feedstock of 211.3 kW MW⁻¹. Whereas dimethyl ether and synthetic natural gas have potential for integration into heat grids, mainly due to their good conversion and simultaneous large heat dissipation. Ammonia and hydrogen should only be considered in combination with carbon capture. Therefore, the key performance indicators determined herein must be considered together with project- and location-specific requirements and the market outlook for the product.

1. Introduction

Reducing greenhouse gas emissions to net zero is only possible by ending the use of fossil fuels as a primary energy source. Private mobility or portions of the heat supply can be covered solely by electricity-based technologies and thereby only rely on renewable power generation, e.g., from photovoltaics or wind turbines. In addition, the transformation from, e.g., fossil to e-mobility leads to an energy demand reduction due to overall higher system efficiencies. However, sectors like freight transport and aviation or the chemical industry are difficult or impossible to be decarbonized, rather only defossilized. While there are already various possible ways of synthesising green fuels, e.g., by using biomass as feedstock, their potentials are limited in terms of sustainable utilization.

In [1], a merit order of the sectors to be electrified is presented, as

well as sectors that cannot be electrified. As a result, an enormous demand for sustainable fuels and chemicals can be identified, where especially the carbon-based demand should be covered by closing the carbon cycles. Waste and biogenic residues are high-value resources that are still underutilized. In comparison, given its high electricity demand and low efficiencies, direct air carbon capture technologies should be used last. As summarized by Jones et al., the utilization of synthesis gas can both be used for sector coupling in future energy systems, and for acceleration of the hydrogen economy by using natural gas as bridging feedstock [2]. From a system perspective, there are blind spots in the analysis of biomass use, thus the hypothesis of a much bigger conflict by assuming today's biomass production as a potential source for energy and chemicals [3]. Therefore, the use of biomass and even biogenic residues must be optimized in all social, economic, and ecological points of view [4]. In addition, further research is needed in the field of biomass

Abbreviations: ASU, Air separation unit; BtL, Biomass-to-Liquids; BtX, Biomass-to-X; CCE, Carbon conversion efficiency; CLAS, Chemical looping air separation; DME, Dimethyl ether; EF, Entrained flow; FT, Fischer-Tropsch; GHG, Greenhouse gas; ITM, Ionic transfer membrane; KPI, Key performance indicator; LPG, Liquefied petroleum gas; MeOH, Methanol; NG, Natural gas; NH₃, Ammonia; PSA, Pressure swing absorption; PtX, Power-to-X; SNG, Synthetic natural gas.

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gasification-based syngas production [4].

Since biomass, both residually and explicitly cultivated, is a high value feedstock, the shape of future energy systems will decide how these limited resources will be used. This paper compares several synthesis routes for the production of various synthetic fuels/energy carriers and chemical feedstock. The predefinition for this comparison is the use of biogenic feedstock, as well as the synthesis gas supply, via entrained flow gasification. The standardized basic requirement in this regard enables a direct comparison of the otherwise (in part) fundamentally different process pathways. The analysis was based on several key performance indicators (KPI), which will be discussed in detail in Section 2.6. Detailed process simulations in Aspen Plus® were used to ensure the in-depth comparability of the processes. The main goal was to identify which process route enables the most promising usage of biomass in context of synthetic fuels and energy carriers from a technical point of view.

In general, based on an analysis of the literature, Biomass-to-X (BtX) has seen a growing level of interest and an increasing number of related publications during recent years. However, in addition to thermochemical conversion technologies like gasification, many different processes based on biological and/or physical methods are also gaining research interest [5,6]. In [5] an extensive review of 1st to 4th generation biofuels via multiple process-pathways is given, thereby highlighting the need for further in-depth research in all disciplines in order to achieve the sustainable usage of current biomass potentials, as well as increase the use of biomass in the long term. In this context, this study focuses solely on the thermochemical pathway, in particular entrained-flow (EF) gasification. Among the various thermochemical routes, gasification is considered to be the most attractive because, for example, the produced syngas offers a variety of possible applications [7]. A comparison of different process routes for biomass based fuels reveals high investment costs as being one of the reasons for the high fuel costs of gasification-based biofuels [6,8]. Nevertheless, gasification, and in particular EF gasification, has numerous advantages [9,10]:

- Deployable for large scale plants
- Almost complete tar conversion
- Mature technology (used in large scale for coal-to-liquid)
- Pressurized operation possible
- Cold gas efficiency up to 90 %
- Expected direct power integration, e.g. plasma torch

In addition, gasification enables the integration of biomass use into polygeneration plants, in which a flexible use of the feedstock for electricity, heat and/or fuel or chemical production is possible, which offers the opportunity to maximize the fuel usage by using excess heat and unused syngas as well as synthesis by-products for power generation [11]. Furthermore, looking at the ongoing demand for power integration from volatile renewables, a future coupling of biomass and power is also possible. For example, using solid oxide cells to couple the process bidirectionally with the power sector can improve the carbon conversion efficiency of one specific process [12]. Additionally, this approach can increase the capacity factor of the plant itself by offering system-serving flexibility [13,14]. Until now, EF based BtX research has often focused on single, location-specific feedstock (e.g., sugarcane [15], palm oil [16], straw [17]) or selected process routes (e.g., Fischer-Tropsch (FT) fuels [12,15,18], ethanol [19], dimethyl ether (DME) [20,21]). There is, for example, a comparison of EF and circulating fluidized bed (CFB) gasification based BtL products which focuses on comparable products [22]. Additionally, there have already been some review articles dealing with topics like biofuel production from biomass gasification in general [9], biofuel generation from livestock waste [23], or comparisons of various thermochemical ways of hydrogen production [24]. In contrast, regarding PtX products, there already exist extensive reviews on the current state of technology [10], as well as detailed technical and economical evaluations [25]. However, there is a lack of a

detailed comparison regarding various BtX products from an energetically and technical perspective. Table 1 provides a comparative summary of the literature found.

Focusing on the currently most used fossil energy carriers, its synthetic equivalents and highly-discussed alternatives, this work compares the following six possible BtX products:

- Ammonia (NH₃)
- Methanol (MeOH)
- Dimethyl ether
- Fischer-Tropsch synthetic crude (FT syncrude)
- Methane (SNG)
- Hydrogen (H₂)

As stated above, EF-based gasification enables the use of a wide range of feedstock. This paper, however, focuses on the analysis and comparison of six different products without examining the influence of feedstock variation. The scope of the study is therefore limited to the central process, starting with fuel pretreatment for the gasification process, and ending with the raw product, before any upgrades.

2. Methods, theory, and simulations

This paragraph introduces the methodology underlying the work, the model description, and the definition of the key performance indicators used. A simplified process scheme is shown in Fig. 1, whereby this study only focuses on the steps from pretreatment (torrefaction) until the synthesis step.

2.1. Feedstock and pretreatment

Biomass and biogenic residues as a carbon source differ over a wide range of characteristics, e.g., elemental composition and physical properties and enable an equally wide range of utilisation paths [4]. Compared to conventional fuels, biomasses tend to have lower energy density, higher proportions of undesirable, aggressive constituents, and are more heterogeneous [27]. As a result, especially for the use in EF gasification, extended pretreatment is required in addition to the conventional steps already being used in coal gasification, such as drying and grinding [27]. Among the most promising pretreatments are hydrothermal carbonization (HTC) and torrefaction, where in both cases the processes and application have been investigated in numerous extensive reviews [27–31].

In order to achieve a better understanding of the most important biomass characteristics relevant to the process simulation, more than 900 samples from two databases [32,33] were used to calculate mean values for the elementary composition and heating values. The subset of data used includes the categories of HTC, torrefied materials, sludge, and untreated wood, with each sample being based on actual laboratory tests. Fig. 2 provides a comparison of the main parameters needed for the simulation. A variation of these should be performed in order to form a generally valid conclusion regarding the usability of various feedstocks in the process variants examined. Given that the aim of the present work is more on a direct comparison of the routes and less on the influence of changing feedstocks, an example feedstock was used. By using untreated beech wood, as defined in Table 2, and simulating the torrefaction process, the comparison of all process routes is ensured without focusing on the feedstock impact. The theoretical background, implementation, and validation of the torrefaction process simulation used was previously described in detail by the authors in [12]. The choice of beechwood as a feedstock, as well as the torrefaction as pretreatment, is based on the existing, validated database of the model.

2.2. Oxygen supply

Oxygen must be supplied to the EF gasifier for oxyfuel gasification.

Table 1

Overview of the existing literature on biomass-to-x, power-to-x, and general gasification-based process routes for sustainable energy carriers.

Scope	Year	Reference	Methodology		Products								Gasifier type*
			Review	Process simulation	Methanol	Methane	Ammonia	FT syncrude	Hydrogen	Dimethyl ether	further fuels		
BtX	2021	[23]	X			X						X	COM
BtX	2021	[16]		(X)									NS
BtX	2020	[8]	X						X			X	NS
BtX	2020	[15]	X						X				COM
BtX	2018	[5]	X									X	NS
BtX	2018	[24]	X							X			COM
BtX	2018	[22]		X	X**			X				X	EF, CFB
BtX	2018	[26]		X				X				X	NS
BtX	2018	[17]		X	X							X	FB
BtX	2016	[4]	X		X	X		X		X		X	NS
BtX	2016	[18]	X					X					COM
BtX	2014	[6]	X				X					X	NS
BtX	2011	[19]		X								X	FB
BtX	2010	[20]		X							X		EF
GAS	2018	[9]	X		X	X	X	X		X	X	X	COM
GAS	2015	[11]	X		X	X		X			X		COM
PBtX	2021	[12]		X				X					EF
PBtX	2019	[14]	X		X	X		X					COM
PtX	2020	[10]	X		X			X			X		-
PtX	2020	[25]		X	X			X		X	X	X	-
This work				X	X	X	X	X		X	X		EF

* EF: entrained flow; FB: fluidized bed; CFB: circulating fluidized bed; NS: not specified; COM: comparison.

** As intermediate product.

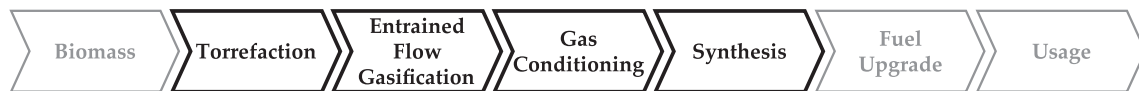


Fig. 1. Simplified process chain with all considered subsystems. Highlighted are the simulated process steps.

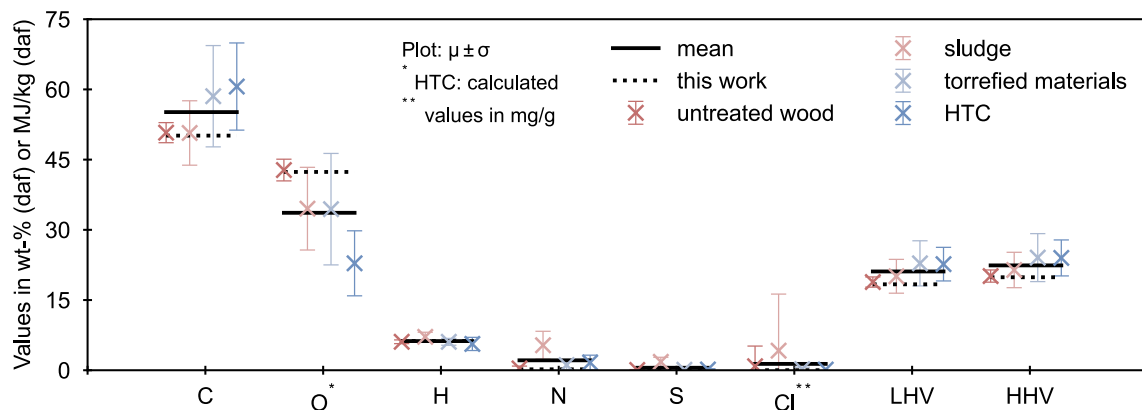


Fig. 2. Comparison of various biomass parameters for the pseudo biomass definition, based on [32,33].

Several options exist for providing the oxygen, including cryogenic air separation (ASU), (vacuum) pressure swing adsorption (PSA), ionic transfer membrane processes (ITM), and chemical looping air separation (CLAS). Currently, industrial scale oxygen production is mainly performed by ASUs, which require 0.16–0.6 kWh/kg O₂ [34,35] at a wide range of scales from 330 t/d to 30.000 t/d [35,36] and can achieve high purities of 93 %–99.8 % [35,37]. PSA can represent an attractive alternative, especially at smaller scales, but at higher specific energy consumptions of 0.2–1.1 kWh/kg O₂ [38,39]. ITM and CLAS, however, are still in their early development stages. Some laboratory tests and modelling studies have been conducted, but larger scale applications are lacking [40–45]. Given the investigated scale of the processes and the high maturity of the technology, oxygen supply by ASU is assumed for this study. Nonetheless, alternatives should be taken into account for

BtX processes at different scales and future developments in oxygen separation technologies as well as e.g. large-scale water electrolysis should be monitored closely.

2.3. Gasification

All BtX processes analyzed are based on a slagging, oxygen-blown entrained flow gasifier lies at the heart of the BtX processes analyzed. Its function is to convert the torrefied biomass into a high quality and mostly tar-free syngas consisting of mainly H₂ and CO. The gasifier model and its auxiliaries in Aspen Plus® is based on the models developed and validated by the authors for the commercially available thyssenkrupp Uhde PRENFLO® process in a previous publication and the respective supplementary information [12].

Table 2
Chemical and physical parameters of the process feedstock used.

Parameter	Unit		Value
<i>Proximate analysis</i>			
Moisture	wt-%	ar* (wet)	35.00
Fixed carbon	wt-%	dry	14.91
Volatile matter	wt-%	dry	84.21
Ash content	wt-%	dry	0.88
<i>Ultimate analysis</i>			
Ash	wt-%	dry	0.88
C	wt-%	dry	50.13
O	wt-%	dry	42.37
H	wt-%	dry	6.26
N	wt-%	dry	0.20
S	wt-%	dry	0.15
Cl	wt-%	dry	0.01
<i>Heat of combustion</i>			
LHV	MJ/kg	daf**	18.36
HHV	MJ/kg	daf**	19.87

* ar: as received.

** daf: dry ash free.

During the gasification process, the torrefied biomass feedstock is fed to the entrained flow gasifier as a finely ground powder with particle sizes below 300 μm [46]. CO_2 as a carrier agent transports the powder pneumatically into the burner of the entrained flow gasifier. In the burner, the biomass feedstock is mixed with the oxygen as the gasifying agent. A well-mixed, entrained stream of torrefied biomass powder, CO_2 as a carrier gas, and oxygen as a gasifying agent then enters the entrained flow gasifier reaction chamber to be converted into syngas. The CO_2 carrier gas is taken from the CO_2 exhaust stream at the acid gas removal stage within the gas conditioning and cleaning system for the BtX process.

A wide range of pyrolysis and gasification reactions take place in the gasification reactor [47]. The first step in the fuel conversion process is the drying and pyrolysis of the fuel particles. This is modelled as an isobaric RYield reactor which turns the biomass feedstock as a non-conventional solid into its basic constituents as conventional components. The main gasification of the fuel is then modelled through an equilibrium reactor (RGibbs), with the pyrolysis products, the CO_2 carrier gas, and the O_2 gasifying agent as inputs. 1 % of the carbon input is assumed to be inert to achieve a carbon conversion of 99 %, which is typical of entrained flow gasifiers [48]. The reactor temperature is kept steadily at 1400 $^\circ\text{C}$ by adjusting the O_2 flow rate as needed. The pressure in the reactor is set at 30 bar to minimize the need for additional compression of the syngas before the subsequent syntheses. Heat losses in the entrained flow gasifier are assumed to depend on the reactor size. For a biomass input of 100 $\text{MW}_{\text{th,LHV}}$, the model assumes heat losses of 2 % for the entrained flow gasification reactor. Subsequent to the entrained flow gasifier, a water-based quench is used to decrease the syngas temperature to 200 $^\circ\text{C}$ and to solidify the molten slag while simultaneously removing most of the particulates and some of the impurities from the syngas [12].

2.4. Gas conditioning and cleaning

After the gasification and quenching steps, the resulting product gas stream still contains a wide range of impurities which need to be removed in order to create a synthesis gas stream that can be processed by the later synthesis stages. The conditioning process entails the removal of syngas impurities in addition to the $\text{H}_2:\text{CO}$ ratio adjustment for the respective subsequent synthesis process. Addressing these issues is the responsibility of the gas conditioning and gas cleaning stage.

The major impurities which must be cleaned from the gas stream include particles, tars, and trace substances like halide compounds,

nitrogen compounds, and sulfur compounds. The failure to remove any of these components according to the respective limits of the downstream processes can cause corrosion, plugging, and fouling of downstream process equipment, as well as catalyst poisoning [46].

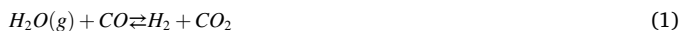
A number of gas cleaning processes can be applied to achieve the required feed gas purity levels. These can be broadly classified into hot (dry) gas cleaning processes and cold (wet) gas cleaning processes. Gas cleaning is considered to be hot gas cleaning according to VDI guideline 3677 if it operates at temperatures of 260 $^\circ\text{C}$ and above [48,49]. Table 3 presents the various treatment methods typically applied by hot and cold gas cleaning processes, whereby tars are neglected since entrained flow gasification leads to a more or less tar-free syngas [46,50].

Hot gas cleaning can achieve increased overall energy efficiencies by several percentage points due to conservation of sensible heat compared to cold gas cleaning. Hot gas cleaning, however, has very high material demands by virtue of the elevated temperatures, which can reach more than 600 $^\circ\text{C}$ for gasification applications [53]. Therefore, capital investment requirements are typically much higher for hot gas conditioning systems than for their low-temperature equivalents. Due to these reasons, hot gas cleaning has not yet become the state of the art and will require further development [46,56].

For the present research, cold gas cleaning was chosen as the main syngas cleaning method because practically all commercially available syngas cleaning methods use cold gas cleaning. The syngas conditioning and cleaning stage of the BtX processes consists of a quench and scrubber, followed by a sour water gas shift (WGS) reactor and subsequent cold acid gas removal. The quench and scrubber remove particulate matter, halides like HCl, and smaller amounts of nitrogen species. The sour WGS reactor adjusts the $\text{H}_2:\text{CO}$ ratio of the syngas in order to fit the requirements of the subsequent synthesis process by either increasing the H_2 (forward WGS) or CO (reverse WGS) content of the synthesis gas via the following reaction: [57–61].

Table 3
Overview of cold and hot gas cleaning systems for syngas conditioning.

Contaminant	Treatment method		Ref
	Cold gas cleaning	Hot gas cleaning	
Particles (e.g., dust, char, ash)	Cyclones, metal filters, moving beds, special scrubbers, fabric bag filters, electrostatic precipitators	Cyclones, metallic foam filters, candle filters	[46]
Oxygen species (e.g., O_2)	Catalytic oxidation, ad- and absorption	Catalytic oxidation, adsorption	[51]
Alkalis	Condensation and washing/leaching, adsorption (e.g., kaolinite, bauxite), getter materials	Adsorption (e.g., kaolinite, bauxite), getter materials	[52]
Halide compounds (e.g., HCl)	Wet scrubbing (e.g., amine scrubber), bag filters	Primary removal within gasifier (e.g., dolomite, limestone), secondary removal via sorbents (e.g., activated carbon, alumina, common alkali oxides, calcium-based powders)	[52,53]
<i>Nitrogen compounds</i>			
NH_3	Aqueous scrubber, absorption	Catalytic decomposition, selective oxidation	[52,54]
HCN	Hydrolysis to NH_3 , absorption	Activated carbon bed	[55]
<i>Sulfur compounds</i>			
H_2S	Absorption	Calcium sorbents, metal oxide sorbents	[46]
COS	Hydrolysis to H_2S	Activated carbon bed	[55]



The purpose of the acid gas removal process is to remove both sulfur compounds and CO₂ from the syngas. There are a wide range of industrial cold acid gas removal processes available, including physical acid gas removal processes such as Rectisol® and Selexol®, chemical acid gas removal processes such as amine scrubbing processes, and hybrid processes such as Sulfinol. Ideally, the acid gas removal process should be both cost efficient and able to separate sulfur compounds, especially H₂S and CO₂, in order to be able to make use of the respective substreams. Therefore, the Selexol® process is chosen for the BtX processes in this work. The Selexol® process uses a mixture of dimethyl ethers of polyethylene glycol with the formula CH₃O(C₂H₄O)_xCH₃, where x is between 3 and 9 [62], as solvents at pressures of 20 up to 130 bar [63] and temperatures between 0 and 40 °C [61]. Selexol® achieves lower costs than Rectisol® due to a lower number of heat exchangers and less need for refrigeration [61,63,64]. It is also more cost efficient than amine scrubbing processes like MDEA for high pressure applications typical of most syntheses in this work [61,63].

The model for the Selexol® process in this work is built on the previous works by Kapetaki, et al. [65], Field, et al. [66], and Adams, et al. [67]. In the chosen two-stage Selexol® pressure swing configuration, the acid gas removal process consists of one set of absorber and steam stripper for H₂S removal and a second set of absorber and air stripper for CO₂ removal. The Selexol® solvent is modelled as a single average molecule with a single vapor pressure curve. In the present research, the dimethyl ether of pentaethylene glycol was chosen to represent Selexol as it is the heaviest available dimethyl ether of polyethylene glycol in Aspen Plus®. The solubilities of H₂S and CO₂ in Selexol® have been validated by Kapetaki, et al. [65] using literature-based experimental data. The respective Henry constants were used with the PR-BM property method, which relies upon the Peng Robinson cubic equation of state with the Boston-Mathias alpha function for estimating thermodynamic properties.

2.5. Synthesis routes

The following section serves both to motivate the selection of the process routes considered and to present the respective processes, operating conditions, kinetics, and implementation in the model. The modelling of the various routes differs only with respect to three aspects: First, in the H₂:CO ratio after the gas conditioning, second in the synthesis section, and third regarding possible heat integration between the various process steps from feedstock pretreatment to syntheses. However, the six process variants only need three different H₂:CO ratios, which are adjusted via the WGS reactor. MeOH, DME, and FT were modelled at a ratio of 2.1/1, methanation at a ratio of 3/1, and the two H₂ variants and NH₃ at a ratio of 17.6. Regarding the heat integration, heat exchangers were used in all models to the extent possible and reasonable in order to minimize the demand for heat supply and removal. This includes heat optimization within the individual subsystems as well as exchanges between the subsystems, e.g., the use of waste heat for the WGS reaction.

2.5.1. Hydrogen

Today, most of the hydrogen (H₂) quantities produced are used for synthesis (e.g., ammonia or methanol) or hydrotreating processes [68]. New developments, e.g., the German national hydrogen initiative, which specifies green H₂ as being one of the most important energy carriers for the energy transition, indicate an increase in demand as well as new production and utilization paths [69]. Nevertheless, the H₂ currently being used for industrial purposes is mainly produced by catalytic reforming of hydrocarbon, especially NG [70]. Given the high power demand per mole of H₂ in the case of water electrolysis, it is not yet economically viable, but this will change in consideration of the greenhouse gas (GHG) reduction targets [69,70]. Furthermore,

hydrogen is being politically promoted as the energy carrier of the future in several countries, with all topics from production and storage to transport and various applications being discussed [71].

2.5.1.1. Model description. In order to obtain hydrogen with a high yield, the synthesis stream at the outlet of the WGS reactor is set to an H₂:CO ratio of 17.59, corresponding to a conversion rate of 92.2 %. Pressure swing adsorption (PSA) is used to purify the hydrogen stream. The target value is the purity specified in DIN EN 17124 for use in mobile fuel cells. With a purity of 99.97 vol% a yield of 80 %, H₂ recovery is assumed according to [72]. Due to the already high pressure from the gas treatment, the PSA does not require any further pressure increase before the adsorption process.

In addition, to the pure H₂ variant a net negative carbon emissions variant is evaluated, since the highest shift towards H₂ leads to the highest CO₂ emissions. By adding a carbon capture unit to the process scheme, the biogenic H₂ can be used with reduced CO₂ emissions. This variant will be referred to as “Hydrogen with Carbon Capture and Storage” (H₂CCS) in the following sections. The capture process itself is already part of the gas conditioning but is extended by a multistage CO₂ compression unit reaching 150 bar in order to address the additional energy and intermediate cooling needed before transportation and storage. The impurity removal additionally required to avoid, e.g. corrosion in pipelines, is disregarded.

2.5.2. Synthetic natural gas

Given its low greenhouse gas (GHG) emissions, natural gas (NG) is considered to be the last fossil fuel during the energy transition into a 100 % renewable energy system [73]. Its current use spreads from power and heat generation to industrial applications. Since power and heat supply tend to be largely covered by renewable sources like solar and wind, a switch to other use cases, e.g. long-term storage, is expected [73]. Since it consists mainly of methane, synthetic natural gas (SNG) is already being produced from a variety of feedstock (fossil, biomass, waste/residues) and process pathways (thermo- and biochemical), as well as solely power-based routes from CO₂ and H₂ (Power-to-SNG) [74].

2.5.2.1. Model description. The TREMP process by Haldor Topsoe is the methanation process chosen, due to its high technology readiness and large-scale application [75]. This process comprises three adiabatic fixed bed reactors which are modelled as equilibrium reactors (RGibbs) in Aspen Plus®. The product gases leave the reactors at different temperatures of 584 °C, 443 °C, and 262 °C. The syngas is first preheated and mixed with the recycle stream. They then enter the first reactor, where the largest amount of H₂ and CO₂ is converted. The product gases leaving the reactor are cooled and split into a recycle stream and the feedstream for the second reactor at a ratio of 85 % to 15 %. The product gases are again cooled after reactor two before entering the final reactor three, where sufficient conversion is reached to achieve an SNG quality that would allow the supply into the gas grid (H-gas quality). For this purpose, the final product is cooled to the standard temperature of 25 °C, and condensed water is separated as a liquid from the SNG gas stream.

2.5.3. Methanol

Methanol (MeOH) is mainly used for chemical synthesis like formaldehyde or acetic acid, although a growing market exists for it as a fuel additive or a precursor for biodiesel and DME synthesis [76]. Currently, it is more or less solely synthesized via the catalytic conversion of syngas [76]. Whereas the majority of syngas currently comes from NG reforming, there is a trend toward coal gasification, especially in China, and research is continuing on syngas from carbon capture CO₂ and electrolysis H₂ [10]. Since the synthesis itself is based on syngas, the process does not differ by changing the carbon source from NG/coal to biomass (apart from the previously discussed gas cleaning and

conditioning).

2.5.3.1. Model description. The methanol synthesis is operated at elevated pressures of 65 bar. Consequently, the syngas is first compressed and then mixed with the recycle stream. Afterwards, the gases are preheated to 235 °C before entering the methanol reactor. The reactor is modelled as a tube bundle reactor (RPlug). The kinetic model of Mignard and Pritchard [77] was implemented to describe the methanol formation process. The kinetic model does not consider by-product formation. Afterwards, the product gases are cooled and methanol as well as water is condensed and separated from the recycle gases. One percent of the recycle gases is purged to avoid the accumulation of inert species in the recycle loop. The pressure of the liquid phase is further reduced in order to remove dissolved gases. The raw methanol then enters the distillation column, which consists of 21 stages, on stage 16 and water is removed. Methanol with a purity fulfilling Grade A specifications is then obtained at the head of the column.

2.5.4. Dimethyl ether

DME is currently mainly used as a propellant in sprays or as a base chemical in further synthesis. Given its similarity to liquified petroleum gas (LPG), it is being discussed as a fuel substitute for gasoline and diesel fuels. The state-of-the-art DME production is based on the dimerization of methanol. [78]

2.5.4.1. Model description. A process using the direct conversion of syngas to DME chosen for the DME synthesis [79]. The reactor is modelled as a tubular flow reactor (RPlug) operated at 260 °C and 50 bar. The formation of methanol and DME within the reactor is described by the kinetic model proposed by Kiendl [80], along with adapted equilibrium constants from Ratamanalaya [81]. The preheated syngas enters the reactor and, after conversion, the product gases are cooled down before entering the absorption column. Within the absorption column, a methanol–water stream is used to absorb methanol, DME, and water from the feedstream. The remaining gases are recycled. The liquid stream is relaxed and further cooled before entering the CO₂ column. Given the similar boiling points of CO₂ and DME, cryogenic conditions are necessary at the top of the column. The separated CO₂ is recompressed and recycled. The bottom product is further cooled before entering the DME column, where DME with a purity over 99 % can be obtained at the top. The bottom products are led to the third and final column, where water and methanol are separated and the purified methanol is recycled to improve carbon conversion.

2.5.5. Fischer-Tropsch synthetic crude

The conventional equivalent to FT synthesis products are crude oil/petroleum constituents as the gasoline-, kerosene- and diesel-fraction, as well as waxes, naphtha, and further heavy components in which the fuel part covers about 90 % of current usage [82]. Due to their almost identical composition, FT fuels are considered to be a direct substitute for the crude-based fuels currently in use. Based on natural gas or coal, FT synthesis has been used for quite some time to produce, e.g., gasoline, diesel, kerosene, and waxes [10]. As a basis for the comparison being presented, all liquid fractions of the FT syncrude will be considered as products in the following evaluations.

2.5.5.1. Model description. The FT synthesis is designed as a low-pressure synthesis at 220 °C and 25 bar. The FT reactor itself is modelled as an isobaric and isothermal RYield reactor. To account for the complex kinetics of the process, the kinetic model is implemented in a separate Python module, which is integrated into the Aspen Plus® model via a FORTRAN subroutine. Finally, the reactor outlet stream is split via a Flash3 separator. The gas phase, mainly unreacted H₂ and CO, as well as further components up to C₄, is fed back to the FT reactor via a steam reformer to increase the yield of liquid FT products. The reformer

is implemented as a REquil module and operated at a steam-to-carbon ratio of 3. A detailed description of the FT model has been published by the authors in the supplementary information of [12].

2.5.6. Ammonia

Ammonia is one of the most important synthetic chemical products. It is mainly used for the production of fertilizers [83]. Currently, it is estimated that ammonia production is responsible for 1–2 % of global energy consumption and 1.6 % of global CO₂ emissions. Over 90 % of the world consumption is still being produced via the Haber-Bosch process, in which nitrogen and hydrogen are converted using an iron catalyst [84]. NG is the main feedstock for the conventional synthesis process due to higher energy efficiency and lower investment cost than other hydrocarbon sources, e.g., naphtha, fuel oil, or coal. Nitrogen is usually supplied from ASU. More recently, the sustainable production of “green ammonia” has been investigated. Green ammonia can be derived from biomass as well as renewable power via water electrolysis [85].

2.5.6.1. Model description. Regarding the ammonia production, it is assumed that the hydrogen outlet of the H₂CCS process is mixed with nitrogen and used as a feedstream for the ammonia synthesis loop. After compression to the operating pressure of 150 bar, the feed is mixed with the recycle gases and preheated before the gases enter the reactor. An indirectly cooled converter is assumed as reactor, with three adiabatic plug flow reactors and intermediary coolers. The product gases are cooled down in several steps to cryogenic conditions of –20 °C (achieved by cooling with liquid ammonia) and liquid ammonia is separated from the unreacted gases. These are recycled, and 1.5 % of the gases are purged to avoid accumulation of inert species (i.e., argon and methane). The kinetic model proposed by Tripodi, et al. [86] is used to describe the reaction and adapted to fit the LHHW form necessary for implementation in Aspen Plus®.

2.6. Key performance indicators

Several key performance indicators (KPI) are defined to evaluate the BtX routes on energetical and technical bases. Table 4 provides an overview of all the KPIs used, and a subsequent detailed definition of each KPI follows.

The KPI definitions are based on Patterson’s recommendations, which state the need for different reference values regarding efficiencies, depending on the application [87]. Thus, purely energetic and exergetic, as well as efficiencies based on physical values, are used.

Based on the lower heating value (LHV) of the fuels used and the synthesis products, respectively, the energy yield (EY) can be calculated as the ratio of outgoing and incoming energy flows (Equation (2)).

$$EY = \frac{\dot{E}_{product}}{\dot{E}_{fuel}} = \frac{\dot{m}_{product} LHV_{product}}{\dot{m}_{fuel} LHV_{fuel}} \quad (2)$$

Table 4

Overview of all key performance indicators used.

KPI	Unit	Definition
\dot{m}_{prod}	$t_{prod} h^{-1}$	Product mass flow
LHV	MJ kg ⁻¹	Lower heating value
EY	–	Energy yield
P_{aux}	MW	Energy demand for auxiliaries
$\Delta\dot{Q}_t$	MW	Heat flow balance
UHF	kW MW ⁻¹	Usable heat per feedstock
CCE	–	Carbon conversion efficiency
HCE	–	Hydrogen conversion efficiency
\dot{m}_{CO_2}	$t_{CO_2} h^{-1}$	CO ₂ emissions
$\dot{m}_{CO_2,spec}$	kg _{CO₂} kg _{prod} ⁻¹	Specific CO ₂ emissions
\dot{m}_{H_2O}	$t_{H_2O} h^{-1}$	Water balance
$\dot{m}_{H_2O,spec}$	kg _{H₂O} kg _{prod} ⁻¹	Water balance
H ₂ : CO	–	H ₂ to CO ratio in syngas stream

where \dot{m}_i is the indicated mass flow and LHV_i is the indicated lower heating value.

As in future energy systems, the focus will be more on the degree of feedstock utilization, but less on the power-driven auxiliaries, so the EY is used instead of an all-inclusive efficiency. Further KPIs are used to account for all of the additional energy demand and losses. P_{aux} can be used to discuss all additional needed incoming energy demands, including the energy demand for sub-ambient cooling.

The usable heat per feedstock (UHF) gives the amount of excess heat, capable for work, per feedstock. As defined in Equation (3), it weights the heat losses of the system by means of its workability. In this case the chemical, kinetic, and potential exergy is disregarded.

$$UHF = \frac{\dot{E}x_{ph,out}}{\dot{E}_{fuel}} \quad (3)$$

The outgoing physical exergy $Ex_{ph,out}$ can be calculated by the product of the respective mass flow \dot{m} with its enthalpy and entropy difference, with 0 indicating the ground state (Equation (5)). All streams above ambient temperature are considered.

$$\dot{E}x_{ph} = \dot{m}[(h - h_0) - T_0(s - s_0)] \quad (4)$$

To evaluate the head demand, the heat balance $\Delta\dot{Q}_i$ is defined as the difference of incoming and outgoing heat (Equation (5)), where \dot{Q}_in can be interpreted as heating and \dot{Q}_out as cooling demands.

$$\Delta\dot{Q} = \sum \dot{Q}_{in} - \sum \dot{Q}_{out} \quad (5)$$

With respect to the goal of reducing CO_2 emissions, the carbon conversion efficiency (CCE) should be maximized in most cases. The CCE is defined as the ratio of the fuels carbon content $n_{C,fuel}$ compared to the products carbon content $n_{C,product}$ according to Equation (6).

$$CCE = \frac{n_{C,product}}{n_{C,fuel}} \quad (6)$$

Directly related to the CCE are the total systems CO_2 emissions (\dot{m}_{CO_2}). These are simply defined as the sum of all outgoing CO_2 streams (Equation (7)), without taking into account additional GHG emitters like fuel transportation, plant construction, etc.

$$\dot{m}_{CO_2} = \sum \dot{m}_{CO_2,out} \quad (7)$$

Likewise, the hydrogen conversion efficiency (HCE) and the overall system water demand (\dot{m}_{H_2O}) are calculated as in Equation (8) and Equation (9), respectively.

$$HCE = \frac{n_{H,product}}{n_{H,fuel}} \quad (8)$$

$$\dot{m}_{H_2O} = \sum \dot{m}_{H_2O,out} \quad (9)$$

Both the overall water balance and the overall CO_2 emissions are additionally calculated as specific emissions per product, indicated by the index “spec”. As a final KPI, the pre-synthesis H_2 to CO ratio needed is also given for the final evaluation.

3. Results and discussion

The KPIs are calculated as described, based on the process simulation results, whereby the following discussion is separated into energetical and material flows.

3.1. Energy efficiency

Fig. 3 summarizes the energetic results of the process simulations. The energy yield is in a range of 40 % for FT to 60 % for DME. Overall, the selective synthesis processes (SNG, MeOH, DME) achieve similar energy yields while the non-selective FT process shows the lowest yield which is partly caused by the low selectivity towards the desired product fraction- NH_3 as the only nitrogen-based product shows a similar low yield as FT fuels, which comes from the requirements for additional nitrogen and the fact that only the hydrogen within the biomass is used. Additionally, as can be seen in Fig. 3 (A), the energy demand for auxiliaries is similar for all products, ranging between 8.3 kW MW^{-1} and 10.2 kW MW^{-1} , besides NH_3 , which peaks at 23.4 kW MW^{-1} . The higher synthesis pressure accounts for roughly 27 % of the additional energy demands. The rest is used for the sub-ambient cooling in the purification step. Since the examined processes are intended for future, 100 % renewable energy systems, it is assumed that the electricity supply will be completely from renewable energies. Therefore, there is no influence on the CO_2 emissions in the following evaluations.

Regarding Fig. 3 (B) one can observe that for all products excess heat is available. However, the UHF shows that the usable amount of this excess heat can be drastically lower. FT synthesis offers the highest amount of excess heat and has the highest UHF of 211.3 kW MW^{-1} . SNG shows relatively low excess heat but has the second highest UHF of 164.6 kW MW^{-1} . In comparison, the hydrogen production, which has a similar high heat balance, provides a much lower UHF of only 84.9 kW MW^{-1} . This shows clearly that the exergetic value of the heat must be considered when comparing different synthesis products. Similar to SNG, DME needs similar cooling as MeOH and H_2/H_2CCS , but offers much higher UHF . The difference between DME and MeOH to some extent is caused by the higher heat demand of the MeOH purification.

In summary, the low energy yield but high UHF indicate that FT fuels are not the most beneficial products from an energetic perspective, but offers the biggest possibilities for coupled processes. Additional to the

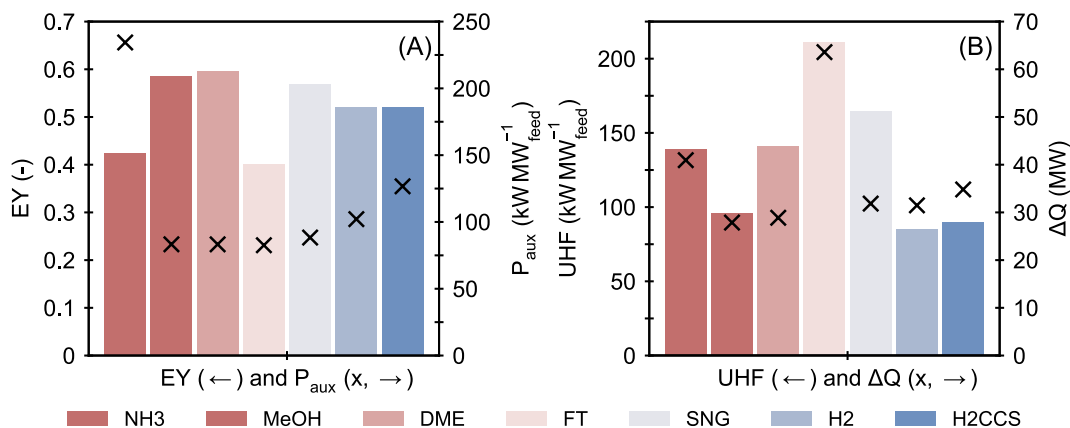


Fig. 3. Comparison of the energy efficiency and energy yield (A) and usable heat per feedstock and heat balance (B) of all considered biomass-to-x routes.

energetical benefits, all the not considered light ends of the FT synthesis can also be of high interest in various further applications. Selective hydrocarbon products seem more promising and show similar efficiencies. The higher potential for heat utilization with regard to DME and SNG might play a role in the product selection, however, it highly depends on the specific projects' conditions and if a suitable heat sink exists at the project location.

3.2. Conversion yield

Fig. 4 shows the relative elementary compositions of the feedstock, syngas variants and all products. From feedstock pretreatment over gasification and quench, the hydrogen and oxygen shares increase due to oxygen input in the gasification step and hydrogen and oxygen input during the raw gas quench. The hydrogen to carbon ratio is adjusted via the water gas shift reactor and the gas cleaning system to match the required subsequent syntheses.

3.2.1. Carbon balance

Effective carbon conversion is essential for high product yields and the minimization of GHG emissions. To give a better sense of where carbon losses occur within the BtX process chains, Fig. 5 shows Sankey diagrams of the carbon flow for the processes having the highest carbon utilization in the sense of carbon capture (H_2 CCS in Fig. 5 (A)) and the lowest CCE (SNG in Fig. 5 (B)), normalized to the carbon input in the feedstock. The values are taken from the Aspen Plus® process simulations, using the carbon content parameter of the respective streams. Due to the use of rounded values in the graphics, the total sum deviates from 100 % in some cases. Since the process chain does not differ at the beginning, both routes exhibited similar losses before the gas cleaning process. A non-negligible amount of carbon is lost during pretreatment as exhaust gases. In comparison, the carbon lost during gasification in the slag plays a minor role. Given that purification of the purge gas is difficult during the synthesis by means of recirculation (e.g., MeOH or FT), the combustion of this gas fraction is assumed, which represents a non-negligible portion of the emissions.

The gas cleaning process is adapted to the downstream synthesis processes or, in the case of H_2 CCS, the lack thereof. As a consequence, the gas cleaning process is one of the main influencing factors determining the CCE. For H_2 CCS, the majority of CO is converted into CO_2 during the WGS step to maximize the hydrogen yield of the route. As intended for CCS, doing so made it possible for a large fraction of the carbon in the feedstock to be removed afterwards as CO_2 in the Selexol

wash. A PSA is used to remove remaining CO_2 impurities in the H_2 . In comparison, it can be seen that the higher CO_2 content in the syngas also results in larger unwanted carbon losses in the Claus process for H_2 CCS. This is one of the main reasons that even H_2 CCS is unable to achieve zero GHG emissions.

In the case of SNG, a syngas with a $H_2:CO$ ratio close to 3 is desired. In comparison to all other considered hydrocarbon products this is the highest required $H_2:CO$ ratio which results in a larger fraction of CO in the syngas that needs to be shifted in the WGS step to achieve this ratio. This explains why such a large amount of carbon is lost as CO_2 during the gas cleaning step, and why the SNG route results in such a low CCE. This also illustrates the limitation of BtX routes with respect to carbon conversion. The high C to H ratio in the biomass feedstock discussed in section 0 always requires that large portions of the carbon be removed as CO_2 before the synthesis step. This limitation can be circumvented to some degree by focusing on products with low H to C ratios, or a total conversion is possible by introducing additional hydrogen somewhere along the process chain.

3.2.2. Hydrogen balance

Similar to the carbon balance, a hydrogen balance is shown in Fig. 6 (A) and (B) for H_2 CCS and SNG, respectively. As can be seen for both routes, the addition of water in the quench as well as in the WGS and AGR plays a significant role in the hydrogen balance. A large fraction of the hydrogen available in the syngas is formed during the quenching of the hot product gases from gasification. The AGR process, however, has no significant effect on the hydrogen balance. In contrast, the share of hydrogen lost during the WGS process in the form of water depends on the desired syngas composition. The more CO is shifted in the WGS step to CO_2 , the less H_2 is lost as water.

Considering the HCE in Fig. 6 (B), however, it can be seen that the H_2 losses during the WGS process do not determine the HCE. For example, SNG still achieves a lower HCE than MeOH, even if a larger fraction of the CO in the syngas must be shifted to achieve the required $H_2:CO$ ratio.

An additional water supply was necessary only for the product routes in which no carbon utilization exists. For all other routes, a positive water balance is achieved. Given that most hydrogen losses occur in the form of water, a lower HCE results in greater net water production (see Fig. 6 (B)).

Fig. 7 (A) shows the specific CO_2 emissions and CCE for all of the processes considered. As expected, a higher CCE is directly related to lower CO_2 emissions. CCE cannot be applied to H_2 CCS and NH_3 because the CO_2 is captured but is not used for any specific application. By scaling the CO_2 emissions on the product stream, NH_3 nevertheless has the lowest specific CO_2 emissions. In contrast, due to the low specific mass of H_2 , H_2 CCS (even with the high carbon capture rate) has non-negligibly high specific CO_2 emissions. However, a direct comparison to the other product routes is only valid if both are considered "negative-emission" technologies, with the removal of atmospheric CO_2 being seen as part of the goal. Considering that renewable carbon sources might become highly valuable in the mid- or long-term, this might become a major downside of both routes. Whereas the specific CO_2 emissions of MeOH and DME are lower than those of FT and SNG, the absolute process emissions are more or less the same (Table 5), something which must be considered for the overall plant design.

Looking at the overall water balances and HCE (Fig. 7 (B)), FT, SNG, and DME exhibits an overall water surplus. The hydrogen supplied in the quench water is not completely utilized in the product formation and is thus discharged as waste water. The H_2/H_2 CCS and NH_3 routes instead depend largely on the additional water integration to maximize the product yield. Consequently, the defining characteristic of these processes can be described as biomass-assisted thermal water decomposition. As expected, the HCE for the two H_2 routes and NH_3 , at over 0.6, is thus higher than for the carbon-based pathways. Despite the higher $H_2:CO$ ratio of the synthesis gas in the SNG route, the HCE is significantly higher for MeOH. FT exhibits the lowest HCE, which is due to both the

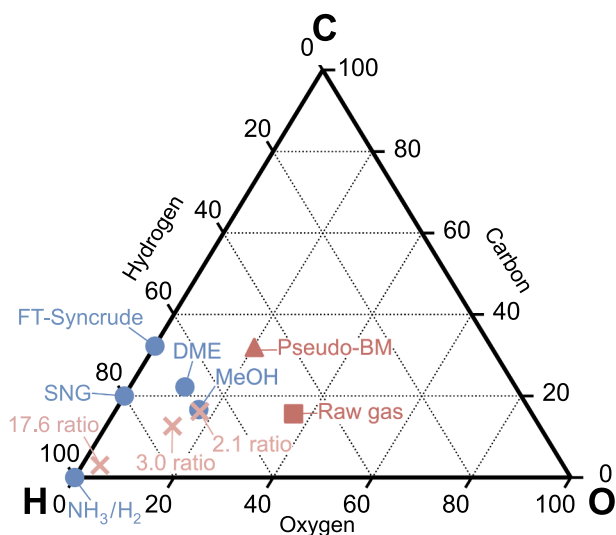


Fig. 4. Ternary diagram, presenting the molar ratio between H, C and O in the feedstock, raw gas, syngas variants and all products.

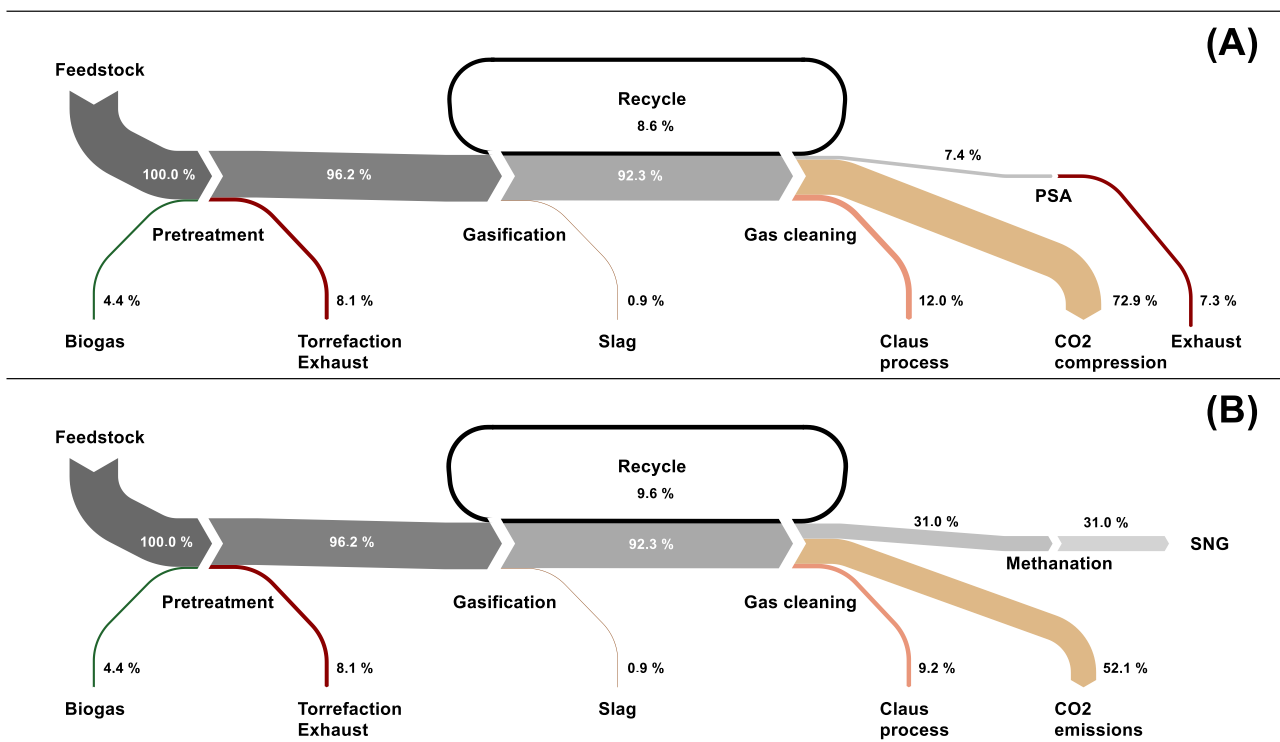


Fig. 5. Carbon balance of biomass-to-H₂CCS and biomass-to-SNG as a Sankey diagram. Recycles during the process step are disregarded.

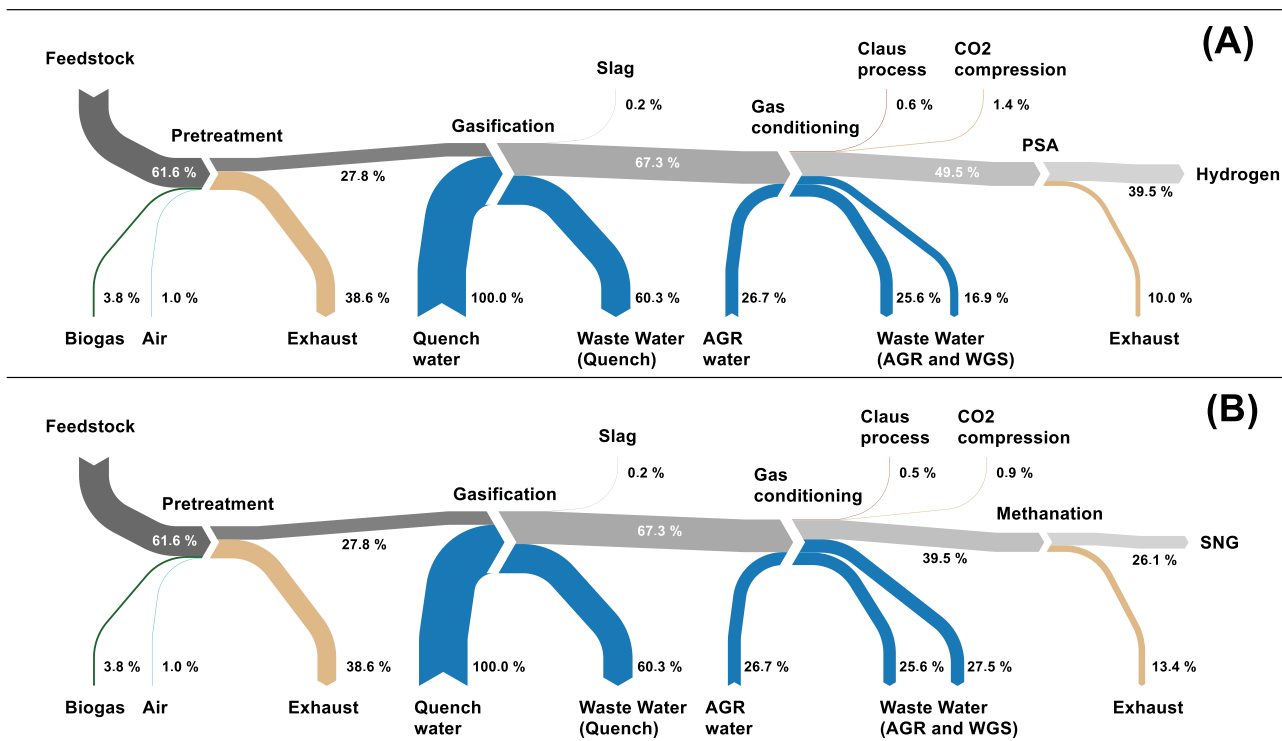


Fig. 6. Hydrogen balance of biomass-to-H₂CCS and biomass-to-SNG as a Sankey diagram. Recycles during the process step are disregarded.

restriction to liquid products and the decreasing hydrogen content in the product with increasing C-chain length.

3.3. Discussion

As seen in the previous sections and as summarized in Table 5, the

energy and material-based KPIs do not necessarily correlate. A high energy yield does not automatically equate to high HCE or CCE, and vice versa. For future applications, the feedstock value in the overarching system must be included. Depending on the higher-level energy system, hydrogen, carbon, or energy in the form of electricity or heat may be the most expensive commodity. In terms of the energy balance, for example,

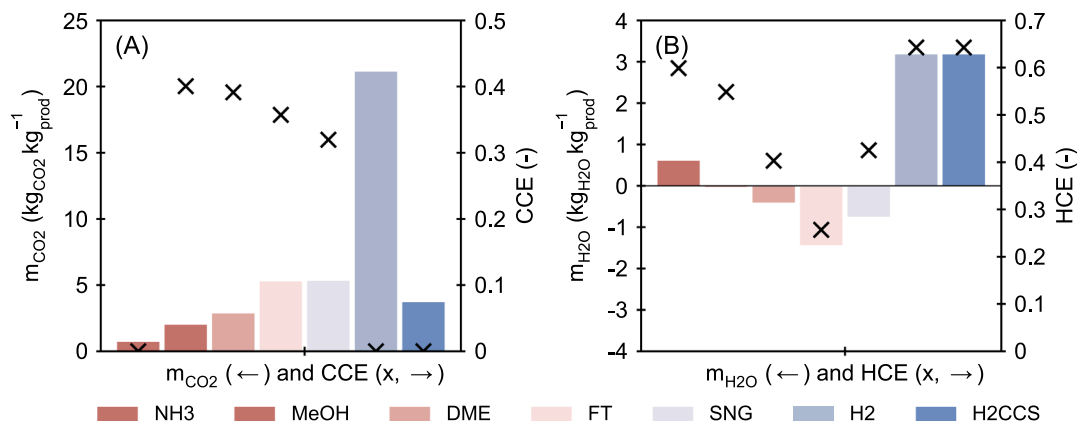


Fig. 7. Comparison of the carbon balance and carbon conversion efficiency (A) and water balance and hydrogen conversion efficiency (B) of all considered biomass-to-x routes.

Table 5

Summary of the simulation boundary conditions and the technical and energetical key performance indicators of all Biomass-to-X routes evaluated, based on 100 MW feedstock input.

KPI	Unit	NH ₃	MeOH	DME	FT	SNG	H ₂	H ₂ CCS
LHV	MJ kg ⁻¹	18.55	19.83	28.73	34.52	45.20	119.43	119.43
\dot{m}_{prod}	t _{prod} h ⁻¹	8.23	10.63	7.47	4.18	4.54	1.57	1.57
EY	-	0.42	0.59	0.60	0.40	0.57	0.52	0.52
P _{aux}	MW	23.44	8.33	8.32	8.26	8.83	10.21	12.67
ΔQ _i	MW	40.95	27.87	28.88	63.60	31.85	31.48	34.81
UHF	kW MW ⁻¹	138.96	96.17	141.03	211.30	164.58	84.90	89.66
CCE	-	-	0.40	0.39	0.36	0.32	-	-
HCE	-	0.60	0.55	0.40	0.26	0.43	0.64	0.64
\dot{m}_{CO_2}	t _{CO₂} h ⁻¹	5.81	21.32	21.31	22.04	24.14	33.14	5.81
\dot{m}_{H_2O}	t _{H₂O} h ⁻¹	4.99	-0.23	-3.01	-5.99	-3.37	4.99	4.99
H ₂ : CO	-	17.57	2.10	2.10	2.10	3.00	17.57	17.57

it is the search for a maximum energy yield with a simultaneous minimum P_{aux} and high UHF per dissipated heat. Such a combination would mean that most of the energy would end up in the product, and the unavoidable waste heat would accumulate at high temperatures and thus be further usable. In contrast, an energy system with a high potential for electricity from renewables would value carbon and hydrogen more highly. In this case, P_{aux} in the form of electricity would be less important, and the focus would be primarily on CCE and HCE.

From a hydrogen point of view, the HCE of MeOH is much higher for MeOH than DME, which is due to the water formation during the DME reaction causing hydrogen losses. Similarly, MeOH has a higher CCE than DME, which is caused by the carbon losses during DME synthesis due to MeOH byproduct formation. If all carbon species are considered, the overall carbon conversion is higher for DME. Whereas SNG, like MeOH and DME, has a high EY and relatively low P_{aux} , the CCE is much lower due to the needed further shift to a higher H₂:CO ratio.

Looking at the hydrogen supply via biomass gasification, only routes combined with carbon capture seem reasonable. However, with a possible future energy system, built on large water electrolysis capacities, this application will no longer be economically feasible. As a result, utilization of biomass-based carbon will be the main aim of gasification systems if no negative emissions are required. On the other hand, the synthesis of NH₃ might still fulfill a field of application for reducing the net emissions of agriculture by offering net negative fertilizers. Additionally, given that the gasification agent in this study is pure oxygen, the oxygen and nitrogen demand can provide a useful dual application for air separation units as an alternative to water electrolysis. However, this needs to be evaluated because the actual future costs for hydrogen, oxygen, and nitrogen cannot currently be estimated. Nevertheless, different kinds of oxygen supply should be taken into account in further studies. The same goes for the direct integration of renewable electrical

power from photovoltaics or wind turbines. As shown in the introduction, a variety of concepts exist for power integration into biomass-to-x processes, which in most cases tend to maximize carbon conversion efficiency. By using water electrolysis, hydrogen can be mixed to the syngas reducing the carbon losses during the water gas shift. Simultaneously, the oxygen provided by the electrolysis can replace the demand for additional air separation units.

One reason for the specific highlighting of UHF and the heat balance is the increasing demand for grid-supported heat supply. Even if individual processes do not have the highest yields in terms of energy or hydrogen/carbon, in individual cases with biogenic residue potential and specific energy carrier requirements, the connection to district heating networks can already bring economic viability. Thus, heat balances of large thermal plants should always be considered in technical and energetical evaluations.

Despite the maximally similar methodology regarding the modelling of the individual process steps, the present evaluation is of course also subject to limitations. First of all, different feedstocks are better suited for individual products, due to their elemental composition. Depending on the feedstock, the required pretreatment also changes, or even a different gasifier concept becomes more attractive. Thus, the focus on only one pretreatment, gasification, and gas conditioning alternative limits the results to the respective plant configuration. In the case of FT synthesis, only liquid products are currently being considered. In reality, such a system integrated into a large chemistry park could probably sell all of the synthesis fractions profitably. Regarding the routes with carbon capture, either storage systems or the utilization of the pure CO₂ stream must be considered in the future. As mentioned before, the carbon stream in a future energy system can be of high value. Finally, an economic evaluation is lacking, as is the inclusion of superordinate system boundary conditions. Without the customer market and

political/societal requirements, no decision can be made regarding the application of one or the other route purely on an energetical and technical evaluation.

4. Conclusion

This research conducted an energetic and technical comparison of six of the most promising BtX routes, based on EF gasification. Detailed process simulations of the routes in Aspen Plus® were created in order to determine the most important KPIs for each route.

From an energetic perspective, the results show that the selective syntheses (SNG, MeOH, DME) achieve similar EY, whereas the non-selective FT route performs worse. Additionally, considering the high amount of usable heat for the FT route, an integration into existing infrastructure where light ends can also be utilized appears to be the most promising option for this route. Further, in locations where heat supply is advantageous, the SNG and DME routes could be seen as the obvious choice. Considering the high value of biogenic carbon in future energy systems, BtX routes that do not utilize the carbon (NH₃, H₂CCS) only represent a solution in the short and medium term as a carbon negative technology. Instead, the future provision of additional hydrogen, e.g. from water electrolysis, might be worth investigating in order to improve carbon conversion. This is true for SNG in particular because the higher required H₂:CO ratio leads to a lower CCE. Regarding the hydrogen balance, the analysis demonstrates the significant influence of quench water on the overall hydrogen utilization. In the case of pure hydrogen production, it even becomes one of the major contributors to the overall product stream.

Overall, no single, optimal BtX route exists. Instead the KPIs demonstrate that each route has different characteristics, making it more suitable in one circumstance and less suitable in another. Therefore, the KPIs determined herein must be considered together with project- and location-specific requirements as well as the market outlook for the product. Therefore, further research will be necessary on the economics of the BtX routes and their market potential.

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CRediT authorship contribution statement

Andreas Hanel: Methodology, Software, Validation, Visualization, Writing – original draft. **Vincent Dieterich:** Methodology, Software, Validation, Writing – original draft. **Sebastian Bastek:** Validation, Visualization, Writing – original draft. **Hartmut Spliethoff:** Funding acquisition, Supervision, Project administration. **Sebastian Fendt:** Conceptualization, Project administration, Supervision.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data availability

Data will be made available on request.

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References

- Ueckerdt F, Bauer C, Dirnmaier A, Everall J, Sacchi R, Luderer G. Potential and risks of hydrogen-based e-fuels in climate change mitigation. *Nat Clim Chang* 2021; 11(5):384–93. <https://doi.org/10.1038/s41558-021-01032-7>.
- Jones MP, Krexner T, Bismarck A. Repurposing Fischer-Tropsch and natural gas as bridging technologies for the energy revolution. *Energy Convers Manage* 2022;267: 115882. <https://doi.org/10.1016/j.enconman.2022.115882>.
- Hahn A, Szarka N, Thrän D. German Energy and Decarbonization Scenarios: “Blind Spots” With Respect to Biomass-Based Carbon Removal Options. *Front Energy Res* 2020;8. <https://doi.org/10.3389/fenrg.2020.00130>.
- Guo M, Song W, Buhain J. Bioenergy and biofuels: History, status, and perspective. *Renew Sustain Energy Rev* 2015;42:712–25. <https://doi.org/10.1016/j.rser.2014.10.013>.
- Ahorsu R, Medina F, Constanti M. Significance and Challenges of Biomass as a Suitable Feedstock for Bioenergy and Biochemical Production: A Review. *Energies* 2018;11(12):3366. <https://doi.org/10.3390/en11123366>.
- Müller-Langer F, Majer S, O’Keefe S. Benchmarking biofuels—a comparison of technical, economic and environmental indicators. *Energy Sustain Soc* 2014;4(1). <https://doi.org/10.1186/s13705-014-0020-x>.
- Sansaniwal SK, Pal K, Rosen MA, Tyagi SK. Recent advances in the development of biomass gasification technology: A comprehensive review. *Renew Sustain Energy Rev* 2017;72:363–84. <https://doi.org/10.1016/j.rser.2017.01.038>.
- Witcover J, Williams RB. Comparison of “Advanced” biofuel cost estimates: Trends during rollout of low carbon fuel policies. *Transport Res Part D: Trans Environ* 2020;79:102211. <https://doi.org/10.1016/j.trd.2019.102211>.
- Molino A, Larocca V, Chianese S, Musmarra D. Biofuels Production by Biomass Gasification: A Review. *Energies* 2018;11(4):1–31. <https://doi.org/10.3390/en11040811>.
- Dieterich V, Buttler A, Hanel A, Spliethoff H, Fendt S. Power-to-liquid via synthesis of methanol, DME or Fischer-Tropsch-fuels: a review. *Energy Environ Sci* 2020. <https://doi.org/10.1039/D0EE01187H>.
- Heidenreich S, Foscolo PU. New concepts in biomass gasification. *Prog Energy Combust Sci* 2015;46:72–95. <https://doi.org/10.1016/j.pecs.2014.06.002>.
- Dossow M, Dieterich V, Hanel A, Spliethoff H, Fendt S. Improving carbon efficiency for an advanced Biomass-to-Liquid process using hydrogen and oxygen from electrolysis. *Renew Sustain Energy Rev* 2021; 152. Doi: 10.1016/j.rser.2021.111670.
- Sigurjonsson HÆ, Clausen LR. Solution for the future smart energy system: A polygeneration plant based on reversible solid oxide cells and biomass gasification producing either electrofuel or power. *Appl Energy* 2018;216:323–37. <https://doi.org/10.1016/j.apenergy.2018.02.124>.
- Schulzke T. Biomass gasification: conversion of forest residues into heat, electricity and base chemicals. *Chem Pap* 2019;73(8):1833–52. <https://doi.org/10.1007/s11696-019-00801-1>.
- Neves RC, Klein BC, Da Silva RJ, Rezende MCAF, Funke A, Olivarez-Gómez E, et al. A vision on biomass-to-liquids (BTL) thermochemical routes in integrated sugarcane biorefineries for biojet fuel production. *Renew Sustain Energy Rev* 2020; 119:109607. <https://doi.org/10.1016/j.rser.2019.109607>.
- Julio AAV, Batlle EAO, Trindade AB, Nebra SA, Reyes AMM, Palacio JCE. Energy, exergy, exergoeconomic, and environmental assessment of different technologies in the production of bio-jet fuel by palm oil biorefineries. *Energy Convers Manage* 2021;243:114393. <https://doi.org/10.1016/j.enconman.2021.114393>.
- Martinez Hernandez E, Ng KS. Design of biorefinery systems for conversion of corn stover into biofuels using a biorefinery engineering framework. *Clean Techn Environ Policy* 2018;20(7):1501–14. <https://doi.org/10.1007/s10098-017-1477-z>.
- Ail SS, Dasappa S. Biomass to liquid transportation fuel via Fischer Tropsch synthesis – Technology review and current scenario. *Renew Sustain Energy Rev* 2016;58:267–86. <https://doi.org/10.1016/j.rser.2015.12.143>.
- He J, Zhang W. Techno-economic evaluation of thermo-chemical biomass-to-ethanol. *Appl Energy* 2011;88(4):1224–32. <https://doi.org/10.1016/j.apenergy.2010.10.022>.
- Clausen LR, Elmgaard B, Houbak N. Technoeconomic analysis of a low CO₂ emission dimethyl ether (DME) plant based on gasification of torrefied biomass. *Energy* 2010;35(12):4831–42. <https://doi.org/10.1016/j.energy.2010.09.004>.
- Wang Z, He T, Li J, Wu J, Qin J, Liu G, et al. Design and operation of a pilot plant for biomass to liquid fuels by integrating gasification, DME synthesis and DME to gasoline. *Fuel* 2016;186:587–96. <https://doi.org/10.1016/j.fuel.2016.08.108>.
- Dimitriou I, Goldingay H, Bridgwater AV. Techno-economic and uncertainty analysis of Biomass to Liquid (BTL) systems for transport fuel production. *Renew Sustain Energy Rev* 2018;88:160–75. <https://doi.org/10.1016/j.rser.2018.02.023>.
- Jung S, Shetti NP, Reddy KR, Nadagouda MN, Park Y-K, Aminabhavi TM, et al. Synthesis of different biofuels from livestock waste materials and their potential as

- sustainable feedstocks – A review. *Energy Convers Manage* 2021;236:114038. <https://doi.org/10.1016/j.enconman.2021.114038>.
- [24] Arregi A, Amutio M, Lopez G, Bilbao J, Olazar M. Evaluation of thermochemical routes for hydrogen production from biomass: A review. *Energy Convers Manage* 2018;165:696–719. <https://doi.org/10.1016/j.enconman.2018.03.089>.
- [25] Schemme S, Breuer JL, Köller M, Meschede S, Walman F, Samsun RC, et al. H₂-based synthetic fuels: A techno-economic comparison of alcohol, ether and hydrocarbon production. *Int J Hydrogen Energy* 2020;45(8):5395–414. <https://doi.org/10.1016/j.ijhydene.2019.05.028>.
- [26] Ibarra-Gonzalez P, Rong B-G. Systematic Synthesis and Evaluation of Thermochemical Conversion Processes for Lignocellulosic Biofuels Production: Total Process Evaluation and Integration. *Ind Eng Chem Res* 2018;57(30):9925–42. <https://doi.org/10.1021/acs.iecr.7b05382>.
- [27] Chew JJ, Doshi V. Recent advances in biomass pretreatment – Torrefaction fundamentals and technology. *Renew Sustain Energy Rev* 2011;15(8):4212–22. <https://doi.org/10.1016/j.rser.2011.09.017>.
- [28] Chen W-H, Peng J, Bi XT. A state-of-the-art review of biomass torrefaction, densification and applications. *Renew Sustain Energy Rev* 2015;44:847–66. <https://doi.org/10.1016/j.rser.2014.12.039>.
- [29] van der Stelt M, Gerhauser H, Kiel J, Ptasiński KJ. Biomass upgrading by torrefaction for the production of biofuels: A review. *Biomass Bioenergy* 2011. <https://doi.org/10.1016/j.biombioe.2011.06.023>.
- [30] Wang T, Zhai Y, Zhu Y, Li C, Zeng G. A review of the hydrothermal carbonization of biomass waste for hydrochar formation: Process conditions, fundamentals, and physicochemical properties. *Renew Sustain Energy Rev* 2018;90:223–47. <https://doi.org/10.1016/j.rser.2018.03.071>.
- [31] Krylova AY, Zaitchenko VM. Hydrothermal Carbonization of Biomass: A Review. *Solid Fuel Chem* 2018;52(2):91–103. <https://doi.org/10.3103/S0361521918020076>.
- [32] TNO Biobased and Circular Technologies. Phyllis2, database for (treated) biomass, algae, feedstocks for biogas production and biochar; Available from: <https://phyllis.nl/>.
- [33] Hansen L. Internal Report: HTC measurements at the Chair of Energy systems. Database and documentation of experiments; 2022.
- [34] Perrin N, Dubettier R, Lockwood F, Court P, Tranier J-P, Bourhy-Weber C, et al. Oxycombustion for Carbon Capture on Coal Power Plants and Industrial Processes: Advantages, Innovative Solutions and Key Projects. *Energy Procedia* 2013;37:1389–404. <https://doi.org/10.1016/j.egypro.2013.06.015>.
- [35] Air Liquide Engineering & Construction. Technology Handbook. [December 11, 2020]; Available from: <https://www.engineering-airliquide.com/de/technology-handbook>.
- [36] Beysel G. Enhanced Cryogenic Air Separation A proven Process applied to Oxyfuel: Future Prospect. In: 1st Oxyfuel Combustion Conference Cottbus. Cottbus; 2009.
- [37] Taniguchi M, Asaoka H, Ayuhara T. Energy Saving Air-Separation Plant Based on Exergy Analysis. In: *Kobelco Technology Review* No. 33; 2015.
- [38] Barcia P. Industrial Application of Adsorption-based Gas Separation Processes. In: *Leipziger Symposium on Dynamic Sorption*. Leipzig; 2019.
- [39] Pacific Consolidated Industries LLC. On-Site oxygen solutions: Industrial Catalog.
- [40] Kriegel R. Sauerstoff-liefernde Keramiken für Verbrennungsprozesse. In: 1. Aachener Ofenbau- und Thermoprocess-Kolloquium. Aachen; 2017.
- [41] Repasky J, McCarthy D, Armstrong P, Carolan M. ITM Technology for Carbon Capture on Natural Gas and Hybrid Power Systems. In: *Workshop on Technology Pathways Forward for Carbon Capture & Storage on Natural Gas Power Systems*. Washington; 2014.
- [42] Armstrong PA. Development of ITM Oxygen technology for intergration in IGCC and other advanced power generation. Allentown 2015.
- [43] Cormos C-C. Techno-Economic Evaluations of Copper-Based Chemical Looping Air Separation System for Oxy-Combustion and Gasification Power Plants with Carbon Capture. *Energies* 2018;11(11):3095. <https://doi.org/10.3390/en11113095>.
- [44] Shah K, Moghtaderi B, Zanganeh J, Wall T. Integration options for novel chemical looping air separation (ICLAS) process for oxygen production in oxy-fuel coal fired power plants. *Fuel* 2013;107:356–70. <https://doi.org/10.1016/j.fuel.2013.01.007>.
- [45] Moghtaderi B. Application of Chemical Looping Concept for Air Separation at High Temperatures †. *Energy Fuels* 2010;24(1):190–8. <https://doi.org/10.1021/ef900553j>.
- [46] Fendt SR. Experimental Investigation of a Combined Biomass-to-Gas / Power-to-Gas Concept for the Production of Synthetic Natural Gas (SNG). 1st ed. München: Verlag Dr. Hut; 2020.
- [47] Dossow M. Simulation and comparison of different synthesis routes for the production of sustainable aviation fuels: A power-and-biomass-to-liquid (PbTL) approach [Master's Thesis]. Munich: Technical University of Munich; 2020.
- [48] Asadullah M. Biomass gasification gas cleaning for downstream applications: A comparative critical review. *Renew Sustain Energy Rev* 2014;40:118–32. <https://doi.org/10.1016/j.rser.2014.07.132>.
- [49] VDI/DIN-Kommission Reinhaltung der Luft (KRdL) - Normenausschuss. Filtering-separators - High-temperature gas filtration(3677 - Sheet 3); 2010.
- [50] Ud Din Z, Zainal ZA. Biomass integrated gasification-SOFC systems: Technology overview. *Renew Sustain Energy Rev* 2016;53:1356–76. <https://doi.org/10.1016/j.rser.2015.09.013>.
- [51] Yan Q, Wan C, Street J, Yan DW, Han J, Yu F. Catalytic removal of oxygen from biomass-derived syngas. *Bioresour Technol* 2013;147:117–23. <https://doi.org/10.1016/j.biortech.2013.08.036>.
- [52] Prabhansu KMK, Chandra P, Chatterjee PK. A review on the fuel gas cleaning technologies in gasification process. *Journal of Environmental. Chem Eng* 2015;3(2):689–702. <https://doi.org/10.1016/j.jece.2015.02.011>.
- [53] Marcantonio V, Müller M, Bocci E. A Review of Hot Gas Cleaning Techniques for Hydrogen Chloride Removal from Biomass-Derived Syngas. *Energies* 2021;14(20):1–15. <https://doi.org/10.3390/en14206519>.
- [54] Mojtahedi W, Ylitalo M, Maunula T, Abbasian J. Catalytic decomposition of ammonia in fuel gas produced in pilot-scale pressurized fluidized-bed gasifier. *Fuel Process Technol* 1995;45(3):221–36. [https://doi.org/10.1016/0378-3820\(95\)00038-9](https://doi.org/10.1016/0378-3820(95)00038-9).
- [55] Andersson KJ, Skov-Skjøth Rasmussen M, Højlund Nielsen PE. Industrial-scale gas conditioning including Tpsos tar reforming and purification downstream biomass gasifiers: An overview and recent examples. *Fuel* 2017;203:1026–30. <https://doi.org/10.1016/j.fuel.2017.02.085>.
- [56] Klimantos P, Koukouzas N, Katsiadakis A, Kakaras E. Air-blown biomass gasification combined cycles (BGCC): System analysis and economic assessment. *Energy* 2009;34(5):708–14. <https://doi.org/10.1016/j.energy.2008.04.009>.
- [57] Chiesa P, Consonni S, Kreutz T. Co-production of hydrogen, electricity and CO from coal with commercially ready technology. Part A: Performance and emissions. *Int J Hydrogen Energy* 2005;30(7):747–67. <https://doi.org/10.1016/j.ijhydene.2004.08.002>.
- [58] Meerman H. Perspectives on gasification systems to produce energy carriers and other chemicals with low CO₂ emissions: Techno-economic system analysis on current and advanced flexible thermo-chemical conversion of fossil fuels and biomass. Universiteit Utrecht; 2012 [PhD thesis].
- [59] Rytter E, Ochoa-Fernández E, Fahmi A. Biomass-to-Liquids by the Fischer-Tropsch Process. In: Imhof P, van der Waal JC, editors. *Catalytic Process Development for Renewable Materials*. Weinheim, Germany: Wiley-VCH Verlag GmbH & Co. KGaA; 2013. p. 265–308.
- [60] Pala LPR, Wang Q, Kolb G, Hessel V. Steam gasification of biomass with subsequent syngas adjustment using shift reaction for syngas production: An Aspen Plus model. *Renew Energy* 2017;101:484–92. <https://doi.org/10.1016/j.renene.2016.08.069>.
- [61] Higman C, van der Burgt M. *Gasification*. 2nd ed. Amsterdam: Elsevier/GPP Professional Publ; 2008.
- [62] Robinson PJ, Luyben WL. Integrated Gasification Combined Cycle Dynamic Model: H₂S Absorption/Stripping, Water-Gas Shift Reactors, and CO₂ Absorption/Stripping. *Ind Eng Chem Res* 2010;49(10):4766–81. <https://doi.org/10.1021/ie901549s>.
- [63] National Renewable Energy Laboratory. Survey and Down-Selection of Acid Gas Removal Systems for the Thermochemical Conversion of Biomass to Ethanol with a Detailed Analysis of an MDEA System: Task 1: Acid Gas Removal Technology Survey and Screening for Thermochemical Ethanol Synthesis; Task 2: Detailed MDEA Process Analysis. San Francisco; 2009.
- [64] Hillestad M, Ostadi M, Alamo Serrano G, Rytter E, Austbø B, Pharoah JG, et al. Improving carbon efficiency and profitability of the biomass to liquid process with hydrogen from renewable power. *Fuel* 2018;234:1431–51. <https://doi.org/10.1016/j.fuel.2018.08.004>.
- [65] Kapetaki Z, Brandani P, Brandani S, Ahn H. Process simulation of a dual-stage Selexol process for 95% carbon capture efficiency at an integrated gasification combined cycle power plant. *Int J Greenhouse Gas Control* 2015;39:17–26. <https://doi.org/10.1016/j.ijggc.2015.04.015>.
- [66] Field RP, Brasington R. Baseline Flowsheet Model for IGCC with Carbon Capture. *Ind Eng Chem Res* 2011;50(19):11306–12. <https://doi.org/10.1021/ie200288u>.
- [67] Adams TA, Salkuyeh YK, Nease J. Processes and simulations for solvent-based CO₂ capture and syngas cleanup. In: *Reactor and Process Design in Sustainable Energy Technology*. Elsevier; 2014. p. 163–231.
- [68] Häussinger P, Lohmüller R, Watson AM. Hydrogen, 6. Uses. In: *Ullmann's Encyclopedia of Industrial Chemistry*. Weinheim, Germany: Wiley-VCH Verlag GmbH & Co. KGaA; 2012.
- [69] Federal Ministry for Economic Affairs and Energy. *The National Hydrogen Strategy*; 2020.
- [70] Häussinger P, Lohmüller R, Watson AM. Hydrogen, 2. Production. In: *Ullmann's Encyclopedia of Industrial Chemistry*. Weinheim, Germany: Wiley-VCH Verlag GmbH & Co. KGaA; 2012.
- [71] Capurso T, Stefanizzi M, Torresi M, Camporeale SM. Perspective of the role of hydrogen in the 21st century energy transition. *Energy Convers Manage* 2022;251:114898. <https://doi.org/10.1016/j.enconman.2021.114898>.
- [72] Fail S, Diaz N, Benedikt F, Kraussler M, Hinteregger J, Bosch K, et al. Wood Gas Processing To Generate Pure Hydrogen Suitable for PEM Fuel Cells. *ACS Sustainable Chem Eng* 2014;2(12):2690–8. <https://doi.org/10.1021/sc500436m>.
- [73] Hanel A, Fendt S, Spliethoff H. Operation of Conventional Power Plants During the German Energy Transition: a Mini Review. *Front Energy Res* 2022;10. <https://doi.org/10.3389/ferng.2022.907251>.
- [74] Fendt S, Buttler A, Gaderer M, Spliethoff H. Comparison of synthetic natural gas production pathways for the storage of renewable energy. *WIREs Energy Environ* 2016;5(3):327–50. <https://doi.org/10.1002/wene.189>.
- [75] Kopyscinski J, Schildhauer TJ, Biollaz SM. Production of synthetic natural gas (SNG) from coal and dry biomass – A technology review from 1950 to 2009. *Fuel* 2010;89(8):1763–83. <https://doi.org/10.1016/j.fuel.2010.01.027>.
- [76] Ott J, Gronemann V, Pontzen F, Fiedler E, Grossmann G, Kersebohm DB et al. Methanol. In: *Ullmann's Encyclopedia of Industrial Chemistry*. Weinheim, Germany: Wiley-VCH Verlag GmbH & Co. KGaA; 2012.
- [77] Mignard D, Pritchard C. On the use of electrolytic hydrogen from variable renewable energies for the enhanced conversion of biomass to fuels. *Chem Eng Res Des* 2008;86(5):473–87. <https://doi.org/10.1016/j.cherd.2007.12.008>.
- [78] Bell DA, Towler BF, Fan M. Methanol and Derivatives. In: *Coal Gasification and Its Applications*. Elsevier; 2011. p. 353–371.

- [79] EPCM Holdings. Direct DME Synthesis From Natural Gas. [June 10, 2022]; Available from: <https://epcmholdings.com/direct-dme-synthesis-from-natural-gas/>.
- [80] Kiendl I. Reaktionstechnische Untersuchungen der Direktsynthese von Dimethylether aus Synthesegas. Munich: Technical University of Munich; 2018 [PhD Thesis].
- [81] Ratamanalaya P, Limtrakul S, Vatanatham T, Ramachandran P. Kinetics Study of Direct Dimethyl Ether Synthesis. In: TIChE International Conference. Hatyai; 2011.
- [82] Alfke G, Irion WW, Neuwirth OS. Oil Refining. In: Ullmann's Encyclopedia of Industrial Chemistry. Weinheim, Germany: Wiley-VCH Verlag GmbH & Co. KGaA; 2012.
- [83] Appl M. Ammonia, 1. Introduction. In: Ullmann's Encyclopedia of Industrial Chemistry. Weinheim, Germany: Wiley-VCH Verlag GmbH & Co. KGaA; 2012.
- [84] Appl M. Ammonia, 2. Production Processes. In: Ullmann's Encyclopedia of Industrial Chemistry. Weinheim, Germany: Wiley-VCH Verlag GmbH & Co. KGaA; 2012.
- [85] Rouwenhorst KHR, Krzywda PM, Benes NE, Mul G, Lefferts L. Ammonia, 4. Green Ammonia Production. In: Ullmann's Encyclopedia of Industrial Chemistry. Weinheim, Germany: Wiley-VCH Verlag GmbH & Co. KGaA; 2000, p. 1–20.
- [86] Tripodi A, Compagnoni M, Bahadori E, Rossetti I. Process simulation of ammonia synthesis over optimized Ru/C catalyst and multibed Fe + Ru configurations. J Ind Eng Chem 2018;66:176–86. <https://doi.org/10.1016/j.jiec.2018.05.027>.
- [87] Patterson MG. What is energy efficiency? Energy Policy 1996;24(5):377–90. [https://doi.org/10.1016/0301-4215\(96\)00017-1](https://doi.org/10.1016/0301-4215(96)00017-1).