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

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Thesis to obtain the Master of Science Degree in

Chemical Engineering

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December 2022

I launch my rockets, between my ears

Hoping an inch of good, is worth a pound of years.

Adapted from

"If only we had taller been"

by Ray Bradbury

Resumo

O processo de liquefacção hidrotérmica (HTL) transforma biomassa num líquido composto por moléculas mais simples e que pode ser usado como biocombustível, constituindo uma alternativa aos combustíveis petrolíferos, tal como é necessário para placar o progresso das Alterações Climáticas.

O producto do processo HTL chama-se biocrude e a sua aplicabilidade como combustível, mesmo após destilação para obtenção das fracções mais adequadas, é muito fraca. O desempenho fraco das fracções de biocrude é atribuída à elevada quantidade de heteroátomos nas suas moléculas constituintes, assim como a elevada proporção de fracções pesadas, de baixo valor. O melhoramento (*upgrading*), especificamente através de hidroprocessamento, do biocrude pode ser uma solução para melhorar a qualidade do biocrude, adaptada da refinação de petróleo. O hidroprocessamento abrange os processos catalíticos em que hidrogénio reage com fracções de petróleo para reduzir a quantidade de heteroátomos (chamado processo de hidrotratamento) ou para partir as moléculas pesadas em moléculas mais leves (chamado processo de hidrocracagem). O presente trabalho procura avaliar a viabilidade tecno-económica de uma unidade de melhoramento para biocrude produzido por HTL a partir de biomassa ligno-celulósica. Determinou-se que um substituto de petróleo com elevada qualidade, apelidado Syncrude, podia ser produzido com um custo de 249€/barril numa unidade com capacidade para 2100 barris/ano. Este custo não é competitivo face ao preço do petróleo (cerca de 80€/barril, 112.85€/bbl considerando o custo das emissões de GHG UE). Os principais factores de custo são o custo do biocrude e a escala pequena da unidade.

Palavras-chave

Melhoramento (*upgrading*)
Liquefacção hidrotérmica (HTL)
Análise tecno-económica
Aspen
Hidrotratamento
Biocombustíveis

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

Declaration

I declare that this document is an original work of my own authorship and that it fulfills all the requirements of the Code of Conduct and Good Practices of the Universidade de Lisboa.

Acknowledgments

This work could not have been made without the people who gave me the opportunities and the support to succeed. To them I present my gratitude.

To engineer Jérôme Majcher, who created the opportunity for an intern to join him at IFP Energies Nouvelles and to participate in an innovative project. I recognize the effort and the risk to your professional reputation that you accepted by allowing an intern near such a project, and I'm extremely thankful for the opportunity. I appreciate all the support and all the concern that you dedicated to my well-being, both inside and outside of work.

To professor Maria Cristina Fernandes, who helped me to get to writing this document so that I could translate all the work that I had done into a final grade and my Engineer's Diploma, and whose work as coordinator of the internship office meant that I could take full advantage of the internship at IFPEN.

To doctor Elodie Devers, who, for several years, has brought the great opportunities of interning at IFPEN to IST students and whose assessment got me to my interview with Jérôme. And who once gave me a ride in her car from Solaize to IFPEN.

To professor Filipa Ribeiro, who has kept the bond between IST and IFPEN alive and well over the years.

To engineers Romina Digne and Alexandre Pagot, who welcomed me into their project and work groups, and who had the patience and the tolerance for the intern's lack of experience.

To engineers Rafaela Oliveira and Marisa Duarte, who helped me feel a little more at home in IFPEN, and who gave me very helpful feedback on my work.

To the recent graduates and other interns of R12: Azhar, Albert, Yu Hsuan, Marie(s), who gave me a place at their table, shared their daily troubles and helped me feel so much less alone in a new world.

To Beatriz Barata, who helped me find a place to live in Lyon, and who's extensive and detailed advice greatly helped me live my day-to-day in France.

To my parents and my sister, who have worked so hard and invested so, so much to allow me to become an engineer. They had patience beyond measure and held on to hope when I had lost all mine.

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List of acronyms

A	Area
ADU	Atmospheric distillation unit / Crude distillation unit
Annum	Same as operating-year (1 annum = 8000 h)
ASME	American Society of Mechanical Engineers
ASTM	American Society for Testing and Materials
bbl	Standard barrel of oil (approx. 159 L)
BP	Boiling point
C1	Methane
C2	Ethane
C3	Propane
C4	n-Butane
CAPEX	Capital expense
CE PCI	Chemical Engineering Plant Cost Index
CHPS	Cold High Pressure Separator (V-202)
CMPS	Cold Medium Pressure Separator (V-209)
CP	Heat capacity at constant pressure
CW	Water from cooling tower
DC	Direct costs
EN	European Norm
EOS	Equation of State
EU27	27 Countries comprising the European Union
FBP	Final boiling point
FCI	Fixed-capital investment
G	Gas flux (common unit: $kg \cdot s^{-1} \cdot m^{-2}$)
GDP	Gross domestic product
GHG	Greenhouse gases
GO	Gasoil
H	Enthalpy
H/D	Height to diameter ratio
HDA	Hydrodearomatization
HDC	Hydrocracking
HDN	Hydrodenitrogenation
HDO	Hydrodeoxygenation
HDP	Hydroprocessing (HDT and/or HDC)
HDS	Hydrodesulfurization
HDT	Hydrotreatment

HeX	Heat Exchanger
HHPS	Hot High Pressure Separator (V-201)
HMPS	Hot Medium Pressure Separator (V-208)
HPS	High pressure steam (saturated at 40 barg)
HPSG	Generation of high pressure steam
HTL	Hydrothermal liquefaction
IAPWS	International Association for the Properties of Water and Steam
IBP	Initial boiling point
ISBL	Inside battery limits
ISO	International Organization for Standardization
Keq	Chemical equilibrium constant
L	Liquid flux (common unit: $kg \cdot s^{-1} \cdot m^{-2}$)
LHSV	Liquid hourly space velocity. Ratio between QV of feed and V of catalyst
LLE	Liquid-liquid equilibrium
LPS	Low pressure steam (saturated at 125°C)
LPSG	Generation of low pressure steam
m	Mass
M&R	Maintenance and repairs
MEK	Methyl ethyl ketone
MFSP	Minimum fuel sale price
MIK	Methyl isopropyl ketone
MMscfd	106 standard (60°F, 14.696 psia) cubic feet per day
MW	Molecular weight
n	Chemical amount (common unit: mol)
NBP	Boiling point at normal pressure
NG	Natural gas
Nth	Ordinal numeral large value. 1 is to 1st as n is to nth.
OL	Operating labor
OPEX	Operating expense
OSBL	Outside battery limits
P	Pressure
PFD	Process Flowsheet Diagram
ppx	Partial pressure of compound x
PR	Peng-Robinson
PT	Total pressure
Q_m	Mass flowrate
Q_n	Molar flowrate
Q_V	Volumetric flowrate

R	Ideal gas constant
SE	Square of error
SimDist	Simulated distillation through chromatography
SMR	Steam methane reforming
SRK	Soave-Redlich-Kwong
SRKKD	SRK-Kabadi-Danner
SSE	Sum of square of errors
T	Temperature
TBP	True boiling point
TCI	Total capital investment
TEMA	Tubular Exchanger Manufacturers Association
TPC	Total product cost
U	Global/Overall heat transfer coefficient
V	Volume
v	Linear velocity
VCU	Vacuum distillation unit
VGO	Vacuum gasoil
VLE	Vapor-liquid equilibrium
VLLE	Vapor-liquid-liquid equilibrium
Vn	Molar volume
VR	Vacuum residue
WABT	Weighted average bed temperature.
WGS	Water gas shift
WWT	Waste water treatment
x	Conversion
α	VLE and VLLE partition coefficient
α_{Hr}	Ratio of reaction enthalpy to amount of hydrogen consumed
ΔH_r	Enthalpy of reaction
λ	Dimensionless number associated with flow regime in reactor (see Equation 6 on p.29)
μ	Dynamic viscosity (common unit: cP)
μ_ℓ	Dynamic viscosity of liquid (common unit: cP)
ν	Kinematic viscosity (common unit: cSt)
ρ	Density
ρ_g	Density of gas
ρ_ℓ	Density of liquid
σ	Surface tension
σ_ℓ	Surface tension of liquid
Ψ	Dimensionless number associated with flow regime in reactor (see Equation 7 on p.29)

1. Introduction

1.1. Background

I applied to an internship offer at IFP Energies Nouvelles, posted by Eng. Jérôme Majcher and divulged at IST by Dr. Elodie Devers. In February 2022, I joined Eng. Jérôme in Solaize, Lyon, France, to work on "*Simulation et dimensionnement d'un procédé d'upgrading de charges liquides issues de la biomasse lignocellulosique et ayant pour produits des bases biocarburants de 2nde génération*".

(…)

1.1.1. Process simulation software

At IFPEN, I worked mostly with AVEVA's PRO/II simulation software, as is common practice there. The PRO/II simulation was given enhanced robustness, meaning that it could reach an acceptable solution with less, or worse quality, initial data. This robustness had a cost in terms of solution time, which could be as high as 20 minutes. In order to tackle this excessive processing time, several simplifications had to be included in the model, but with the safeguard that they could be validated against the more rigorous, and slower, model.

The data already collected by the team at IFPEN only allowed for a limited degree of precision in the simulation, with plans for further measures of the process reality only to take place after my departure.

(…)

PRO/II has a library of compounds much less extensive than Aspen. This led to the need to devise a new way to model the biocrude, different from the mixture-of-pure-compounds employed by most sources. Although it is common practice in Academia to take the values in Aspen's databases as accurate, it should be noted that AspenTech gives no guarantees as to the accuracy of those values. It seems that the approach necessary for any project of industrial relevance must include the experimental characterization of the relevant compounds and mixtures, lest the results have very little meaning.

With some of the data obtained from the PRO/II simulation, the simulation in Aspen Plus could be made in less time, due to increased familiarity with the process, but also due to less need for robustness.

Simulation sequence is of critical importance in sequential-modular process simulators, like Aspen Plus and PRO/II. In this aspect, Aspen is much, much stronger in its ability to automatically determine a viable calculation sequence, but its manual controls of the sequence are confusing, disorganized and intimidating, leading users to avoid using or even learning about these functionalities. In opposition, PRO/II's automatic sequencer is defeated by simpler simulations, but the tools to manually set the sequence are visually prominent and much easier to learn and use.

The simulation in Aspen Plus used User2 models with Excel spreadsheets to represent the reactor, whereas the PRO/II simulation used simpler (and faster) calculator blocks. This was done due to insufficient knowledge, at the time, of the relevant functionalities of Aspen, which leads me to point that Aspen does not allow access to good learning resources to users of the academic version. More details about the challenges encountered using Aspen software are given in Annex 7.

1.2. Objectives of the dissertation

The primary, inescapable, objective of this dissertation is to satisfy the coursework requirements and to allow me to graduate as a Chemical Engineer. In writing it, I sought to showcase the technology of hydrothermal liquefaction and I worked to demonstrate the necessary path to economic viability of the process to produce a crude oil substitute from biomass.

1.3. Structure of the dissertation

The experimental hypothesis investigated for the dissertation is quite self-evident: “is the process lucrative?”. (…)The methodology describes the Aspen simulation’s construction, focusing on the parts that required more ingenuity (including outside of Aspen), followed by an explanation of the methods used in the economic analysis. The results are then presented (…) by following a structure very close to that used to describe how they were calculated. Interspersed with the results are segments of text commenting the importance of certain results, including how they are relevant for results further ahead. The economic analysis concludes with an attempted demonstration of a case where the process would be viable.

The conclusion summarizes the comments made on the results and points to the work that would be necessary to improve the accuracy of the estimations, as well as approaches to improve the economic outcome of the process.

1.4. Societal context

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 (IPCC WG 3, 2021a, sec. 2.7) [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 (Ferella et al., 2019). 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 (IPCC WG 3, 2021b, chap. 15).

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[1] In an environmental context, the term used for this problem is “carbon lock-in”. In financial context, the corresponding term used is “stranded assets”.

2. State of the art

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[2], and it is formed alongside a gas phase of mostly CO_2, an aqueous phase and a solid phase (Biller and Ross, 2016).

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 (Dimitriadis and Bezergianni, 2017; Gollakota et al., 2018; Ramirez et al., 2015).

The reaction has been studied at temperatures ranging from 250°C to 450°C and pressures from 100 bar to 350 bar (Lozano et al., 2022); these ranges include the subcritical and supercritical states of water (critical temperature: 373.9 °C; critical pressure: 220.6 bar (Haynes, 2017)). Lower temperature favors the formation of solids i.e., charcoal, and when this is the desired product, the process is called hydrothermal 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 hydrothermal gasification, when this gas mixture is the main desired product (Biller and Ross, 2016). The elevated pressure is broadly agreed to facilitate the reaction by reducing heat and mass transfer limitations throughout the biomass particles.

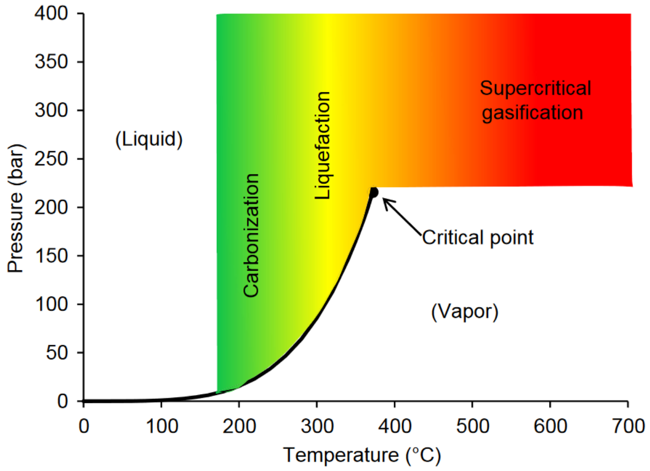

Figure 1 - Hydrothermal processing conditions in the water phase diagram. Figure adapted from Biller and Ross, 2016.

The product of interest, biocrude, is a very complex mixture of organic compounds including many oxygenated species. The degree of complexity of the mixture that is biocrude is of the same order of magnitude as that of crude oils, however it is superior. A growing ordering of the complexity of mixtures can be suggested starting from binary mixtures to mixtures typical of stream in industrial chemical processes, to crude oil (and biocrude) and ending in mixtures typical of biological processes.

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[2] Sometimes spelled “bio-crude” e.g., Ramirez et al., 2015; other times called “bio-oil” e.g., Akhtar and Amin, 2011, or even “biooil” Maschmeyer and Humphreys, 2013

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 Pedersen et al., 2017; Treese et al., 2015

	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. Catalysts for HDT always have some effectiveness in HDC as well (the reverse is also true), so it is considered that both processes always happen, even if to different degrees depending on the catalyst and process conditions (Robinson and Dolbear, 2006; Treese et al., 2015).

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

2.1. Environmental impact

The importance and potential of biofuels to reduce anthropogenic greenhouse gas (GHG) emissions has been extensively explored and has evolved over time. From a simplistic point of view, it can be said that plants grow by absorbing carbon dioxide from the atmosphere and that an equal amount of carbon dioxide is release back to the atmosphere when the biofuel is burned, therefore, the atmospheric concentration of GHGs should not increase as a result of the usage of biofuels (Gustavsson et al., 1995).

This reasoning is flawed since the GHG emissions related to the cultivation, harvest and transport of the biomass are not taken into account, neither are those associated with the energy and material needs of the conversion process, or those associated with biofuel distribution. Additionally, there are concerns about the climatic impact of land-use change and economic concerns since energy crops compete against food crops for productive land and other farming resources (de la Rúa Lope and Lechón, 2018).

Biofuels produced from ligno-cellulosic feedstocks are considered advanced biofuels since they are not produced using material fit for human consumption and therefore have less potential to compete with food crops for the land on which they grow best (Neiva Correia et al., 2018; Riazi and Chiaramonti, 2018).

The report by Tews et al., 2014, includes a life-cycle assessment of the GHG emissions associated with the entire production and distribution (scopes 1, 2 and 3 (US EPA, 2016)) 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) (Tews et al., 2014). 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 (Bhandari et al., 2014; Luo et al., 2020).

2.2. 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.

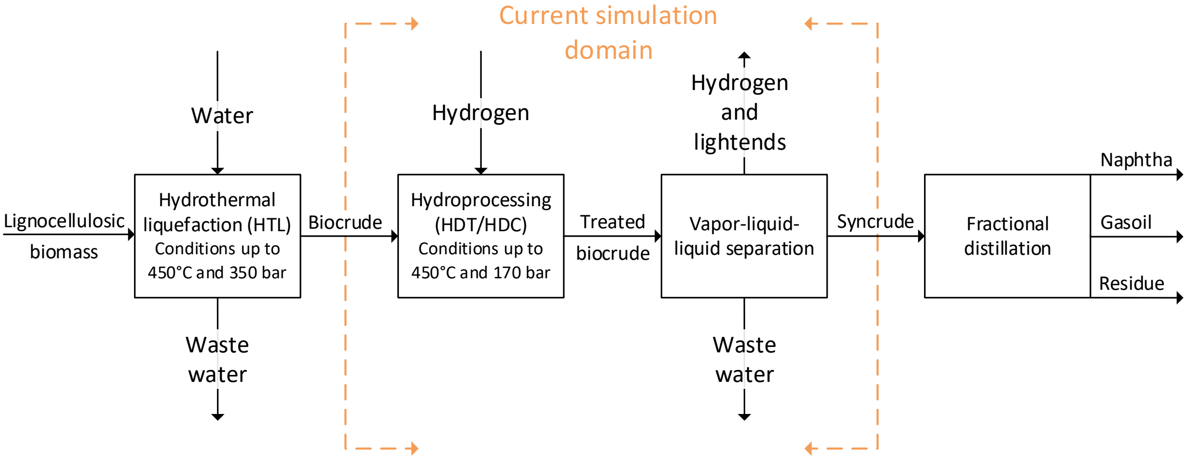


Figure 2 - Diagram of biomass to fuels HTL pathway

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.

2.2.1. Hydrotreatment

Hydrotreatment is the process of using hydrogen, over a suitable catalyst, to react with undesirable substances present in crude oil fractions, in order to allow the effective removal of the contaminants. Hydrodesulfurization is a type of hydrotreatment that targets the removal of sulfur and is one of the most employed, in terms of hydrogen consumption. The process results in the formation of hydrogen sulfide, which being a gas, is easily separated from liquid fractions, such as diesel or fuel-oil (Kokayeff et al., 2015). An example of the scheme for a commercial hydrotreatment process is shown in Figure 3. Some notable differences, from the process proposed in this work for biocrude, include the injection of cold water before the cold high-pressure separator (CHPS; cold separator in the figure) and the use of air coolers instead of water coolers between the hot and cold parts of the separators section. The biocrude process dispenses the addition of water to "wash away" the ammonia since so much is already produced as reaction products and the need to cool to lower temperature justifies the usage of water cooling rather than air cooling.

In terms of terminology, in the figure the high-pressure separators are called "separators" and the low-pressure separators are called "flash drums".

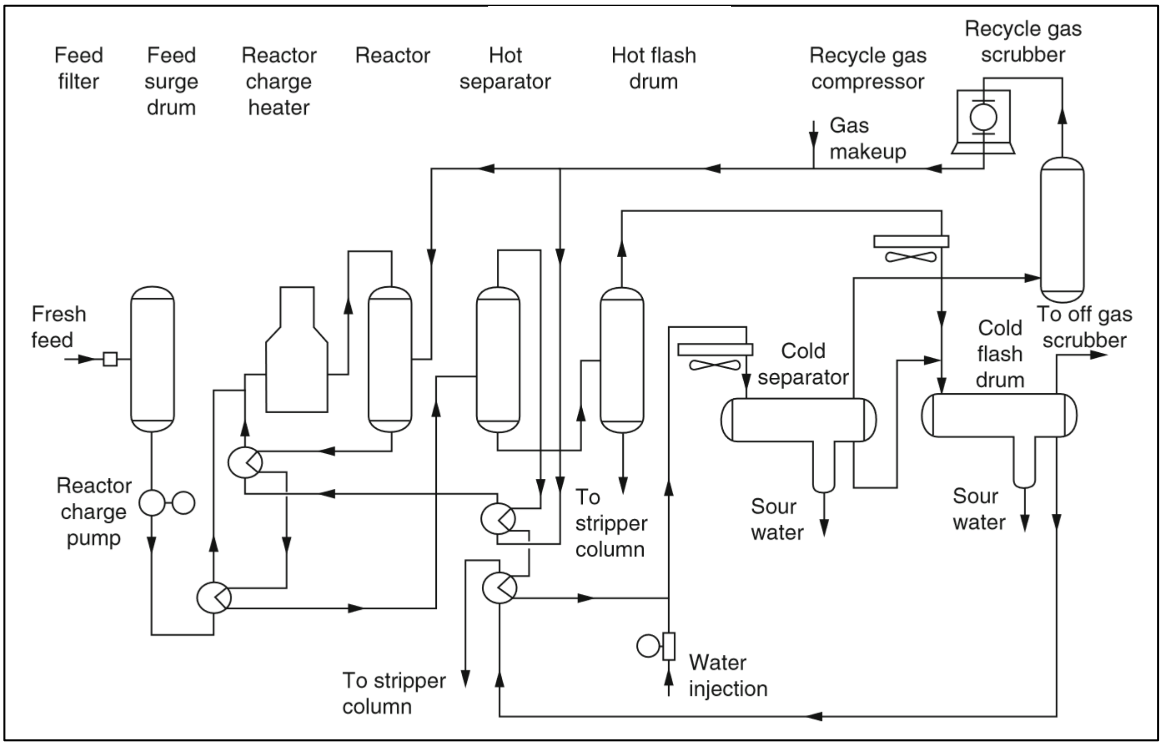


Figure 3 - Schematic flow diagram of vacuum gasoil (VGO) Unionfining^{TM} (a type of HDT) unit. Adapted from Treese et al., 2015, p. 367

2.2.2. Hydrocracking

Hydrocracking, sometimes considered a subtype of hydrotreatment (Kokayeff et al., 2015), while other times considered a different process altogether (Bricker et al., 2015), is the process of reacting heavy fractions of crude oil with hydrogen, over a suitable catalyst, to produce lighter fractions, for which there tends to be much higher demand, and thus fetch a higher price at market. An example of hydrocracking would target transforming the residue of the vacuum distillation of crude oil, a very heavy substance, into a gasoil blendstock, that is to say, a product with the comparatively lower boiling point range typical of gasoil and that can be mixed with other blendstocks to produce Diesel engine fuel compliant to standards ((EN590, CEN/TC 19, 2022) in the European Union) (Bricker et al., 2015; Treese et al., 2015).

A scheme for a typical HDC unit is shown in Figure 4.

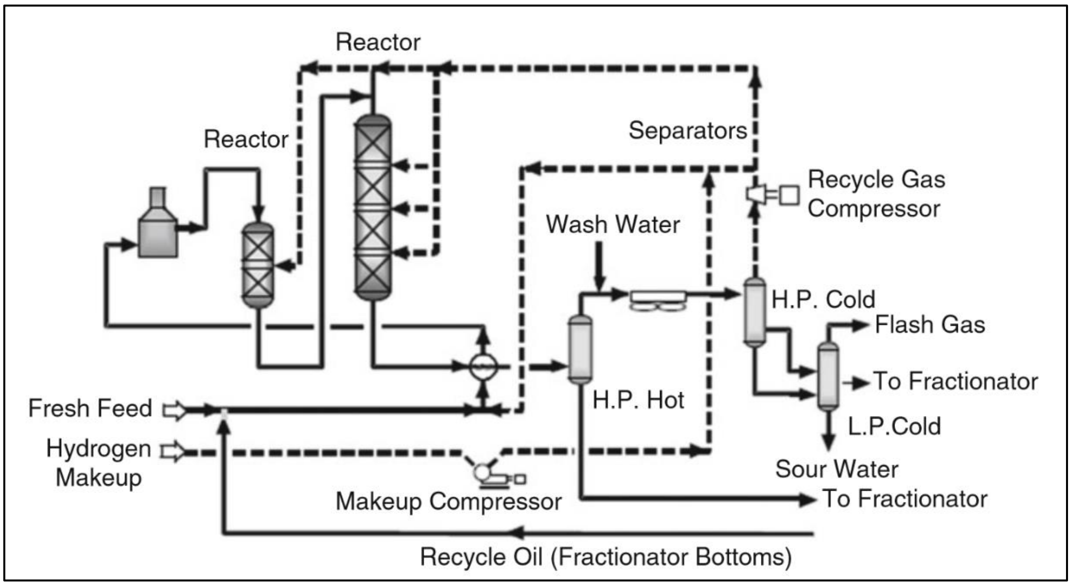


Figure 4 - Typical flow diagram of reactor section of single-stage hydrocracking unit. Adapted from (Treese et al., 2015, p. 325).

The "single-stage" refers to the fact that both the depicted reactor shells are directly in series. In a "two-stage" design, the "Recycle Oil" is hydrocracked in a separate reactor and the products of the two reactors are then mixed before the separators. The alternative where no recycle oil is hydrocracked is called the "once-through" configuration. Figure 4 shows a reactor design with two shells, with the first having 2 catalytic beds and the second having 4. The usage of two beds can be justified by several criteria, but the most common is height limit of a single shell (around 50 m). In cases where a high gas flow rate is needed to quench between the beds, having two reactor shells allows that the first shell be of smaller diameter and thus cheaper to build (more details on the importance of this matter is given in the section dealing with sizing and costing of the reactor (p.29)

2.3. Differences of common practice in chemical *versus* petroleum engineering

As mentioned before, the simulated process deals with extremely complex mixtures. This complexity means that, using the usual simulation characterization strategy of selecting pure components and then estimating the mixture properties, it is near-impossible to get a stream with accurate properties. This approach has been tried by some authors (Lozano et al., 2019; Pedersen et al., 2018; Penke et al., 2021; Snowden-Swan et al., 2017; Taghipour et al., 2022), but the work focus almost exclusively on untreated Biocrude and important parameters for equipment sizing, like density and viscosity, are rarely or never considered.

For this work, an approach closer to that used in modelling petroleum processes was used. This approach is focused more on the directly measured properties of the petroleum, rather than pure chemical compounds and their interactions. Modelling tools, like Aspen Plus, have special functionalities so as to accommodate this approach and, by employing dedicated physical property models, can achieve accurate representations of petroleum.

In the crude oil industry, the boiling point distribution (TBP curve) of feed and products is the most important descriptor of a substance. This is reasonable, since the volatility characteristics of a fuel are critical to its applicability in a specific type of engine or burner, and the TBP curve is also strongly correlated with other important parameters like viscosity and density. Information about a substance's TBP curve and specific gravity is combined to form the minimal useful assay data.

The treated biocrude, with has lost most of its oxygen, was considered to be a petroleum and to be adequately described by the oil correlations.

A point must also be made about scales, since it is well-established that economies of scale are one of the most important contributing factors to reducing total product cost in the process industries. Chemical plants often have their production described in terms of kton/year, with common, large scale, chemical process usually producing around 200 kton/year of product. In oil refining, capacities are usually described in terms of thousands of barrels per day (kbbl/day or kbpd), which makes the comparison of scale difficult and obfuscates the order-of-magnitude difference between chemical plants and refineries. According to Robinson and Dolbear, 2006, the average crude distillation unit has a capacity of 114 kbbl/day, which is approximately equivalent to 5800 kton/year, and the average HDT unit has a capacity of 1440 kton/year (30.6 kbbl/year). By designing this unit for a capacity of 100 kton/year (2.1 kbbl/year), more in line with chemical plant scale than with refinery scale, the economic results may show a lack of competitiveness with fossil fuels.

3. Process scheme for the biocrude upgrading process

The configuration of the process studied for this dissertation was based on a hydrocracker of heavy oil cuts.

The process scheme is described by 4 blocks as can be seen in Figure 5. 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, composed mostly of hydrogen, 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 (WWT),

    - 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.

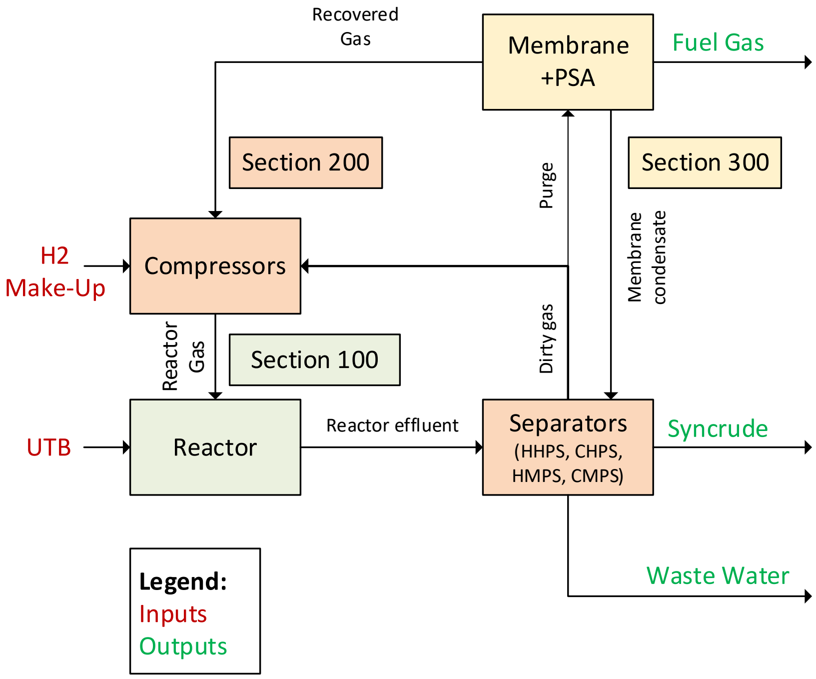


Figure 5 - Block flow diagram of the process

The simulation domain has two streams entering and three streams leaving:

- Process inputs:
    - UTB: untreated HTL biocrude feedstock
    - H2 Make-up: hydrogen to compensate what is consumed in the reaction and lost from the recycle loop in the output streams
- Process outputs
    - Waste water: formed in the reaction and requiring WWT
    - Syncrude: stream of valuable hydrocarbons destined for fractionation
    - Fuel Gas: PSA tail, containing high concentration of C1

4. 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,
- ensuring that the simulation converged, despite the presence of customized blocks, multiple design specs and a large recycle stream.

The solutions tried, some of which were found adequate while others where not, are described in the following sections.

4.1. Physical and chemical characterization

The description of the substances involved was not simple. The approach taken in published literature, as mentioned on p.7 , 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. (…). 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. (…)

The model of UTB started from the pure component triolein and then the viscosity and density were adjusted.

(…)

Treated biocrude was modelled as an assay with discrete lights. The pseudo-component property estimation was done using the default "ASPEN" property method. The boiling points where extracted, from the chart presented in the reference, using WebPlotDigitizer (Rohatgi, 2022) and the values are presented in Table 2. The points selected on the chart are shown in Annex 6.

Table 2 - D2887 assay data of treated (pine) biocrude from Jarvis et al., 2018

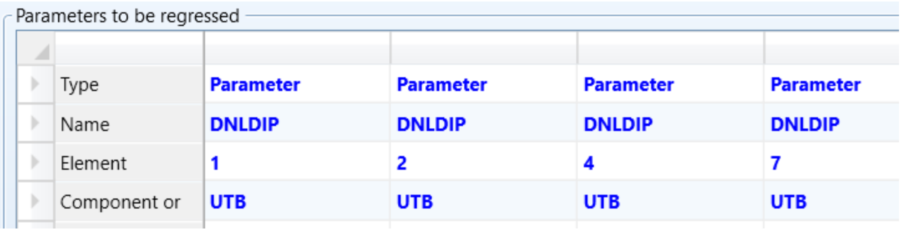
%Mass recovered	Boiling point (°C)
1	37
5	82
10	103
15	125
20	146

25	167
30	188
35	211
40	231
45	252
50	272
55	290
60	307
65	323
70	339
75	359
80	381
85	407
90	440
95	483
99	542

The specific gravity considered was 0.9 (Jarvis et al., 2018). The Aspen input code of the implementation of the assay pseudocomponents is given in Annex 3.

Following the recommendation in Peters et al., 2003, p. 218, the Soave-Redlich-Kwong (SRK) property method was initially selected. By consulting the "Aspen Plus V11 Help," 02/19, 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), as this is the most computationally efficient method and the approximation is suitable for mixtures where it is known that the water is contaminated, but it's not critical to know what the contaminants are. This is valid since the waste water treatment plant (WWTP) is not part of the simulation domain.

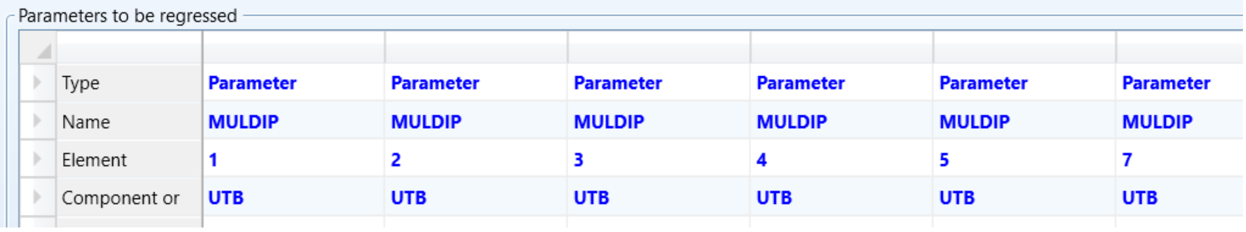
The SRK-KD method uses the *ESSRK0* model for molar volume and the *MUL0ANDR* model for viscosity and it is not possible, in Aspen Plus V11, to adjust the parameters of components in these models with the SRK family of methods, so in order to perform the adjustment to the experimental data by regression, the IDEAL method was selected for the process section before the reactor (up to stream 10). The IDEAL method also uses *MUL0ANDR* for viscosity, but uses *VL0RKT* for the molar volume, and the parameters of these models can be adjusted by regression. In order to work with the regressed parameters, the Route by which IDEAL calculates the molar volume of mixtures (*VLMX*) had to be changed to *VLMXQUAD*. The "Regression" run mode was selected and the data from **Erro! A origem da referência não foi encontrada.** and **Erro! A origem da referência não foi encontrada.** were introduced and the parameters for regression were indicated as shown below:



Parameters to be regressed

Type	Parameter	Parameter	Parameter	Parameter
Name	DNLDIP	DNLDIP	DNLDIP	DNLDIP
Element	1	2	4	7
Component or	UTB	UTB	UTB	UTB

Figure 6 - Selection of density/molar volume parameters to be regressed



Parameters to be regressed

Type	**Parameter**	**Parameter**	**Parameter**	**Parameter**	**Parameter**	**Parameter**
Name	**MULDIP**	**MULDIP**	**MULDIP**	**MULDIP**	**MULDIP**	**MULDIP**
Element	**1**	**2**	**3**	**4**	**5**	**7**
Component or	**UTB**	**UTB**	**UTB**	**UTB**	**UTB**	**UTB**

Figure 7 - Selection of viscosity parameters to be regressed

(…)

The regression of viscosity required a loosening of convergence tolerance from 1E-4 to 2E-4 and an increase of the maximum number of iterations in the Main algorithm.

(…)

4.2. Characterizing the reaction

Hydrotreatment involves not only a great number of possible reactants but also several different chemical pathways. In their effort to model the upgrading process, Penke et al., 2021, utilized a set of 85 equilibrium reactions to attempt to obtain a representative model reactor. This approach, almost brute force, is of questionable value as described earlier. Instead, the thermal characterization of the reactor was performed by estimating the industry standard of heat released per mol of hydrogen consumed.

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

In literature it is possible to find a range of values for α_{Hr} from 14 kcal/mol to 32 kcal/mol (Robinson and Dolbear, 2006).

The hydrodeoxygenation reaction, which consumes the most hydrogen, and thus is responsible for most of the heat released, can be generalized by the following equation:

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

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.

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

These reactions were simulated using Aspen's RSTOIC model, at the process conditions at the end of each bed, to obtain the α_{Hr} for each reaction.

Table 3 – α_{Hr} for model compounds

A	x	B	y	α (kcal/mol H_2)
Catechol	2	Benzene	2	15.5
Phenylacetic acid	3	Ethylbenzene	2	14.8
4-Ethyl-2-methylphenol	1	3-Ethyltoluene	1	18.9
2-Hydroxyphenethyl alcohol	2	Ethylbenzene	2	21.1
Stearic acid (C18)	3	Octadecane	2	14.8
Ethanol	1	Ethane	1	23.1
MEK	2	Propane	1	17.8
MIK	2	I-Hexane	1	18.6
Glycerol	3	Propane	3	20.1
tert-Butylhydroquinone	2	t-Butylbenzene	2	17.7

For equivalent table with structural formulas, see Annex 1.

Based on this data, $\boldsymbol{\alpha_{Hr}}$ was estimated to be **19 kcal/mol**$_{H2}$. The estimate was obtained by the average of the different values for α, rounded up to the nearest integer. (…)

4.3. 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 (Robinson and Dolbear, 2006).

Several strategies, in addition to, or combination with, the most conventional were considered as possible effective solutions.

1. **Hydrogen quench** – after each catalytic bed, cold hydrogen is added to the reaction mix in such an amount that the resulting stream has the desired temperature. This is the more conventional approach, but results in a high flowrate of gas in the reactor (…).

   - Advantages
     - Well know approach
     - High pp_{H2} due to dilution of contaminants formed
     - Possible reduction of total pressure, while still maintaining an acceptable pp_{H2}
   - Disadvantages
     - High gas flowrate requires a larger recycle compressor
     - Large diameter of reactor is necessary to avoid flooding the reactor with gas, i.e., moving to the pulsed flow or spray flow regimes, which are of unknown adequacy to the reaction

2. **Chilled hydrogen quench** – the reactor gas that is used to quench is cooled to a low temperature (e.g.: -20°C) using a refrigeration utility
   - Advantages
     - Less gas flowrate is needed and so a smaller and cheaper reactor can be used
   - Disadvantages
     - Need for a refrigeration utility, increasing costs
3. **Recycle of the fractionation bottoms** – the bottom product of fractionation (not included in the current simulation) is pumped to provide thermal ballast for the 1^{st} bed and to quench in the quench boxes. This strategy is currently used in full-conversion hydrocrackers of heavy oil cuts (Robinson and Dolbear, 2006).
   - Advantages
     - Increase in liquid flowrate increases margin of safety relative to spray-flow regime
     - Cracking of VGO, increasing the value of the total reactor effluent
     - No cracking of naphtha or GO, since those are removed in the fractionation
     - Increases concentration of Aromatics in the reactor (aromatics tend to stay in the heavier cuts), favoring hydrodearomatization (HDA), which is an equilibrium reaction. High aromatic content in gasoil means it to be of "less quality" by lowering the cetane number, among other effects (Luning Prak et al., 2021).
   - Disadvantages
     - Currently unpredictable increase in hydrogen consumption, the main cost driver for hydroprocessing of oil cuts
     - More catalyst is necessary since some of the catalyst will be "busy" with additional cracking
     - Increased size of all units in separations train, including fractionation columns
     - Difficulties in mixing with the reactor internal streams due to high viscosity of heavy cuts.
4. **Integrated crossflow heat exchangers** – in each quench box are placed a series of U-tubes with cold streams on the inside. This hypothesis resembles putting a TEMA DXU HeX in each quench box.
   - Advantages
     - Reduces necessary gas flowrate, allowing for lower diameter reactor and smaller compressor
     - Reduces size of HeXs after reactor
     - No increase in hydrogen consumption
     - Less variation in fluid flowrates throughout the reactor, leading to less unnecessary space in the reactor (better capital efficiency)
   - Disadvantages

  - Untested design – low velocities in the reactor internal stream may cause a low U, requiring a large heat exchange area
  - Need to occlude parts of the reactor cross-section in order to prevent bypass of the tubes and to increase velocity
  - Some hydrogen quench may still be necessary, with accompanying control systems, meaning that instrumentation cost is not avoided
  - More complex layout to allow for thermal integration (e.g., it would be difficult to bring the atmospheric column bottom stream to the reactor quench box and then send it back to the column)
  - Complex design and, based on experience with embedded-tube Fischer-Tropsch reactors (see Guettel et al., 2008), complex operation

5. **Increasing the number of beds**
   - Advantages
     - By having more beds, the duty that must be assigned to the first bed is lower and this allows for a lesser amount of gas to be needed as ballast there, allowing for a smaller reactor
   - Disadvantages
     - Additional quench box, bed supports, distributors, etc. with direct increase in cost of the reactor
6. **More than one reactor shell –** by breaking the reactor into multiple shells in series, it is possible to replace one hydrogen quench with a HeX, per additional shell
   - Advantages
     - If a quench box is replaced with a HeX, the increase of quenching gas flow does not happen so the reactor diameter doesn't need to be so great
     - Each shell can be of a different diameter and so it's possible to reduce the amount of material needed for construction of all shells
   - Disadvantages
     - The cost of the additional shells and HeXs may overcome the achieved savings
7. **Single shell with multiple diameters**
   - Advantages
     - Combines some of the savings of multiple shells with different diameters and the material savings of having a single shell
   - Disadvantages
     - Unorthodox solution. Although multiple diameter columns are reasonably common, multiple diameter reactors are less so.

  - ○ Mixing of quench gas with reactor internal stream can become more complicated

With current knowledge, the most conservative solution is number 1, since the increase in the hydrogen consumption, predicted in alternative 3, can easily compromise the economic viability of the process. Solution 4 would require thorough study, starting with CFD modelling, before being realistically considered, and so is placed outside the scope of this work. Solutions 2, 5, 6 and 7 merit further consideration since they do not require analysis with tools that fall beyond those already used in this work.

4.3.1. Base case design

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

- Maximum temperature: 400°C (Jarvis et al., 2018)
- (…)
- Number of shells: 1
- Number of beds/shell: 5 (maximum according to Bricker et al., 2015)
- (…)
- LHSV: 0.21 h-1 (Jarvis et al., 2018)
- Catalyst void fraction: 40%
- Acceptable approach to spray flow regime: 70%

Before introduction into Aspen, the reactor initialization parameters were estimated with a conventional enthalpy balance in Excel. These were the assumptions used for the balance:

- Reference temperature for ΔH is 0°C and physical states are liquid for the liquid stream and gas for the gas stream
- C_P of condensable phase is considered constant at 0.65 kcal/kg/K
- C_P of gas fed to reactor is 2.33 kcal/kg/K
- C_P of total mixtures is calculated by weighted average based on weight
- Q_m and ρ of condensable phase are considered to vary linearly in proportion to conversion, from the values known for the liquid feed to the values calculated by Aspen for the syncrude.
- Densities used were at 15°C
- (…)

(…)

- (…)
- The split of this gas into each quench box was as indicated
- The duty for each bed was as calculated in the balance

The distribution of duties across the beds is an important output variable to keep under consideration. It is assumed that in each bed there will be as much duty as will produce an increase of temperature $(\ldots)$. As previously explained, the amount of quench gas is that which will reduce the total stream temperature $(\ldots)$. The total duty is also fixed through the hydrogen consumption and the assumption of conversion as proportional to duty.

Given these fixed variables, the duty on beds 2 to 4 becomes a fully dependent variable. The duty on bed 5 is constrained by what has been the duty in previous beds and the maximum duty (the duty in bed 5 is "what remains") and so must have one less imposition than previous beds. For bed 5, the requirement that the feed be at $(\ldots)$ is removed, replaced by the constraint that the temperature increase in bed 5 must be less than or equal to $(\ldots)$ (it cannot be greater than $(\ldots)$ due to mechanical constraints).

The first bed has one degree of freedom, the variable of its duty, and by varying this duty, the duty in the other beds and the temperature of the stream entering bed 5 changes as a response. Other imposed duties were tried.

(…)

It is visible that reducing the duty in bed 1 can lead to an overall reduction in H2/HC ratio, but in order to stay in line with the limit ΔT, another bed would have to be added and, since we're already at limit of 5 beds in one shell, a 6th bed would require a second shell, which would be economically unattractive. This limit of 5 beds per shell can perhaps be substituted by a maximum shell height and maximum height per bed, in which case many more than 5 beds can be fitted into a shell.

Once the simulation had converged, the values determined using Aspen were compared with the ones calculated using the enthalpy balance.

(…)

It was specified that the Reactor gas should have a molar fraction of hydrogen of at least (…), so that its partial pressure would remain high without the need for high total pressure, which requires thicker reactor vessel walls and thus increases CAPEX. According to Kokayeff et al., 2015, it is important to remove as much CO, CO_2 and CH_4 as possible from the Reactor Gas stream since these will react in the Steam Methane Reforming and Water-Gas Shift reactions (Equation 4 and Equation 5, respectively). According to equilibrium calculations, these reactions will both occur dominantly in the inverse direction. The reactions are very fast and highly exothermic and can cause thermal runaway, as well as tending to wastefully consume hydrogen when it is in high abundance, as is the case.

$$H_2O + CH_4 \rightleftharpoons 3H_2 + CO \qquad \text{Equation 4}$$

$$H_2O + CO \rightleftharpoons H_2 + CO_2 \qquad \text{Equation 5}$$

These reactions are sometimes given little consideration since the gas fed to experimental, small-scale reactors, is mostly pure hydrogen. In the simulated model, as in industrial application, the contaminants present in the gas fed to the reactor will increase the relevance of the SMR and WGS reactions.

(…)

The equilibrium was introduced as a “Chemistry” in the Properties environment, but it was not selected for every block, since it was considered only to happen in appreciable amounts in the presence of the catalyst. Instead, the chemistry was enabled only for the blocks that represent the quench boxes and, in the case of the last bed, the block that introduces the HDT reaction duty into the stream (further details given below, in section 4.4.3, in the part where M104 is described).

4.4. Process simulation

With the process scheme decided, based on the BFD and on vacuum residue HDC units, a diagram with more detail is proposed in Figure 8. It details the main pieces of equipment necessary to the process. (…) This flowsheet was the basis for the implementation in Aspen Plus and the Aspen flowsheet is given in Annex 8.

Table 4 - Equipment list

E-101	E-102	E-103	E-104	E-105	E-201	E-202	E-203	E-204	E-205	H-101	H-102	K-201	K-202
LOWER UTB VISCOSITY FROM STORAGE	REACTOR EFFLUENT-LIQUID FEED	REACTOR EFFLUENT-REACTOR GAS FEED	SPLIT FEED PRE-HEATER	REACTOR GAS QUENCH COOLER	COOLER BEFORE CHPS	COOLER HYDROGEN FROM DISTRIBUTION	H2 MAKE-UP LP STAGE INTERCOOLER	H2 MAKE-UP MP STAGE INTERCOOLER	COOLER BEFORE CMPS	FIRED HEATER TRIM HUCLEAR FEED	FIRED HEATER TRIM REACTOR GAS	RECYCLE GAS COMPRESSOR	H2 MAKE-UP COMPRESSOR LP STAGE

K-203	K-204	P-101	R-101	SC-301	SC-302	SC-303	V-201	V-202	V-205	V-206	V-207	V-208	V-209
H2 MAKE-UP COMPRESSOR MP STAGE	H2 MAKE-UP COMPRESSOR HP STAGE	FEED PUMP	HDT/HDC UPGRADING REACTOR	MEMBRANE CONDENSATION	MEMBRANE PERMEATION/RETENTION	PRESSURE SWING ABSORBTION	HOT HIGH PRESSURE SEPARATOR	COLD HIGH PRESSURE SEPARATOR	H2 M.U. LP STAGE SUCTION K.O. DRUM	H2 M.U. MP STAGE SUCTION K.O. DRUM	H2 M.U. HP STAGE SUCTION K.O. DRUM	HOT MEDIUM PRESSURE SEPARATOR	COLD MEDIUM PRESSURE SEPARATOR

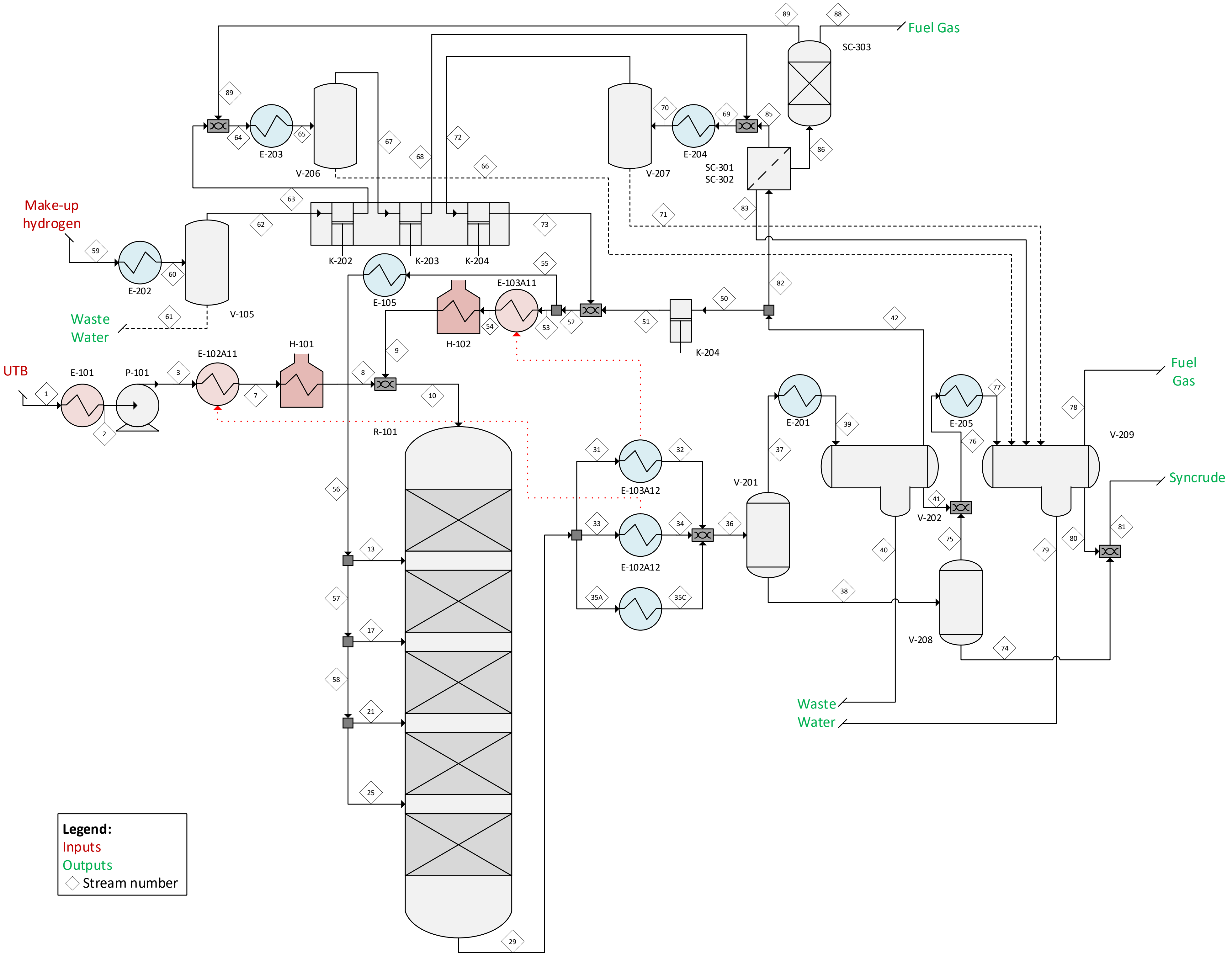


Figure 8 - Process flowsheet diagram

Table 5 - Stream summary table (PFD table).

(…)

The following is a description of how the process was translated into the simulator.

4.4.1. Upstream of the reactor

The section that processes the untreated biocrude (UTB), up to the point where it is mixed with the hydrogen before entering the reactor, uses the IDEAL property method with adapted properties as described previously, allowing for more rigorous sizing of the exchangers and pump. This is done by having this section's blocks in a separate flowsheet section, UTB-SECT, depicted in Figure 9.

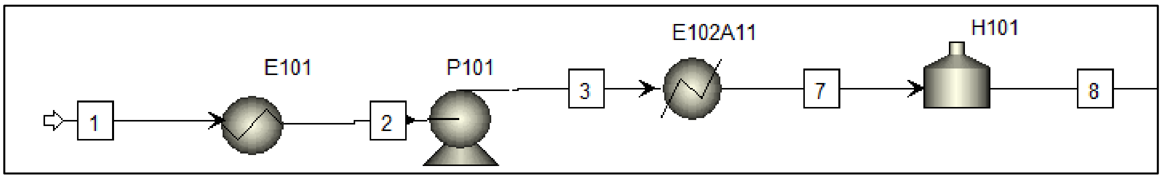


Figure 9 - Section of flowsheet that uses IDEAL property method

The gas fed to the reactor comes from stream 52, but this stream will change as the simulation is solved since it includes a large amount of recycled unreacted hydrogen. This stream, despite not being a boundary stream, should have its input parameters defined in order to give an initial value to the iterative solution of the flowsheet. (…)

Because the pseudocomponent generation was not instructed to "Generate component IDs", it is not possible to specify initial values for the pseudocomponents, leading to a lower limit on the difference between stream 52 in the first and second iteration which is substantially high. Had the component ID generation been used, the simulation convergence should have been faster and more reliable.

These values have already been subjected to reconciliation, meaning they were changed based on the final results from a previous run. The value of the molar flowrate of stream 52 with which the simulation is initialized affects the temperature of stream 29 (…).

The trim heater H102 may seem dispensable, but (like H101) was kept as an actuator for a control loop that targets the temperature of the gas-liquid mixture entering the reactor. In the simulation this control was achieved by having a set-point on the temperature of stream 10 and varying the temperature of stream 9 through H102. The control of the temperature in stream 10 is particularly important since block M101 mixes a stream coming from the IDEAL property method with another using the SRKKD method, which tends to generate unreal variations in stream variables.

E102A11 and E103A11 represent the cold sides of heat exchangers E102 and E103, respectively. The HeXs are broken up like this to facilitate an eventual heat integration study. In the current simulation they are imposed the symmetric duty of their other halves E102A12 and E103A12. This is in the complex part of the flowsheet (i.e., involving recycling and solved iteratively). For the sizing of the HeXs, the results from the solved loop are cloned and the relevant streams exchange heat directly in blocks E102 and E103.

4.4.2. Reaction product

It was necessary to create a stream with the composition of the experimental effluent based on the data from literature. This was done in three parts with one stream containing the petroleum pseudocomponents in the form of the JARVIS assay, another stream with the light products of the reaction and another with the water.

(…) The combined streams form stream R-EFFLU0 and this stream is run through a Mult block where it is shrunk by 0.5% to ensure that the final mass balance is achieved (this should become clearer after the explanation of the reactor model).

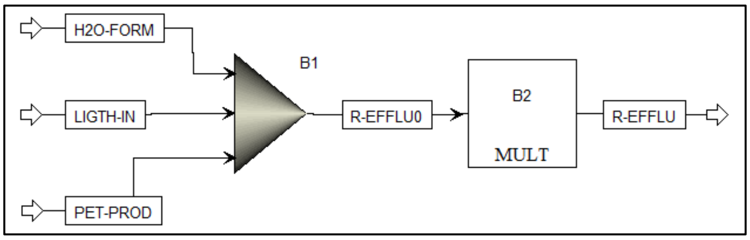


Figure 10 - Flowsheet section that defines the reaction product

4.4.3. Reactor

Aspen Plus does not possess a convenient, built-in, solution for modelling reactors dealing with oil products, so it was necessary to resort to User Models. This is the approach shown in Haydary, 2019, for the relevant example. The approach used in the previous simulation, in PRO/II, had also been to use custom code and the computation strategy was largely kept the same, except that based in Excel rather than Fortran.

The reactor is simulated as repeating sets of separate components. The first set R101A is composed of a User2 block (R101A11) where the conversion of reactants into products takes place, followed by a Heater block (R101A12) that introduces the reaction enthalpy into the stream, as arbitrated in **Erro! A origem da referência não foi encontrada.**. The first conversion block uses its own excel file, which was developed following the example in (“Aspen Plus V11 Help,” 02/19 Getting started with Aspen Plus>Tutorials>Customizing Unit Operation Models>Creating an Excel Unit Operation Model).

(…)

In addition to stream 10 (connected to the block), streams 1 and R-EFFLU are also referenced through the “Streams” tab since some of their parameters will be needed in the Excel sheet. The option to flash the outlet stream, once its parameters have come back from Excel, is also selected, but the Pressure and Temperature are left blank since they are supplied by Excel.

Inside the excel sheet, the conversion is calculated as being equal to the duty fraction, then, the amount of remaining hydrogen and UTB is calculated and then the other compounds, including the pseudocomponents, are calculated by adding a fraction of the R-EFFLU stream.

The stream temperature doesn’t change, but the pressure is reduced by the estimated pressure drop. The resulting stream then has its other variables (enthalpy, vapor fraction, entropy, density, MW, etc.) calculated by the flash algorithm in Aspen. Next, the duty is added in R101A12. Since this is the first bed, the temperature after the reaction duty is controlled by changing the amount of excess gas which is added to the reactor feed. DS2M101 is the design-spec that manipulates the amount of gas in the feed to achieve a set-point (…) in stream 12.

M104, SP105 and DS3QB1 comprise the first quench box and its control loop. The controlled variable is the temperature of the stream leaving the quench box and going into the second catalytic bed, stream 14, and the set-point is (…), bellow the final bed temperature. The manipulated variable is the flowrate of reactor gas, which is at 40°C, that is added. M104 is the only block in this section that has the SMR+WGS chemistry enabled, so that the changes in composition and reaction enthalpy are considered when determining the amount of quench gas.

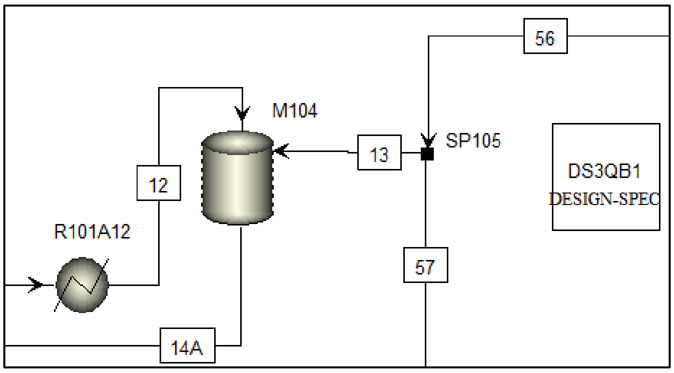


Figure 11 - Blocks and streams simulating the first quench box

The second reactor bed can be said to be more generic, since it is cloned to make beds 3 through 5, all using the same spreadsheet file. R101B10 is the "0th part" of the second bed and it had to be added to solve a bug in Aspen: as the recycle loop was iterated through, the first call of Excel wasn't responding properly, and so the actual 1st bed, R101B11, was just being bypassed. The solution works by having this dysfunctional operation happen in a block that also calls the Excel sheet, but only does a vestigial conversion of 0.002%. If the block works correctly, it doesn't have any impact, if it doesn't, then it still serves to "reset" the Excel call mechanism to proper working order.

R101B11, as well as R101C11 through R101E11, use only a single user parameter, which is the duty in that specific bed and, in regard to referenced streams and flash options, it is equal or equivalent to R101A11. The spreadsheets used in these beds have the other values that were supplied in R101A11 (see **Erro! A origem da referência não foi encontrada.**) as numbers hard-coded into the sheet, meaning that their adjustment can't be done inside Aspen Plus, but must be made directly in the Excel file. This approach is not the most flexible, but it is adequate to a context in which the simulation will not be used by multiple users. A more robust approach would, for instance, include transfer block to move the data from the first bed block to the others.

The "addition" of the reaction heat to the stream and the quench box control loop work just as described for the first bed, with the exception of the 4th and final quench box, in which there is no control loop since the flowrate is simply that which flows in stream 52 but hasn't previously been added to the reactor stream; as mentioned on page 22, in order to control the temperature of block M110, the initial value of molar flowrate in stream 52 must be manipulated. Improved robustness of this point would require a Design-Spec to perform the control, which, due to the fact that it only matters in the first pass of the iterative resolution, would require a full custom sequence, and so it was not deemed to be priority.

4.4.4. Cooling of the reactor effluent

The reactor effluent follows next to the separation section of the process, but before that, it must be cooled. The stream leaving the reactor, stream 29, is the most valuable stream in terms of useful heat (it carries all of the heat generated by the reaction, along with the heat supplied to the reactants and no longer needed). Only the most elementary form of heat integration, the heating of reactants with reaction products (Smith, 2016), was performed in the scope of the work, but it allows us to see that there is enough heat to eschew the use of a heating utility for the reactants.

(…)

(…). In order to preserve as much high-grade heat as possible, the streams passing through E102 and E103 are limited in their flowrate at SP109. DS6S31 adjusts the flowrate in stream 31 so that, having cooled, it will be at (…). DS7S33 does the same for stream 33.

Stream 35A is the remainder between stream 29 and the other two outlets of SP109, and it allows us to see that over (…) MW of heat are still available at (…). In the simulation, the heat in E104 is used to generate high-pressure steam. While this probably isn't realistic from a process point of view, it allows an economic value to be placed on the high-grade heat. E106 does the final cooling in order to meet the objective, generating low-pressure steam.

The original idea was to place all these heat exchangers in series. In the development of this work, it was shown that having the heat exchangers in series would not allow the second reactant stream to be heated to such a high degree, since only the first reactant stream would be heated with the product stream at (…) and the stream remaining after heating all reactants would have a higher amount of heat, but of heat at a lower temperature. This would limit its ability to produce the utilities of the highest added value and it would require larger heat exchangers to harvest the heat, since the available temperature difference would be lower.

The split was suggested by Aspen Energy Analyzer during an initial attempt to perform heat integration of the process. This attempt had to be given low priority and was eventually abandoned.

4.4.5. Separators section

(…)

V201 is the hot high-pressure separator and its aim is to remove the hydrogen and most of the water from the product stream. Its pressure must be as high as possible since it is a part of the recycle loop of hydrogen and if the loss of pressure can be avoided, then it won't need to be compensated by the recycle compressor, saving substantially on costs. The higher the temperature, the more hydrogen is recovered, but a temperature that is too high will cause the hydrogen stream to be more contaminated, so a balance was found (…).

The vapor stream is then condensed using cooling water as cooling utility, which allows for a temperature in V202 of 40°C. V202 is the cold high-pressure separator and its objective is to separate out the water from the hydrocarbons and the gas to be recycled. The separation is more effective with lower temperature, since the solubility of water in the organic phase decreases, as does its vapor pressure.

V208 is the hot medium-pressure separator and its task is to remove as much non-condensable combustible gases as possible from the product. The removal of these very light compounds is important to improve the quality of the naphtha produced from processing of the syncrude, since gasoline standards have maximum limits on volatility.

The cooling done in E205 and the separation in V209, the cold medium-pressure separator, tries to recover some suitably heavy organics, preventing these valuable products from being burned and it removes as much water as possible from the fuel gas stream, thus increasing its LHV.

4.4.6. Compressors section

The gas stream to be recycled must have the adequate purity and pressure to be useful to the reactor. Additionally, fresh hydrogen must be added to make-up for that which was consumed in the reactor and lost dissolved in the liquid products or with the fuel gas. It was considered that the hydrogen used for make-up was available as pure (purified by the hydrogen plant or resulting from electrolysis) and with a pressure of 25 barg. The make-up compressor was simulated as separate parts, rather than an MCompr block, to facilitate solution of the simulation. The fact that, between the stages of compression, more hydrogen is added coming from the purification system, causes that a different mass is fed to each stage and that makes solving the MCompr block quite difficult and unpredictable.

Despite the varying mass feeds, the compression ratio in each stage was set as the same as for the first stage, through the use of a calculator block (a transfer block would also have worked). A criterium of maximum temperature at the outlet of each stage was set (…) as is common with hydrogen compression. To reach the reactor pressure, it was thus necessary to have 3 compression stages, with intercooling. The intercooling is achieved using cooling water, since the cooled temperature of 65°C, where air coolers are most economical (Towler and Sinnott, 2022), is not adequate to only three compression stages.

4.4.7. Recycle gas purification

The purity of the gas leaving the CHPS is only (…)l and it was established that the reactor gas should have a purity of at least (…).

(…)

5. Sizing and costing

The costing of the equipment was done using Aspen Process Economic Analyzer (APEA) 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.

With APEA's requirements in consideration, the sizing of those pieces of equipment, that required more information than that provided by Aspen Plus/in the PFD, was done. The wall thickness of pieces of equipment was calculated using EN 13445 (CEN/TC 54, 2021) and other applicable codes such as ASME BPVC (American Society of Mechanical Engineers, 2021).

5.1. Heat exchangers and furnaces

Tube-and-shell heat exchangers were sized roughly using Aspen Exchanger Design and Rating and heuristics from Coker and Ludwig, 2007. Most values were left at their default.

U-tubes where selected whenever high temperatures, and thus high thermal expansion of the metal, was relevant.

A213C steel, the tube variant of 2.25Cr-1Mo, was chosen for tubes containing high-pressures. A387D, also a 2.25Cr-1Mo, was the equivalent option for the shells.

It bears mentioning that "Tube length extended" is double for U-tubes versus straight tubes.

SS316 cladding with a thickness of 3 mm was used to protect the shells that are exposed to untreated biocrude from corrosion. (…) EDR suggested that running the UTB on the shell might imply half the cost of running it through the tubes.

For the exchangers condensing sour water, namely E201 and E205, the condensation was set to occur on the tube side, and with tubes made of SS316, due to the expected corrosion potential. The parameters required by APEA are given **Erro! A origem da referência não foi encontrada.** for the HeXs in section 100, and in **Erro! A origem da referência não foi encontrada.** for section 200.

(…)

5.2. Reactor

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.

Önsan and Avci, 2016, states that staying in trickle flow regime is dependent on gas and liquid fluxes as well as properties of the fluids, namely density, viscosity and surface tension. The source gives the following chart relating the variables:

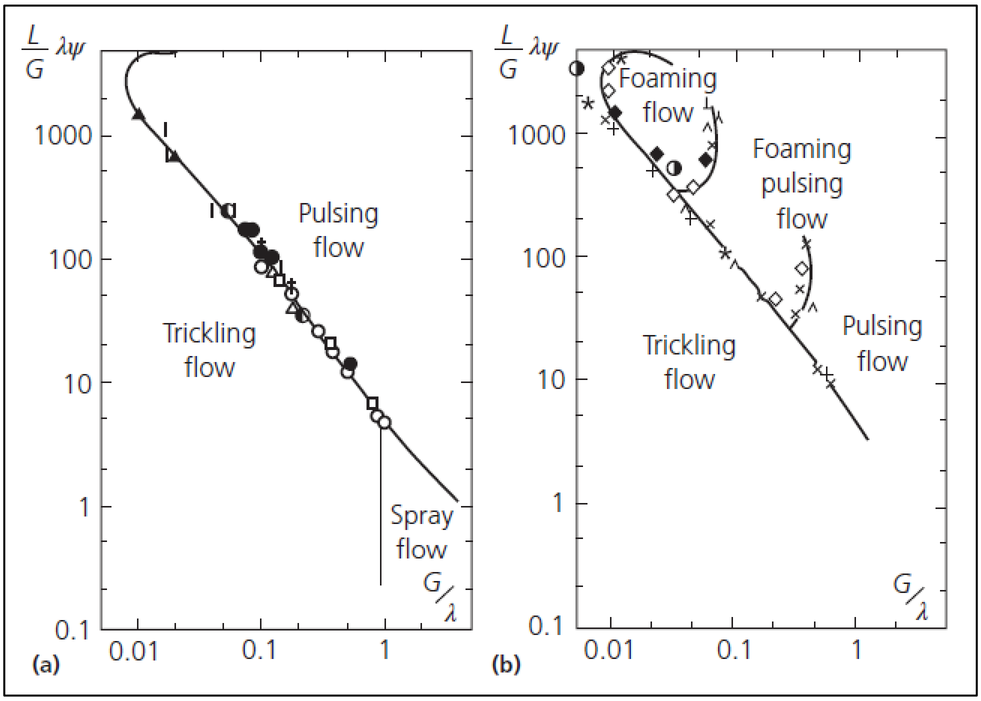


Figure 12 – Hydrodynamic regimes for two-phase downflow in fixed beds; nonfoaming (a) and foaming (b) liquids. Adapted from Charpentier and Favier, 1975; Önsan and Avci, 2016.

Where:

$$\lambda = \left(\frac{\rho_g}{\rho_{air}} \cdot \frac{\rho_\ell}{\rho_{water}}\right) \qquad \text{Equation 6}$$

$$\Psi = \frac{\sigma_{water}}{\sigma_\ell}\left[\frac{\mu_\ell}{\mu_{water}}\left(\frac{\rho_{water}}{\rho_\ell}\right)^2\right]^{0.33} \qquad \text{Equation 7}$$

An approach to “flooding” (Kister, 1992; Zhu, 2014), like that used for distillation columns, was arbitrated at 70% of gas velocity that causes spray flow, for the calculated (L/G)·λ·Ψ. The calculation sequence to size the reactor is given in Table 6. The data which is considered uniform throughout the reactor, including the results of the final iterative solution, is given in **Erro! A origem da referência não foi encontrada.**.

The amount of gas increases throughout the reactor due to the hydrogen quenches. Because of this, the gas/liquid proportion increases monotonically. This allows those problems deriving from high or low gas/liquid rates only need to be analyzed at the first and at the final bed, and this data that varies throughout the reactor is what is shown on **Erro! A origem da referência não foi encontrada.**. The spreadsheet used to perform the calculation is given in Annex 9 .

Table 6 - Calculation sequence for sizing of the reactor

Data from PFD	Qm
Arbitrate initial value	G in 1st bed assuming 100% voidage
Calculate	A empty cross-section
Data from literature	Bed voidage
Calculate	A free in packed cross-section
Calculate	Diameter
Calculate	L in packed bed
Calculate	G in packed bed
Data from PFD	Qv
Calculate	Linear velocity of liquid
Data from process conditions	LHSV
Calculate	Volume catalytic beds
Calculate	Height of all beds
Data on properties of air	ρ (…)
Data on properties of water	ρ, μ, σ (…)
Data props of process stream	ρ, μ, σ
Calculate	λ
Calculate	Ψ
Calculate	(L/G)*λ*Ψ
Mark on chart (Figure 12)	(L/G)*λ*Ψ
Read from chart	Limit (G/λ)
Calculate	Limit G
Choose	G_max/G_limit=(aproach to flood)
Calculate	G_max
Calculate	SE=(G packed bed - G_max)^2
Calculate	SSE
By changing	G in 1st bed assuming 100% voidage
Respecting	G packed bed ≤ G_max for that bed
Minimize	SSE
Read final	**Diameter**
Read final	**Height of all beds**
Data from literature	Non-bed height (f(n_beds))
Calculate	**TL/TL height**
Data from literature	ρ bulk catalyst
Calculate	**Mass of catalyst**

(…)

This data, along with those already presented in the PFD table, are sufficient to feed into the model for a packed tower in APEA and get a cost estimate.

(…)

5.3. Purification of recycle gas (Membrane and PSA)

The system of purification that comprises section 300 was costed by following the method used in Snowden-Swan et al., 2017, and that consists in using the hydrogen flowrate of the purified stream to define capacity and an exponential factor (n) of 0.8.

$$Scaled\ equipment\ cost = cost\ at\ original\ capacity \times \left(\frac{new\ capacity}{original\ capacity}\right)^{n} \qquad \text{Equation 8}$$

The reference is of a very similar process, although extending to HTL as well as the upgrading. (…)

5.4. Compressors

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

(…)

5.5. Raw materials

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 (IEA, 2021) 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., 2017, has a value of 0.744€/kg, Tews et al., 2014 calculates 0.60€/kg and Penke et al., 2021 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.

5.6. Utilities

The prices of electricity and natural gas were obtained from DGEG, 2022, for the 2nd half of 2021 for the European Union. These values are given in Table 7.

Table 7 - Price of electricity and natural gas in EU27 (DGEG, 2022).

Grid utility	**Usage**		**Price**	
Electricity	(…)	MWh/annum	0.1092	€/MWh
Natural Gas	(…)	GJ/annum	8.4173	€/GJ

Using the prices given in Turton et al., 2018, sec. 8.3.1, for other utilities and their relation to the public grid utilities, the following prices were calculated. The prices of HPSG and LPSG were calculated as -0.9x the reference. The calculated cost of the remaining utilities are given in Table 8.

Table 8 - Price of utilities based on grid utilities. Based on Turton et al., 2018

Utility	HPS	Fired	HPSG	LPSG	CW
Cost (€/GJ)	15.08	10.52	-13.57	-6.01	0.612
Dependent on	NG	NG	HPS	LPS	Electricity

Wastewater treatment was not considered since, according to Snowden-Swan et al., 2017; Tews et al., 2014, the amount of wastewater produced in the upgrading process is minimal compared to the one from HTL.

5.7. Estimation of Total Capital Investment and Total Product Cost

From the purchased-equipment costs, the TCI and TPC were calculated by using the factors method described in Peters et al., 2003, pp. 272–274. The exact factors used are indicated in Table 9 and Table 10.

Table 9 - Factor used in calculation of total capital investment from equipment costs. Adapted from Peters et al., 2003

	Factor	**of**	Notes
Purchased-equipment cost (ISBL)			
Delivery	0.1	ISBL	
Installation	0.48	ISBL	
Instrumentation	0.36	ISBL	
Piping	0.68	ISBL	
Electrical	0.25	ISBL	
Buildings	0.4	ISBL	
Yard improvements	0.1	ISBL	
Service facilities (OSBL)	0.7	ISBL	A high value was selected to account for the need for a hydrogen plant among the rest
Land	0.06	ISBL	
Direct costs (DC)			
Engineering	0.2	DC	
Legal	0.02	FCI	
Construction expense and contractor's fee	0.15	FCI	
Contingency (Nth of a kind plant)	0.1	FCI	
Indirect costs			
Fixed-capital investment (FCI)			
Working capital	0.15	TCI	
Total capital investment (TCI)			

Table 10 - Factors used in the calculation of the total product cost. Adapted from Peters et al., 2003

	Factor	**of**	Notes
Raw materials			
Operating labor (OL)	0.15	TPC	
Direct supervisory and clerical labor	0.15	OL	
Utilities			
Maintenance and repairs (M&R)	0.07	FCI	High value to account for corrosiveness and other difficulties of the fluids, as well as catalyst replacements
Operating supplies	0.15	M&R	
Laboratory charges	0.15	OL	
Patents and royalties	0.03	TPC	
Direct production costs			
Depreciation (20 year straight-line)	0.05	FCI - Land	Used preliminarily and kept once it was decided not to deepen the economic analysis (see Results)
Local taxes	0.025	FCI	
Insurance	0.075	FCI	
Rent	0		
Financing interest	0.05	FCI	
Fixed charges			
Plant overhead costs	0.1	TPC	
Manufacturing cost			
Administrative costs	0.035	TPC	
Distribution and marketing costs	0.05	TPC	A low value was chosen as the product should be easy to sell to a small number of clients
Research and development costs	0.05	TPC	High value due to high potential/need of process improvement
General expenses			
Total product costs (TPC)			

5.8. 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.

5.9. Sensitivity analysis

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

Table 11 - 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 11 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 (IEA, 2021))
- 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 Dolbear, 2006, the average capacity of an HDT unit is 30.6 kbbl/day. Adjustment was made using an exponential factor of 0.6 (see Equation 8).

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 (…).

6. Results and discussion

6.1. Simulation results concerning streams

(…)

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

6.2. Equipment costs (ISBL)

Equipment costs are given for the uninstalled pieces of equipment, since factors are then used to calculate delivery, installation, instrumentation, piping and electrical costs, derived from the uninstalled cost.

6.2.1. Heat Exchangers

All heat exchangers were considered to be of tube-and-shell type. While this leaves some possibility of further reducing costs, by replacing the HeXs that are smaller with other types, the gains should not be very impactful, given that the smaller HeXs already have small costs. The sizing and costing results from APEA are given in **Erro! A origem da referência não foi encontrada.**.

(…)

At this scale of production, most heat exchangers are quite small (<5m^2) and could possibly be replaced by pre-engineered or concentric-tube types, further reducing costs.

6.2.2. Compressors

Considering their pressure ratios and volumetric flowrates, all compressors were chosen to be of reciprocating type (positive-displacement). None are expected to encounter corrosive gases, so the material of construction should be carbon steel. It bears mentioning that compressors K202, K203 and K203 are individual units, rather than a single multistage unit, due to the different quantities of gas being compressed in each “stage”.

(…)

At a larger scale, the use of centrifugal/axial compressors becomes clearly cheaper (including in terms of maintenance (Coker and Ludwig, 2015)). It is shown, further ahead, that the cost of compressors weighs heavily (>35%) on the total ISBL cost and so there are great economies of scale to be realized at the level of this equipment.

Great cost improvements can be achieved if it is possible to have the make-up compressors in a single case with a common crankshaft, even if efficiency is reduced, but this determining if this is possible would require consulting with manufacturers. Reducing the flowrate of gas to the reactor would allow a reduction in the size of K201.

6.2.3. Pump

Although only a single pump is considered in this analysis, it should be pointed out that it must handle a high flowrate (…), and that its operation is crucial to the functioning of the unit. The details concerning the pump are given in **Erro! A origem da referência não foi encontrada.**.

(…)

The single pump currently considered in the scheme is another strong point of potential for economies of scale. A quick experiment shows that an increase of scale of 10x results in a cost increase of under 2x.

6.2.4. Drums

According to the simulation, no liquid is present in the knock-out drums and they could not be sized with the information currently available. Their cost should not be great, so ignoring them should not have a great effect on economic considerations.

(…)

6.2.5. Reactor

The reactor cost is sensitive to the pressure, which is hard to reduce while maintaining effectiveness, to LHSV, which implicates the need for a taller reactor, and to the gas flowrate, since it is the key to calculating the diameter, as described previously. The diameter affects the amount of material necessary for construction, not just in the obvious way, but also because, for a fixed pressure, the larger the internal diameter of the cylinder, the greater must be the wall thickness (EN13445, 2021).

The economies of scale possible for the reactor are limited by the diameter, through the gas flowrate. According to Turton et al., 2018, the maximum H/D for a reactor of this size category is 1.8. If we increase the capacity of the reactor, the height must remain the same, since it only depends on LHSV and other fixed parameters (like non-bed height/number of beds). This causes that as capacity increases, diameter increases to maintain the same mass fluxes and H/D decreases towards the minimum of 1.8. The maximum diameter is 5.35 m (…) (Equation 8, n=0.42, calculated from APEA experiment results). For further capacity increases it would be necessary to add reactors in parallel, with less intense economies of scale. For a 15x capacity increase, it would be necessary to conduct thorough cost optimization of number of reactors vs diameter, which falls outside the scope of this work. Additional cost reductions might be achieved by adding a 6th bed, cooling the reactor gas to a lower temperature and using a shell with multiple diameters.

The result of costing with the base case design are given in **Erro! A origem da referência não foi encontrada.**.

(…)

6.2.6. Purification of recycle gas

The economic justification for the purification system is widely acknowledged in literature (Alfke et al., 2012; Hsu and Robinson, 2006; Treese et al., 2015).

The specification of (…) purity in hydrogen for the gas fed to the reactor should be questioned, since lowering the purity should reduce the size of the purification system, which has a substantial impact on total ISBL.

(…)

The cost of the purification system is over 20% of total ISBL. It is based on prices from 2004 and so it can be hoped that in the interim the technology has improved and costs have decreased. Data on this type of equipment is difficult to find in published literature.

6.2.7. Correction for inflation

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. ("Plant Cost Index," 09/22), available in Annex 2, was used to correct the values to December 2021, the same date as the prices of electricity and NG from DGEG, 2022. The values before and after correction for inflation are shown in Table 13

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 12.

Table 12 - 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	

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 13 – (...)

It is evident that the equipment costs are dominated by the compressors, followed by the reactor and the purification system. As discussed in their respective sections, it may be possible to reduce the cost of these pieces of equipment.

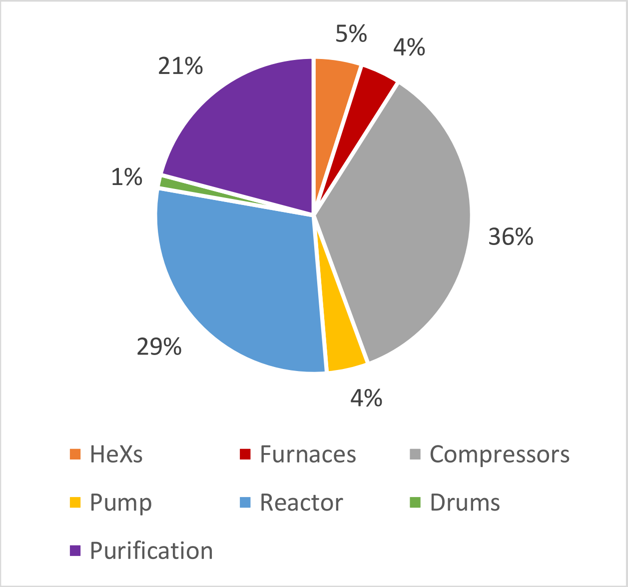


Figure 13 - Distribution of equipment costs

6.3. Total Capital Investment

As explained in the relevant section of the methodology, additional costs were calculated following the factors given in Peters et al., 2003.

Table 14 – Calculation of total capital investment and its sub-parcels

	Factor	of ↓	Cost
Purchased-equipment cost (ISBL)			13 230 812 €
Delivery	0.1	ISBL	1 323 081 €
Installation	0.48	ISBL	6 350 790 €
Instrumentation	0.36	ISBL	4 763 092 €
Piping	0.68	ISBL	8 996 952 €
Electrical	0.25	ISBL	3 307 703 €
Buildings	0.4	ISBL	5 292 325 €
Yard improvements	0.1	ISBL	1 323 081 €
Service facilities (OSBL)	0.7	ISBL	9 261 568 €
Land	0.06	ISBL	793 849 €
Direct costs			**54 643 254 €**
Engineering	0.2	DC	10 928 651 €
Legal	0.02	FCI	1 796 491 €
Construction expense and contractor's fee	0.15	FCI	13 473 679 €
Contingency (Nth of a kind plant)	0.1	FCI	8 982 453 €
Indirect costs			**35 181 273 €**
Fixed-capital investment			**89 824 527 €**
Working capital	0.15	TCI	15 851 387 €
Total capital investment			**105 675 914 €**

6.4. Cost of raw materials

The cost of biocrude and hydrogen, which have been detailed in section 5.5, are given in Table 15. Figure 14 presents the relative importance of these two raw materials in terms of cost.

Table 15 – (...)

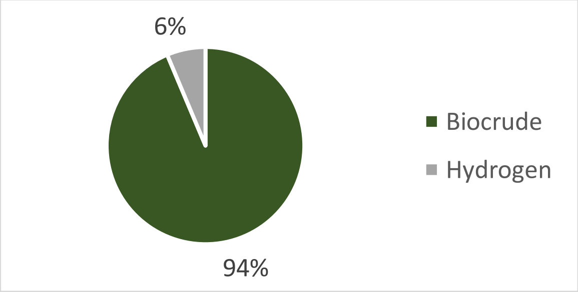


Figure 14 - Distribution of cost of raw materials

The cost of raw materials is clearly dominated by the biocrude. In a longer-term perspective, the price of biocrude may decrease significantly since the associated technology is quite recent and further research may yield large improvements to the production process. The outlook for improvements in hydrogen is more limited since the technology is more mature. The refining industry’s shift to Green Hydrogen may cause prices to rise, including by benefiting less of the economies of scale possible in SMR+WGS.

6.5. Cost of utilities

The utilities involved in the process are given in **Erro! A origem da referência não foi encontrada.**, along with the net cost resulting from adding the utilities which are consumed with those that are produced. The strategy of valuing the generated utilities as if they were to be sold is a shortcut calculation that allows for an appreciation of available heat and its quality. It could be more efficient to use the high temperature heat (used to generate steam) instead to directly heat the HTL feed or reactor, as an example. Figure 15, Figure 16 and **Erro! A origem da referência não foi encontrada.** show the balance of utilities and the relative importance of each utility. Details on the calculation of the unit cost of each utility are given section 5.6.

(…)

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.

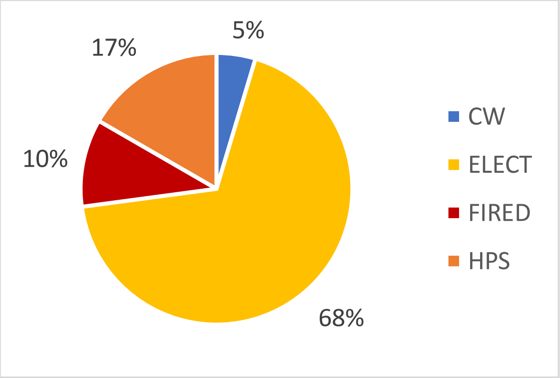


Figure 16 - Cost distribution of consumed utilities

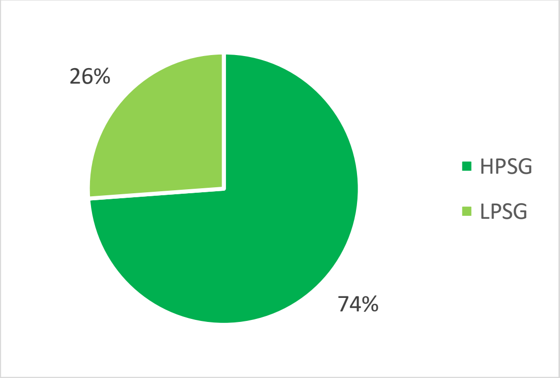


Figure 15 - Earnings distribution of produced utilities

6.6. Total product cost

The results of the calculation of the total product cost are given below, in Table 16. In order to show the relative importance of different cost drivers, the parcels of cost were aggregated into raw materials, utilities, those that depend only on fixed-capital investment, which is to say those parcels which aren't affected by the cost of raw materials and utilities, and those that are affected by all cost drivers. The relative importance of each of these categories is given in Figure 17.

Table 16 - Total product cost and parcels from which it is calculated

	Factor	of ↓	Cost (€/annum)
Raw materials			69 474 682
Operating labor	0.15	TPC	26 391 487
Direct supervisory and clerical labor	0.15	OL	3 958 723
Utilities			378 584
Maintenance and repairs	0.07	FCI	6 287 717
Operating supplies	0.15	M&R	943 158
Laboratory charges	0.15	OL	3 958 723
Patents and royalties	0.03	TPC	5 278 297
Direct production costs			**116 671 370 €**
Depreciation (20 year straight-line)	0.05	FCI-Land	4 451 534
Local taxes	0.025	FCI	2 245 613
Insurance	0.075	FCI	6 736 840
Rent	0		-
Financing interest	0.05	FCI	4 491 226
Fixed charges			**17 925 213**
Plant overhead costs	0.1	TPC	17 594 325
Manufacturing cost			**152 190 908**
Administrative costs	0.035	TPC	6 158 014
Distribution and marketing costs	0.05	TPC	8 797 162
Research and development costs	0.05	TPC	8 797 162
General expenses			**23 752 338**
Total product cost			**175 943 246**

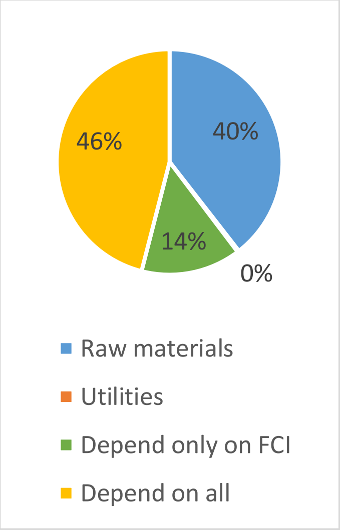


Figure 17 - Distribution of cost based on precedent parcel

Considering the TPC and the parcels that lead to it, it is possible to point quite clearly to the 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.

6.7. 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 17.

Table 17 - Income breakdown and necessary product price to balance with costs

Sell price of fuel gas	7.5756	€/GJ
Production of fuel gas	305 155	GJ/annum
Income from fuel gas	2 311 724	€/annum
Syncrude production	698 552	bbl/annum
Total product cost	175 943 246	€/annum
Necessary syncrude price	**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. A quality comparison of syncrude and Brent is presented after the Sensitivity Analysis.

6.7.1. The cost of carbon dioxide emissions

Under Portuguese legislation, biofuels are exempt from having to pay for associated emissions of greenhouse gases (Despacho n.º 17313, 2008). 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 18.

Table 18 - Adjustment of the price of crude oil by the cost of its emissions in the EU. Data from Despacho n.º 17313, 2008 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

6.8. 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 19 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 19 - 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**

As expected from Figure 17, 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 (see Compressors), 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 (Tews et al., 2014), 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., 2014.

For comparison, a though experiment is proposed: the total land area of Portugal is about 9 million ha and the refinery at Sines processes 220 kbbl/day, so to feed it would require over 80% of the nation’s land area. The

European part of France has an area of 55 million ha and French refineries can process 1250 kbbl/day, so the French would only need to sacrifice 75% of their land area.

This short hypothetical has some very rough approximations, such as assuming a productivity of 10 ton/ha/annum of pine wood (pine is mentioned since it is the type of lignocellulosic biomass that was by Jarvis et al., 2018) and considering that pine could be planted for the sole purpose of producing biocrude, but it still serves the purpose of showing that Syncrude technology is clearly still far from replacing crude oil, and it is critical to improve the land area requirements of biofuels. The usage of wastes, including agro-forestry wastes, as feedstocks is also a much more environmentally sound approach to producing biofuels and that is consistent with the approach taken by most researchers (Lozano et al., 2022; Snowden-Swan et al., 2017, etc.).

6.9. Quality of syncrude

The quality of a crude oil can be assessed, in a preliminary fashion, by looking at its boiling point distribution and figuring out much of each type of fuel it would yield. The smaller the heavy fraction, the better the quality. It must be stressed that this approach leaves out other fundamental quality characteristics such as cetane number of the gasoil cut or the octane number of the naphtha cut. The true boiling point distributions of some reference crude oils along with that of Syncrude is given in Figure 17 and the obtainable cut are given in Table 20.

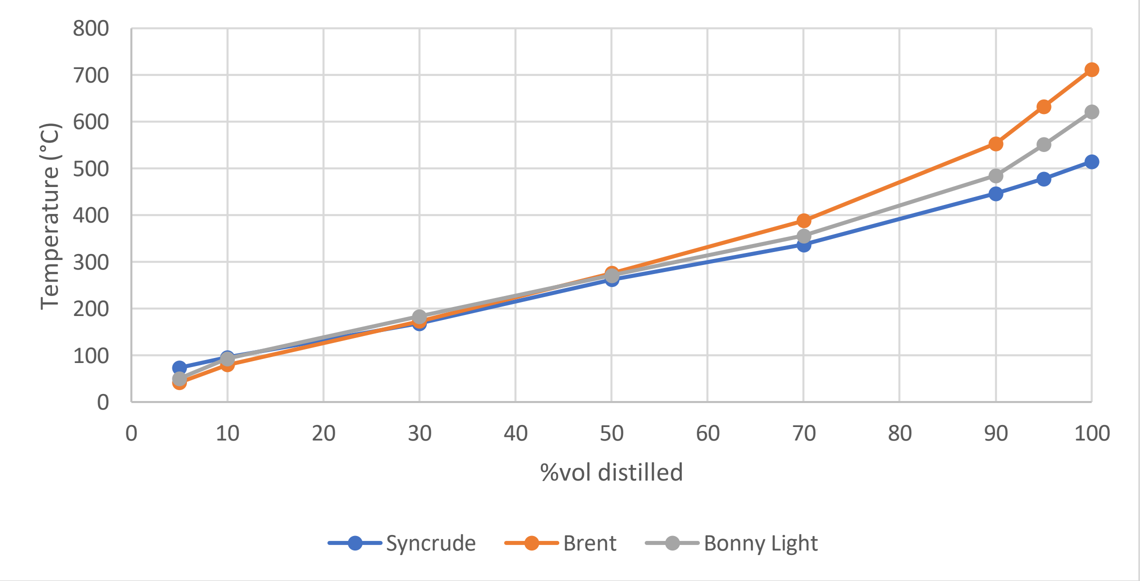


Figure 18 - TBP distribution of reference petroleum (Brent), Nigerian Bonny Light and Syncrude (from assay data supplied with Aspen Plus V11)

Table 20 - Cuts obtainable from Syncrude, Brent and Bonny Light. Prices from "Oil Price Charts," 2022.

	Syncrude	**Brent**	**Bonny Light**
%vol Naphtha (IBP-180°C)	31	30	30
%vol Gasoil (180°C-350°C)	37	25	30
%vol VGO (350°C-540°C)	32	28	34
%vol VR (540°C-FBP)	0	17	6
Price on 17/10/2022		91.62	92.56

Syncrude is estimated to be more expensive than Brent, but a higher price tag may be justified, and not just through the reduced environmental impact. Most noticeably, the simulated Syncrude has a fraction of Gasoil much higher than Brent and no vacuum residue. This translates simply to a feedstock which is cheaper to process into saleable fuels. This is, however, a superficial analysis of the quality of the fuels that would result from further processing of Syncrude. It allows us to state that 37% vol has the correct boiling points for Diesel, but if, for instance, the cetane index is very low, then that would negatively affect the price.

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 (Peters et al., 2003; Riazi and Chiaramonti, 2018).

7. Conclusions and follow-up work

Throughout the execution of the work described in this document, several improvements to the methods were identified, but their employment was not prioritized. These improvements are described next:

I strongly discourage the usage of Excel models in Aspen Plus for tasks of this level of complexity (not very high). The same result could have been achieved by:

1. Having the generation of pseudocomponents generate component IDs.
2. Using Calculator Blocks and importing/exporting stream Vectors.

This approach would have produced a simulation that runs much faster, doesn't conflict with other open Excel instances or with the Copy-Paste function of the entire computer while the simulation is running.

The usage of a Calculator to determine make-up hydrogen flowrate (or of a Balance block) is not a simple option, since it would involve programming the Calculator not to run on every pass of the recycle loop and it would probably require manual sequencing of Design-specs, Tear loops, Calculators along with all the rest.

At earlier stages of the development, several reactor designs were sized and costed. These included designs were the shell had two different diameters, using refrigeration to lower the quench gas temperature to -20°C and/or adding additional beds. These results were not presented due to a shortage of time to make them coherent with the final version of the base case.

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 parts (see Smith, 2016), 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 on page 14. 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.

It is shown that that the final product, Syncrude, has very favorable quality characteristics compared to Brent crude or even the high-quality Nigerian Bonny Light and can therefore justify a higher market price. Additionally, 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. At present, much of the solution to reducing emissions from liquid fuels rests on replacing the machines that consume those fuels with new ones, designed to operate on electricity or hydrogen. This solution requires not only that individuals and companies invest in new, (for the moment) more expensive vehicles and machines, but also that new infrastructure be deployed to supply the energy to users. Then there must also be consideration for the time and investment necessary to ramp up production of everything from batteries to electrolyzers, that require not just factory capacity but, due to the scale that they must achieve to solve the global emissions problem, also require an expansion of production of basic raw materials: everything from copper and steel to noble metals and rare-earth minerals.

All the necessary investment will probably make the solutions based on electricity and hydrogen unaffordable for people in developing countries. Many poorer countries are yet to be able to deploy a stable, reliable and all-reaching electrical grid. How can it be expected that they sign-up to electric mobility?

In addition to the high environmental performance, Syncrude can also bring economic benefits, especially in countries without any oil reserves, as is the case of Portugal. Currently, countries without their own oil are dependent on imports of crude oil or fuels. In such countries, the production of Syncrude can allow for greater energy independence, stabilizing the prices than then get propagated to all sectors of the economy. If we consider the expenditure approach to calculating GDP, where it is defined as the sum of consumption, investment, government expenditure and net exports (exports - imports), then reducing the import bill for crude oil can have a heavy impact on the growth of the economy.

The section on “Correction for inflation”, as well as Annex 2, show the impact of large variation in prices on the economic viability of industrial projects: at the start of the project, a hypothetical product will break-even at an arbitrary 100€/unit , but 2 years later, when it’s halfway to the delivery of a working factory, a price of 140€/unit is needed for viability, a price that the market may not accept, in which case two years of work may have to go to waste, even if they were done with the highest of competence and to the highest of standards.

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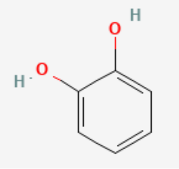
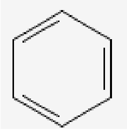
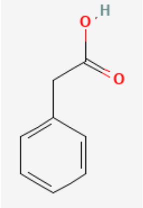
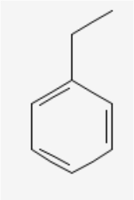
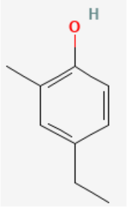
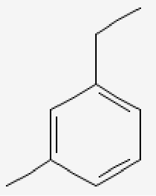
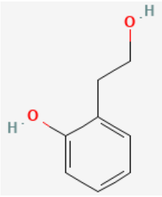
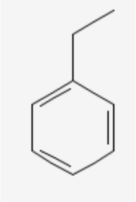
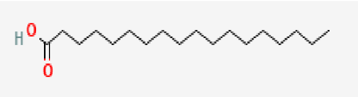
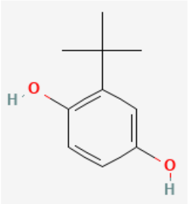
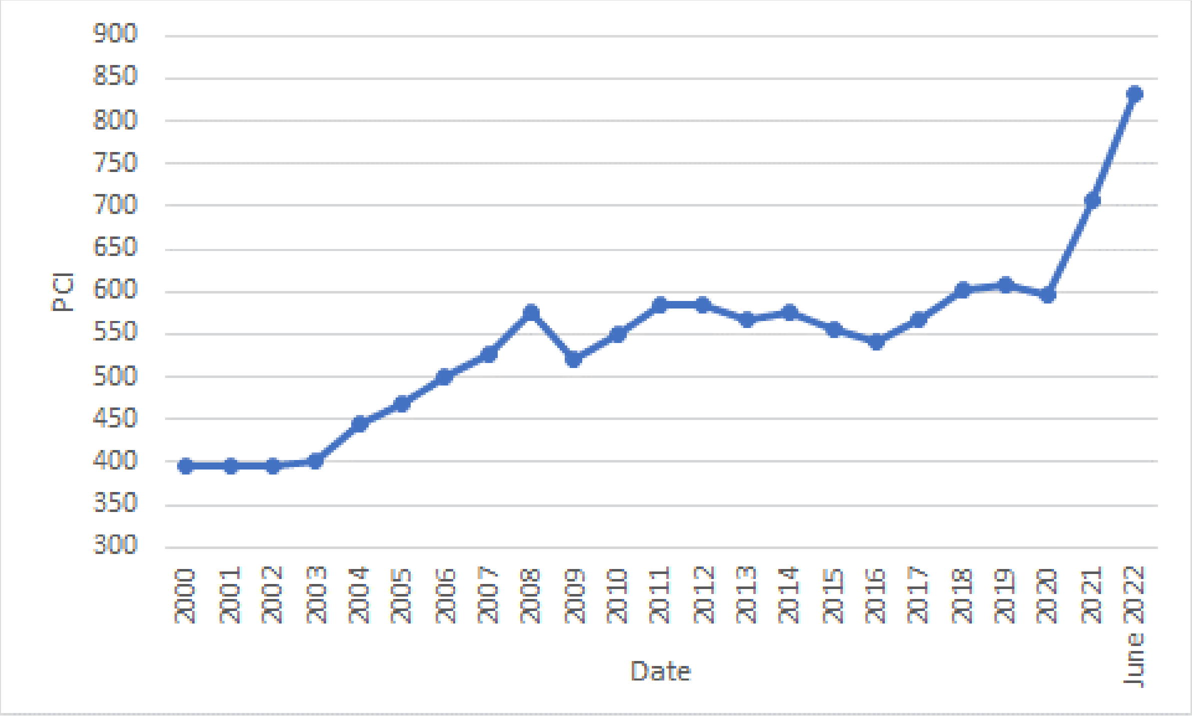
Annex 1 – model compounds for HDO

$$A + x \cdot H_2 \rightarrow B + y \cdot H_2O$$

A		x	B		y	α (kcal/mol H2)
Catechol		2	Benzene		2	15.5
Phenylacetic acid		3	Ethylbenzene		2	14.8
4-Ethyl-2-methylphenol		1	3-Ethyltoluene		1	18.9
2-Hydroxyphenethyl alcohol		2	Ethylbenzene		2	21.1
Stearic acid (C18)		3	Octadecane		2	14.8
Ethanol		1	Ethane		1	23.1
MEK		2	Propane		1	17.8
MIK		2	I-Hexane		1	18.6
Glycerol		3	Propane		3	20.1
tert-Butylhydroquinone		2	t-Butylbenzene		2	17.7

Annex 2 – Plant Cost Index from *Chemical Engineering* magazine

Year	PCI
2000	394.1
2001	394.3
2002	395.6
2003	402.0
2004	444.2
2005	468.2
2006	499.6
2007	525.4
2008	575.4
2009	521.9
2010	550.8
2011	585.7
2012	584.6
2013	567.3
2014	576.1
2015	556.8
2016	541.7
2017	567.5
2018	603.1
2019	607.5
2020	596.2
2021	708.0
June 2022	832.6



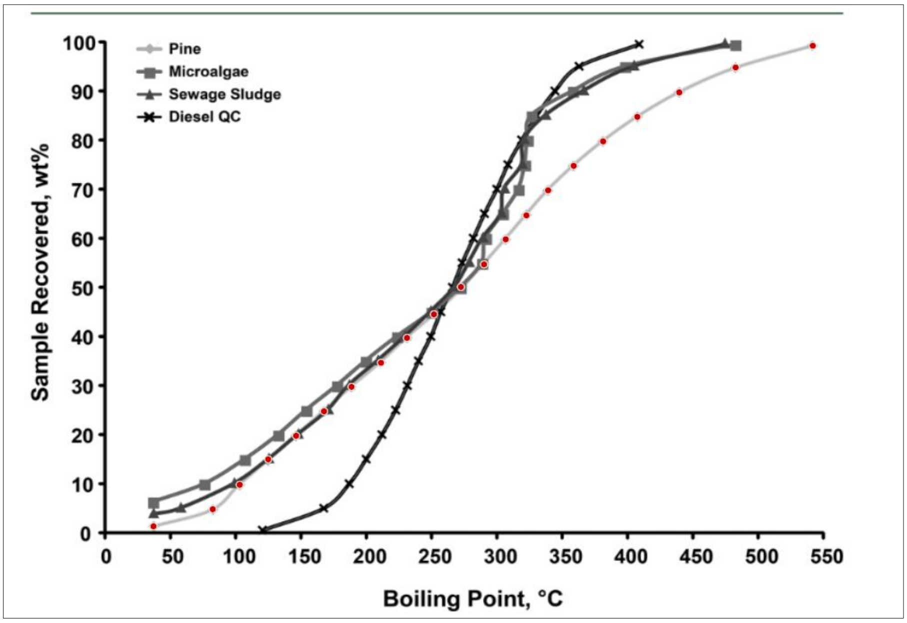
Annex 3 – Aspen Plus input code for pseudocomponents

```
PC-CALC
  PC-SET JARVIS
  CUTS LTEMP=50.00000000 UTEMP=400.0000000 INCR=10.00000000 /  &
    UTEMP=2000.000000 INCR=25.00000000
  PC-IDS OPTION=NBP
  OPTIONS PC-GEN-OPT=IN-RANGE

ADA-SETUP
  ADA-SETUP PROCEDURE=REL9 EP=99.5

ASSAY JARVIS
  ASSAY-DATA GRAV=0.9
  DIST-CURVE D2887 1.36 36.71000000 / 4.82 82.13000000 /  &
    9.81 102.8100000 / 14.99 124.5900000 / 19.79  &
    146.0100000 / 24.78 167.4300000 / 29.77 188.4800000 /  &
    34.66 211.0000000 / 39.74 230.9500000 / 44.54  &
    251.6200000 / 50.11 272.3000000 / 54.71 290.0300000 /  &
    59.8 306.6500000 / 64.69 322.5300000 / 69.78  &
    339.1400000 / 74.77 358.7100000 / 79.75 381.2400000 /  &
    84.74 407.4600000 / 89.73 439.5900000 / 94.82  &
    482.7900000 / 99.23 541.8800000
```

Annex 4 – (…)

Annex 5 – (…)

Annex 6 – Points extracted from Jarvis et al., 2018



%Mass recovered	Boiling point (°C)
1	37
5	82
10	103
15	125
20	146
25	167
30	188
35	211
40	231
45	252
50	272
55	290
60	307
65	323
70	339
75	359
80	381
85	407
90	440
95	483
99	542

Annex 7 – About my challenges with Aspen

In developing the simulations for this work, I had to expand considerably my knowledge of how to use AspenTech software, beyond that which I had gained through previous school courses. I'm aware that classroom time is very limited and that choices must be made about what to leave out of the curriculum. I also recognize that those who make decisions about what to teach students have concerns about leaving said students overly dependent on a particular piece of software, lest they prove incompetent in a setting outside of school where they must use an alternative tool. The following are arguments, some stronger than others, of course, about the importance of knowing certain things relating to process simulators, including some accounts of personal experience.

Going from using Aspen Plus to using PRO/II was not difficult. The online video training, that AVEVA provide as part of the software license contract, was adequate to allow me to get on with developing the simulation. This smooth transition also applied to other software substitutions, such as going from Aspen Process Economic Analyzer to a similar proprietary tool of IFPEN. Where I did struggle was with tasks that I neither knew how to do in Aspen or PRO/II.

Understanding and controlling **convergence** is very important in any simulation that has Design-Specs, recycle streams (tear streams), rigorous distillation columns, etc. The importance of this topic earns it a distinct place in the knowledge requirements for certification[3] as an "Aspen Plus Certified User", the most basic certification level available from AspenTech (EAP101).

From talking to fellow students, I have found that only about half the times are their difficulties with process simulation based in inadequate process choices, with the other half being based on an inability to get the software to solve a problem that is perfectly coherent from an engineering perspective. Lack of understanding and control over Convergence leaves students frustrated and doubting their skills in Chemical Engineering, which is understandable when Aspen appears to be finding incomprehensible faults in their work.

The competency objectives related to Convergence given in Aspen's study guide (see address in footnote 3) are adequate, in my opinion, to allow any user to understand if their simulated process has an actual engineering flaw or if the problem exists only because process simulators are imperfect.

Understanding and control of the **sequence** in which the software perform the calculations relates strongly to the previous points about convergence. Aspen as developed a reasonably good system to determine in what sequence it should perform the calculations, but, when complexity increases, it's quite easy for the automated system to get disastrously confused by a matter that is perfectly straightforward to the user's human brain. I think that this confusion of the software often leads users to simplify their process scheme, in an attempt not to overwhelm the sequencing capabilities, leaving substantial computational power locked up. Why should a simulation with 5 recycle streams and 15 design specs be an impossibility? If the engineering is sound, the sequence has been correctly set and the convergence adjusted, then let the computer crunch numbers until it reaches a solution!

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[3] See https://www.aspentech.com/-/media/aspentech/home/cst-certification/aspen-plus-certification/study-guide-aspen-plus-basics

User models allow the implementation of every variety of complex system with any degree of precision, so long as the adequate knowledge is available to those who develop the model! They also allow us to cheat on realism when we have limited information. It's hard to dispute that a low-accuracy solution is better than none at all. In my senior project course, my group worked on equipment sizing and costing for a process that produced polyols incorporating 20% weight of CO_2, and since the process was quite recent there was very little published information. We did not have the information on the kinetics of the heterogeneously catalyzed reaction and so we couldn't go by the book (Haydary, 2019) in simulating the polymer production process and so we spent much valuable time trying to work around the fact that, as far as we knew, there was no way to make an Aspen simulation for our process. If I had the knowledge that I now have about User Models, we would have employed the same approach that I used in this work (described in section 4.4.3) with some partial adjustments, since we had about as much information.

The following no longer concerns "basic" Aspen knowledge, but I would also like to say some things about its importance.

Equation-oriented (EO) modelling is a process simulation approach that is different from the sequential-modular approach normally used by Aspen and PRO/II, but it is available in the normal Aspen Plus environment. AVEVA's newest offering in process modeling, AVEVA Process Simulator, which aims to replace PRO/II, works exclusively through an equation-oriented approach and my first experience of EO modeling software was their demonstration at IFPEN during my internship. It seemed quite easy to use, but of course in a competent demonstration there was no other possibility. Equation-oriented modelling works by solving the flowsheet as a system of equations, instead of going block by block. This approach should be easily recognizable as the one used to solve mass and energy balances using pen and paper (and calculator). When calculating recycle flows, no engineer thinks to calculate the result of each unit operation in a loop until the results "stop changing". In fact, when calculating the flow of make-up streams, there is no proper way other than equation-oriented (the only alternative is trial-and-error), but this is implemented in Aspen using Calculators rather than the EO tools, so it goes unnoticed. I've never used EO tools, but these examples lead me believe that there might be substantial gains, both in processing and simulation development time, from learning more about the subject.

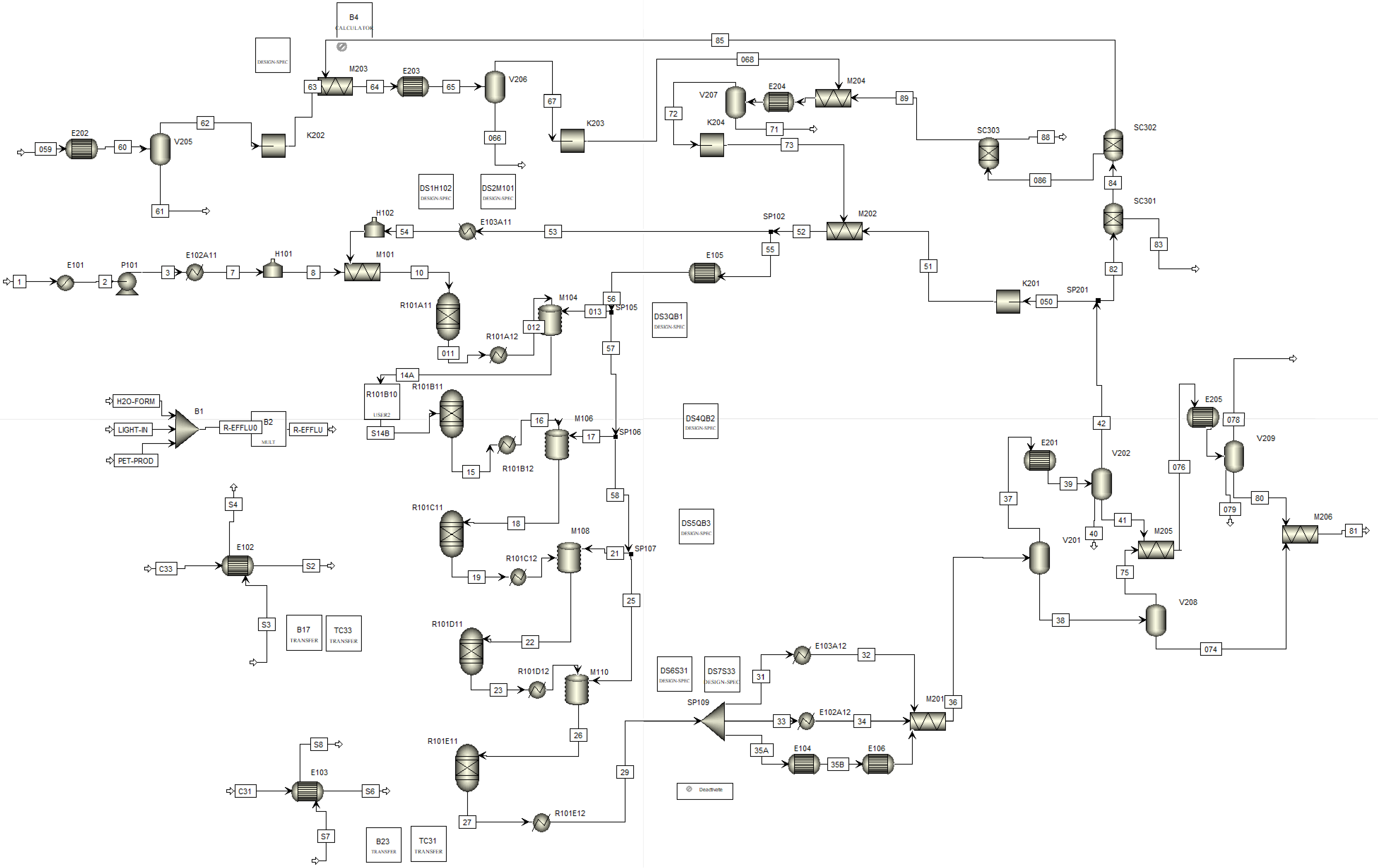
Dynamic simulation has an important role in process control, but I would like to point out its great potential as an instructional tool. Some time ago, I found a forum message from a process operator that was asking for help understanding the concept of reflux in a distillation column, since it was his job to manually operate the reflux valve while they waited for a replacement for the automatic control valve, and he was struggling to, in his words "do the job properly". I could not easily think of a suitable explanation, but I did think that if I knew how to make interactive dynamic simulations, I could make a visual model to show how the relevant variables relate to each other, and how they respond to control inputs. Operators, students, non-chemical engineers… There is a long list of people who could learn faster and better if they could be given a moving process diagram. Alas, I do not know how to make dynamic simulations. Yet.

There is a paucity of books and data on the economics of plant design and equipment costs. (Peters et al., 2003) is considered one of the best sources, yet its latest edition dates from 2003. If the book was in high demand, there should be new editions or other books should have taken its crown… so how are economic studies being performed outside of schools? The answer is that the common practice is to use software like **Aspen Process Economic Analyzer** (APEA) or an equivalent tool, where the chemical engineer inputs the calculated equipment size, or the sizing procedure, and the software gives an estimate of the mechanical engineering calculations and equipment cost. Students should be taught to use the more modern and extensive tools, rather than their archaic ancestors like matche.com and mhhe.com/engcs/chemical/peters/data/.

Lastly, I would like to mention **Aspen Energy Analyzer** (AEA). FI^2EPI (“FI2EPI,” n.d.; Pereira et al., 2016) is much more straightforward to use and produces results, alas, its development was cut and the capabilities with stream splitting where never extended to give a complete tool. Aspen Energy Analyzer is the best alternative if we want to study heat integration with the possibility of stream splitting. The split at the exit of the reactor in process scheme used in this work, I think, is a good example of the importance of stream splitting.

I find it reasonable to conclude by saying that process simulation can greatly help students to better understand Chemical Engineering and that “getting along” better with Aspen can help to improve the enthusiasm of graduates for the profession.

Annex 8 – Flowsheet in Aspen Plus



Annex 9 – (…)