EXECUTIVE SUMMARY

Techno-economic analysis of a process for upgrading HTL biocrude into a crude oil substitute

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Abstract

HTL is a process that transforms biomass into a liquid containing simpler molecules and that can be used as a biofuel, displacing liquid, petroleum based, fuels, as is needed to reduce the advancement of climate change. The product of HTL is called biocrude and its applicability as a fuel, even after distillation into the appropriate cuts, is very poor. The poor performance of biocrude cuts is attributed to the high amount of heteroatoms in its constituent molecules, as well as a high amount of low-value heavy cuts. The upgrading, specifically through hydroprocessing, of biocrude is a potential solution, adapted from petroleum refining, to improve the quality of biocrude. Hydroprocessing encompasses the catalytic processes where hydrogen is reacted with petroleum cuts to reduce their content in heteroatoms (hydrotreatment) or to crack the heavy molecules into lighter ones (hydrocracking). The present work aims to assess the techno-economic viability of an upgrading unit for biocrude produced by HTL of lignocellulosic biomass. A process simulation was constructed in Aspen Plus, based on a hydrocracking unit for heavy oil cuts and adapted to the new feedstock. It was determined that a crude oil replacement of high quality, called Syncrude, could be produced at a break-even price of 249€/bbl in a unit producing 2.1 kbbl/day. This value is uncompetitive with petroleum (approx. 80€/bbl, 112.85€/bbl considering the cost of GHG emissions in the EU). The main cost drivers are the cost of biocrude and small scale of the unit.

Keywords: Upgrading, HTL, Techno-economic assessment, Aspen, Hydrotreatment, Biofuels

1. Introduction

The IPCC AR6 shows that there is already too much investment into fossil fuels to meet the targets of the Paris Agreement. In other words, this means that if all fossil fuel installations currently in operation were to continue functioning according to historic trends and until their currently projected decommissioning date, then they would emit an amount of greenhouse gases (GHGs) that would catastrophically alter the Earth's climate[1].

Biofuels can allow for a great reduction in the climate impact of assets that were originally meant to work with fossil fuels. For example, biogas from anaerobic fermentation, after purification, can replace fossil natural gas, with minimal need for changes to pipelines, compression stations, storage equipment, distribution lines or client equipment[2]. Many older coal power plants are currently being replaced by more efficient and cleaner gas-powered plants, but no matter how high the achieved efficiency, the amount of carbon in the atmosphere will continue to increase, so long as it is being removed from underground.

If a technically and economically viable alternative to crude oil could be found, then all of the currently existing assets in its economic network could be kept in operation, from refineries to tractors, greatly increasing the efficiency of invested capital and reducing the cost of environmental sustainability[3].

Hydrothermal liquefaction (HTL) is a process in which a feedstock, usually a solid in suspension, reacts with water at high temperature and very high pressure to produce an organic liquid with high energetic potential and similar to petroleum in its potential to be converted to hydrocarbon fuels. This product is called biocrude (sometimes "bio-crude"[4],"bio-oil"[5] or "biooil"[6]), and it is formed alongside a gas phase of mostly CO_2, an aqueous phase and a solid phase[7].

Several feedstocks have been explored for the production of biocrude, including algae, ligno-cellulosic biomass, wastewater treatment sludge and plastic wastes, but the greatest focus has been on algae, followed by lignocellulosic biomass [4,8,9].

The reaction has been studied at temperatures ranging from 250°C to 450°C and pressures from 100 bar to 350 bar[10]; these ranges include the subcritical and supercritical states of water (critical temperature: 373.9 °C; critical pressure: 220.6 bar[11]). Lower temperature favors the formation of solids i.e., charcoal, and when this is desired product, the process is called hydro-thermal carbonization. Higher temperatures favor the formation of gas, which contains more methane and a slightly smaller fraction of CO_2, compared to the gas produced in the preferred range for HTL. The process is called hydro-thermal gasification, when this gas mixture is the main desired product[7]. The elevated pressure is broadly agreed to facilitate the reaction by reducing heat and mass transfer limitations throughout the biomass particles.

Biocrude differs markedly from petroleum in its content of heteroatoms, particularly oxygen and sulfur:

Table 1 - Oxygen and sulfur in crude and biocrude. Data from [12,13]

	Crude oils	Biocrude
Oxygen (%wt.)	<2	>9
Sulfur (%wt.)	0.1-3	0.01-0.03

The high content of heteroatoms is considered to be one of the main causes of the poor properties of biocrude, or of its distillation cuts, as fuels. Another reason for the poor performance, as well as a factor depressing the value of biocrude, is that it contains a large fraction of high-boiling cuts. This lowers the value of the biocrude since high-boiling cuts have less market demand due to their limited applicability. The process for the removal of heteroatoms from crude oil is called hydrotreatment (HDT) and consists of reacting oil with hydrogen over a catalyst leading to the formation of H_2S, H_2O, NH_3, etc., which can be easily separated from the organic liquid phase containing the valuable hydrocarbons. The process of reacting heavy oil cuts with hydrogen, over a catalyst, to yield lighter cuts is called hydrocracking (HDC). The two families of processes can be further grouped into the hydroprocessing (HDP) super-family[13,14].

The upgrading of biocrude, through HDP, is seen as the best way to improve its potential yield of quality fuels.

The report by Tews *et al.*[15], includes a life-cycle assessment of the GHG emissions associated with the entire production and distribution (scopes 1, 2 and 3[16]) of biofuels produced from waste woody biomass, using either HTL or fast pyrolysis as the liquefaction process. The authors estimate that HTL gasoline and diesel can result in a 70% reduction in emissions compared to fossil-based fuels. The main drivers of these emissions, accounting for 90% of the them, are the electricity consumed by the process (based on an electricity mix with 70% fossil fuel sources) and the transportation of the feedstock from forest to factory (distance of 120 km)[15]. It can be reasonably predicted that the utilization of renewable-based electricity and bio-fuels can lead to even greater reductions of emissions than the 70% previously mentioned. In other words, if the HTL diesel that is produced is used to fuel the forestry and transport machinery, and “clean” energy is used to run the process, then **it may be possible to reduce the GHG impact of liquid hydrocarbon fuels by over 97%**.

This possibility seems too good to be true, but it can, nonetheless, show the dire importance of investigating HTL biofuels. At a minimum, this possibility should be given as much credibility as is given to claims about the GHG impact of Green Hydrogen[17,18].

1.1. The upgrading step (also known as hydroprocessing)

The upgrading step fits into the overall HTL-fuels process as a way to convert the product of HTL itself, biocrude, into a substance, called syncrude, that can be refined to yield fuels compliant to the applicable norms. This syncrude is this work’s titular “crude oil substitute” and it differs from biocrude by the fact that it yields betters fuels after fractionation, being easier/cheaper to handle due to its greater stability, much lower viscosity, weaker corrosive tendency and having other improved properties.

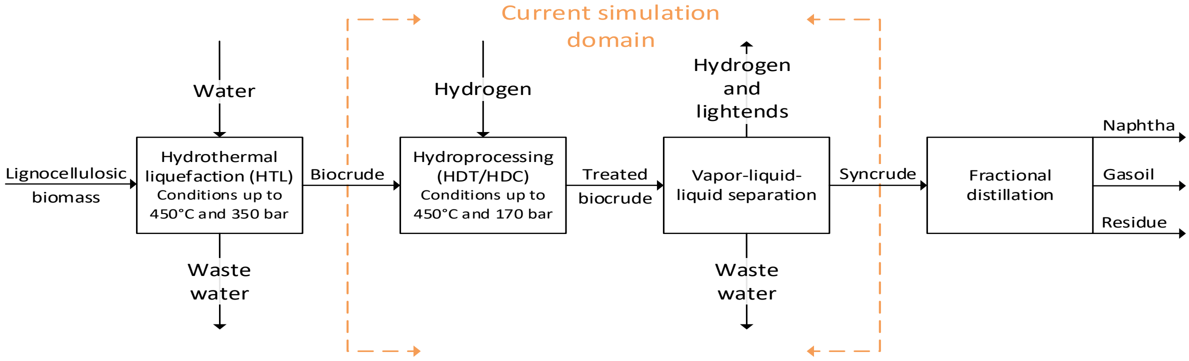

Figure 1 - Diagram of biomass to fuels HTL pathway

Upgrading is done through an adapted version of the hydrotreatment and hydrocracking processes, which are processes that are applied to crude oil fractions e.g., hydrodesulfurization of diesel and hydrocracking of residue from vacuum distillation. The basis for the adaptation were the diagrams given in Treese *et al.* [13, pp.: 325, 367].

2. Process scheme for the biocrude upgrading process

The configuration of the process was based on a hydrocracker of heavy oil cuts.

The process scheme is described by 4 blocks as can be seen in Figure 2. The following is a description of those blocks:

Reactor: in this section the reactant streams (UTB and Reactor Gas) are heated to adequate temperatures, the gas is mixed with liquid feed and the mixture is run through the reactor with its beds of solid catalyst. Between each bed, additional gas, at a temperature lower than the reaction mix, is added in order to reduce the temperature of the stream (quench) before the reaction proceeds in the following bed.

Separators: the reactor effluent stream is cooled and expanded is a series of drums in order to separate out:

- water, which goes to waste water treatment,
- a stream of gas rich in hydrogen and with some contaminants, including carbon dioxide, carbon monoxide and methane (this stream is called Dirty Gas),
- a stream of liquid hydrocarbons with properties and product potential similar to crude oil, termed Syncrude.

Membrane+PSA: the Dirty Gas is separated into a stream enriched in hydrogen, the Recovered Gas, a Waste Gas stream, with mostly carbon dioxide and water vapor (not depicted), and a stream concentrating the contaminants, including substantial non-condensable hydrocarbons, which is sent to the Fuel Gas system.

Compressors: the Recovered Gas is joined by the H2 Make-Up stream and compressed to form the Reactor Gas stream.

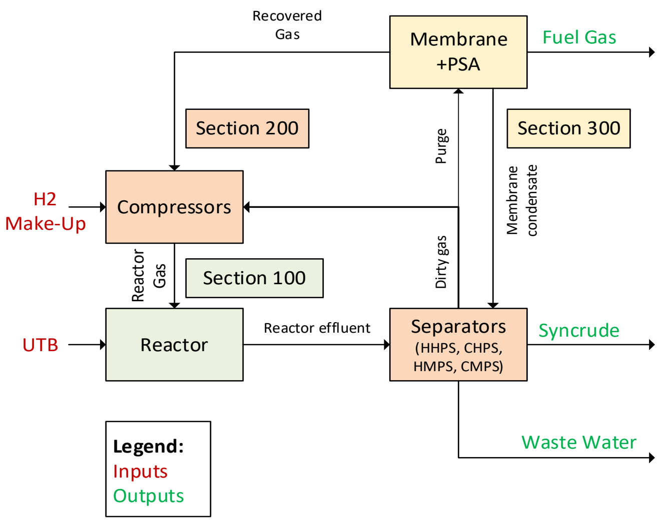

Figure 2 - Block flow diagram of the process

3. Methodology

Developing the simulation involved several challenges, namely: describing the feedstock and reaction products, choosing a physical property method, estimating the reaction enthalpy, choosing an adequate design for the reactor, modelling the reactor with limited knowledge of the reaction, identifying the best process option for purification of the hydrogen to be recycled and ensuring that the simulation converged, despite the presence of customized blocks and multiple design specs and a large recycle stream.

3.1. Physical and chemical characterization

The description of the substances involved was not simple. The approach taken in published literature, based on mixtures of pure compounds, was found to fall short of the desired accuracy, either because it didn't characterize the entirety of the mixture (often TBP curves where only analyzed up to 350°C due to constraints in the available equipment) or because only a sub-set of the parameters necessary was targeted (viscosity and density were often left out).

For this simulation, the choice was made to model the untreated biocrude (UTB) with only the density and viscosity being accurate. This choice was based on the available data and the properties relevant to the section of the process that handles UTB. As can be seen in the PFD, the UTB stream only undergoes heating and pumping before the reactor and, for the sizing of the involved pieces of equipment, the most relevant properties are C_P, thermal conductivity, viscosity, density. There were no available data on the first two, at the time the simulation was developed, so only density and viscosity were accurate.

The model of UTB started from the pure component triolein and then the viscosity and density were adjusted to the measured values by using the Regression function of Aspen.

Treated biocrude was modelled as an assay with discrete lights. The pseudo-component property estimation was done using the default "ASPEN" property method.

Following the recommendation in Peters *et al.*[19], the Soave-Redlich-Kwong (SRK) property method was initially selected. By consulting the Aspen Help[20], and considering that the process has a substantial step of water-organic separation, the Kabadi-Danner mixing rules were selected (SRKKD).

As per the software documentation, the method for the properties of water was selected as STEAMNBS.

The liquid-liquid equilibrium calculations were performed using the "Free water" approach and the water solubility using the SRK-KD method, rather than rigorous liquid-liquid equilibrium (LLE). This is valid since the waste water treatment plant (WWTP) is not part of the simulation domain order allow the adjustment by regression of the stated parameters, the section that handles UTB was set to use the IDEAL property method.

3.2. Characterizing the reaction

The thermal characterization of the reactor was performed by estimating the industry standard of heat released per mol of hydrogen consumed (Equation 1).

In literature it is possible to find a range of values for α_{Hr} from 14 kcal/mol to 32 kcal/mol[14]. The hydrodeoxygenation reaction, which consumes the most hydrogen, and thus is responsible for most of the heat released, can be generalized by Equation 2.

The estimation of the heat duty of the reactor was based on the reaction enthalpy for a simplified hydrodeoxygenation (Equation 3) of compounds thought to be present in biocrude.

The $\boldsymbol{\alpha_{Hr}}$ was estimated to be **19 kcal/mol**$_{H2}$. This translates to an **exothermicity of (…)** for the full-scale reactor.

$$\Delta H_r = \alpha_{Hr} \cdot (Q_{n,H_2,in} - Q_{n,H_2,out}) \quad \text{Equation 1}$$

$$A + x \cdot H_2 \rightarrow B + y \cdot H_2O + w \cdot CO_2 + z \cdot CO \quad \text{Equation 2}$$

$$A + x \cdot H_2 \rightarrow B + y \cdot H_2O \quad \text{Equation 3}$$

3.3. Reactor design

The large amount of energy released by the reaction is one of the central points around which the reactor must be designed. The conventional strategy to keep the reaction mixture near the target temperature is to break up the catalytic bed and to add cold hydrogen between the beds. These spaces before another bed are called the quench boxes. Some reactors, with several beds per shell and multiple shells, exist that have as many as 30 catalytic beds[14].

The reactor for the base case was simulated with the following assumptions:

- Maximum temperature: 400°C[21]
- (…)
- Number of shells: 1
- Number of beds/shell: 5 (maximum[22])
- (…)
- LHSV: 0.21 h^{-1} [21]
- Catalyst void fraction: 40%
- Acceptable approach to spray flow regime: 70%

4. Sizing and costing

The costing of the equipment was done using Aspen Process Economic Analyzer V11. This piece of software prompts the user to input a series of mandatory and optional dimensions of the pieces of equipment in order to estimate its cost.

The reactor was the only piece of equipment that required a highly manual approach to sizing.

Sizing of the reactor was based on ensuring trickling flow regime, which is the regime generally encountered in HDT/HDC processes.

The system of purification that comprises section 300 was costed by following the method used in Snowden-Swan *et al.*[23], and that consists in using the hydrogen flowrate of the purified stream to define capacity and an exponential factor (n) of 0.8.

The compressors were sized and costed considering several individual single stage reciprocating compressors.

The process requires untreated biocrude and make-up hydrogen as raw materials. The cost of hydrogen was set at 1000€/ton, typical for hydrogen used in refineries[24] and produced via SMR and WGS.

The cost of untreated biocrude was set at 0.581€/kg. There is high uncertainty in this value, perhaps as much as ±50% on a mass basis. Snowden Swan *et al.*[23], has a value of 0.744€/kg, Tews *et al.*[15] calculates 0.60€/kg and Penke *et al.*[25] reports a value of 0.40€/kg of treated biocrude (the implied value of untreated biocrude must be lower), so an average of these values was used.

The prices of electricity and natural gas were obtained from DGEG[26], for the 2nd half of 2021 for the European Union

Wastewater treatment was not considered since, according to literature[15,23], the amount of wastewater produced in the upgrading process is minimal compared to the one from HTL.

4.1. Estimation of income

Three streams are considered valuable: the Syncrude stream and the two Fuel Gas streams.

The Fuel Gas streams had their value calculated based on the LHV, the price of Natural Gas and a discount factor of 90% to account for the difficulties in burning a non-standard fuel.

The price of Syncrude was calculated so that the gross earnings were 0. This price isn't rigorously the same as the Minimum Fuel Selling Price, which could only be obtained from a more extensive economic analysis and should be higher than the calculated price.

4.2. Sensitivity analysis

A sensitivity analysis was performed to quantify the impact of several key parameters on the necessary Syncrude price.

Table 2 - Parameters studied in the sensitivity analysis

Parameter	Base case value	Units	Values for other cases
UTB price	0.581	€/kg	1; 0.4
Hydrogen price	1000	€/ton	2500; 800
Operating labor costs	0.15	of TPC	0.135; 0.165
LHSV	0.21	h-1	0.3; 0.5
ISBL	13	M€	16; 9
Production volume	2.1	kbbl/day	5; 30

The following are justifications of the choice of values presented in Table 2 for the other cases.

- As previously described, the price of UTB can vary greatly between the estimates of different authors
- The alternative where Green hydrogen, produced by electrolysis, is represented by the 2500€/ton value (optimistic, 24)
- Greater mechanization and automation may allow a reduction in the number of operators required per shift
- It may be possible to reduce the consumption of hydrogen, while achieving the same degree of HDO. This hypothesis rests on the HDC reactions happening to a lesser extent.
- LHSV used in more conventional hydroprocessing.
- According to Robinson and Dolbear14, the average capacity of an HDT unit is 30.6 kbbl/day. Adjustment was made using an exponential factor of 0.6.
- Combinations of the most impactful variations were also tried.

The original simulation, in PRO/II, allowed for more variables to be experimented with, due to its higher robustness. Recreating this robustness wasn't a priority in the Aspen simulation and so it isn't possible to comment quantitively on, for example, the impact of changing the purity of the gas fed to the reactor (in the particular case of this example, the analysis would be of limited usefulness since the reaction kinetics and thermodynamics are also not known, at present time).

5. Results and discussion

Along with the cost information of each equipment, several other values of importance are given in the tables of following subsections.

All costs from APEA where referenced to the first quarter of 2018 (taken to mean March 2018), while the cost of the purification system was referenced to 2004. Chemical Engineering's Plant Cost Index[27],was used to correct the values to December 2021, the same date as the prices of electricity and NG from DGEG[26].

It bears mentioning that inflation has increase drastically in recent times. A comparison of inflation over periods ending near the present date is given in Table 3.

Had the trend held, of 2% per year, which happened between 2004 and 2018, the current value would have been 612.0, or 26% lower than it is. This is quite relevant when considering published techno-economic evaluations that, logically, had no way of predicting the price increases that came to pass, but nonetheless are of limited value in terms of their conclusions.

Table 3 - Value of the Chemical Engineering Plant Cost Index and its increase between key start dates and the present time

Start date	CE PCI	Increase to June 2022
2004	444.2	87%
March 2018	588.0	42%
December 2021	776.3	7%
June 2022	832.6	

The equipment costs are dominated by the compressors, followed by the reactor and the purification system. It may be possible to reduce the cost of these pieces of equipment.

5.1. Expenses

Additional costs were calculated following the factors given in Peters *et al.*[19].

Table 4 – Calculation of total capital investment and its sub-parcels

	Cost
Purchased-equipment cost	13 230 812 €
Direct costs	**54 643 254 €**
Indirect costs	**35 181 273 €**
Fixed-capital investment	**89 824 527 €**
Working capital	15 851 387 €
Total capital investment	**105 675 914**

The balance of utilities is quite favorable, as it results in a small total expense. Further improvements might be possible by using the excess steam to directly drive equipment or to produce electricity.

The results of the calculation of the total product cost are given below, in Table 5.Table 5 - Total product cost and parcels from which it is calculated

	Cost (€/annum)
Direct production costs	**116 671 370 €**
Fixed charges	**17 925 213**
Manufacturing cost	**152 190 908**
General expenses	**23 752 338**
Total product cost	**175 943 246**

Considering the TPC and the parcels that lead to it, it is possible to point to the direct production cost (raw material) as the main cost driving factor. This shows the importance of further development of the HTL process, as well as integration of all upstream operations with the upgrading unit. Operating labor and its dependent elements are the next most impactful cost drivers, further demonstrating the well-known importance of economies of scale and automation in chemical processes.

5.2. Income

With the purpose of calculating the necessary syncrude price, the gross earnings, considering the sale of all products, is imposed as 0. Then the necessary syncrude price can be calculated using the values shown in Table 6.

Table 6 - Income breakdown and necessary product price to balance with costs

Income from fuel gas	2 311 724	€/annum
Syncrude production	698 552	bbl/annu
Total product cost	175 943	€/annum
Necessary syncrude	**248.56**	**€/bbl**
Gross earnings	**0**	

The calculated necessary syncrude price is very high compared to benchmark crude oil (Brent) prices of around 80 USD/bbl (at present time, 1€ is exchangeable for approximately 1 USD). It must be noted that these gross earnings have not taken into account the time value of money and that the final MFSP may be higher.

Under Portuguese legislation, biofuels are exempt from having to pay for associated emissions of greenhouse gases[28]. The price of biocrude can therefore have some more market advantage if the cost of petroleum is adjusted for its emissions. The values of this adjustment are given in Table 7.

Table 7 - Adjustment of the price of crude oil by the cost of its emissions in the EU. Data from legislation[28] and Aspen Plus V11

Emissions Brent	3099.6	kg_CO2e/ton
Price of emissions	80	€/ton_CO2e
Density of Brent	132.5	kg/bbl
Cost of emissions	32.85	€/bbl
Adjusted price of Brent	**112.85**	€/bbl

5.3. Sensitivity analysis

Within the framework of the simulation developed for this work and the spreadsheets used to produce the previously presented results, it is possible to experiment with different scenarios. In Table 8 the results of changing the specified variables is shown in term of its economic results. Additionally, in the last line of the table, a scenario is presented in which the target is to reach 100€/bbl syncrude, and the necessary price of untreated biocrude is determined.

Table 8 - Results of sensitivity analysis. The numbers on the leftmost column indicate the conditions that are then combined for the scenarios at the bottom of the table.

		New value		**Necessary syncrude price (€/bbl)**
	Base case (BC)			**249**
1)	UTB price	0.4	€/kg	195
	BC value: 0.581	1	€/kg	373
	Hydrogen price	2500	€/kg	265
	BC value: 1000	800	€/kg	246
4)	OL costs	0.135	of TPC	240
	BC value: 0.15	0.165	of TPC	258
	LHSV	0.3	h-1	246
	BC value: 0.21	0.5	h-1	243
2)	ISBL	9	M€	227
	BC value: 13	16	M€	263
	Production volume	5	kbbl/day	238
3)	BC value: 2.1	30	kbbl/day	205
1+2+3				144
1+2+3+4				138
2+3+4	**UTB price**	**0.266**	**€/kg**	**100**

The cost of biocrude can have the most effect on the necessary price of syncrude. The LHSV, which might seem worryingly low to those experienced in HDT/HDC, is estimated to have only a small impact on the final cost. The benefits of scale-up to 30 kbbl/day might be understated due to the application of the simplest technique. Over a 15x increase in capacity equipment does not just need to get bigger, it may be most economical to use other types of the same equipment, but this analysis fell outside the scope of this work. It must also be admitted that scaling up a supply of biomass to make UTB can present negative economies of scale, after a certain point. Considering a mass yield of 27.4% dry basis[15], it would be necessary to supply over 10 Mton/annum of wet biomass to feed a syncrude unit producing 30 kbbl/day. To produce that much biomass, at a productivity of 10 ton/ha/year, would require over 1 million ha, which is the area of a circle with 57 km of radius, less than the 120 km average transport distance considered by Tews *et al.*[15]. The “Green Premium” will likely have to play a big role in the economic viability of Syncrude. This may be achieved through greatly increased carbon trading prices, incorporation of biofuels mandated by legislation or fiscal benevolence through excise tax breaks[19,29].

6. Conclusions and follow-up work

Further investigation is needed into the production of Syncrude and, in particular, the present work can lead to further valuable information through follow-up works. The following are suggestions of key points to be further researched:

- The entire biomass-processing plant should be modelled together. The HTL and upgrading processes should not be compartmentalized due to the advantages that can be gained through heat integration over both parts30, as well as through the sharing of OSBL costs.
- Experimental studies are needed to properly understand the hydrodynamics of the reactor. It seems necessary to operate at a very low LHSV and high gas flowrate, which causes a need for a large diameter reactor. The boundaries of the operating zone need to be experimentally determined. Operation outside the trickle-flow regime show also be investigated.
- Several strategies for dealing with the heat released by the reaction are proposed. These should be further investigated and consideration should be given to the fact that

the most economical solution may change markedly with scale.

- More data is necessary to accurately characterize the fluids involved in terms of thermodynamic and transport properties (AspenTech (and simulator developers in general, I suppose) assume no responsibility for the accuracy of the property parameters that they provide with their software; it is expected that the user supplies their own parameters if the simulation results are expected to be accurate).

The present work supports the technical viability of the upgrading of biocrude from HTL to produce a renewable, low-emissions alternative to petroleum and that can be fed into conventional refineries for processing into marketable fuels.

Clients may place additional value on Syncrude due to its much smaller environmental impact. It can, possibly, translate to as much as 97% less greenhouse gas emissions, compared to fossil crude oil, while needing very little additional distribution infrastructure and being compatible with conventional engines.

The production of drop-in replacement, low-carbon fuels (those that can be used in engines from the previous century all the way to modernity) will probably be a crucial steppingstone in the path to global decarbonization.

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