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Fischer-Tropsch kinetics comparison and sensitivity analysis for a pilot-scale jet fuel production reactor

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Abstract

Decreasing CO₂ emissions is vital to achieve a sustainable world energy transition. One way to achieve that goal is to replace our current fossil-based carbon products with defossilized ones. Fischer-Tropsch (FT) technologies can contribute towards this goal by transforming captured CO₂ and green hydrogen into a wide array of hydrocarbon chains. Under optimized conditions, a high concentration of long-chains hydrocarbons can be produced and further upgraded into jet fuel. Thus, difficult to electrify sectors of the economy such as the aviation sector could have a defossilized supply of fuel. In this context, the end objective of our research is to design, install, operate and optimize a FT reactor to serve as core of a future Power-to-Jet Fuel pilot-scale implementation at the University of Liège (ULiège).

In a previous study [1], the FT kinetics proposed by Iglesia et al. [2] and the stoichiometry reported by Hillestad et al. [3] were used to model said pilot-scale FT installation. Rouxhet et al. [4] then proceeded to use a more complex set of kinetics and stoichiometry reported by Ma et al. [5] for the same purpose. In the present study, the kinetics proposed by Yates et al. [6] are used to design the same FT installation and the results are compared to the ones obtained with the other two sets of kinetics.

The Yates kinetics using a Co/MgO on SiO₂ catalyst were deemed the best suited for the design of the FT facility. Then, a sensitivity analysis is performed to determine the influence of multiple process variables on the conversion of the reactants.

Keywords: Fischer-Tropsch; Jet Fuel; Aspen Custom Modeler; Simulation.

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Nomenclature

| | |
|-----------------|---------------------------------|
| CO ₂ | Carbon Dioxide |
| FT | Fischer-Tropsch |
| RWGS | Reverse Water Gas Shift |
| ULiège | University of Liège |
| FBR | Fixed Bed Reactor |
| ASF | Anderson-Schulz-Flory |
| NS | Not specified |
| α | Chain growth probability |
| CSTR | Continuous stirred-tank reactor |
| CH ₄ | Methane |
| H ₂ | Hydrogen |
| CO | Carbon Monoxide |
| GHSV | Gas hourly space velocity |

1. Introduction

The European Commission aims to lower CO₂ emissions by 55 % compared to 1990 by 2030. In 2016, the aviation sector accounted for 3.6% of overall emissions and 13.4% of transport emissions in the European Union [7]. The sector also has the lowest share of renewables, with only 6% [8]. Thus, innovative alternatives such as using green hydrogen as fuel or producing jet fuel in sustainable ways are considered to defossilize this means of transportation. Sustainable jet fuel could become an adequate substitute of its traditional counterpart by providing at least 70% life-cycle carbon reductions [9].

The present study is carried out in the framework of further improving the Power-to-Jet Fuel value chain and developing a pilot-scale facility. By utilizing hydrogen and carbon monoxide as feedstock, a Fischer-Tropsch (FT) reactor synthesizes jet fuel as a liquid energy vector. This chemical pathway is rendered more sustainable when the hydrogen is produced from renewable energy sources via water electrolysis. Similarly, the carbon monoxide should be obtained from the Reverse Water Gas Shift (RWGS) of said hydrogen and captured carbon dioxide.

Although the production of sustainable FT fuels has already been studied [10, 11], most of these studies do not focus on the maximization of jet fuel production. Moreover, previous studies mostly focus on reaction modeling, and less work has been carried out regarding process study. To do so, the present work uses Aspen Custom Modeler™. First, it allows the use of the vast properties database that AspenTech provides. Second, it allows a detailed modeling of the reaction linked to complex kinetics, catalysts and reactor configurations. Likewise, there is no comprehensive data available on FT at a pilot-scale for the maximization of jet fuel production. Information such as catalyst mass, catalyst configuration, kinetics used for the design, sizing of the reactor, etc; are partially or not provided at all in previous references. The resulting design of this present study will then serve as input for the construction of a pilot-scale reactor at the University of Liège (ULiège). The operation and results obtained from the facility will retroactively improve the model itself.

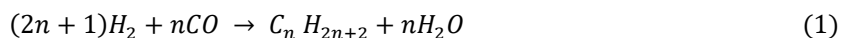
On the other hand, there are multiple commercially available catalysts and, in tandem, kinetics linked to these catalysts have been proposed to portray the behavior of the reaction. Thus, when designing a FT facility, choosing the right catalyst and kinetic model is mandatory to have an accurate depiction. From the wide array of kinetics available, the kinetics of Iglesia et al. [2], Yates et al. [6] and Ma et al. [5] were chosen, analyzed and implemented to design the pilot-scale facility. The catalysts linked to these kinetics (see details below) are effective for the maximization of jet fuel production via FT.

In this paper, the main properties of the FT reaction and the main features of the different sets of kinetics selected to describe it are first portrayed. Then, these kinetics are compared by modeling the pilot-scale fixed bed reactor (FBR) at the ULiège in compliance with the electrolysis capacity available on site. The most suitable catalyst and model are selected based on the amount of catalyst mass, and thus the inherent costs of this design, as well as maximum conversion values attainable. A sensitivity analysis is performed on the selected model to determine the influence of multiple process variables on the conversion of the reactants.

2. Model description

2.1. Theoretical framework

The FT reaction is highly exothermic and transforms syngas into a wide array of hydrocarbon products. The main products of this reaction are paraffins and olefins of different lengths, as portrayed by Equation 1 and 2 respectively. In both equations, n is a real integer that can assume values theoretically from 1 to infinite. Jet fuel, the main focus product of this present study, has a desirable composition of 75-85 vol% consisting of paraffins, iso-paraffins and cycloparaffins and the remaining 15-25% of olefins and aromatics. Jet fuel also encompasses hydrocarbon chains of 10 to 18 carbon atoms [12]. There are many technological configurations that enable the FT reaction but to maximize the production of C_{12-20} chains, the use of low temperatures (200-230°C) and of cobalt as catalyst is preferred [13].



From the wide array of kinetics available that describe the rate of consumption of carbon monoxide for the FT reaction, the kinetics of Iglesia et al. [2], Yates et al. [6] and Ma et al. [5] were chosen; all of them were obtained for low temperature FT and utilizing cobalt catalysts, although slightly different. In Table 1, the main characteristics of these kinetic models are featured, including the operation condition ranges in which these kinetics were validated. In both Iglesia et al. and Ma et al., the methanation reaction (See Eq. 3) is also considered in parallel to the FT reaction.



Table 1. Main features of Fischer - Tropsch kinetics.

| Feature | Iglesia et al. [2] | Yates et al. [6] | Ma et al. [5] |
|------------------|---------------------------------|---|--|
| Catalyst | Co catalyst on SiO ₂ | Co/MgO on SiO ₂ . 21.4% Co, 3.9 wt% Mg. | 25% Co on Al ₂ O ₃ |
| Reactor | NS | Slurry reactor | Continuous Stirred Tank Reactor (CSTR) |
| Reactions | FT and methanation | FT | FT and methanation |
| FT Stoichiometry | Appendix A.1 | Appendix A.1 | Appendix A.3 |

Table 2. Main features of Fischer-Tropsch kinetics (Continued).

| Feature | Iglesia et al. [2] | Yates et al. [6] | Ma et al. [5] |
|-------------------------------|---|--|--|
| Temperature range | 200 - 210 °C | 220 - 240 °C | 220°C |
| Pressure range | 0.1 - 3 MPa | 0.5 - 1.5 MPa | 1.42 - 2.13 MPa |
| H ₂ /CO ratio | 1 - 10 | 1.5 - 3.5 | 1 - 2.5 |
| GSHV | NS | 0.48 – 5 NL/gcat/h | 3 - 16 NL/gcat/h |
| Conversion | <15% | 6 - 68 % | 3 - 52 % |
| CO reaction rate ¹ | $R_{CO,CH_4} = \frac{a_1 P_{CO}^{0.05} P_{H_2}}{1 + b_1 P_{CO}}$ $R_{CO,FT} = \frac{a_2 P_{CO}^{0.05} P_{H_2}^{0.6}}{1 + b_2 P_{CO}}$ | $R_{CO} = \frac{a_3 P_{CO}^{0.5} P_{H_2}}{(1 + b_3 P_{CO})^2}$ | $R_{CO} = \frac{a_4 P_{CO}^{-0.31} P_{H_2}^{0.88}}{1 - 0.24 \frac{P_{H_2O}}{P_{H_2}}}$ |

In a previous study [1], the developed reactor model used kinetics from Iglesia et al. further adapted by Panahi et al. [14] and the stoichiometry proposed by Hillestad et al. [3] based on the Anderson-Schulz-Flory (ASF) distribution. The ASF model proposes a statistical distribution of FT products based on the chain growth probability (α). The Hillestad stoichiometry makes some simplifications. It only considers the methanation reaction in parallel to the FT reaction and the production of linear paraffins by the FT reaction. Likewise, it models all products with carbon atom number below 21 as individual units. On the other hand, components with carbon atom number from 21-30 were put together in a component designated C₂₁₊. The lumped component C₂₁₊ is modeled as C₃₀H₆₂ due to similar properties. The resulting stoichiometry implemented in this study for Iglesia et al. is shown in Appendix A.1.

For Yates et al., the stoichiometry proposed by Hillestad et al. and a similar α were used as well. It is important to highlight that Yates et al. only consider the conversion of CO due to FT and no methanation. The kinetics were first validated by obtaining similar reaction rate values as the ones obtained by their experiments, as shown in Appendix A.2. It is noticeable that the Yates kinetics were developed based on experimental data gathered by using a slurry reactor. This could be a potential source of error when implementing them on our FBR model due to the inherently different mass and heat transfer interactions in both configurations. However, as described by Visconti et al. [15], a slurry and a FBR provide similar conversion values for the FT reaction when operated at similar process conditions. Thus, there is a low chance for error when this kinetic model is implemented in a FBR in that regard.

For Ma et al., the stoichiometry implemented in this model contemplates the production of both paraffins and olefins containing between 1 and 45 carbon atoms. The stoichiometry is determined following the ASF distribution, except for the methane for which an additional production is considered through the methanation reaction (see Appendix A.3). Then, the kinetics were also validated by comparing reaction rate values with their experimental data.

¹ Where, R_{CO} is the reaction rate. In the case of Iglesia et al., there is a reaction rate linked to the FT reaction and one for the methanation reaction (CH₄). In the case of Ma et al., the R_{CO} encompasses both the methanation and the FT reactions. P_{CO}, P_{H₂} and P_{H₂O} are the partial pressures of carbon monoxide, hydrogen and water respectively. The a and b constants are kinetic parameters, different in value, for each consumption rate. In the case of Yates et al., they vary with the temperature.

The kinetics include a reaction rate describing the overall CO consumption, including the overall methane production. The specificity of this kinetic model is the presence of a kinetic water effect factor at the denominator of the kinetic expression, which favors CO consumption. It is important to highlight that the kinetics of Ma were developed based on experimental data from a CSTR. No more details are provided but it could imply a continuous agitation of the catalyst support. Thus, when implemented in a FBR there is a chance for error in the results; no references were found that suggest otherwise.

2.2. Case study - ULiège model

The previously defined kinetics are used to simulate a pilot-scale project at ULiège. The feed of the ULiège model is composed of hydrogen and carbon monoxide. The hydrogen feed is based on the total hydrogen production capacity of the 3 electrolyzers at ULiège, 67 mol H₂/h (1.5 Nm³/h). Based on a 2.1 H₂ to CO ratio, a molar flow of 32 mol CO/h (0.71 Nm³/h) is required.

Ideally, for most chemical engineering operations, a high conversion of the limiting reactant in conjunction with a high selectivity of the desired product is preferred. For the FT reaction, it has been reported that conversions higher than 70% result in a lower selectivity for C₅₊ [16]. This can explain why most FT reactors operate at conversions lower than 90% worldwide [17]. Likewise, as previously displayed on Table 1, the studied kinetics were only validated in low to medium conversion ranges; up to 68% for Yates et al., for example. Modelling a reactor that reaches higher conversion rates than the ones obtained experimentally could lead to inaccurate results. Thus, a conversion of 65% was chosen for all the kinetic models. This is a conversion value reported by multiple FT set ups [17], including a similar capacity FT pilot-scale plant developed during the Soletair project [18]. It is also a value comprised by the Yates et al. validation conversion range (6 - 68%) and not so distant from the maximum conversion value achieved by the Ma et al. study (52%). Nonetheless, this is not the case for Iglesia et al. study, where the maximum conversion achieved only reached 15%. Even though Iglesia's model has been used for simulation studies with high conversions [19], it is disclosed that this can be a significant source of error. Thus, results from this kinetic model should be addressed accordingly.

It should also be specified that the kinetics of Ma et al. are less precise at high conversion values (>75%). It is a consequence of integrating the water kinetic effect factor in the model. Indeed, this model leads to high conversion values in the presence of water, neglecting the fact that the CO consumption rate should decrease at high conversion. In this case, the conversion increase has not a declining effect on the consumption rate as the denominator tends toward 0 when H₂O partial pressure increases (see Table 1). Thus, the integration of the water kinetic effect in this model is seemingly artificial. Therefore, the results obtained with this kinetic model for conversion values higher than 52% (the maximum experimental conversion reached by Ma et al.) do not represent reality appropriately.

The operation conditions of the FT pilot-scale plant are displayed in Table 3. To guarantee an almost isothermal operation of the reactor, a single tube FBR with a cooling jacket having a high inlet flow of water is chosen. Via iteration, the mass of the catalyst and the volume of the reactor for each set of kinetics were obtained. The porosity of the catalytic bed was assumed to be 0.5 as this is the average value reported by Vervloet et al. [20]. The catalyst density was assumed as 2000 kg/m³ as reported by Panahi et al. (2012). This allows the estimation of the volume of the catalytic bed volume via Eq. 13 in Appendix A.4.

Table 3. Process conditions of the pilot-scale FT plant for the selected kinetic models.

| Process variable | Value |
|--------------------|------------|
| T | 220 °C |
| P | 20 bar |
| H ₂ /CO | 2.1 |
| Total molar flow | 0.1 kmol/h |

3. Results

3.1. Kinetic models comparison

The simulation of the ULiège case study was performed with every single kinetic model. Table 4 portrays the results.

Table 4. Comparison of the results obtained with the kinetic models.

| | Iglesia et al. [2] | Yates et al. [6] | Ma et al. [5] |
|--------------------------------|--------------------|------------------|---------------|
| Mass of the catalyst | 3.5 kg | 1.77 kg | 1.05 kg |
| GHSV | 0.63 NL/h*g | 1.24 NL/h*g | 2.10 NL/h*g |
| Volume of the catalytic bed | 3.5 L | 1.77 L | 1.05 L |
| Selectivity of C ₅₊ | 62.71% | 65.93% | 84.51% |

It is noticeable that depending on the catalyst type the same conversion is achieved with different quantities of catalyst, even though they are all cobalt-based. Thus, this highlights the importance of supporters and promoters in improving the FT reaction. Using the 25% Co/Al₂O₃ catalyst together with the kinetics of Ma et al., result in the least amount of catalytic bed volume and mass needed. Additionally, a higher selectivity is achieved as well. Likewise, cobalt catalysts purely supported on alumina incur in lower costs (966.38 USD for 500 gr) than those supported on silica (996.38 USD for 500 gr) [21], while no information was found on the costs of cobalt promoted with magnesium and supported on silica. Due to these reasons, the 25% Co/Al₂O₃ catalyst makes the most sense for a potential real-life implementation at the conversion limit chosen, 65%. Nonetheless, as stated before, because this catalyst and kinetics were not validated at such high conversions and the GSHV of the pilot-scale plant, their effectiveness is inaccurate.

As reported by Lillebo et al. [16], for a cobalt-based catalyst in a FBR using similar process conditions the best possible trade-off between selectivity and conversion is situated at around 80%. Thus, for the next step focusing on the sensitivity analysis of the pilot plant the Yates kinetics were chosen instead. This kinetic model was validated at much higher conversion values, up to 68%, which is close to the ideal operation value. The other kinetics (Yates et al. and Iglesia et al.) were not validated at high conversion values. Moreover, Ma's model is physically accurate due to

the counterintuitive water effect at high conversion values, so it was avoided for the next step. Even though the Yates kinetic were not validated at 20 bar like Ma et al.'s, the operation pressure has a much lower influence on conversion than the temperature and the GHSV [15].

3.2. Sensitivity analysis

A sensitivity analysis is carried out to study the influence of process variables on the reactor to be designed, integrating the kinetics of Yates et al. for the Co/MgO on SiO₂ catalyst. Figure 1 displays the influence of the percentage of the GHSV (on the top-left), the temperature (on the top-right), the H₂/CO ratio (on the bottom-left) and the pressure (on the bottom-right) on conversion values.

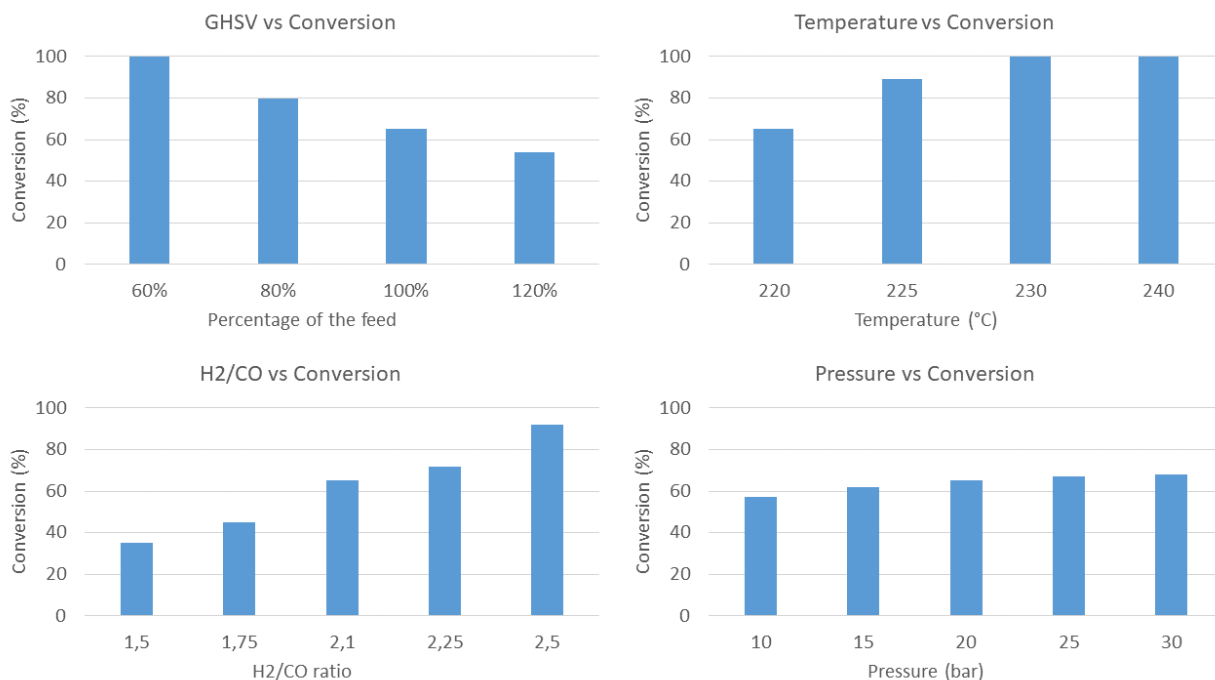


Figure 1. Sensitivity analysis of the percentage of the GHSV (on the top-left), the temperature (on the top-right), the H₂/CO ratio (on the bottom-left) and the pressure (on the bottom-right) on conversion values.

For the GHSV analysis, percentages ranging from 60 to 120% of the original GSHV were studied. These were chosen because the electrolyzers at ULiège are able to operate at capacities that range from 60 to 100%. Additionally, in case of having a recycle of unreacted tail gas coming from the reactor, the inlet feed could be increased to up to 20%. In the present study, it is observed that when the GHSV increases the CO conversion decreases considerably. It has been reported that the effects of space velocity on product selectivity are minor. On the other hand, olefin selectivity increases with GHSV as a consequence of the lower readsorption probability [15]. Therefore, 80% of the GHSV is preferable overall.

For the temperature analysis, it is important to notice that 220 and 240°C were chosen because these are the only two temperature values Yates et al. provided kinetic parameters for. The *a* and *b* parameters for temperatures 225°C and 230°C were obtained via regression of the original values provided by Yates et al. In this temperature range, CO conversion increases drastically with temperature. Even though a complete conversion of carbon monoxide is achieved at 230°C, as previously mentioned, high conversion values deviate the selectivity of the reaction towards lighter

hydrocarbons [17]. The same pattern is perceived with temperature increases in a FT system using a cobalt catalyst [15]. Thus, a temperature of 225 °C provides an effective trade-off between conversion and selectivity.

When the H₂/CO ratio increases, the conversion increases significantly. However, it has been reported that CH₄ selectivity increases with an increasing H₂/CO ratio, while the selectivity towards waxes and olefins extensively declines with increasing H₂ concentration at the inlet [15]. Thus, a ratio of 2.25 provides an effective trade-off between conversion and selectivity in this case.

For the pressure range analyzed, the conversion of CO is significantly high at low pressures. An increase from 10 bar to 30 bar results in a conversion increase of almost 10%, which is not as impactful as varying other process variables. Nonetheless, at higher pressures the solubility and readsorption rate of olefins in the liquid products increases leading to their transformation into heavier hydrocarbons [15]. Consequently, operating at 20 bar provides a trade-off between conversion and selectivity while not incurring in higher utility costs linked to operating at higher pressures.

It is important to highlight that the kinetics of Yates et al. in the present study are linked to a fixed chain growth probability factor (α). Thus, the selectivity of products doesn't change with the variation of other process variables. The variation of the selectivity towards C₅₊ would be a crucial factor to further decide between altering one process condition or another when operating the pilot scale plant.

4. Conclusions

Three kinetics models associated to three different catalysts were utilized for the simulation of a FT pilot scale installation. The 25% Co/Al₂O₃ catalyst together with the kinetic model developed by Ma et al. appear as the most appropriate set for a FT pilot scale implementation at medium conversion ranges. Indeed, this choice leads to less catalyst for achieving the same conversion levels compared to other catalysts. However, the kinetic model of Ma et al. is not appropriate for high conversion rates, which are preferred for FT. The development of a kinetic model for the 25% Co/Al₂O₃ catalyst that describes the behavior of the reaction at higher conversion rates is required.

As a consequence, the kinetics of Yates et al. and the Co/MgO on SiO₂ catalyst were preferred for further sensitivity analysis studies of the FT reactor. This model was the only one validated experimentally at higher conversion values, up to 68%, which is the closest to the recommended 80%. After performing a sensitivity analysis of the model, it was confirmed that increasing the temperature, the pressure and inlet H₂/CO values had a positive on conversion values, as well as decreasing the GHSV. Nonetheless, the chain growth probability factor (α) could be linked to the temperature as it was performed with the Ma et al. model to have a better understanding of the influence of process variables on the selectivity. A detailed optimization of the model will offer the combination of operation conditions that maximizes conversion and C₅₊ selectivity without hindering the reaction in other ways, e.g. coke production, etc.

To have a more accurate comparison of FT kinetic models it is recommended to guarantee that all of them are validated in a similar range of operation conditions. However, this is unfortunately rarely the case in the practice and such comparative study of different kinetics for the Fischer-Tropsch reaction targeting jet fuel production could not be retrieved in the literature. As a consequence, the present study compared three different kinetic models at given process conditions of the pilot scale plant to be built, highlighting the impact that the selection of a kinetic model may have on the reactor's design. Nonetheless, one should also note that these catalysts could be more effective at a different combination of temperature, pressure, H₂/CO and GHSV.

Future work will focus on further improving the accuracy and the performance of the simulation for jet fuel production maximization. A new model will be developed using more detailed kinetics such as the one proposed by Pandey et al. [11] for the 20%Co/0.5Re γ -Al₂O₃ catalyst, achieving up to 75% conversion rates. This commercially available catalyst has reached 85% at lab scale without having a significant drop in selectivity for C₅₊ [16]. It has also been successfully scaled up by Loewert et al. [10] to 0.27 L, but not to the capacity analyzed in the present study (1.77

L). The results of the simulation using the 20%Co/0.5Re γ -Al₂O₃ catalyst will then be compared with the ones presented in this study. Additionally, the influence of the presence of carbon dioxide and water in the inlet stream of the reactor will be taken into consideration. Later phases will focus on improving the integration of the carbon capture, electrolysis, RWGS, recycle and post-treatment sub-processes to the reactor. Finally, the more detailed design will then serve as input for the construction of a pilot scale reactor at ULiège. The operation and results obtained from the facility will retroactively improve the model itself.

Acknowledgements

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Appendix A. Calculations

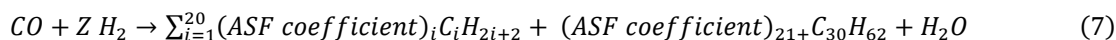
A.1. Alpha value and stoichiometric factors calculation for Iglesia and Yates kinetic models

For low-temperature cobalt FT, a constant α value of 0.9 is assumed, as done by Hillestad et al. [3]. Based on Eq. 4, this leads to a H₂/CO ratio (Z) of 2.1. By using Eq. 5 and Eq. 6, the ASF coefficients for every single potential hydrocarbon that can be produced via FT are estimated, where C_i refers to the number of carbon atoms of the hydrocarbon. These coefficients are then used in Eq. 7 to provide the full stoichiometry of the FT reaction.

$$Z = \frac{H_2}{CO} = 3 - \alpha \quad (4)$$

$$ASF\ coefficient_i = (1 - \alpha)^2 * \alpha^{i-1} \quad for\ C_i, i = 1, 2, 3 \dots 20 \quad (5)$$

$$ASF\ coefficient_{21+} = (1 - \alpha) * \alpha^{20} \quad for\ C_{21 \rightarrow 30} \quad (6)$$



A.2. Yates model validation

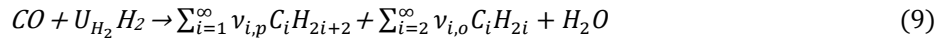
At 240°C, 0.79 MPa, H₂/CO = 2 and a Synthesis Gas Feed Rate of 0.067 NL/min*g cat, Yates et al. [6] obtained these reaction rates: 0.678, 0.68, 0.694 mmol/ (min*g cat) at different operation times. The Yates model here implemented obtained 0.638 mmol/ (min*g cat) by following the model proposed by Yates et al. With an error of 6.5%, the model was deemed validated.

A.3. Alpha value and stoichiometry calculation for the Ma et al. [5] model

For Ma's model, the α value is calculated by accounting for its temperature and syngas ratio dependency following the model developed by Vervloet et al. [20], as shown in Eq. 8.

$$\alpha = \frac{1}{1 + k_{\alpha} * \left(\frac{C_{H_2}}{C_{CO}}\right)^{\beta} * \exp\left(\frac{\Delta E_{\alpha}}{R} * \left(\frac{1}{493.15} - \frac{1}{T}\right)\right)} \quad (8)$$

Where k_{α} equals 0.0567, C_i is the concentration of component i , β equals 1.76, ΔE_{α} equals 120.4 kJ/mol, R equals 8.314 J/mol/K and T is the temperature in K. The chain growth probability α is used to specify the stoichiometry of the FT reaction, portrayed in Eq. 9, which accounts for the production of paraffins and olefins according the ideal ASF model.



The $v_{i,p}$, $v_{i,o}$ and U_{H_2} factors are calculated via Eq. 10, Eq. 11 and Eq. 12, respectively. $v_{i,p}$ accounts for the production of paraffins. $v_{i,o}$ accounts for the production of olefins. U_{H_2} denotes the hydrogen usage ratio.

$$v_{i,p} = \frac{\alpha^{i-1} * (1-\alpha)^2}{1 + e^{-0.3}} \quad (10)$$

$$v_{i,o} = \frac{e^{-0.3} * \alpha^{i-1} * (1-\alpha)^2}{1 + e^{-0.3}} \quad (11)$$

$$U_{H_2} = 2 + \frac{1-\alpha}{1 + e^{-0.3}} \quad (12)$$

The $e^{-0.3}$ term translates the ratio between the amount of paraffins and olefins for a given chain length.

A.4. Calculation of the volume of the catalytic bed

$$\text{Volume of the catalytic bed} = (1 - \text{porosity}) * \frac{\text{mass of the catalyst}}{\text{density of the catalyst}} \quad (13)$$

References

- [1] Morales A, Leonard G. Simulation of a Fischer-Tropsch reactor for jet fuel production using Aspen Custom Modeler; 2021.
- [2] Iglesia E, Reyes SC, Madon RJ. Reaction-Transportation selectivity models and the design of Fischer-Tropsch catalysts. *Computer-Aided Design of Catalysts*; 1993. p. 199-257.
- [3] Hillestad M. Modeling the Fischer-Tropsch distribution and model implementation. *Chem. Prod. Process Model*; 2014. Vol 10, p. 147-159.
- [4] Rouxhet A, Leonard G. Modelling and kinetic study of a Fischer-Tropsch reactor for the synthesis of e-kerosene; 2022.
- [5] Ma W, Jacobs G, Sparks DE, Spicer RL, Davis BH, Klettlinger JL and Yen CH. Fischer-Tropsch synthesis: Kinetics and water effect study over 25%Co/Al₂O₃ catalysts. *Catalysis Today* 228; 2014. p. 158–166.
- [6] Yates IC and Satterfield CN. Intrinsic Kinetics of the Fischer-Tropsch Synthesis on a Cobalt Catalyst. *Energy & Fuels*; 1991. Vol 5, p. 168 – 173.
- [7] EASA. European Aviation Environmental Report; 2019. DOI: 10.2822/309946.
- [8] European Commission. Communication from the commission to the European parliament, the council, the european economic and social committee and the committee of the regions; 2020. Available at: <https://eur-lex.europa.eu/legal-content/EN/TXT/?uri=CELEX%3A52020DC0066> [Accessed 26 August 2022].

- [9] Sustainable Aviation. Sustainable aviation fuels road-map; 2019. Available at: https://www.sustainableaviation.co.uk/wp-content/uploads/2020/02/SustainableAviation_FuelReport_20200231.pdf [Accessed 26 August 2022].
- [10] Loewert M, Hoffmann J, Piermartini P, Selinsek M, Dittmeyer R, Pfeifer P. Microstructured Fischer-Tropsch reactor scale-up and opportunities for decentralized application. *Chemical Engineering & Technology*; 2019. Vol 42, p. 2202-2214.
- [11] Pandey U, Runnigen A, Gavrilovic L, Jorgensen EA, Putta KR, Rout KR, Rytter E, Blekkan EA, Hillestad M. Modeling Fischer-Tropsch kinetics and product distribution over a cobalt catalyst. *AIChE Journal*, 7; 2021. Vol 67, e17234.
- [12] Doliente S, Narayan A, Tapia JFD, Samsatli NJ, Zhao Y, Samsatli S. Bio-aviation fuel: A comprehensive review and analysis of the supply chain components; 2021. DOI: <https://doi.org/10.3389/fenrg.2020.00110>.
- [13] Dieterich V, Buttler A, Hanel A, Spliethoff, Fendt S. Power-to-Liquid via synthesis of methanol, DME or Fischer-Tropsch-fuels: a review. *Energy & Environmental Science*, 10; 2020.
- [14] Panahi M, Rafiee A, Skogestad S, Hillestad M. A natural gas to liquids process model for optimal operation. *Industrial & Engineering Chemistry* 51; 2012. p. 425-433.
- [15] Visconti CG, Lietti L, Tronconi E, Rossini S. Kinetics of low-temperature Fischer-Tropsch synthesis on cobalt catalysts: Are both slurry autoclave and tubular packed-bed reactors adequate to collect relevant data at lab-scale? *The Canadian Journal of Chemical Engineering*; 2016. Volume 94, Issue 4, p. 685 - 695.
- [16] Lillebo A, Rytter E, Blekkan E, Holmen A. Fischer-Tropsch Synthesis at High Conversions on Al₂O₃-Supported Co Catalysts with Different H₂/CO Levels. *Ind. Eng. Chem. Res*; 2017. Vol 56, p.13281-13286.
- [17] ETIP Bioenergy. Biomass to liquids (BtL) via Fischer-Tropsch – a brief review, 2021. Available at: https://www.etipbioenergy.eu/images/ETIP_B_Factsheet_BtL_2021.pdf [Accessed 26 August 2022].
- [18] Vidal F, Koponen J, Ruuskanen V, Bajamundi C, Kosonen Antti, Simell P, Ahola J, Frilund C, Elfving J, Reinikainen M, Heikkinen N, Kauppinen J, Piermartini P. Power-to-X technology using renewable electricity and carbon dioxide from ambient air: SOLETAIR proof-of-concept and improved process concept. *Journal of CO₂ Utilization*; 2018. Vol 228, p. 235 – 246.
- [19] Rafiee A, Panahi M. Optimal Design of a Gas-to-Liquids Process with a Staged Fischer-Tropsch Reactor. *Chemical Engineering & Technology*; 2016. Vol 39, Issue 10, p. 1778 – 1784.
- [20] Vervloet D, Kapteijn F, Nijenhuis J, Van Ommen JR. Fischer-Tropsch reaction-diffusion in a cobalt catalyst particle: aspects of activity and selectivity for a variable chain growth probability. *Catalysis Science & Technology*; 2012. Vol 2, p. 1221-1233.
- [21] Riogen. Catalyst for Chemicals & Energy. Available at: <https://shop.riogeninc.com/main.sc> [Accessed 26 August 2022].