

# Outline of a 10,000 t/a PtL plant: Technological Assessment and Upscale-Study

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## Summary

To mitigate climate change there is a strong need to reduce CO<sub>2</sub> emissions in the transport sector. Synthetic fuels from power-to-Liquid (PtL) pathways are a promising strategy, especially for sectors that are challenging to electrify. In this contribution, the outline of a 10.000 t/a PtL plant is presented. Therefore, the needed technology steps - H<sub>2</sub> and CO<sub>2</sub> supply, synthesis gas formation, fuel synthesis, and downstream/refining - were identified and different options were evaluated. With regard to the technology selection, certain general assumptions were taken into consideration, such as the TRL, the robustness of the technologies and their commercial availability. Amine scrubbing from biogenic sources was chosen for CO<sub>2</sub> capture. For H<sub>2</sub> production PEM and alkali electrolysis were assessed as best options. For synthesis gas production the reverse water gas shift (RWGS) reaction is the most promising technology, while for fuel synthesis, a Co-catalyzed low temperature Fischer-Tropsch reaction was selected. For refining of the FT-crude to fuels compliant with the given standards, hydrocracking, hydrogenation, isomerization and distillation were identified as necessary steps.

## 1. Introduction

Due to the progressing climate change, mankind has to solve the great challenge of transforming its industrial processes as well as the transport, heat, and energy sector towards climate neutrality. Among others, the goal for the German transport sector is a complete defossilization, ergo a transformation away from crude oil towards renewable sources and CO<sub>2</sub> neutrality. While in Germany the industry could already reduce their greenhouse gas (GHG) emissions by 31 - 33 % compared to 1990, there is no noteworthy GHG emission reduction in the German transport sector (i.e. road traffic, aviation, and shipping) [1]. To reach the climate goals of the German government, a fast action is necessary to reduce the CO<sub>2</sub> emis-

sions in short-time. Especially, as the German government is even encouraging their aims for GHG emission reduction in this sector from 42 % [2] to 48 % [3] until 2030, compared to 1990. The replacement of fossil-based gasoline, diesel, and kerosene by PtL fuels is a good option to achieve this fast GHG emission reduction. If PtL fuels are produced from green hydrogen and CO<sub>2</sub> from the atmosphere or from point or biogenic sources, such as biogas or bioethanol plants, they combust CO<sub>2</sub> neutral. Even if the Well-to-Wheel efficiency with 13 % is low (69 % e-mobility) [4], PtL fuels have the great advantage that they can be used as direct replacement in the existing car, truck, aircraft or ship fleet (drop-in fuels) or with minor reconstructions (near-drop-in fuels), as they are chemically identical or similar to fossil-based fuels.

As such they can be used in the existing fuelling infrastructure [5]. Because of their good gravimetric and high volumetric energy density [6], PtL fuels are a promising strategy, especially for sectors that are challenging to electrify, like long-haul air transport, marine applications or long-distance haulage. As a sufficient replacement of the existing car fleet to fuel cell or electric vehicles until 2030 is not to expect, PtL fuels could also play a key role in road transport as an intermediate solution for CO<sub>2</sub> emission reduction.

Currently several research projects are conducted, addressing the production of PtL fuels, e.g. the Kopernikus project P2X [7], the PtM Miniplant in Freiburg (Germany) [8] and the C<sup>3</sup>-Mobility project [9]. But the scales are still quite far off from industrial scale. In some cases, like in P2X, decentralized production approaches are investigated. Larger PtL plants for centralized production are in planning at the moment, e.g. in Frankfurt-Höchst (Germany) with a capacity of 3,500 t/a e-fuel [10] or the Haru Oni project in Chile with about 130,000 l/a e-gasoline at the beginning [11].

This contribution presents the conceptual outline of a first of its kind 10,000 t/a demonstration PtL plant, based on a study conducted for the German Federal Ministry for Transport and Digital Infrastructure (BMVI). If built, the main goal is to gain experience with regard to process integration and optimization as well as to lay the foundation for a potential later scale up to commercial plant size, which would be in the order of at least 100,000 t/a. The PtL plant features a modular design, allowing single components of the process chain to be exchanged with other technologies at a later stage. Water electrolysis is used to produce H<sub>2</sub> from renewable energy, while CO<sub>2</sub> can stem from point sources or direct air capture. Syngas is generated via a reverse water gas shift reaction (RWGS) or a Co-Electrolysis. For the synthesis step a Fischer-Tropsch process and the methanol/DME based route are considered. The upgrading of the received intermediate (i.e. syncrude or methanol/DME) to standard conform fuels is achieved via a varying combination of refining steps, e. g. hydrocracking, hydrogenation, isomerization, and distillation. In the following sections the different technology options for each process step are referred to as “technology blocks”.

A technical evaluation of the different technologies for each block, based on literature review and in-house expert judgement, was performed with respect to the technological readiness level (TRL), the scalability, conformity, integrability into the PtL plant, specific energy demand and costs, as well as accruing waste streams and byproducts. Based on this technology screening, the most promising technologies for the 10,000 t/a PtL plant were selected. Special focus is dedicated to the connection of the different technology components. Based on these results a selection of mature and robust technologies for this first of its kind plant is presented. Furthermore, highly innovative but yet not sufficiently developed com-

ponents for the 10,000 t/a PtL plant were identified and will be further investigated in a parallel construction of a smaller research plant (scale: <1 % of demo plant).

## 2. Evaluation method

In the following section the evaluation method for the different technologies is described. Six criteria were defined. As first criterion the “accordance with the goal of the PtL concept”, ergo the feasibility for a discontinuous operation with renewable (fluctuating) electrical energy was assessed. Second, the technical readiness of the technology for its application in a 10,000 t/a PtL plant was evaluated, based on the investigated TRL of the desired technology as well as on the availability of the technology in the desired scale and potential scaling problems. The third criterion was the specific energy (electric and thermal energy) and reactant demand, based per kg product. The fourth criterion was the possibility of integrating the desired technology into the PtL plant energy management and the possibility of connecting the technology to upstream, reaction, and downstream steps for the production of a fuel compliant with given standards (i.e. process integration). The fifth point was the formation of by- and waste products, and the last point the specific costs per kg product for the specific technology.

The needed information for evaluating the different technology blocks related to these criteria were obtained from literature research and in-house expert judgement. If one or more of these points were not applicable for a technology block, they were excluded from the evaluation.

An evaluation system from 0 points “unsuitable” to 5 points “very good” was defined and each technology was rated quantitatively, based on the results of the literature research and in-house expert knowledge, per criterion and then compared to competing technologies within a technology block (cf. Fig. 1). Finally, the average points of the technologies were compared. Thereby, the selection of mature and robust technologies for each process step, resp. technology block, for the initial equipment of the 10,000 t/a PtL plant was performed.

Very good	good	medium	low	very low	unsuitable
5	4	3	2	1	0

Fig. 1: Evaluation system for the different technology blocks

Afterwards a first interconnected process layout based on the selected technologies including all utility units, material flows and peripheral systems was developed.

Technologies that were not chosen for the initial equipment but have a high innovation potential were considered for a smaller research plant (scale: <1% of demo plant). The layout of the research plant was conceived in parallel but is not within the scope of this contribution. Main goal of the research plant is to further investigate these high potential technologies separately as well as in

line with other technology steps in terms of an optimized process integration to develop them for later use in the 10,000 t/a plant.

### 3. Results and discussion

#### 3.1 H<sub>2</sub> production

For H<sub>2</sub> production five different technologies were identified as potentially interesting for the 10,000 t/a PtL plant. The alkaline electrolysis (AEL), the proton exchange membrane electrolysis (PEMEL), the high temperature electrolysis (SOEL), methane pyrolysis, and steam reforming in combination with carbon dioxide capture and storage (CCS). Through literature research results, in-house expert knowledge and physical-chemical calculations, the electric and thermal energy demand, the TRL level, operation temperature, further reactant and product streams as well as the ramp-up time from standby, the H<sub>2</sub> purity and the specific H<sub>2</sub> costs per kg were investigated. The results are shown in Table 1.

Based on these values the evaluation shown in Table 2 was performed. Steam reforming with CCS is not in accordance with the PtL concept, as it cannot directly implement renewable electricity as main source of energy. Additionally, steam reforming is available on industrial scale, but the necessary CCS infrastructure does not yet exist in Germany. Thus, steam reforming with CCS is not a suitable option for the 10,000 t/a PtL plant, even

if the specific energy demand is low (no electric and low thermal energy demand), the only used additional reactant besides methane is water and the H<sub>2</sub> production costs are low. Also, methane pyrolysis is no option for the PtL plant, due to its low technological readiness and its specific energy demand. As byproduct carbon black is formed that has to be separated and used, except by total oxidation, which would again result in significant CO<sub>2</sub> emissions. The specific H<sub>2</sub> costs would be in the same region as for steam reforming, but additional gas cleaning would be necessary. During methane pyrolysis, there would be an option for the direct formation of synthesis gas (CO, H<sub>2</sub>) by partial oxidation of the carbon black. Thereby, and by the low H<sub>2</sub> costs, methane pyrolysis can become an interesting technology after further investigation, using biogas as green methane source.

Thus, the remaining technology is the water electrolysis, for which the before mentioned three options were evaluated. The AEL is the highest developed technology, followed by the PEMEL. SOEL is still at demonstration level. Even if the SOEL has a higher thermal energy demand, due to the reaction temperature of 550 to 850 °C, its electric energy demand is lower. While heat can be provided from the exothermic Fischer-Tropsch reaction, for example, electricity has to be produced in a renewable manner. This is a great advantage, leading to a better ranking of the SOEL compared to AEL and PEMEL, for the criterion of “Integration in the PtL system”, where

**Table 1: Process data for H<sub>2</sub> production [Investigated using in-house expert knowledge and literature]; LHV: Lower heating value; CCS: Carbon dioxide capture and storage; \*Calculated with an electricity rate of 7 ct/kWh, 7000 Full load hour/a and literature values for CAPEX & OPEX; References: [12-19].**

	Energy demand [kWh/kg H <sub>2</sub> ]			TRL	Temperature	Reactant demand	Ramp-up time from standby (cold)	Product gas quality	Specific costs [€/kg H <sub>2</sub> ]
	el.	therm.	chem.						
<b>Alkaline electrolysis (AEL)</b>	54	0.15	-	9	60 - 80 °C	Water: 12 kg/kg H <sub>2</sub> Byproduct: O <sub>2</sub>	1 - 2 h	H <sub>2</sub> -purity 99 - 99.8 %	4.5 - 5.2*
<b>Proton exchange membrane electrolysis (PEMEL)</b>	58	0.35	-	7 - 8	50 - 80 °C	Water: 12 kg/kg H <sub>2</sub> Byproduct: O <sub>2</sub>	5 - 10 min	H <sub>2</sub> -purity >99.99 %	5.5 - 6.3*
<b>High temperature electrolysis (SOEL)</b>	41	9.37	-	6	550 - 850 °C	Water (vapor): 12 kg/kg H <sub>2</sub> Byproduct: O <sub>2</sub>	Several hours	H <sub>2</sub> -purity 99.8 %; Synthesis gas formation possible (Co-Electrolysis)	~5*
<b>Methane pyrolysis</b>	9.5	-	62.5 (CH <sub>4</sub> , LHV)	5 - 6	800 - 2000 °C	Byproduct: C (carbon black)	-	Gas cleaning necessary; Synthesis gas formation possible	2.5 - 3
<b>Steam reforming (with CCS)</b>	-	0.5-0.58	46.7 (CH <sub>4</sub> , LHV)	9	820 - 880 °C	Water: 7.5 - 15 kg/kg H <sub>2</sub> Exhaust: CO <sub>2</sub>	-	Synthesis gas formation possible	2 - 2.5

**Table 2: Evaluation of the different H<sub>2</sub> production technologies; CCS: Carbon dioxide capture and storage.**

	In accordance with the goal of the PtL-concept	Technological readiness	Specific energy and reactant demand	Integration in the PtL system	By-/Waste products	Specific costs	Ø
<b>AEL</b>	4	5	3	3	5	3	3.8
<b>PEMEL</b>	5	4	2	3	5	2	3.5
<b>SOEL</b>	3	2	4	4	4	3	3.3
<b>Methane pyrolysis</b>	1	1	1	4	3	4	2.3
<b>Steam reforming (+ CCS)</b>	0	5	5	5	1	5	3.5

PEMEL and AEL are evaluated equally, and for the criterion “specific energy and reactant demand”. Regarding PEMEL and AEL, the AEL was ranked higher according to the latter criterion. As reactant for all three electrolysis technologies, only water is needed, while oxygen is formed as byproduct. The latter can be sold to improve the business plan of the plant. The H<sub>2</sub> is gained in very high purity >99.8 %, but the H<sub>2</sub> price with 4.5 (AEL) to 6.3 €/kg (PEMEL) is comparatively high. For the 10,000 t/a plant, the AEL needs to be upscaled to about 30 MW. Thanks to its high TRL, this upscaling is not critical. For PEMEL a numbering up of smaller modules would lead to the 30 MW requirement. For PEMEL Iridium (Ir) is needed as raw material for the electrodes, which might be critical for a state-of-the-art use of PEMEL, especially for its use in various industrial PtL plants. Even if a numbering up to 30 MW for SOEL would be possible, the complex technology, a challenging heat management as well as occurring degradation make the SOEL not suitable for the initial equipment for the first of its kind 10,000 t/a PtL plant. However, it is an interesting technology for the future and the research plant. Thus, for H<sub>2</sub> production in the 10,000 t/a PtL plant, the best options are AEL and PEMEL, which are ranked nearly equally to one another and show low upscale and operational problems. Therefore, both technologies shall be used in the PtL plant.

### 3.2 CO<sub>2</sub> capture

For CO<sub>2</sub> separation, seven technology options were investigated for CO<sub>2</sub> exploitation from two different sources. First, the membrane separation, water washing, amine scrubbing, and pressure swing adsorption for CO<sub>2</sub> separation from biogenic point sources, such as digester gases (e.g. biogas plant or bioethanol plant). Second, the high temperature aqueous solution DAC (direct air capture), the low temperature DAC with temperature swing adsorption, and the low temperature DAC with moisture swing adsorption for CO<sub>2</sub> separation from the atmosphere. Via in-house expert knowledge, physical-chemical calculations, and literature research the energy demands, the TRL levels, the CO<sub>2</sub> purity, the specific CO<sub>2</sub> costs, the requisite auxiliary materials, as well as waste/byproducts were investigated (cf. Table 3). The evaluation of the technologies according to the defined criteria (cf. Chapter 2) is shown in Table 4. The three direct air capture (DAC) methods fit opti-

mal to the PtL concept, as CO<sub>2</sub> from the atmosphere is used, thus being more flexible than biogenic CO<sub>2</sub> capture which has to rely on the operation of a biogas or bioethanol plant. But the DAC methods are of much lower technical readiness than the methods for separation from biogenic digester gases. The highest TRL has the low temperature DAC with temperature swing adsorption (TRL 8) and would be thereby the only possible DAC option for a 10,000 t/a PtL plant. But the CO<sub>2</sub> costs are very high (155 €/t<sub>CO<sub>2</sub></sub> compared to 50 - 100 €/t<sub>CO<sub>2</sub></sub>) as well as the energy demand, that is much higher than for the CO<sub>2</sub> separation from biogenic sources. Therefore, the low temperature DAC with temperature swing adsorption is a promising option for CO<sub>2</sub> exploitation from air, but it has to be further investigated (lower energy demand, lower price, higher TRL, etc.) before it is applicable for large PtL plants and will only be considered for the research plant.

Thus, for the 10,000 t/a PtL plant a biogenic CO<sub>2</sub> source, e.g. a biogas or bioethanol plant, must be chosen. The technological readiness is fairly developed for all methods shown (TRL 9), except the membrane separation (TRL 6-8), which makes scaling up difficult and eliminates this technology as an option for the 10,000 t/a PtL plant. Water washing, amine scrubbing, and pressure swing adsorption can be scaled without problems to 10,000 t/a fuel scale, but with water washing a very impure CO<sub>2</sub> is obtained (14 - 22 vol%), which makes this technology not applicable. Pressure swing adsorption and amine scrubbing can both be used for the 10,000 t/a PtL plant. In the end, amine scrubbing was chosen, as higher CO<sub>2</sub> purities are obtained along with the lowest CO<sub>2</sub> costs.

### 3.3 Synthesis gas formation

The next step in the PtL process is the formation of synthesis gas (CO, H<sub>2</sub>) (syngas) from H<sub>2</sub> and CO<sub>2</sub>. For this process, four technologies were considered: water electrolysis, e.g. AEL, in combination with a reverse water gas shift reaction (RWGS), co-electrolysis, dry biogas reforming and autothermal reforming of FT-tail gas. The investigated data, based on literature research, in-house expert knowledge, and physical-chemical calculations, includes the necessary reactants, the energy demand, the TRL, and the residue/waste products (cf. Table 5). The evaluation according to Chapter 2 is shown in Table 6.

The co-electrolysis is suitable for the Fischer-Tropsch (FT) route, as it directly converts CO<sub>2</sub> and H<sub>2</sub>O to syn-

thesis gas; however, it does not fit for methanol synthesis from CO<sub>2</sub> and H<sub>2</sub>. The “AEL plus RWGS” process fit for both cases: for FT-synthesis, AEL and RWGS are put in line; for methanol synthesis, the RWGS is bypassed.

Co-electrolysis could possibly be scaled up to the desired scale by numbering up, but with a low TRL of 4, many difficulties must still be faced (e.g. membrane stability or degradation), while for RWGS, with a TRL of 6 the technology is more mature. Scaling up to the 10,000 t/a scale should, therefore, be possible. The biggest problem appears to be a CO<sub>2</sub> neutral heat supply, as the energy demand is quite high, even a bit higher than for co-electrolysis. As compared to co-electrolysis for syngas formation with AEL + RWGS, two reaction steps are needed instead of one. The “integration into the PtL system” is thereby ranked higher for co-electrolysis.

Waste products of AEL + RWGS are O<sub>2</sub> and H<sub>2</sub>O. The first can be sold and the latter used in the AEL again. Also, for the co-electrolysis, the byproduct is O<sub>2</sub>.

The “autothermal reforming of FT-tail gas” is a commercially available option, but for its application a tail gas must already exist. Thus, this reaction is an option for tail gas recycling and thereby for process optimization, but not for main synthesis gas production. Also, the dry reforming of methane and CO<sub>2</sub> is an interesting option for synthesis gas production, but, since the methane from biogas plants is mostly used in other ways (e.g. power generation), the methane from the biogas plant is limited. Thus, grey methane from natural gas would be needed, making it incompatible with a green PtL plant. Additionally, no renewable electricity would be intro-

**Table 3: Process data for CO<sub>2</sub> capture [Investigated using in-house expert knowledge and literature]; DAC: Direct air capture; References: [ 20-30 ].**

		Energy demand [kWh/kg CO <sub>2</sub> ]		TRL	Purity CO <sub>2</sub> [vol%]	Spec. CO <sub>2</sub> costs [€/t CO <sub>2</sub> ]	Auxiliary material	Waste/ Byproducts
		el.	therm.					
Biogenic digester gas	Membrane separation	0.34	-	6 - 8	75	~95	-	-
	Water washing	0.2	-	9	14 - 22	No utilizable CO <sub>2</sub>	Additive absorbents	Waste water
	Amine scrubbing	0.01	0.63 (120 - 140 °C)	9	90 - 99.9	50 - 75	Treated absorbent	Used absorbent
	Pressure swing adsorption	0.2	-	9	87 - 99.9	~100	Adsorbent	Used adsorbent
Atmosphere	High temperature aqueous solution DAC	1.5 - 1.8	-	6	~97 %	186	Potassium hydroxide, Water (4.7 l/kg CO <sub>2</sub> ), Calcium carbonate	Waste water CaCO <sub>3</sub>
	Low temperature DAC with temperature swing adsorption	0.3 - 0.65	1.5 - 2.0 (100 °C)	8	>99.9 %	155	Amine based sorbent	Waste Water
	Low temperature DAC with moisture swing adsorption	0.3	-	5	n.s.	144	n.s.	n.s.

**Table 4: Evaluation of the different CO<sub>2</sub> capture technologies; DAC: Direct air capture; \*No data available.**

		In accordance with the goal of the PtL-concept	Technological readiness	Specific energy and reactant demand	Integration in the PtL system	By-/Waste products	Specific costs	Ø
Biogenic digester gas	Membrane separation	4	3	3	2	5	4	3.5
	Water washing	4	5	4	0	3	0	2.7
	Amine scrubbing	4	5	3	5	3	5	4.2
	Pressure swing adsorption	4	5	4	3	3	4	3.8
Atmosphere	High temperature aqueous solution DAC	5	2	1	2	2	1	2.2
	Low temperature DAC with temperature swing adsorption	3	4	2	5	4	2	3.3
	Low temperature DAC with moisture swing adsorption	5	0	3	*	*	2	2.5

duced into the system. Thus, as the most suitable option for synthesis gas generation, a coupling of water electrolysis (e.g. AEL) and RWGS was chosen for the initial equipment of the 10,000 t/a PtL plant. The co-electrolysis will be closer investigated at the research plant.

### 3.4 Fischer-Tropsch synthesis

After synthesis gas formation comes the synthesis step. One very promising option for producing PtL fuels is the Fischer-Tropsch synthesis (FTS).

Three different process ways were examined: the low temperature FTS with Fe-catalyst, the low temperature FTS with Co-catalyst, and the high temperature FTS with Fe-catalyst. The investigated process data are shown in Table 7: CO and H<sub>2</sub> demand, investment (invest) costs, TRL, reaction temperature, residue/waste products and syncrude composition. Table 8 shows the evaluation of these values. Easy to see is that the high temperature FTS is not suitable for a PtL plant, as the main products are short chain hydrocarbons with a chain length from C1 - C4 (57 %), which is even too small for gasoline. With the low temperature FTS, the formed chain length is longer: 45 % waxes (>C22) and 42 % hydrocarbons with a chain length between C5-C22 are obtained by Co-catalyzed FTS; 50 % waxes (>C22) and 32 % hydrocarbons between C5 and C22 are obtained for the Fe-catalyzed FTS, depending on the chosen process conditions.

In both cases, scaling up is not the problem to solve, but rather the scaling down to 10,000 t/a fuel scale, as FTS is used in the industry in large scales for years,

like the Sasol process [31] or the Pearl GTL process from Shell [32]. The core challenge is to run the FTS with acceptable costs in this small scale. The needed scale for the 10,000 t/a PtL plant is not available on the market and must, therefore, be developed. One core challenge of the FTS is its bad performance to load flexible operation. This problem has to be solved for the desired PtL plant either by optimizing the FTS synthesis to work with fluctuating reactant input, or by installing a synthesis gas buffer to compensate the fluctuation. As reactor, a tube bundle reactor or microstructure reactors with fixed catalyst beds can be used. Microstructure reactors have the benefit of well controlled heat development, but for a 10,000 t/a fuel scale, a huge number of reactors would be needed. Therefore, for the 10,000 t/a plant, a tube bundle reactor shall be used.

For low temperature FTS, the Co-catalyzed route was chosen, as it has a slightly lower reactant (CO, H<sub>2</sub>) demand and has a slightly higher yield in hydrocarbons with chain lengths  $\geq$ C5 (87 % to 82 %).

### 3.5 Downstream/ Refining of FT syncrude

After the FTS, a crude mixture of alkanes, alkenes, alcohols, and other organic compounds with different chain lengths are obtained, denoted as FT-crude or syncrude. This syncrude cannot be used as fuel immediately, but must be processed in several downstream/refining process steps (cf. Table 9). As those processes are mandatory to fulfill the given fuel specifications, no eva-

**Table 5: Process data for synthesis gas (syngas) formation [Investigated via in-house expert knowledge and literature]; LT: Low temperature; \*Assumed syngas composition: H<sub>2</sub>/CO = 2/1; \*\*Assumed syngas composition: H<sub>2</sub>/CO = 1/1; References: [33-44].**

	Reactants	Energy demand		Reactant demand	TRL	Residues/ Waste products	
		el.	therm.				
LT electrolysis + RWGS	AEL	H <sub>2</sub> O	54 kWh/kg H <sub>2</sub>	0.15 kWh/kg H <sub>2</sub>	12 kg H <sub>2</sub> O/kg H <sub>2</sub>	9	~8 kg O <sub>2</sub> /kg H <sub>2</sub>
	RWGS	H <sub>2</sub> + CO <sub>2</sub>	-	0.4 - 0.5 kWh/kg CO at 700 - 1000 °C	~0.07 kg H <sub>2</sub> /kg CO ~1.6 - 1.7 kg CO <sub>2</sub> /kg CO	6	~0.65 kg H <sub>2</sub> O/kg CO
	Overall process	H <sub>2</sub> O + CO <sub>2</sub>	~10 kWh/kg syngas*	~0.47 kWh/kg syngas*	~1.5 kg H <sub>2</sub> O/kg syngas* ~1.5 kg CO <sub>2</sub> /kg syngas*	6	1 kg O <sub>2</sub> /kg syngas* 0.57 kg H <sub>2</sub> O/kg syngas*
Co-electrolysis	H <sub>2</sub> O + CO <sub>2</sub>	~8.8 kWh/kg syngas*	0.75 - 1 kWh/kg syngas*	~1.6 kg CO <sub>2</sub> /kg syngas* ~1.2 kg H <sub>2</sub> O/kg syngas*	4	O <sub>2</sub> Waste heat (550 - 850 °C)	
Dry biogas reforming	Biogas	Methane demand: 0.3 kg/kg CO		~0.75 kg CO <sub>2</sub> /kg syngas** ~0.28 kg CH <sub>4</sub> /kg syngas **	5 - 6	-	
Autothermal reforming of FT-tail gas	FT-tail gas	-	-	~0.4 - 0.6 kg CH <sub>4</sub> /kg syngas* ~0.25 kg O <sub>2</sub> /kg syngas* ~0.875 kg H <sub>2</sub> O/kg syngas* ~0.17 kg CO <sub>2</sub> /kg syngas*	9	-	

**Table 6: Evaluation of the different synthesis gas formation technologies; LT: Low temperature; †Data availability not sufficient for qualitative comparison.**

	In accordance with the goal of the PtL-concept	Technological readiness	Specific energy and reactant demand	Integration in the PtL system	By-/Waste products	Specific costs†	Ø
LT electrolysis + RWGS	4	3	3	4	5		3.8
Co-electrolysis	3	0	4	5	5		3.4
Dry biogas reforming	0	3	5	3	4		3.0
Autothermal reforming of FT-tail gas	3	5	5	5	4		4.4

**Table 7: Process data for Fischer-Tropsch synthesis (FTS) [Investigated using in-house expert knowledge and literature]; HC: Hydrocarbons, References: [12; 33; 45-47].**

	CO demand [kg CO/kg syncrude]	H <sub>2</sub> demand [kg H <sub>2</sub> /kg syncrude]	Invest costs [k€/MW]	TRL	Temperature	Residues/Waste products	Syncrude-composition
Low temperature FTS with Fe-catalyst	2.3 - 2.5	~0.17	450 - 725 Cheap catalyst	9	220 - 230 °C	Waste water, Tail gas	~50 % Waxes (>C22) ~32 % HC C5-C22 ~18 % HC C1-C4
Low temperature FTS with Co-catalyst	2.2 - 2.4	~0.16	450 - 725 Expensive catalyst	9	220 - 230 °C	Waste water, Tail gas	~45 % Waxes (>C22) ~42 % HC C5-C22 ~13 % HC C1-C4
High temperature FTS with Fe-catalyst	4.5 - 4.7	~0.33	500 - 800 Cheap catalyst	9	320 - 340 °C	Waste water, Tail gas	<3 % Waxes (>C22) ~40 % HC C5-C22 ~57 % HC C1-C4

**Table 8: Evaluation of the different Fischer-Tropsch synthesis (FTS) technologies; \*Criterion not evaluated, as not meaningful for this process step.**

	In accordance with the goal of the PtL-concept*	Technological readiness	Specific energy and reactant demand	Integration in the PtL system	By-/Waste products	Specific costs	Ø
Low temperature FTS with Fe-catalyst		5	4	4	4	5	4.4
Low temperature FTS with Co-catalyst		5	5	5	4	4	4.6
High temperature FTS with Fe-catalyst		5	2	1	2	4	2.8

luation of the specific technologies was carried out. Essential for the refining of the FT-crude is the hydrocracking that cleaves long chain hydrocarbons (e.g. waxes (>C22)) to the desired chain length. For kerosene the range of C9 - C17 and for diesel the range of C9 - C22 is desired. Nevertheless, it is not possible to crack the crude to only one fraction, so that always several fractions are obtained, e.g. gasoline (C5 - C11) and kerosene. Furthermore, through the addition of hydrogen, double bonds can be hydrogenated and alkenes are converted to alkanes. Organic acids, aldehydes and alcohols in the crude are also reduced to alkanes. If after hydrocracking alkenes or alcohols remain in the cracked crude, or if the original FT-crude should not be cracked, an (additional) hydrogenation is necessary to reduce all oxygen compounds and unsaturated compounds to alkanes. Afterwards an isomerization is needed to branch the alkanes and to adjust the desired i-alkane/n-alkane ratio. Hydrogenation and isomerization can be performed in parallel in one process step.

Afterwards several distillations are necessary to obtain the desired fuel fractions, which must be compliant with the given standards. For synthetic kerosene, the ASTM 7566 is applicable, for Diesel the DIN EN 590 and for gasoline the DIN EN 228.

### 3.6 Methanol (MeOH) synthesis and further processing to fuels

Methanol can be produced via two processes. Directly from CO<sub>2</sub> and H<sub>2</sub> or from synthesis gas (CO, H<sub>2</sub>). The first process has the benefit, that CO<sub>2</sub> must not be converted to CO by means of co-electrolysis or RWGS. Thus, energy could be saved by avoiding the high temperatures for these applications (550 - 1000 °C).

The investigated data for these two methods are shown in Table 10 and the evaluation according to Chapter 2 is shown in Table 11.

For the second process, in this study an RWGS was combined with the methanol synthesis from synthesis

**Table 9: Downstream methods for FT-crude (syncrude) refining to fuels [Investigated via in-house expert knowledge and literature]; References: [48-57].**

	TRL	Function	Usage	Energy demand [kWh/kg jet fuel]		H <sub>2</sub> demand [kg/kg jet fuel]
				electric	thermal	
<b>Hydrocracking</b>	9	Catalytic conversion of long chain hydrocarbons to shorter hydrocarbons and hydrogenation of double bonds, alcohols, etc.	<ul style="list-style-type: none"> <li>Cracking of FT-product to the desired chain length distribution (solid waxes to liquid products)</li> <li>Conversion of alkenes, alcohols, etc. to alkanes</li> </ul>	0.01 (wax pumps)	-0.1 (exotherm)	for FT-waxes: 0.05 - 0.15
<b>Hydrogenation</b>	9	Hydrogenation of double bonds, alcohols, etc.	Conversion of alkenes, alcohols, etc. to alkanes	-	(exotherm)	0.03
<b>Isomerization</b>	9	Catalytic conversion of linear alkanes and alkenes to branched alkanes and alkenes.	Optimizing of freezing point	-	0.1 (reactant heating)	0.05

gas. In this case, the technological readiness of the direct methanol synthesis from CO<sub>2</sub> is a bit higher (TRL 6 - 8) than for the synthesis gas synthesis (TRL 6), due to the required RWGS. Both processes have similar reactant (CO<sub>2</sub>, H<sub>2</sub>) as well as similar energy demands (electric and thermal), as long as for the synthesis gas based process the waste heat and heat demand are optimally integrated. In both cases, due to the exothermic methanol synthesis, waste heat is produced, which can be used in an integrated manner in the PtL plant to cover other heat demands. In both cases, the specific investment costs are very high (5500 and 6300 - 6670 €/kg MeOH/h). For both processes waste water is produced, which can be reused in the electrolysis after purification. For the direct methanol synthesis, exhaust gases like methane and CO are formed. Regarding these arguments, the direct methanol synthesis from CO<sub>2</sub> and H<sub>2</sub> is the more promising option. However, the further processing of the methanol to fuels is challenging (cf. Table 12). While Methanol-to-Gasoline (MtG) is well known, and scaling up to the 10,000 t/a

scale would be possible by numbering up, this technology is not conducive if kerosene is the target product. Therefore, the Methanol-to-Jet (MtJ) process must be applied, which is still being researched on lab scale (TRL 4 - 5). According to the alcohol-to-jet process, also for MtJ the three reaction steps dehydration (Methanol-to-olefins (MtO)), oligomerization and hydrogenation are under investigation [58], but problems occur producing sufficiently long enough chain length (>C6), even if the individual process steps are well understood. As the main focus of this PtL plant is kerosene production, the methanol route (methanol synthesis + MtJ) will be further considered at the smaller research plant. However, it is not a suitable option for the 10,000 t/a PtL plant. Thus, the FT-route was selected for the demonstration plant.

### 3.7 DME synthesis

A third alternative to FTS and the methanol route is the dimethyl ether (DME) synthesis. DME can be produced

via three ways. By dehydration of methanol, from synthesis gas or directly from CO<sub>2</sub> and H<sub>2</sub>. The investigated process parameters are shown in Table 13, and the evaluation in Table 14. For DME synthesis from methanol, the methanol must first be formed from CO<sub>2</sub> and H<sub>2</sub>. This reaction also limits the TRL of this process to 6 to 8. TRL 6 is reached for the synthesis gas DME synthesis, as the synthesis gas has to be formed before by a co-electrolysis or, as in this study, with a RWGS limiting the TRL. On the other side, the direct synthesis of DME from CO<sub>2</sub> and H<sub>2</sub> has an even lower TRL of 4 - 5. The reactant demand (CO<sub>2</sub>, H<sub>2</sub>) is quite similar for direct and syngas synthesis and higher for synthesis based on methanol. The excess heat is nearly equal for all three methods, if the heat integration is optimum for DME from synthesis gas (-0.6 - -0.8 kWh/kg DME). The excess heat can be used as heat source for other process steps. For the DME from methanol route, additional electric energy is needed (methanol synthesis). However, the specific DME investment costs are, as for methanol synthesis, very high (7900 - 9460 €/ (kg DME/h)). As a residue, waste water is formed for all DME synthesis routes, which can be reused in the electrolysis. For synthesis via methanol additional exhaust

gas is produced during methanol synthesis (CO, CH<sub>4</sub>) and for syngas-DME synthesis additional CO<sub>2</sub>.

The workup to fuels would be identical to the methanol route, MtG or MtJ, and would face the same problems.

Thus, no reaction route is particularly promising for the 10,000 t/a PtL plant. Furthermore, DME is an intermediate product of the MtG and MtJ process [59] and is produced during the methanol route. While the methanol route will become part of the research plant, the DME route will not be considered at all.

### 3.8 Initial equipment of the 10,000 t/a PtL plant

After the evaluation of the single technology steps for the 10,000 t/a PtL plant, the best technologies steps were combined within a PtL process.

For water electrolysis two technologies were chosen, AEL and PEMEL, which will produce H<sub>2</sub> in equal amounts (50 % each). CO<sub>2</sub> will be obtained from biogenic digester gases (biogas plants or bioethanol plants) via amine scrubbing, while the synthesis gas formation will be performed by RWGS. As fuel synthesis step, the

**Table 10: Process data for methanol synthesis [Investigated via in-house expert knowledge and literature]; MeOH: Methanol; References: [26; 45; 60-67].**

		Reactant demand			TRL	Energy demand		Specific investment costs	Residues/ Waste products
		H <sub>2</sub>	CO <sub>2</sub>	CO		electric	thermal		
<b>Methanol from CO<sub>2</sub> &amp; H<sub>2</sub></b>		~0.2 [kg/kg MeOH]	1.4 - 1.5 [kg/kg MeOH]	-	6 - 8	0.11 - 0.17 [kWh/kg MeOH]	~0.4 [kWh/kg MeOH] (210 - 300 °C)	~5,500 [€/ (kg MeOH/h)]	Waste water (0.57 kg/kg MeOH) Exhaust gas, e.g. CO & CH <sub>4</sub> (0.91 kg/kg MeOH)
<b>Methanol from CO &amp; H<sub>2</sub></b>	<b>RWGS</b>	~0.07 [kg/kg CO]	1.6 - 1.7 [kg/kg CO]	-	6	-	0.4 - 0.5 [kWh/kg CO] with 700 - 1000 °C	1,300 [€/ (kg CO/h)]	Waste water (~0.65 kg/kg CO)
	<b>MeOH- synthesis</b>	~0.13 [kg/kg MeOH]	-	0.6 - 0.9 [kg/kg MeOH]	9	0.15 [kWh/kg MeOH]	~0.75 [kWh/kg MeOH] (240 - 270 °C)	~5,500 [€/ (kg MeOH/h)]	Waste water (~0.14 kg/kg MeOH)
	<b>Overall process</b>	~0.2 [kg/kg MeOH]	1.0 - 1.5 [kg/kg MeOH]	-	6	0.15 [kWh/kg MeOH]	Heat Demand: 0.24 - 0.45 Waste heat: -0.75 [kWh/kg MeOH]	6,300 - 6,670 [€/ (kg MeOH/h)]	Waste water (~0.73 kg/kg MeOH)

**Table 11: Evaluation of the different methanol synthesis technologies.**

	In accordance with the goal of the PtL- concept	Techno- logical readiness	Specific energy and reactant demand	Integration in the PtL system	By-/Waste products	Specific costs	Ø
<b>Methanol from CO<sub>2</sub> &amp; H<sub>2</sub></b>	3	3	5	4	3	5	3.8
<b>Methanol from CO &amp; H<sub>2</sub></b>	3	2	5	3	3	4	3.3

**Table 12: Evaluation of the different methanol to fuel technologies; \*Criterion not evaluated, as not meaningful for this process step; †Data availability not sufficient for qualitative comparison.**

	In accordance with the goal of the PtL-concept*	Technological readiness	Specific energy and reactant demand†	Integration in the PtL system	By-/Waste products†	Spec. costs†	Ø
<b>Methanol-to-Gasoline (MtG)</b>		5		0			
<b>Methanol-to-Jet (MtJ)</b>		0		5			

**Table 13: Process data for dimethyl ether (DME) synthesis [Investigated via in-house expert knowledge and literature]; References: [45; 62; 65-70].**

		Reactant demand				TRL	Energy demand		Specific investment costs	Residues/Waste products
		H <sub>2</sub>	CO <sub>2</sub>	CO	MeOH		electric	thermal		
DME from methanol	Methanol-synthesis	~0.2 [kg/kg MeOH]	1.4 - 1.5 [kg/kg MeOH]	-	-	6 - 8	0.11 - 0.17 [kWh/kg MeOH]	~0.4 [kWh/kg MeOH] (210 - 300 °C)	~5,500 [€/kg MeOH/h]	Waste water (0.57 kg/kg MeOH) Exhaust gas, i.e. CO & CH <sub>4</sub> (0.91 kg/kg MeOH)
	DME-synthesis	-	-	-	1.4 - 1.7 [kg/kg DME]	9	-	(-0.03) - (-0.14) [kWh/kg DME]	-	Waste water (~0.4 kg/kg DME)
	Overall process	0.28 - 0.34 [kg/kg DME]	1.96 - 2.55 [kg/kg DME]	-	-	6 - 8	0.15 - 0.29 [kWh/kg DME]	(-0.6) - (-0.8) [kWh/kg DME]	-	Waste water (1.2 - 1.4 kg/kg DME) Exhaust gas (1.3 - 1.6 kg/kg DME)
DME from CO & H <sub>2</sub>	RWGS	~0.07 [kg/kg CO]	1.6 - 1.7 [kg/kg CO]	-	-	6	-	0.4 - 0.5 [kWh/kg CO] with 700 - 1000 °C	1,300 [€/kg CO/h]	Waste water (~0.65 kg/kg CO)
	DME-synthesis	~0.17 [kg/kg DME]	-	~1.2 [kg/kg DME]	-	9	-	-1.24 [kWh/kg DME]	~7,900 [€/kg DME/h]	Waste water (~0.4 kg/kg DME) CO <sub>2</sub>
	Overall process	~0.25 [kg/kg DME]	1.9 - 2.0 [kg/kg DME]	-	-	6	-	Need: 0.48 - 0.6 Waste: -1.24 [kWh/kg DME]	9,460 [€/kg DME/h]	Waste water (~1.2 kg/kg DME) CO <sub>2</sub>
DME from CO <sub>2</sub> & H <sub>2</sub>	Overall process	~0.25 kg/kg DME	~1.9 kg/kg DME	-	-	4-5	-	-0.74 kWh/kg DME	~7,900 [€/kg DME/h]	Waste water (~1.2 kg/kg DME)

**Table 14: Evaluation of the different dimethyl ether (DME) synthesis technologies; \*No data available**

	In accordance with the goal of the PtL-concept	Technological readiness	Specific energy and reactant demand	Integration in the PtL system	By-/Waste products	Specific costs	Ø
<b>DME from methanol</b>	3	3	3	3	2	*	2.8
<b>DME from CO &amp; H<sub>2</sub></b>	3	2	3	3	3	2	2.7
<b>DME from CO<sub>2</sub> &amp; H<sub>2</sub></b>	3	0	3	1	3	3	2.2

Co-catalyzed low temperature FT-synthesis was chosen. As refining steps, to obtain the desired fuel (gasoline, diesel and especially kerosene), a hydrocracker, a hydrogenation and an isomerization unit, as well as distillation units were integrated.

Fig. 2 shows the resulting flow sheet and the detailed coupling of the single technologies selected for the 10,000 t/a PtL plant. The 10,000 t/a fuels are divided into a kerosene fraction (C<sub>9</sub> - C<sub>16</sub>; target product), a diesel fraction (C<sub>17</sub> - C<sub>25</sub>), and a naphtha fraction (C<sub>6</sub> - C<sub>8</sub>; usable for gasoline

after further processing). For hydrogen production, the two electrolysis units were coupled in parallel. The produced  $H_2$  and captured  $CO_2$  are fed into the RWGS. The synthesis gas is then led into the FT reactor. The formed FT-crude (syncrude) is fed to a hot separator, where the waxes are separated from the remaining crude. The waxes are then hydrocracked and afterwards fed to a Middle distillate(M)-rectification unit. The remaining FT-crude is fed into a cold separator. The light products are fed back to the RWGS, and the heavier products are fed to the M-rectification. The head product of M-rectification runs to a Naphtha(N)-rectification, where the head product is fed back to the RWGS, the bottom product is the naphtha fraction. The bottom product of the M-rectification is fed to a hydrogenation unit, where the isomerization takes place in parallel, followed by a kerosene(K)-rectification. The head product is the kerosene fraction, and the bottom product is fed to a Diesel(D)-rectification. Here, the head product builds the diesel fraction. The bottom product is fed back to the hydrocracker.

#### 4. Conclusion

The conceptual outline of a 10,000 t/a PtL plant is presented. The needed technology steps were identified, and the

different technological options were evaluated. With regard to the technology selection, certain general assumptions were taken into consideration, such as the TRL, the robustness of the technologies, and their commercial availability. As result the initial equipment consists of an AEL and PEMEL for water electrolysis ( $H_2$  production) and an amine scrubbing for  $CO_2$  capture from biogenic sources (biogas plant, bioethanol plant).

Via a RWGS, the  $CO_2$  and  $H_2$  is converted to synthesis gas ( $CO$ ,  $H_2$ ), followed by a Co-catalyzed low temperature Fischer-Tropsch synthesis. The crude is then refined by hydrocracking, hydrogenation, isomerization, and distillation to achieve the three fuel fractions: kerosene, diesel, and naphtha. Furthermore, the coupling of these technologies was investigated and an integrated process flowsheet was developed.

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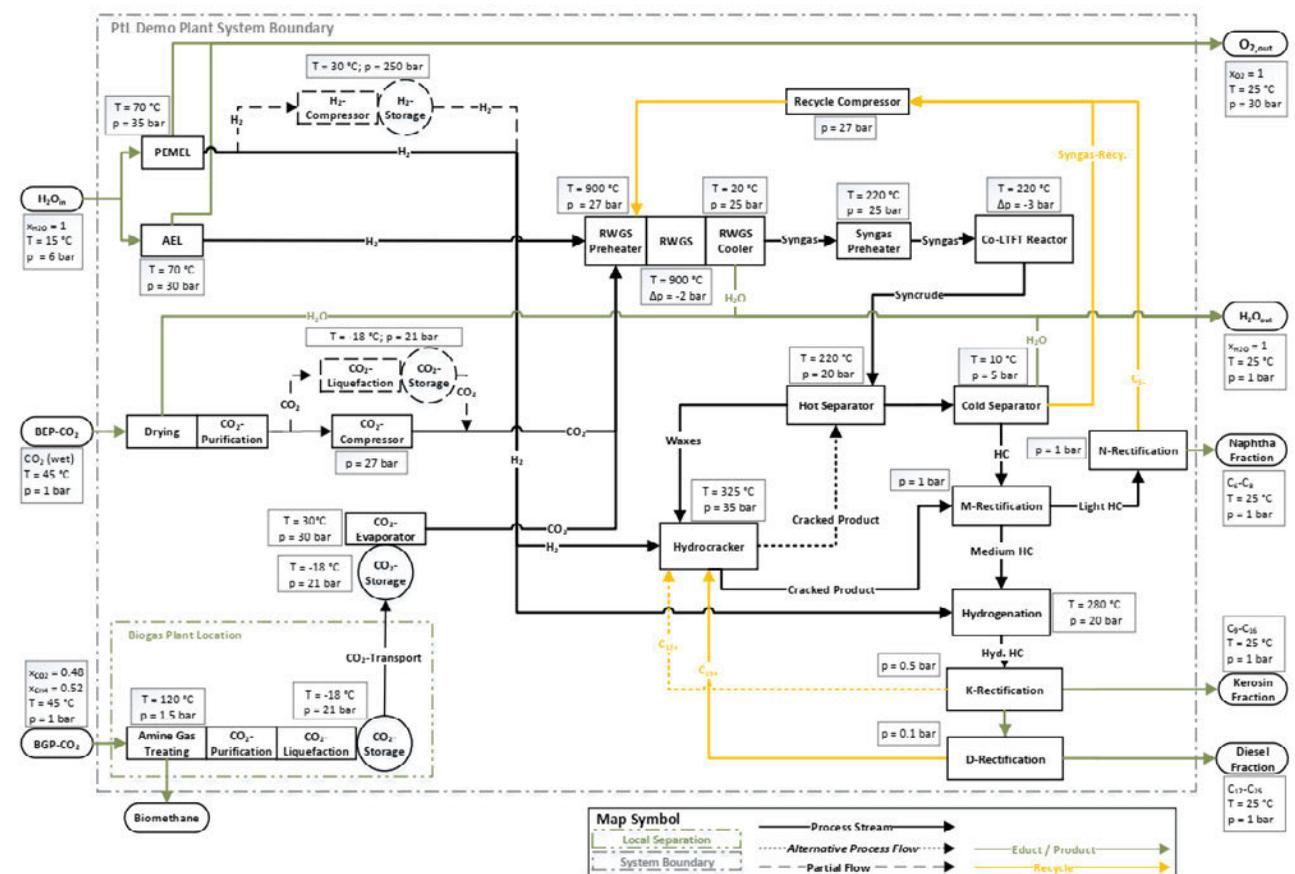


Fig. 2: Process scheme of a 10,000 t/a PtL plant; BGP: Biogas plant; BEP: Bioethanol plant; AEL: Alkaline electrolysis; PEMEL: Proton exchange membrane electrolysis, RWGS: Reverse water gas shift reaction, Syngas: Synthesis gas ( $CO$ ,  $H_2$ ); Co-LTFT: Cobalt catalyzed low temperature Fischer-Tropsch synthesis; Syncrude: Fischer-Tropsch (FT)-crude; M-Rectification: Middle-distillate rectification; HC: Hydrocarbons; Hyd.: hydrogenated; K-Rectification: Kerosene rectification; D-Rectification: Diesel rectification.

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