Techno-economic Study of the Storage of Fluctuating Renewable Energy in Liquid Hydrocarbons

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20 Analysis, Synthetic fuels

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ABSTRACT

Liquid hydrocarbons are considered as an option to store renewable energy while decoupling the supply and demand of renewable resources. They can also be used as transportation fuel or as feedstock for the chemical industry and are characterized by a high energy density. A process concept using renewable energy from fluctuating wind power and CO_2 to produce liquid hydrocarbons was modeled by a flowsheet simulation in Aspen Plus®. The capacity of the plant was set to 1 GW_{LHV} of hydrogen input, using water electrolysis, reverse-water-gas-shift reaction (RWGS) and Fischer-Tropsch (FT) synthesis. A feed of 30 t/h of H_2 generated 56.3 t/h (12,856 bbl/d) of liquid hydrocarbons. A Power-to-Liquid efficiency of 44.6 % was calculated for the base case scenario. Net production cost ranged from 12.41 $\$/GGE$ to 21.35 $\$/GGE$ for a system powered by a wind power plant with a full load fraction of about 47 %, depending on the assumed electricity feedstock price and electrolyzer capital cost. For systems with full load fractions between 70 % and 90 %, the production cost was in the range of 5.48 $\$/GGE$ to 8.03 $\$/GGE$.

1. Introduction

In 2012, a total of $1{,}133\ TWh$ of renewable power was generated worldwide, corresponding to 5.0 % of the total electricity generated [1]. Depleting, finite fossil fuel reserves and the goal to reduce CO_2 emissions led to a transition to alternative power generation technologies. Therefore, an increasing number of renewable energy installations is now being observed. It is predicted that from 2014 to 2035, the renewable generation capacity will double to about $3{,}930\ GW$ of installed capacity [2]. Over the past decade, conventional power plants accounted for about 68 % of the investment in the power sector. By 2035, however, about 62 % of the investment is predicted to be in renewable technologies [2].

In conventional energy systems, power generation follows the energy demand [3]. In contrast, wind and solar power generation follows natural conditions, with hourly, daily, weekly or seasonal fluctuations [4]. Hence, long-term seasonal storage applications with a high capacity, low storage losses, well-established and safe storage tanks and low space requirements are required. Liquid hydrocarbons are considered an option to store renewable energy while decoupling supply and demand. They are characterized by a high energy density, are used in the transportation sector and exhibit little to no loss during long-term storage. Additionally, liquid hydrocarbons have an existing infrastructure, can be easily transported and also be used as transportation fuel or as feedstock for the chemical industry.

The generation of liquid hydrocarbons was investigated by several studies [5], [6], [7], [8] and [9]. Current research focuses on the optimization of the generation of fuels and olefins from biomass and natural gas [10]. On the other hand, the use of CO_2 for the production of synthetic fuels demonstrates a real greenhouse gas sink. This technology combines CO_2/steam-mixed reforming and CO_2-active iron catalysts in Fischer-Tropsch synthesis in Gas-to-Liquid processes [11]. The generation of liquid transportation fuels by combining a solid oxide electrolyzer cell and Fischer-Tropsch (FT) synthesis was investigated by [6] and [7]. Mignard et al. investigated the generation of alcohols from marine energy and CO_2 [5]. Jess et al. suggest generating liquid fuels from solar energy and CO_2 [8]. A rating of several Power-to-Liquid (PtL) technologies was proposed by Tremel et al [9]. The aforementioned references assume a continuous supply of energy and reactant to the fuel production plant.

The present work investigates the techno-economic effect of an option to couple continuous fuel production with fluctuating energy sources, considering present realistic assumptions and future technological developments.

The economic potential of storing fluctuating renewable energy in liquid hydrocarbons is of special interest for renewable power station operators and for the prediction of future energy scenarios. Renewable liquid hydrocarbons may contribute to the fuel supply for aviation as well [12]. A techno-economic study was carried out, starting with a detailed process model of the generation of liquid hydrocarbons by FT synthesis. The model was analyzed by pinch point analysis and the economic performance was estimated on the basis of capital and operation cost estimations.

2. Scope of Evaluation and Process Description

The evaluation focuses on the production of liquid hydrocarbons from renewable excess power and CO_2. The system boundary and the block flow diagram of the process concept are shown in **Fehler! Verweisquelle konnte nicht gefunden werden.**.

The focus on fluctuating renewable energy requires a highly flexible electrolyzer unit. A proton exchange membrane (PEM) electrolyzer can be operated at high current densities (above 2 A/cm^2) and cover a nominal power density range from 10 % to 100 % [13]. A storage cavern acts as the link between the highly fluctuating source, the electrolyzer unit and the continuous chemical synthesis. Hydrogen is stored if excess power is available and used when the hydrogen demand exceeds its generation. The liquid product is stored in tanks for later use. The economic analysis comprises the cost estimation for the electrolyzer unit, the hydrogen storage cavern and the chemical plant, including auxiliary units and utilities.

Fehler! Verweisquelle konnte nicht gefunden werden. illustrates a more detailed flowsheet of the process concept. The PEM electrolysis and the cavern are not modeled in the flowsheet. The capacity of the plant is set to 1 GW of hydrogen input based on its lower heating value (LHV). H_2 from electrolysis and CO_2, which is delivered by a pipeline, are fed to the plant. CO_2 and H_2 are converted in the reverse-water-gas-shift (RWGS) reactor to syngas, which is composed of H_2 and CO. The syngas is then further

converted to hydrocarbons in the FT synthesis. The hydrocarbon syncrude is upgraded and separated from unreacted feed and gaseous hydrocarbons to make the final product.

3. Simulation Model

A flowsheet simulation model was developed in Aspen Plus®. Heat losses of reactors, heat exchangers and piping were neglected. Furthermore, the electrolyzer and the storage cavern are not included in the flowsheet model. The pressure losses in the process are lumped in the recycle stream and are assumed to be $0.2\ MPa$ [14].

3.1. Components and thermodynamic model

The model is based on the pure components H_2, CO_2, CO, and H_2O and the n-alkanes CH_4 through to $C_{30}H_{62}$, which were selected from the Aspen database. Coke is represented by solid carbon. Hydrocarbon products are represented only by n-alkanes, since the main products of cobalt based low temperature FT synthesis are n-alkanes [15]. CH_4 through to C_4H_{10} are gases, C_5H_{12} through to $C_{20}H_{42}$ are liquids and hydrocarbons with a chain length longer than C_{20} are waxes. In this work, the Peng-Robinson equation of state in combination with the Boston-Mathias alpha function is used to describe the phase behavior in the process [16], [17]. The Peng-Robinson equation of state is widely applied in gas processes, refining and FT modeling studies [14], [18], [19].

3.2. Reverse water-gas-shift reactor

The reverse water-gas-shift (RWGS) reaction (1) is the endothermic hydrogenation of CO_2 to CO [20].

$$CO_2 + H_2 \rightleftharpoons CO + H_2O \quad \Delta H_R^0 = 41.2\ kJ/mol \tag{1}$$

The RWGS reactor model comprises a Gibbs energy minimization reactor model and an adiabatic burner model. The Gibbs energy minimization reactor model assumes thermodynamic equilibrium for the RWGS, which is a reasonable assumption at high temperatures [8], [20]. The operation temperature and pressure are assumed to be $900\ °C$ and $2.5\ MPa$, respectively [21]. In addition to the fresh feed, the external recycle (see **Fehler! Verweisquelle konnte nicht gefunden werden.**) is fed to the RWGS

reactor. The external recycle contains unreacted reactants and gaseous hydrocarbons from the FT synthesis. Hence, steam reforming of the gaseous hydrocarbons occurs as a side reaction in the RWGS reactor. The external recycle is a split of the total recycle (from flash F-5, see **Fehler! Verweisquelle konnte nicht gefunden werden.**), whose split fraction is determined by the fuel demand of the burner (FG-1). The adiabatic burner model supplies heat to the RWGS reactor.

To reduce coking in the reformer, the carbon safety factor (CSF) was introduced [14], [22]. The CSF determines the amount of steam required to achieve a constant distance from the coking equilibrium. The CSF is calculated by equations (2) and (3).

$$CSF = \frac{y_{CO_2}}{y_{CO}^2} \cdot \frac{1}{P} \cdot K(T) \tag{2}$$

$$K(T) = e^{-\frac{\Delta G_R^0(T_0)}{R \cdot T_0} - \frac{\Delta H_R^0(T_0)}{R} \cdot \left(\frac{1}{T} - \frac{1}{T_0}\right)} \tag{3}$$

y_{CO_2} and y_{CO} are the molar fraction of CO_2 and CO, respectively. P is the overall pressure and $K(T)$ the temperature dependent equilibrium constant. $K(T)$ is calculated by the Gibbs reaction enthalpy (ΔG_R^0), the reaction enthalpy (ΔH_R^0), the ideal gas constant R, the temperature T and the standard temperature $T_0 = 25°C$. To achieve an O/C ratio greater than 2, the criterion $CSF = 3$ must be met.

3.3. Fischer-Tropsch synthesis

In FT synthesis, CO and H_2 are polymerized to long chain hydrocarbons over a catalyst (4).

$$i \cdot CO + 2i \cdot H_2 \rightarrow (-CH_2-)_i + i \cdot H_2O \quad \Delta H_R^0 = -152\ kJ/mol \tag{4}$$

The chain growth probability, α, is a measure if whether chain propagation or termination occurs (5) and is connected to the weight fraction, w_n, by the Anderson-Schulz-Flory distribution [15], which determines the product distribution.

$$w_n = \frac{(1-\alpha)}{\alpha} \cdot \alpha^n \cdot n \tag{5}$$

The reaction scheme of a cobalt-based catalyst at low temperatures was selected for this work, since the yield of n-alkanes is high for this kind of catalyst [15], [23]. The FT synthesis was modeled by a stoichiometric reactor model. The model comprises 30 reactions for the generation of hydrocarbons from CH_4 to $C_{30}H_{62}$. The molar fractional conversion of each reaction is determined by α, the corrected methane yield and the per-pass conversion of CO as displayed in the supplementary information (SI) Table S1. The H_2-to-CO ratio, the molar fraction of the reactants and the operation temperature and pressure are fixed and also reported in Table S1 (of the SI). The ratio of H_2 feed to CO_2 feed is adjusted to meet the H_2-to-CO ratio criteria. The molar fraction of the reactants is adjusted by the internal recycle, which is determined by the amount of gaseous product taken from the fourth flash (F-4).

3.3. Product separation and upgrading section

The targeted products of the plant are liquid hydrocarbons with a chain length ranging from C_5 to C_{20}. Therefore, hydrocracking is required to crack the waxes into shorter chain hydrocarbons in the desired range. The hydrocracker model is based on a yield distribution [24]. It operates at 6.0 MPa and $T_{HC} = 350\,°C$. A five step product separation section is modeled to represent the separation of liquid products from the gaseous byproducts, reaction water, unreacted gases and inserts [15]. The separation temperatures are: $T_{F-1} = 145°C$, $T_{F-2} = 100°C$, $T_{F-3} = 100°C$, $T_{F-4} = 10°C$ and $T_{F-5} = -30°C$. The liquid products of the separation stages F-2 through to F-5 are collected and brought together with the product of the hydrocracker to ambient conditions in the flash drum F-6. The gaseous byproduct is additional fuel for the burner.

4. Model Results and Process Performance

4.1. Model results

The operation parameters of the 1 GW_{LHV} H_2 input plant are described in the simulation model section. About $270\,t/h$ of H_2O and $236\,t/h$ of CO_2 are required to generate about $56\,t/h$ of liquid hydrocarbons. The mass flow block diagram is displayed in Figure S1 of the supplementary information (SI). The main share of the liquid hydrocarbon product is in the range of C_5 to C_{10}. The detailed product distribution is shown in Figure S2 in the SI.

153

154 *4.2. Heat integration*

155 The cooling and heating requirements are determined by pinch point analysis. The composite curves are
156 shown in **Fehler! Verweisquelle konnte nicht gefunden werden.** and indicate that the heating demand
157 of the process can be satisfied by internal heat exchange. A total cooling demand of $431.5\ MW$ must be
158 realized to cool down the remaining hot streams of the process. Refrigeration, chilling and cooling water
159 are selected as cooling utilities. A detailed record of the selected utility types, their characteristics and
160 thermal loads is listed in Table S2 of the SI.

161 *4.3. Process performance*

162 Five parameters are used to assess the process performance: three process efficiencies, a chemical
163 conversion and a recycle ratio (see **Fehler! Verweisquelle konnte nicht gefunden werden.**). The
164 chemical conversion efficiency, η_{CCE}, accounts for losses when converting H_2 and CO_2 into liquid
165 hydrocarbons. The plant efficiency, η_{Plant}, considers the in-plant losses due to compression, pumping
166 and utilities (P_U). The Power-to-Liquid efficiency, η_{PtL}, relates the total energy input to the chemical
167 energy content of the liquid products and considers the energy demand for electrolysis and AC/DC
168 conversion. The carbon conversion, η_C, is a measure of the overall conversion of carbon atoms into
169 hydrocarbons. The recycle ratio allows the evaluation of the size of the recycle streams. **Fehler!**
170 **Verweisquelle konnte nicht gefunden werden.** summarizes the five process performance parameters
171 and their respective calculation formulae.

172 The energy demand of electrolyzing water to hydrogen is predicted to be 4.3 kWh/Nm^3 for large-scale
173 electrolyzer systems [25]. Thereby, the power demand for electrolysis is calculated as $1{,}450\ MW$.
174 Assuming a conversion efficiency of 96 % for the AC/DC conversion, the power input to the process is
175 calculated as $1{,}512\ MW$. The electrical demand for chilling and refrigeration results from the respective
176 thermal loads and coefficients of performance. **Fehler! Verweisquelle konnte nicht gefunden werden.**
177 summarizes the results of the flowsheet simulation. Additionally, the results of the performance
178 parameters are shown.

The plant efficiency η_{Plant} of 65.9 % is lower than the reported value of 69.3 % [9], which was calculated based on an idealized reaction scheme of 100 % conversion. The Power-to-Liquid efficiency η_{PtL} of 44.6 % is lower than the reported value of 51 % [6], where instead of a PEM electrolyzer a solid oxide electrolyzer is applied, which uses excess heat directly to decrease the energy losses due to electrolysis. Apart from the liquid hydrocarbons, about 431.6 t/h (184 MW) of steam is produced as a byproduct.

5. Economic Analysis

A cost estimation was carried out for the proposed concept. The cost basis is the US dollar ($, December 2014).

5.1. Methodology and results

Methodology and accuracy comply with classes three and four of the Association for the Advancement of Cost Engineering for cost estimation in the process industry [26].

The component prices are estimated by equation (6) according to [27] and [28]. Scaling factors account for the economies of scale. Prices from previous years are updated via the Chemical Engineering Plant Cost Index (CEPCI).

$$PC = PC_{ref} \cdot \left(\frac{S}{S_{ref}}\right)^{D} \cdot \left(\frac{CEPCI_{2014}}{CEPCI_{ref}}\right) \cdot F \cdot z(S_{max}) \tag{6}$$

The equation gives the purchased cost (PC) of equipment at the scale (S) required for the proposed capacity in the year 2014. PC_{ref} is the purchased cost in the reference year at the reference scale (S_{ref}). The scaling factor (D) accounts for scaling effects. $CEPCI_{2014} = 576.1$ and $CEPCI_{ref}$ are the cost indices for the year 2014 and the reference year, respectively [27], [29]. F is a factor accounting for high pressure and special materials, where applicable. The quantity (z) is the number of parallel trains dependent on the maximum scale S_{max}.

The installed capacity of the electrolyzer and the H_2 cavern depends on the fluctuating renewable power production pattern. Therefore, the electrolyzer capacity is calculated based on the amount of H_2 required per year and the full-load fraction of the fluctuating renewable energy source. An offshore wind power plant in the North Sea is selected as the fluctuating renewable energy scenario [30]. The wind pattern shows short-term and seasonal fluctuations from $0.03\ GW$ to $3.2\ GW$ (see Figure S3 of the SI). Based on the generation pattern, an annual full-load fraction of $46.8\ \%$ is calculated, which leads to a required electrolyzer capacity of $3.2\ GW$; the capacity of the cavern is calculated to $29.1\ kt$, or equivalent to $11\ \%$ of the annual H_2 consumption. The filling level of the cavern is shown in Figure S3 of the SI. Due to the fluctuating pattern of power generation, the cavern must be partially filled for the start-up. Assuming that the same wind pattern applies each year, the required start-up amount of hydrogen is determined to be $22.5\ kt$.

Fehler! Verweisquelle konnte nicht gefunden werden. lists the capacities of the main components and the respective parameters required to calculate the purchased cost. The prices of the other process equipment are based on literature values [28].

The total purchased cost (TPC) of the plant is $3{,}150\ M\$$. The TPC is multiplied by ratio factors to account for installation, instrumentation, piping, electrical systems, buildings, yard improvements and service facilities [28]. Adding engineering, construction, legal expenses and contractor's fees, the fixed capital investment (FCI) for the chemical plant can be calculated by (7). The reported cost for the electrolyzer includes instrumentation, piping, electrical systems, service facilities, engineering and construction. Hence, the FCI of the electrolyzer is calculated by (8).

$$FCI_{Chemical\ Plant} = 4.60 \cdot TPC_{Chemical\ Plant} \tag{7}$$

$$FCI_{Electrolyzer} = 1.83 \cdot TPC_{Electrolyzer} \tag{8}$$

Including contingencies, working capital and the start-up expenses for the cavern, the total capital investment (TCI) is $8{,}690\ M\$$ (9). The start-up expenses for the cavern are $158\ M\$$.

$$TCI = 1.25 \cdot FCI_{Total} + Cost_{Start-up\ Cavern} \quad (9)$$

Assuming an interest rate of 7 % and a life time of 30 years for the electrolyzer unit and the chemical plant, as well as 80 years for the cavern, the annualized capital cost (ACC) is calculated as $560\ M\$/a$ by (10) [27].

$$ACC = FCI \cdot \frac{IR \cdot (1+IR)^{PL}}{(1+IR)^{PL} - 1} \quad (10)$$

The operation costs are the costs for maintenance, insurance, taxes, reactants, materials, utilities and revenues for byproducts. The maintenance cost for the chemical plant components is assumed to be 7 % of FCI of the chemical plant [28]. The maintenance effort for the electrolyzer is calculated based on the reconditioning period, which is reported to be 15 % of the FCI of the electrolyzer unit and must be carried out every 60,000 hours of operation [31]. Insurance and taxes are 2 % of the overall FCI [28]. The prices for utilities, reactants and byproducts are listed in Table S3 in the SI.

The total operation cost (TOC) is $2{,}800\ M\$/a$. The total annualized cost (TAC) is the sum of the TOC and the ACC. The net production cost (NPC) is $18.62\ \$/GGE$ ($6.83\ \$/kg, 4.51\ \$/l$). Water electrolysis and intermediate storage in the cavern account for about 89 % of the NPC.

Fehler! Verweisquelle konnte nicht gefunden werden. depicts the distribution of the total capital investment and the net production cost on the different cost categories. With all of the above mentioned realistic assumptions for an $1\ GW_{LHV}$ H_2 input PtL plant, the annual capital cost and the cost for electricity to power the electrolysis account for about 85 % of the net production cost.

5.2. Sensitivity analysis

The effect of several economic parameters on the production cost of liquid hydrocarbons is shown in **Fehler! Verweisquelle konnte nicht gefunden werden.**. The steeper the slope is, the larger the parameter's effect on the overall economics is. **Fehler! Verweisquelle konnte nicht gefunden werden.** shows that both the capital cost of the electrolyzer and the cost of electricity have the highest slopes. As shown in **Fehler! Verweisquelle konnte nicht gefunden werden.**, these are the cost categories with the

highest share of the production cost. If offshore wind power was available for half of the assumed 186 $\$/MWh$, the NPC would shrink to 11.81 $\$/GGE$. Assuming excess power free of charge, the NPC drops to 5.00 $\$/GGE$. The effect on the revenues due to selling O_2 has a larger impact on the production cost than the purchase of CO_2. The effect of changing the costs of the cavern is small compared to the O_2 revenue. The critical factor for intermediate H_2 storage is therefore not its cost, but the local availability. The sensitivity analysis proves that the cost of the electrolyzer and wind power are the main expenses in this production process. The sensitivity analysis shows that NPC ranges from 15.90 $\$/GGE$ to 21.35 $\$/GGE$.

The effect of the interest rate, the maintenance cost, taxes, insurance expenses and the ratio factor for the chemical plant is depicted in **Fehler! Verweisquelle konnte nicht gefunden werden.**. The interest rate and the ratio factor selected for the chemical plant have the largest effect on the NPC. Depending on the assumed economic parameters, the net production cost varies by about $\pm$ 5.0 %.

Cost reductions can be observed by taking the overload functionality of the PEM electrolyzer into account. An assumed overload functionality of 5.0 % of the installed capacity leads to a capital cost reduction of 3.6 %. Due to a high share of the electricity cost, the NPC is reduced by 0.9 % (18.45 $\$/GGE$). Further technology development is expected to reduce the energy demand of electrolysis to about 4.1 kWh/Nm^3 [25], which will cut the net production cost by 4.6 % (17.77 $\$/GGE$). Additionally, electrolyzer capital cost is predicted to drop to about 380 $\$/kW$ [32] and electricity generation cost of offshore wind power plants may drop to 136 $\$/MWh$ [33]. Taking higher efficiency, overload capability and the predicted lower prices into account, the production cost could drop by $1/3$ to about 12.41 $\$/GGE$ in an optimistic future scenario (see "Future Case", **Fehler! Verweisquelle konnte nicht gefunden werden.**).

The full load capacity of the electrolyzer is highly dependent on the chosen renewable power source and its location. Hence, the outcome of the effect of the full load fraction on the net production cost is presented in **Fehler! Verweisquelle konnte nicht gefunden werden.**. With rising full load hours, the net production cost decreases due to lower expenses for the electrolyzer and the intermediate storage.

The share of the annual capital cost of total annual cost declines from 36 % at a full load fraction (FLF) of 10 % to about 11 % at a continuous power input (100 % FLF). The net production cost curve shows a high cost reduction potential when the FLF is increased up to 70 %.

5.3. Fields of application and substitution potentials

FT-based liquid hydrocarbons allow for a wide variety of applications. Fields of application include fuel for stationary gas turbines for power generation, in the transportation sector, or as feedstock for the chemical industry. FT-based syncrude does not fulfill the specifications for gasoline, kerosene or diesel without upgrading. They may be sold to refineries that already operate units for further processing and upgrading to transportation fuels. Alternatively, they could be used as renewable drop-in to conventional fuels. In the chemical industry, a pure feedstock is mainly required; therefore, additional distillation would be required to generate pure feedstock for further processing. Gas turbines allow for a wide variety of liquid mixtures as fuel [34]. PtL hydrocarbons provide renewable generated sulfur and nitrogen-free fuels for gas turbines. **Fehler! Verweisquelle konnte nicht gefunden werden.** compares the market feedstock prices with the calculated net production cost for the base case and a future predicted value.

Fehler! Verweisquelle konnte nicht gefunden werden. indicates that economic viability cannot be achieved for the proposed process at present. The production cost for the base case is about 7 times today's market prices of fuels and chemicals; for the future case it is about 4 times. Generation of electricity, when no renewable power is available, by using liquid hydrocarbons, which were produced from renewable electricity, reveals prices of about 4.5 times today's feedstock market prices. Taking the optimistic future case, about 3 times today's market price applies. Synthetic fuels can achieve crude oil market prices (93 $\$/bbl$) at power costs of 8.70 $\$/MWh$ if electrolyzer capital cost of 380 $\$/kW$ and a full load fraction of 100 % are assumed.

The net production cost ranges from 12.41 $\$/GGE$ to 21.35 $\$/GGE$, depending on the assumed electricity feedstock price and electrolyzer capital cost. Strong dependence of the net production cost on the applied assumptions of the electrolyzer capital cost and the electricity price complicates the

296 comparison of the calculated costs with other studies. Becker et al. reports fuel production cost of
297 4.66 $/GGE$ to 18.30 $/GGE$ for FLFs in the range of 20 % to 100 % and electricity prices of 20 $/
298 MWh to 80 $/MWh$ [6]. Applying a FLF of 90 % and electricity cost of 20 $/MWh$, net production
299 cost of 5.48 $/GGE$ is calculated (see "20 $/MWh$ Case", **Fehler! Verweisquelle konnte nicht**
300 **gefunden werden.**), which is comparable to the reported value of 5.44 $/GGE$ [6]. The combination of
301 high full load fractions and low energy prices allows the generation of liquid fuels at about twice the
302 market prices of today (see **Fehler! Verweisquelle konnte nicht gefunden werden.**). The generation of
303 various liquid fuels from H_2 and CO_2 proposing the decoupling of the H_2 generation from the chemical
304 plant was investigated [9]. Tremel et al. reports syncrude production cost of 7.50 $/GGE$ for FLF of
305 70 % and a H_2 feedstock price of 4 $/kg$. The model of the present study determines a production cost
306 of 8.06 $/GGE$ under these assumptions.

307

308 **6. Conclusion**

309 A process concept using renewable power from fluctuating wind power and CO_2 to produce liquid
310 hydrocarbons was modeled by a flowsheet simulation. The economic performance of the process was
311 evaluated. A Power-to-Liquid efficiency of 44.6 % was calculated for a 1 GW_{LHV} H_2 input PtL plant.

312 The economic analysis indicates that economic viability of the process cannot be achieved under current
313 market prices for neither fuels nor chemicals. Net production cost ranges from 12.41 $/GGE$ to
314 21.35 $/GGE$ for a wind-powered system if electrolyzer cost vary in the range of 340 $/kW$ to 1275 $/
315 kW and the wind power cost from 136 $/MWh$ to 223 $/MWh$. Systems with FLFs between 70 % and
316 90 % and low electricity feedstock cost yield production costs in the range of 5.48 $/GGE$ to 8.03 $/
317 GGE. The economic methodology underlays an inherent uncertainty of $\pm$30 %. Sensitivity analyses
318 show that the main effect on the production costs comes from the electrolyzer capital cost, the wind
319 power costs and the FLF. Therefore, reducing the costs for electrolyzer systems and electricity feedstock
320 are the key factors for creating an economically viable production scenario of liquid hydrocarbons from
321 renewable power and CO_2. Additionally, economic viability is more realistic for systems operating at

high FLFs, as they decrease the capital costs for high installed capacities of the electrolyzer and the intermediate storage. Hence, a minimum FLF of 70 % is recommended for liquid hydrocarbon processes based on renewable power.

The technical assessment revealed a large amount of excess heat, which is assumed to be sold. The approach of the conversion of thermal energy into electricity by a steam cycle is proposed, but this concept reveals only a small overall efficiency increase due to the low efficiency of the steam cycle. In a subsequent study, the direct thermal use of the excess heat and its effect on the process efficiency and economics will be investigated. The technical and economic potential of CO_2 sources will be examined to evaluate the limitations of their availability. Additionally, the technical options and the cost of upgrading products from liquid hydrocarbons to jet fuels is of special interest to the authors and will be assessed.

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NOMENCLATURE

AC	Alternate current
ACC	Annualized capital cost
ASF	Anderson-Schulz-Flory distribution
α	Chain growth probability
CEPCI	Chemical Engineering Plant Cost Index
COP	Coefficient of performance
CSF	Carbon safety factor
DC	Direct current
EL	Electrolysis
η_C	Carbon conversion
η_{CCE}	Chemical conversion efficiency
η_{Plant}	Chemical plant efficiency
η_{PtL}	Power-to-Liquid efficiency
f_{H_2+CO}	Molar fraction of H_2 and CO
FCI	Fixed capital investment
FLF	Full load fraction
FT	Fischer-Tropsch
FTS	Fischer-Tropsch synthesis reactor
GGH	Gasoline gallon equivalent
ΔH_R^0	Standard enthalpy of reaction (kJ/mol)
LH	Liquid hydrocarbons
LHV	Lower heating value
LP	Low pressure steam
$\dot{m}$	Mass flow (t/h)
MP	Medium pressure steam
n	Carbon number
NPC	Net production cost
p	Pressure (MPa)
P	Power (MW)
PC	Purchased cost
PEM	Proton exchange membrane
PtL	Power-to-Liquid
R	Recycle ratio
$R_{H_2/CO}$	H_2-to-CO ratio
RWGS	High temperature reformer, reverse water gas shift reaction
T	Temperature $(°C)$
TAC	Total annualized cost
TCI	Total capital investment
TOC	Total operation cost
TPC	Total purchased cost
w	Mass fraction

378 REFERENCES

379

[1] International Energy Agency, "Key World Energy Statistics," International Energy Agency, Paris, 2014.

[2] International Energy Agency, "World Energy Investment Outlook," International Energy Agency, Paris, 2014.

[3] P. Denholm, E. Ela, B. Kirby and M. Milligan, "The Role of Energy Storage with Renewable Electricity Generation," National Renewable Energy Laboratory, Golden, 2010.

[4] C. Ekman and S. Jensen, "Prospects for large scale electricity storage in Denmark," *Energy Conversion and Management,* vol. 51, pp. 1140-1147, 2010. DOI:10.1016/j.econman.2009.12.023.

[5] D. Mignard and C. Pritchard, "Processes for the synthesis of liquid fuels from CO2 and marine energy," *Chemical Engineering Research and Design,* vol. 84, pp. 828-836, 2006. DOI:10.1205/cherd.05204.

[6] W. Becker, R. Braun, M. Penev and M. Melaina, "Production of Fischer-Tropsch liquid fuels from high temperature solid oxide co-electrolysis units," *Energy,* pp. 99-115, 2012. DOI:10.106/j.energy.2012.08.047.

[7] J. Stempien, M. Ni, Q. Sun and S. Chan, "Thermodynamic analysis of combined solid oxide electrolyzer and Fischer-Tropsch processes," *Energy,* vol. 81, pp. 682-690, 2015. DOI:10.1016/j.energy.2015.01.013.

[8] A. Jess, P. Kaiser, C. Kern, R. Unde and C. von Olshausen, "Considerations concerning the energy demand and energy mix of global welfare and stable ecosystems," *Chemie Ingenieur Technik,* vol. 83, pp. 1777-1791, 2011. DOI:10.1002/cite.201100066.

[9] A. Tremel, P. Wasserscheid, M. Baldauf and T. Hammer, "Techno-economic analysis for the synthesis of liquid and gaseous fuels based on hydrogen production via electrolysis," *Int. J. Hydrogen Energy,* p. in press, 2015. DOI:10.1016/j.ijhydene.2015.01.097.

[10] O. Onel, A. Niziolek, J. Elia, R. Baliban and C. Floudas, "Biomass and Natural Gas to liquid transportation fuels and olefins (BGTL+C2_C4): Process synthesis and global optimization," *Ind. Eng. Chem. Res.,* vol. 54, pp. 359-385, 2015. DOI:10.1021/ie503979b.

[11] C. Zhang, K.-W. Jun, R. Gao, Y.-J. Lee and S. Kang, "Efficient utilization of carbon dioxide in gas-to-liquid process: Process simulation and techno-economic analysis," *Fuel,* vol. 157, pp. 285-291, 2015. DOI:10.1016/j.fuel.2015.04.051.

[12] R. Kivits, M. Charles and N. Ryan, "A post-carbon aviation future: Airports and the transition to cleaner aviation sector," *Futures,* vol. 42, pp. 199-211, 2010. DOI:10.1016/j.futures.2009.11.005.

[13] M. Carmo, D. Fritz, J. Mergel and D. Stolten, "A comprehensive review on PEM water

electrolysis," *Int. J. Hydrogen Energy,* vol. 38, pp. 4901-4934, 2013. DOI:10.1016/j.ijhydene.2013.01.151.

[14] D. König, N. Baucks, G. Kraaij and A. Wörner, "Entwicklung und Bewertung eines Verfahrenskonzeptes zur Herstellung flüssiger Kohlenwasserstoffe unter Nutzung von CO2," *Chemie Ingenieur Technik,* no. 86, p. 1351, 2014. DOI:10.1002/cite.201450066.

[15] A. de Klerk, Fischer-Tropsch Refining, Weinheim: Wiley-VCh Verlag, 2011. ISBN:978-3-527-32605-1.

[16] D. Peng and D. Robinson, "A new two-constant equation of state," *Ind. Eng. Chem. Fundam.,* no. 15, pp. 59-64, 1976. DOI:10.1021/i160057a011.

[17] J. Boston and P. Mathias, "Phase Equilibria in a Third-Generation Process Simulator," *Proceedings of the 2nd International Conference on Phase Equilibria and Fluid Properties in the Chemical Process Industries,* pp. 823-849, 17-21 March 1980.

[18] M. Sudiro and A. Bertucco, "Production of synthetic gasoline and diesel fuel by alternative processes using natural gas and coal: Process simulation and optimization," *Energy,* no. 34, pp. 2206-2214, 2009. DOI:10.1016/j.energy.2008.12.009.

[19] R. Baliban, J. Elia and C. Floudas, "Toward novel hybrid biomass, coal, and natural gas processes for statisfying current transportation fuel demands: 1: Process alternatives, gasification modeling, process simulation and economic analysis," *Ind. Eng. Chem. Res.,* no. 49, pp. 7343-7370, 2010. DOI: 10.1021/ie100063y.

[20] R. Unde, "Kinetics and reaction engineering aspects of syngas production by the heterogeneously catalysed reverse water gas shift reaction," University of Bayreuth, Bayreuth, 2012.

[21] W. Verdegaal, S. Becker and C. von Olshausen, "Power-to-Liquid: Synthetisches Rohöl aus CO2, Wasser und Sonne," *Chemie Ingenieur Technik,* vol. 87, pp. 340-346, 2015. DOI:10.1002/cite.201400098.

[22] A. Melman and N. Woudstra, Eds., Solid oxide fuel cell systems study, Apeldoorn: Commission of the European Communities, 1991. ISBN:92-826-1960-5.

[23] A. Steynberg and M. Dry, Eds., Fischer-Tropsch Technology, Amsterdam: Elsevier B.V., 2004. ISBN:978-0-444-51354-0.

[24] Y. Liu, K. Murata, K. Okabe, M. Inaba, I. Takahara, T. Hanaoka and K. Sakanishi, "Selective hydrocracking of Fischer-Tropsch waxes of high-quality Diesel fuel over Pt-promoted polyoxocation-pillared montmorillonites," *Top Catal,* vol. 52, pp. 597-608, 2009. DOI:10.1007/s11244-009-9239-8.

[25] T. Smolinka, M. Günther and J. Garche, "Stand und Entwicklungspotenzial der Wasserelektrolyse zur Herstellung von Wasserstoff aus regenerativen Energien," NOW GmbH, Berlin, 2010.

[26] Association of the Advancement of Cost Engineering, "Cost Estimate Classification System - as applied in engineering, procurement, and construction for the process

industries," AACE International, Morgantown, 2011.

[27] S. Towler and R. Sinnott, Chemical Engineering Design, Burlington: Elsevier Inc., 2008. ISBN:978-0-7506-8423-1.

[28] M. Peters, K. Timmerhaus and R. West, Plant Design and Economics for Chemical Engineers, New York: McGraw-Hill, 2004. ISBN:007-124044-6.

[29] Chemical Engineering, "Chemical Engineering Plant Cost Index," *Chemical Engineering,* p. 64, January 2015.

[30] Y. Scholz, "Renewable energy based electricity supply at low costs: development of the REMix model and application for Europe," University of Stuttgart, Stuttgart, 2012.

[31] C. Ainscough, D. Peterson and E. Miller, "Hydrogen production cost from PEM electrolysis," Department of Energy USA, Washington, DC, 2014.

[32] J. Levene, B. Kroposki and G. Sverdrup, "Wind energy and production of hydrogen and electricity - opportunities for renewable hydrogen," National Renewable Energy Laboratory, Golden, 2006.

[33] International Energy Agency, "Technology Roadmap Wind energy," International Energy Agency, Paris, 2013.

[34] C. Soares, Gas Turbines, Oxford: Butterworth-Heinemann, 2015. ISBN:978-0-12-410461-7.

[35] G. Saur, "Wind-to-hydrogen project: electrolyzer capital cost study," National Renewable Energy Laboratory, Golden, 2008.

[36] O. van Vliet, A. Faaij and W. Turkenburg, "Fischer-Tropsch diesel production in a well-to-wheel perspective: A carbon, energy flow and cost analysis," *Energy Conversion Management,* vol. 50, pp. 855-876, 2009. DOI:10.1016/j.enconman.2009.01.008.

[37] D. Steward, G. Saur, M. Penev and T. Ramsden, "Lifecycle cost analysis of hydrogen versus other technologies for electrical energy storage," National Renewable Energy Laboratory, Golden, 2009.

[38] U.S. Energy Information Administration, "www.eia.gov," 2015. [Online]. Available: http://www.eia.gov/dnav/pet/hist/LeafHandler.ashx?n=pet&s=rwtc&f=m. [Accessed 31 03 2015].

[39] Platts, "Solventswire," The McGraw-Hill, Houston, vol. 35. 2012.

[40] U.S. Energy Information Administration, "www.eia.gov," 2015. [Online]. Available: http://www.eia.gov/dnav/pet/pet_pri_gnd_dcus_nus_a.htm. [Accessed 31 03 2015].

[41] P. Kaiser, F. Pöhlmann and A. Jess, "Intrinsic and effective kinetics of cobalt-catalyzed Fischer-Tropsch synthesis in view of a Power-to-Liquid process based on renewable energy," *Chemical Engineering Technology,* vol. 37, pp. 964-972, 2014. DOI:10.1002/ceat.201300815.

[42] R. Swanson, A. Platon, J. Satiro and R. Brown, "Techno-economic analysis of Biomass-to-Liquids production based on gasification," *Fuel,* vol. 89, pp. 11-19, 2010. DOI:10.1016/j.fuel.2010.07.027.

[43] Dutch Association of Cost Engineers, Price Booklet, vol. 30, Den Haag: BIM Media, 2014. ISBN: 978-94-62-45051-6.

[44] P. Markussen, J. Austell and C. Hustad, "A CO2-infrastructure for EOR in the North Sea (CENS): Macroeconomic implications for host countries," *Sixth Int. Conference on Greenhouse Gas Control Technologies,* vol. 324, 2002.

[45] G. Ulrich and P. Vasudevan, "How to estimate utility costs," *Chemical Engineering,* pp. 66-69, 2006.

[46] P. Rao and M. Muller, "Industrial oxygen: its generation and use," *ACEEE Summer Study on Energy Efficiency in Industry,* vol. 6, pp. 124-135, 2007.

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382 References [43] to [46] refer to citations in the supplementary information (Table S3).