Optimisation and Scale-up of the System Based on Simulation

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Disclaimer

Summary

This deliverable details the scale-up and optimization of the FFW chemical processes with the main aim of obtaining diesel and synthetic natural gas as part of the task 4.4. Other valuable by-products, such as naphtha fraction, have been obtained and can be used for other purposes.

The document is mainly structured in the description of two optimised scenarios: the first is the base case, where the post-gasification products, which are going to be processed, come from a gasification using air (in presence of nitrogen). The second scenario describes the process where the gasification has been carried out in absence/low concentration of nitrogen, which implies the use of a previous separation of oxygen from air or steam.

The post-gasification products are the raw material for Fischer-Tropsch (FT) synthesis process. FT reaction allows the synthesis of different product distribution: alkanes, waxes, olefins and alcohols. The FT reaction process has been designed in order to obtain long chain hydrocarbons (waxes) through a low temperature reaction in a slurry bed reactor (SBR). The products are separated in different cuts following a process similar to a conventional petroleum refinery (atmospheric distillation, vacuum distillation and hydrocracking). The aim of these operations is to refine the maximum amount of diesel. In despite of being out of the main aims of the project, a valuable naphtha fraction is obtained in atmospheric distillation and hydrocracking as well, which can be used for the potential energy generation in the plant or be sold.

Synthetic natural gas (SNG) is obtained using a catalytic methanation process, using CO and H_2 as reactive, where several adiabatic reactors with intermediate cooling enable the production of methane. Water is also produced as by-product and it is removed after the reactors. This SNG effluent must be treated in the base case scenario by means of a membrane and a CO_2 absorber column to reduce the nitrogen and CO_2 content, respectively, whilst in the case study is used a CO_2 absorber column only in order to comply with the current natural gas composition requirements (due to the low concentration of nitrogen).

This process generates significant amounts of energy in some sections, due to the exothermic reactions carried out, which is used to generate medium or high pressure steam and which can be used to heat other parts of the process (by energy integration) or generate electricity.

The main outputs obtained along this document are the design and the amount of the different valuable products, as well as the comparison between the two scenarios: the base case and the case study.

The case study represents the same processes that take place in base case. However, the gasification as first stage (refers to D.3.4) is performed using oxygen instead of air (lower nitrogen concentration). This case study reports smaller equipment and even the absence of some of them, such as the membrane system for nitrogen removal, e.g. during methane upgrading. A gasification in presence of oxygen/steam also was considered. Nevertheless, the quality of the obtained syngas was not sufficient to be used as raw material in Fischer-Tropsch process.

An energetic integration of the entire process (including chemical pre-treatment) has been developed both for base case and case study. Important energy savings are achieved.

At the end of the current document, a comparison between both optimised base case and optimised case study along with the summary of each scenario are found.

Contents

Tables

Figures

1 Introduction

1.1 Purpose and Scope

This deliverable forms part of Work Package 4 (WP4. Development of technical solutions for SNG-diesel production) of the FFW project, which aims to develop novel catalysts which will enhance the overall performance of the FFW process. The deliverable's two main objectives are:

- Support the design of unit operations and piping for both the synthesis stage and pre-treatment stage of the FFW demonstration process.
- Enable evaluation of the best industrial scale process set-up - by providing input into Task 6.1 - 'Life cycle analysis of the FFW system' which will help to determine the viability of the industrial FFW process.

The simplified block flow diagram in Figure 1 shows the major synthesis steps required to produce diesel and synthetic natural gas from the synthesis gas produced in the FFW pre-treatment process.

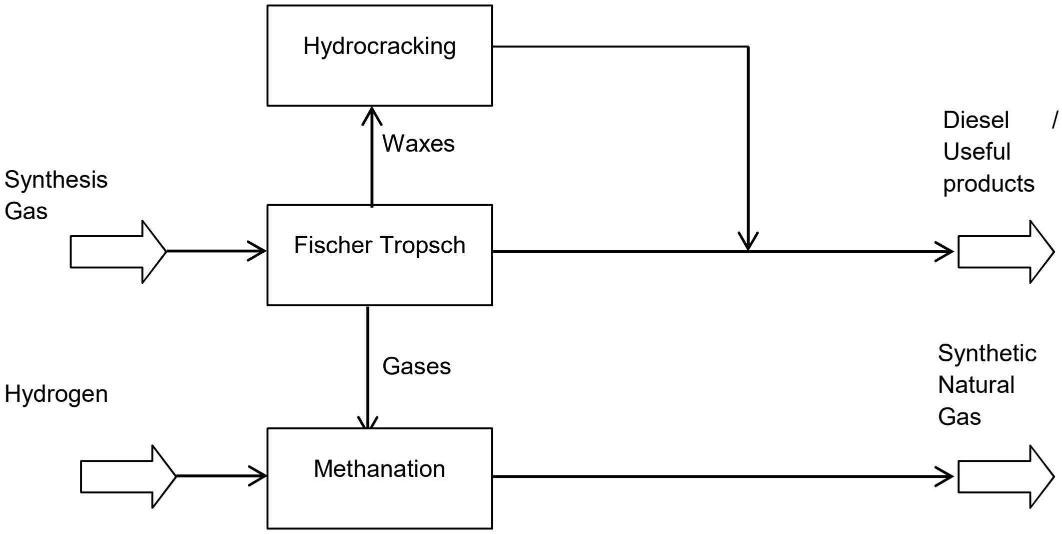


Figure 1.Simplified synthesis block flow diagram

An overview of each of the stages and available process solutions is provided within this document. Based on the requirements of the project, each process is modelled using Aspen HYSYS software and the processes are optimised. Required intermediate steps are added and discussed within each section (heat exchangers, compressors, etc.). This initial evaluation represents the 'base case' scenario. The base case considers:

- Utilisation of synthesis gas produced from gasification with air (as per the content of D.3.4)

Certain restrictions with the base case scenario meant that the set-up elaborated as part of the base case was not believed to be the most optimum from a techno-economic point of view due to high exergy loss in the post separation of the nitrogen. As a result, taking into consideration available experimental results and requirements of the industrial scale system, an improved process is considered. This improved process differs from the base case by considering:

- Utilisation of synthesis gas produced from gasification with oxygen/steam – considers air separation unit (ASU) through the cryogenic distillation of air.

For the improved process, additional process operations are evaluated and selected. Alterations to previous operations are made and each unit operation optimised. Feasibility of the industrial FFW process is discussed.

1.2 Implementation

For simulation and optimisation of the chemical synthesis process, Aspen HYSYS is used. Aspen HYSYS is a flowsheet simulation software capable of simulating chemical processes – including refinery processes. Different unit operations are placed on a flowsheet and connected with mass and energy streams. The software sequentially solves each unit operation. Numerous iterations can be carried out where a feedback or recycle loop is present.

Fluid packages are used to define the components and property model utilised by the flowsheet (or flowsheet section). The simulation considers several different process sections according to the main operations which take place in these sections – some of these sections utilise different fluid packages (and property models). The following property models are utilised in the flowsheet:

Table 1. Utilised property models

Section	Property model used in fluid package	Selection criteria
2, 3, 4, 7, 8, 9 ,10, 11, 12	PRSV	This is a two-fold modification of the Peng-Robinson (PR) equation of state that extends the application of the original PR method for moderately non-ideal systems. It is successfully extended to handle non-ideal systems giving results as good as those obtained using excess Gibbs energy functions like the Wilson, NRTL, or UNIQUAC equations.
5, 6,	PC-SAFT (Acid gas)	The PC-SAFT equation includes an association term that accounts for strong intermolecular forces which can better predict system behaviour with associating compounds. It is a proven model that can represent a wide range of compounds, including hydrocarbons, inorganic gases present in natural gas streams, water, and other polar and associating components. The model can fit vapor pressure, liquid density, and liquid heat capacity very well without requiring volume translation terms. Often both VLE and LLE can be represented with the same binary interaction parameters.
13	HCRSRK (based on Soave-Redlich Kwong)	Thermodynamic model used by HYSYS in hydrocracking to solve the lump kinetics.

Several different HYSYS unit operations are used. They are listed below in Table 2.

Table 2. Unit operation model used in FFW simulation

Unit Operation Model	Description
Absorber-Acid gas cleaning model	This model simulates an absorption operation. The basic Absorber column has two inlet and two exit streams. When used alone, the Absorber has four boundary streams and so requires four Pressure Flow specifications. The Acid Gas page on the Parameters tab is enabled if the fluid package associated with the column uses the Acid Gas property package.
Adjust	The Adjust operation varies the value of one stream variable (the independent variable) to meet a required value or specification (the dependent variable) in another stream or operation.
Distillation column subflowsheet	The Column is a special type of subflowsheet in HYSYS. A subflowsheet contains equipment and streams, and exchanges information with the parent flowsheet through the connected internal and

Unit Operation Model	Description
	external streams. From the main simulation environment, the Column appears as a single, multi-feed multi-product operation. In many cases, you can treat the column in exactly that manner.
Component splitter	With a Component Splitter, a material feed stream is separated into two component streams based on the parameters and split fractions that you specify. You must specify the fraction of each feed component that exits the Component Splitter into the overhead product stream.
Compressor	The Centrifugal Compressor operation is used to increase the pressure of an inlet gas stream with relative high capacities and low compression ratios. Depending on the information specified, the Centrifugal Compressor calculates either a stream property (pressure or temperature) or a compression efficiency.
Distillation column	The basic Distillation column has one inlet and two or three exit streams, depending on the condenser configuration. When used alone, the Distillation column has three or four boundary streams but requires four or five pressure-flow specifications; generally one pressure and three or four flow specifications.
Expander	The Expander operation is used to decrease the pressure of a high pressure inlet gas stream to produce an outlet stream with low pressure and high velocity. An expansion process involves converting the internal energy of the gas to kinetic energy and finally to shaft work. The Expander calculates either a stream property or an expansion efficiency.
Gibbs reactor	The versatility of the Gibbs Reactor allows it to function solely as a separator, as a reactor which minimizes the Gibbs free energy without an attached reaction set or as a reactor which accepts equilibrium reactions. When a reaction set is attached, the stoichiometry involved in the reactions is used in the Gibbs Reactor calculations.
Heat Exchanger	The Heat Exchanger performs two-sided energy and material balance calculations. The Heat Exchanger is very flexible, and can solve for temperatures, pressures, heat flows (including heat loss and heat leak), material stream flows, or UA.
Heater	The Cooler and Heater operations are one-sided heat exchangers. The inlet stream is cooled (or heated) to the required outlet conditions, and the energy stream absorbs (or provides) the enthalpy difference between the two streams. These operations are useful when you are interested only in how much energy is required to cool or heat a process stream with a utility, but you are not interested in the conditions of the utility itself.
Hydrocracker	The Hydrocracker model in HYSYS Refining is a state-of-the-art Hydrocracker Unit simulation system that can be used for modelling a single-stage, two-stage Unicracker, or two-stage Isocracker hydrocracker unit as a standalone unit operation or as part of a refinery-wide flowsheet. The Hydrocracker includes feed characterization system, reactor section(s), recycle gas loop(s), product separation, and product mapper. The reactor model is based on rigorous kinetics. The feed characterization system and product mapper are designed to work together with the HYSYS Refining assay system so the Hydrocracker model can be simulated in a refinery-wide flowsheet.
Mixer	The Mixer operation combines two or more inlet streams to produce a single outlet stream. A complete heat and material balance is performed with the Mixer. That is, the one unknown temperature among the inlet and outlet streams is always calculated rigorously.
CSTR	The CSTR is a vessel in which Kinetic, Heterogeneous Catalytic, and Simple Rate reactions can be performed. The conversion in the reactor depends on the rate expression of the reactions associated with the reaction type. The inlet stream is assumed to be perfectly (and instantaneously) mixed with the material already in the reactor, so that the outlet stream composition is identical to that of the reactor contents.
Spreadsheet	The Spreadsheet applies the functionality of spreadsheet programs to flowsheet modelling. With essentially complete access to all process variables, the Spreadsheet is extremely powerful and has many applications in HYSYS.
Component splitter	The Splits page lets you specify the separation fraction of the outlet streams. The Splits, or separation fractions ranging from 0 to 1, must be specified for each component in the overhead stream exiting the Component Splitter.
Tank	Multiple feeds, one liquid and one vapor product stream. The Tank is generally used to simulate liquid surge vessels.
3-phases separator	Multiple feeds, one vapor and two liquid product streams. The 3-Phase Separator operation divides the vessel contents into its constituent vapor, light liquid, and heavy liquid phases.

Unit Operation Model	**Description**
Separator	Multiple feeds, one vapor and one liquid product stream. In Steady State mode, the Separator divides the vessel contents into its constituent vapor and liquid phases.
Tee	The Tee operation splits one feed stream into multiple product streams with the same conditions and composition as the feed stream, and is used for simulating pipe tees and manifolds
Valve	HYSYS performs a material and energy balance on the inlet and exit streams of the Valve operation. HYSYS performs a flash calculation based on equal material and enthalpy between the two streams. It is assumed that the Valve operation is isenthalpic.
Petroleum distillation column	The focus of the Petroleum Column is to model the imperfect separation of crude and other feeds that occur in the refining industry as accurately as possible. The modelling of imperfect fractionation plays a very important role in refinery economics. Conversely the focus is not to use the tool as a detailed design tool.
Equilibrium reactor	The Equilibrium reactor is a vessel which models equilibrium reactions. The outlet streams of the reactor are in a state of chemical and physical equilibrium. The reaction set which you attach to the Equilibrium Reactor can contain an unlimited number of equilibrium reactions, which are simultaneously or sequentially solved.

2 FFW Base Case

The base case scenario considers an up-scale of the demonstration processes. I.e. it considers a process where synthesis gas is produced from gasification of biomass, in this case olive residues, with air (Refer to deliverables 3.1, 3.4, 5.1 and 5.2). A certain amount of freedom is afforded in the process design since the demonstration processes only consider gasification and syngas cleaning - and then Fischer-Tropsch synthesis and methanation. The required intermediate steps are designed and then simulated. The design of these intermediate steps is thus selected based on the overall requirements of the process. The main factors that shape the overall base case design are:

- SNG specification, which requires SNG to have no more than 30% nitrogen, means that if gasification of biomass with air is used (as per demo), sufficient nitrogen has to be removed from the process at some point to ensure compliance. High concentrations of N_2 result increased compression costs and exergy losses.
- Difficulty in removing nitrogen from product gas (containing CO and H_2) means that if gasification with air (as per demo) is used, it is only viable to separate N_2 from H_2. In any case, H_2 is required for hydrocracking of waxes and must be produced in the process.
- To remove sufficient amounts of N_2 from the process, utilisation of WGS reactor to shift the H_2:CO ratio to 3:1 for methanation reactor resulted in insufficient amounts of N_2 shifted from the process. Instead, H_2 must be produced from some of the product gas by shifting all CO and then removing the N_2 (membrane is utilised due to suitability for small and medium process).
- Conversion of synthesis gas to fuel in the Fischer-Tropsch process needs to be limited to avoid concentrating the remaining nitrogen in the off-gas since the off-gas is used for methanation. i.e. lower conversion results in lower concentrations of N_2 in the off-gas. Even then, produced SNG contains high levels of N_2 and must be removed by an upgrading process.

2.1 Fischer-Tropsch Synthesis

Fischer-Tropsch process has been modelled through one reactor only. Following the reactor, has been developed a separation product section composed by phase separator equipment, in order to remove the water mainly, and distillation towers (atmospheric and vacuum), prior to the hydrocracking section.

2.1.1 Process Overview

The Fischer-Tropsch process is, in principle, a carbon-chain-building process, where in the presence of a suitable catalyst, methylene groups are attached to the carbon chain. The detailed behaviour of the actual reactions is not known however the main reaction is (1):

$$2H_2 + CO \rightarrow -CH_2- + H_2O \qquad -165.0\ \text{kJ/mol}$$

As shown, all the reactions involved in the shown above reaction are overall an exothermic reaction, and to avoid an increase in temperature, which results in lighter hydrocarbons, the Fischer-Tropsch reactor is cooled, to secure stable reaction conditions (2). The excess energy can be used to increase steam temperature which can be used elsewhere in the process or as heating medium.

In general, the approximate product distribution of hydrocarbons formed during the Fischer–Tropsch process follows an Anderson–Schulz–Flory (ASF) distribution (1) :

$$W_n/n = (1-\alpha)^2\, \alpha^{(n-1)}$$

Where W_n is the weight fraction of hydrocarbon molecules containing n carbon atoms; α is the chain growth probability or the probability that a molecule will continue reacting to form a longer chain. In general, α is largely determined by the catalyst present and the process conditions. In accordance with the above equation methane will usually be the largest single product; however, by increasing α close to one, the total amount of methane formed can be minimised and the reaction can be driven towards the production of long chain hydrocarbons as required by FFW project (1).

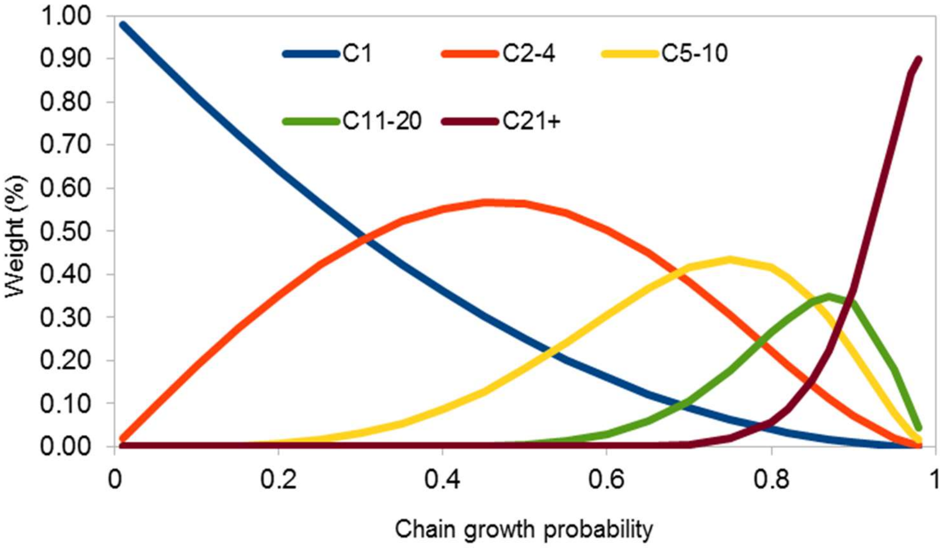


Figure 2. Anderson-Schulz-Flory distribution

The Fischer-Tropsch process either takes place at high temperature or low temperature where different catalysts are favoured for different temperatures (2). The FFW process uses low temperature process.

2.1.1.1 Catalysts

Fischer-Tropsch synthesis does not occur in the absence of appropriate catalysts. Various metals, including but not limited to iron, cobalt, nickel, and ruthenium, alone and in conjunction with other metals, can serve as Fischer–Tropsch catalyst. Nickel and ruthenium are not considered within the FFW project due to high selectivity to methane and high cost respectively. Cobalt has high selectivity to heavy hydrocarbons suitable cracking and for production of diesel fuel. Iron has the advantage of being readily available and relatively inexpensive but also has the disadvantage (or advantage if desired) of greater water–gas shift activity (1).

Fischer–Tropsch catalysts are very sensitive to poisoning by sulphur containing compounds. The sensitivity of the catalyst to sulphur is greater for cobalt-based catalysts than for their iron counterparts. Some of these mechanisms are unavoidable and others can be prevented or minimized by controlling the impurity levels in the syngas (1).

Carbon deposition can also cause catalyst deactivation but can be reduced by addition of promoters to catalysts, which most commonly used are Pt, Re, and Ru, and control of reaction temperature and pressure. In general, because of its high activity, the coke deposition rate is higher for an iron catalyst than a cobalt catalyst. Consequently, cobalt catalysts have longer lifetimes (1).

2.1.1.2 Reactors

The main Fischer-Tropsch reactor types are: the multi-tubular fixed-bed, the slurry reactor, and the fluidised-bed reactor (with either a fixed bed or a circulating bed). A reactor similar to the Sasol slurry phase distillate reactor (slurry reactor or bubble column reactor) has been chosen for the FFW project purpose, although the multitubular fixed bed was considered for the simulations due to its easy scale-up.

The selection of the reactor is associated with the operation regime. There are two main regimes considered most promising: low-temperature Fischer-Tropsch (LTFT), which usually operates at 200-250 ºC and it is characterised by long-chain molecules; and high-temperature Fischer-Tropsch (HTFT), which operates at 320-375 ºC and its products are shorter chain molecules. The correct path to choose the reactor depends on the catalyst, the conditions and the distribution of products that is desired. When the regime selected is HTFT, commonly the reactor operates with iron catalysts using two-phase fluidised bed reactor. When the regime is LTFT, either iron or cobalt in three-phase slurry or tubular fixed bed reactor can be used. It is an important point to assure a successful FT plant (3).

- Multitubular Fixed Bed Reactor (MFBR)

Due to the high exothermal reaction of CO hydrogenation which takes place in the FT process (heat around 140-160 kJ/mol CO converted) and since the sensitivity associated with the temperature for the product selectivity, it is important to take into account that the reactor types are restricted by the heat management requirements. It is necessary to consider the deactivation rate of the catalyst and the replacement strategy, this point has not been considered for the reactor design though.

There are two types of LTFT fixed bed based reactors with multitube configuration in operation. One is based on Fe catalyst (Arbeitsgemeinschaft Ruhrchemie-Lurgi, or Arge), and the other is based on Co catalyst (Shell middle distillate synthesis, or SMDS).

For the Co-LTFT multitube reactor, there are several considerations, which are analogous to Arge reactor (Fe-based catalyst). On one hand, cobalt is better for the lasting lifetime and higher activity. In opposition of other potential technologies, multitubular fixed bed technology is more robust and easier in order to develop and scale-up. Although the loading and unloading of the catalyst might be onerous, it is not a problem due to the several years of lifetime. Other advantages of this kind of reactor are listed below (4):

- This reactor is very robust in operation, with the backing of many years of industrial experience.
- A high resistance to contaminants presented in the syngas, such as H_2S, which are adsorbed by the top layer of the catalyst.
- Absence of separation problems between wax and catalyst.
- The scale-up from the pilot plant data using a single tube reactor is quite simple and robust.

Shell made a large scale-up of the Arge reactor, which operates in Sasol 1 (South Africa) with a catalyst of iron (current production 35,000 tonnes/year), into larger multitubular fixed bed reactors 7 meters in diameter used in the Shell Pearl GTL project with a total capacity of 6,000,000 tonnes/year (140,000 bbl/day), combined with the production of LPG condensates and ethane that are piped from Qatar (5). The raw material for this process (Shell) is natural gas, whilst in Sasol process is coal.

In 2012, Linde bought and developed the Choren based process *Choren Carbo-V ® Process.* This process is based on three gasification stages plus a FT technology to covert biomass to liquid (BtL). This process was designed following the Shell Middle Distillate Synthesis technology (SMDS). The capacity of the plant is 15 kt/year and the biomass source is wood chips. (6)

On the other hand, there are some drawbacks associated with the use of multitubular reactors for FT process:

- The control of the temperature inside the reactor axially and radially can be problematic.

- Large multitubular reactors tend to have high construction costs.
- A low efficiency of the catalyst is shown when the catalyst particles have 3-5 mm due to internal transfer limitations.
- There are labour-intensive catalyst replacement requirements.

The multitubular fixed bed remains the dominant technology of LTFT process for industrial capacity, in despite of the drawbacks listed upon. This technology is considered promising for processing of syngas from biomass with a relatively small capacity installed.

In Figure 3 a multitubular fixed bed reactor is represented. This reactor is similar to a shell and tube heat exchanger, where the tubes are filled of catalyst. The external walls of the tubes are surrounded by boiling water, which remove the reaction heat, and through the steam pressure is possible to control the reactor pressure. Feed (syngas) is introduced into the top of the reactor and it passes through the catalyst placed in the tubes. At the bottom, heavy waxes and gaseous streams are separated, the gaseous product is leaving at the top of the reactor and the waxes at the bottom, whilst the catalyst remains fixed.

The most important point for this reactor design is the maintenance of a good control of temperature. This point requires 50 mm as the maximum diameter of the tubes (7) (8).

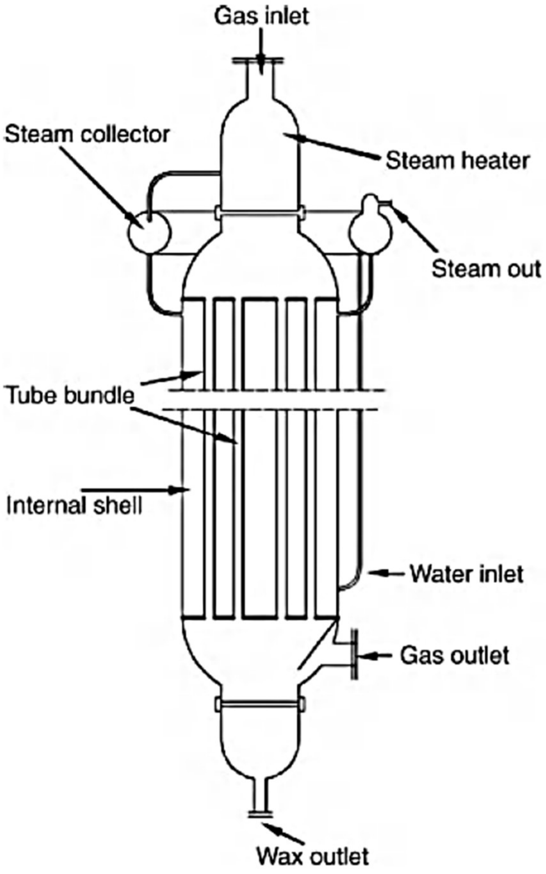


Figure 3. Multitubular Fixed Bed FT Reactor (Example of Original Arge Reactor) (9)

- ➢ Slurry Bed Reactor (SBR)

Slurry bubble column reactors have been used in large-scale application for iron-based Fischer-Tropsch process since 1993 by Sasol. Sasol also applied this reactor in an industrial scale for Co-based Fischer-Tropsch reaction (LTFT), nevertheless some problems appeared in regards with catalyst fines.

Fischer carried out the earliest studies about slurry bed reactors in 1932. Years later, Rheinpreussen AG and Koppers GmbH developed a slurry reactor at semi-commercial scale using a low H_2:CO ratio and 0.1 m/s superficial gas velocity. The first commercial scale for slurry bed FT reactors had 1.5 m diameter and 7.7 m height, and the working volume was 10 m^3. Due to the difficult separation of the waxes from the catalyst and the poor knowledge in hydrodynamics about FT catalyst, this technology was not attractive for industrial application.

During the late 1980s and the early 1990s, 1 m diameter fixed fluidized bed (FFB) reactor was adapted by Sasol into a pilot-scale slurry reactor using the SAS technology. The catalyst used in this revamping was similar to Arge multitubular fixed bed reactor, but manufactured as finely divided particles. At that moment, the understanding about slurry hydrodynamics and methods for catalyst particle separation from liquid had increased.

This reactor was successful and recommissioned as the slurry bubble column at commercial scale in Sasol 1. The production capacity of this equipment is 12,500 t/a and was adapted for a Co-based FT catalyst instead of precipitated iron catalyst lately. After a scale-up, the diameter of the reactor is 10 m and 45 m height. The design capacity for this plant is between 750-850 kt/a. Escravos GTL plant, which is being built in Nigeria, is based on this technology. Some difficulties have been reported about this technology.

Based on iron catalyst, Synfuels China scaled up a slurry reactor for FT products in 2000, with 1 kt/a pilot plant capacity in Taiyuan. Demonstration plants shown successful results during the projects carried out with capacities of 200-225 kt/a and 5.3-5.8 internal diameter and 57 m height reactors during 2005, these plants were commissioned between 2008-2009 and are still in operation.

In Figure 4 is represented a common slurry bed reactor. At the bottom of the equipment, the syngas is introduced into the gas distributor, and the FT reaction starts when the slurry phase takes place. At the top, the reacting gas is leaving the reactor, after going throughout the bed.

There is a slurry free space at the top, this space enables to separate any mist carried over by the gaseous stream. Light FT fractions that remain in the gaseous streams are recovered downstream and heavy waxy products are extracted by filtration (in situ).

Heat exchangers inside the slurry bed allow to remove the reaction heat with high efficiency.

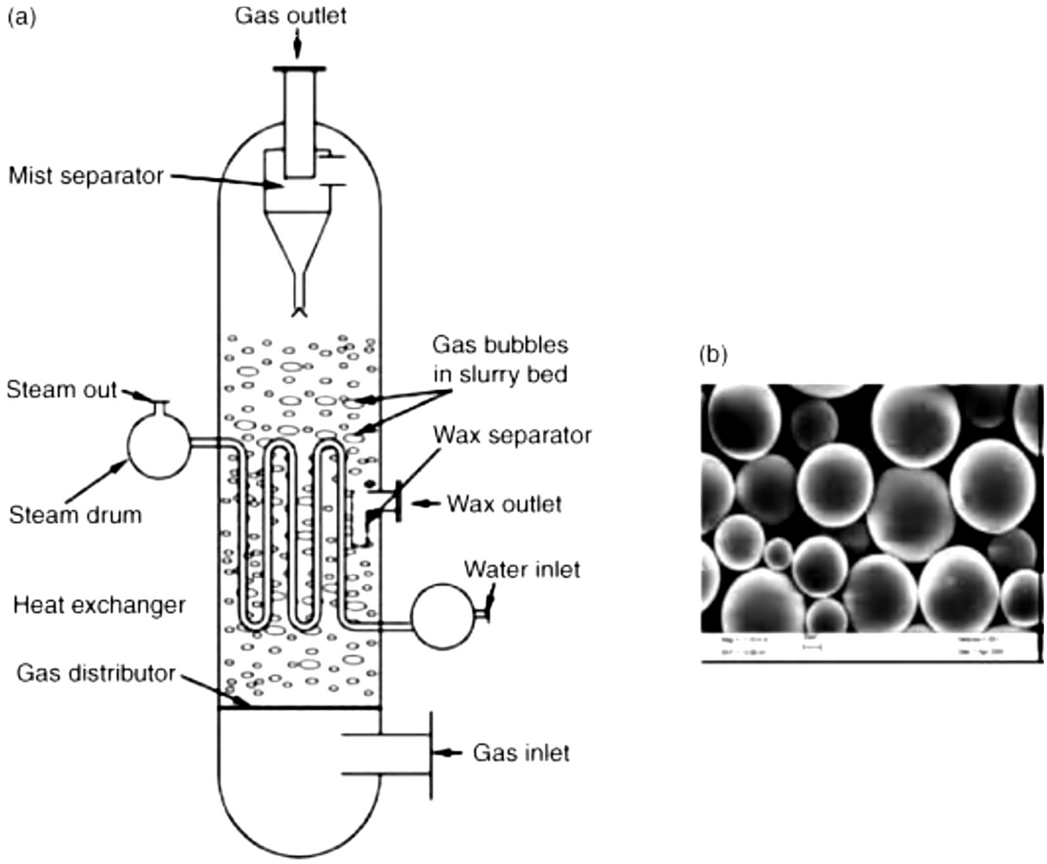


Figure 4. a)Slurry fixed bed reactor scheme b) bubble particle size (9)

The advantages of the slurry bed reactor over the multitubular fixed bed reactor are listed below:

- The smaller particle size of the catalyst enhances the mass and heat transfer and makes a decrease in the consumption per ton of product of the catalyst.
- It is possible to meet more isothermal conditions.
- The pressure drop is not a problem (a quarter of fixed bed pressure drop)
- Online removal and addition of catalyst.
- It is possible to achieve higher selectivity to heavy products and lower selectivity to methane.
- Low cost in comparison to MFBR for the same capacity.

The main drawbacks are:

- Remaining contaminants in syngas can spread over the catalyst and contribute significantly to a fast deactivation.
- The flow reactor model is closer to a continuous stirred tank reactor (CSTR) than a plug flow reactor, which is less efficient.
- Erosion and attrition of the catalyst appear as consequence of movement and collision of catalyst particles. This phenomena increases the viscosity of the slurry phase and makes more difficult the waxes and catalyst separation.
- Liquid/solid separation is one of the main problems when the hydrodynamic regime is considered. This part could increase the separation cost of the process.

Some companies, such as Eni IFPEN, have carried out some studies to minimize the operation risks and the results shown as the favourite configuration the external filtration unit for the wax outlet and the recycle of the catalyst to the reactor bottom, which will keep uniform and controlled the catalyst concentration (9).

2.1.2 Modelling Review

Damartzia and Zabaniotou (10) provide a decent (and relatively recent) overview of Fischer-Tropsch modelling with several references to Aspen PLUS (but not HYSYS). More recently Floudas *et al* undertook a review on production of liquid transportation fuels which again refers to many instances of modelling of Fischer-Tropsch processes using Aspen PLUS (but not HYSYS) (11). Approaches usually adopt a kinetic approach, but often the product distribution is defined by the ASF equation.

Prins *et al* undertook a study on the exergetic (available energy) optimisation of a production process for Fischer–Tropsch fuels using Aspen PLUS (not HYSYS) (12). The Fischer-Tropsch Reactor hydrocarbon distribution adhered to the ASF equation where (alpha) the chain growth probability factor was calculated according to a rate based equation dependant on rate constants for: adsorption of carbon monoxide, desorption of paraffins and desorption of olefins from active site, and also partial pressures of carbon monoxide and hydrogen. The equation was for an iron catalyst, although Prins *et al* speculate that the model would be useful for cobalt catalysts as well. Interestingly, from the perspective of the FFW project, they noted alpha values fell for synthesis gas diluted with nitrogen.

Finally, although C M Masuka *et al* (13) did not model the FT process using Aspen, they did give a good overview of the accuracy of various equations of state and product distribution according to different equations should they need to be considered further. They highlighted the popularity of the Soave-Redlich-Kwong equation for use in the Fischer-Tropsch process due to its capability to generate reasonably accurate equilibrium ratios in VLE calculations.

2.1.3 FFW Process Fischer-Tropsch Design

FT scale-up process developed in FFW project through Aspen HYSYS software has been designed by means of one continuous stirred tank reactor (CSTR) only and a series of equipment in order to obtain the separation: three phase separator, an atmospheric distillation tower and a vacuum distillation tower (previous to the hydrocracking section).

The reactor used for this purpose is a *Continuous Stirred Tank Reactor (CSTR).* This model has been selected based on information detailed above (See 2.1.1.2. Reactors), where the flow is described closer to this model than a plug flow reactor (PFR). Considerations to be taken into account for this reactor model are:

- Pressure drop is previously supposed/calculated
- The reactor orientation can be selected. For this configuration the reactor is vertical.
- Heterogeneous kinetics (only available for PFR and CSTR in Aspen HYSYS).
- No catalyst information is taken into account for the reactor modelling (only for the kinetic modelling).

Reaction system has been modelled through the kinetics expression provided by KTH:

$$r_{FT} = k \cdot p_{H_2}^{\alpha} \cdot p_{CO}^{\beta} \cdot p_{H_2O}^{\gamma} \tag{1}$$

$$\boxed{k = A \cdot exp\left(-\frac{Ea}{RT}\right)} \tag{2}$$

Where the values are shown in Table 3:

Table 3. Kinetic parameters for FT reaction

Results (at 210 °C)	
K, mol/gcatalyst·s·bar$^{-0.4}$	4.806E-06
α	0.5
β	-0.25
γ	0.1499
Arrhenius Results	
Ea, kJ/kmol	103.9
A, mol/gcatalyst·s·bar$^{-0.4}$	8.19E+05

The effect of the catalyst concentration on conversion ratio was studied by Krishna et al. (2001) (14). Increasing catalyst concentration increases conversion ratio and a 40 % of catalyst loading in the liquid is considered the limit for feasible commercial operation of FT plant (14). For this design, 35 % is considered to maximize conversion within reasonable margin from the limit.

Heterogeneous catalytic reaction set has been chosen as reaction set. Thermodynamic model chosen has been PSRV due to there is a mixture of polar and non-polar components (due to the presence of alcohols) mainly in vapour phase (15).

2.1.3.1 Assumptions

Fischer-Tropsch (FT) product distribution follows the experimental distribution. The FT product distribution is based on KTH results with a fine powder catalyst at 40 % conversion. The same product distribution is expected for the catalyst at 60 % conversion (see 2.7. Base Case Summary for comparison details). Other assumptions made during the reactor design are listed below:

- Process is under steady-state and isothermal conditions (210 ºC).
- Input flow rate of synthesis gas is constant.
- Catalyst deactivation is negligible.
- Intra-particle mass and heat transfer resistances are negligible.
- Good mixing between gas and liquid products.
- Catalyst sphericity is 1 (perfect sphere).
- Irreversible kinetics.
- Gas holdup remains unaffected if the length to diameter ratio is ≥ 6.
- One dimensional model.
- Waxes and gases leave the reactor in the same side within the simulation.
- Catalyst separation (filter) has not been considered for this design.

2.1.3.2 *Pressure drop*

Aspen HYSYS PFR uses Ergun Equation for pressure drop calculation. However, for CSTR model, the pressure drop needs to be supposed or calculated in previous stages and it needs to be introduced (it is not calculated).

Espinoza *et al* summarised the differences between fluidized and fixed bed, highlighting the pressure drop in multitubular fixed bed in the range 3-7 bar and less than 1 bar for slurry bed reactors (16). This is aligned with the different reviews about FT process, where always is mentioned and foreground the lower pressure drop as an advantage over MTFB. The design of the reactor has been done using HYSYS and using as data 1 bar pressure drop.

2.1.4 Unit Specification and Analysis

In Figure 5, FT Reaction section is represented.

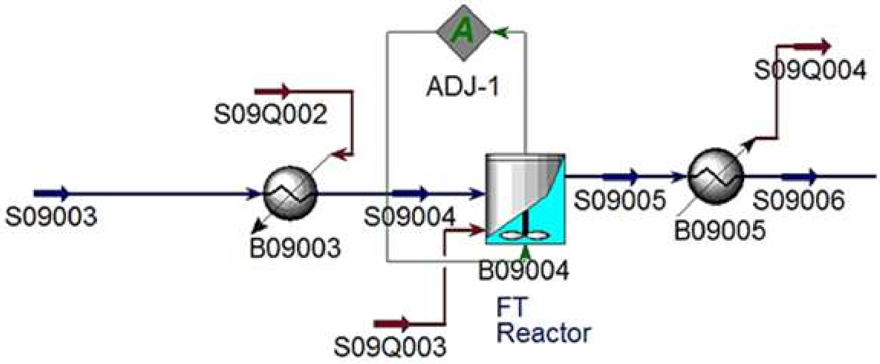


Figure 5. FT reaction section

2.1.4.1 *Design Inputs*

The design inputs introduced for FT reaction in Aspen HYSYS are shown in Table 4. Low temperature and relatively high pressure used since the conditions inhibit formation of short chain hydrocarbons. Long chain hydrocarbons and high yield are achieved at these conditions. The maximum conversion, specified as conversion through an *adjust* tool (used to calculate the total volume of the reactor) is 60 %.

Table 4. Fischer-Tropsch Model Inputs

Input	**Value**
CSTR Inlet temperature, ºC	210
CSTR outlet temperature, ºC	210
Inlet Pressure	33.7
Pressure drop, bar	1
Activation energy of catalyst, kJ/kmol	103.9
Reaction Exponent - CO	0.5
Reaction Exponent – H_2	-0.25
Specified possible paraffin length	1-30. 32. 36.
Specified possible olefin length	2-20. 22. 24

Input	Value
Reactor volume, m^3	10.18
Reactor Length, m	8.50
Liquid Volume, % (m^3)	85 (9.8)
Catalyst particle Diameter, μm	53-90
Catalyst Loading, % in wt.	35
Particle Sphericity	1
CO Mass Flow, kg/h	3810
H_2 Mass Flow, kg/h	575
Total Mass Flow (including other components such as N_2 and CO_2), kg/h	12,918

Peng Robinson-Stryjek and Vera (PRSV) or Enhanced Peng Robinson equation is used as the property model since it is useful in calculating VLE thermodynamic properties. Some references texts use Redlich-Kwong Soave (RKS), however this equation is not valid for this system due to the presence of alcohols, and HYSYS is not able to use part of the component list (oxygenated compounds) if this model is applied.

Paraffins and olefins available on Aspen HYSYS are limited so paraffins of carbon chain length 31, 32 and 33 are all represented by C32H66, the amount of which is dependent on the number of mols of carbon atoms present in total by the 3 carbon chain lengths. Paraffins with carbon chain length 34-39 are all represented by C36H74, the amount of which is dependent on the number of mols of carbon atoms present in total by the 6 carbon chain lengths. The distribution used for olefins shows no olefins with a carbon chain length over C24.

2.1.4.2 Outputs

The different outputs in the FT reactor design along with the mass balance are shown in Table 5 and Table 6.

Table 5. FT reactor design outputs

Output	Value
Conversion-CO, %	60
Diameter, m	1.23
Catalyst loading, kg	6,379
Productivity, kg HC/kg catalyst[1]	0.21
MP steam generation, kg/h	6,575
Heat flow, MJ/h	-13,028

---

[1] As HC products are referred paraffins, olefins and alcohols

Table 6. FT reactor mass fraction outputs

Component	Mass flow, kg/h
H_2O	1,403.59
H_2	227.69
CO	1,523.77
CO_2	1,467.09
N_2	6,975.13
C1OH	10.28
C2OH	3.12
C3OH	1.50
C4OH	1.43
C5OH-C10OH	38.24
C11OH-C15OH	17.22
C1	266.57
C2	11.21
C3	15.38
C4	23.72
C5-C10	196.18
C11-C20	316.78
C21+	220.06
C2=	1.01
C3=	33.25
C4=	33.31
C5= - C10=	92.46
C11= - C20=	32.11
C21= +	7.58

Heat exchangers are modelled for this process in FT reaction process. They are necessary to heat the FT feed and to chill the effluent before the three phase separator (after FT reaction and as part of the FT product separation section). The first approach of these heat exchangers (without any energetic integration) is represented in Table 7

Table 7. Heat exchanger designs for FT reaction section

Heat Exchanger	T inlet, ºC	T outlet, ºC	Service	T inlet service, ºC	T outlet service, ºC	Mass flow service, kg/h
B09003	-12.67	210	Water (vapour lo liquid)	333.9	233.9	2826
B09005	210	15	Chilled water	5	25	70,554

2.1.4.3 Validation

In their summary about fixed bed for FT process, in addition to the stating of the typical pressure drop for this system, Spinoza *et al* mentioned the conversion for a once through process that is up to 80 % is possible. The conversion chosen as maximum is 60 % for this case.

As mentioned in previous sections, one of the advantages of slurry bed reactors is the relatively cheap construction in comparison with the multitubular fixed bed. Typically particle sizes are between 40-150 µm, and the bed height will depend on the production selected (17).

A numerical comparison among reactors is not possible, the trends are the same though. The comparative data for this kind of reactors is provided by Sasol 1 site, which is 5 m diameter and 22 m high (18).

Figure 6 represents the slurry bed reactor scale-up. Taking into account the production of SASOL plant (≈ 17,000 barrels per day) and the production of the FFW project scale-up plant (≈140 barrels/day), the results shown in 2.1.4.2 Outputs are within the range. The size of this FT reactor could be considered within the pilot plant scale (the use of biomass limits the amount of raw material due to logistic issues, but SASOL treats higher volumes of syngas coming from coal).

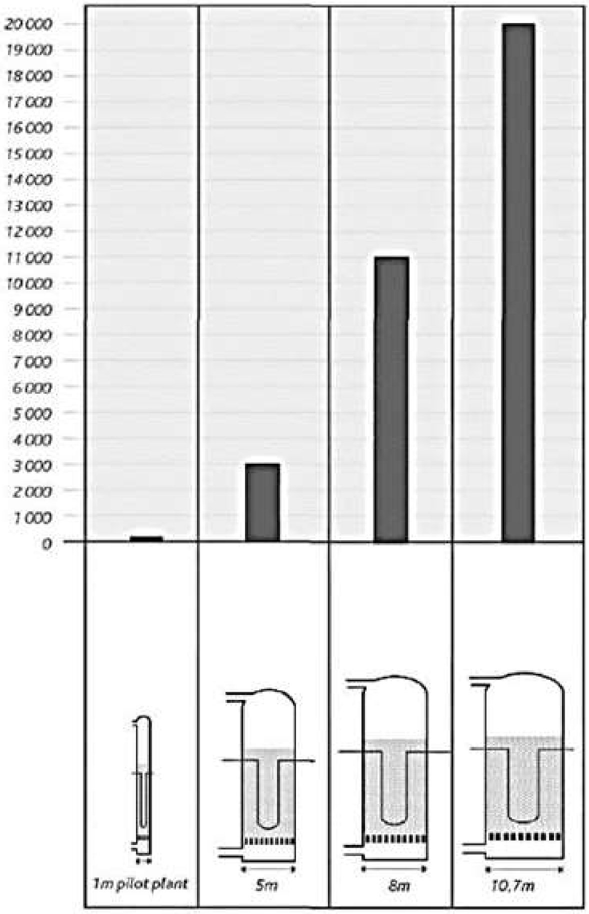


Figure 6. Scale up of SAS slurry bed reactor (y axis: barrels/d, x axis: 1, 5, 8 and 10.7 m reactor diameter) (17)

2.2 Fischer-Tropsch Product Separation

This section describes how the FT reaction products are fractionated into different valuable products before waxes are hydrocracked.

The main target of this section has been the maximum obtaining of diesel as valuable product. However, naphtha fraction is obtained as well as an off-gas stream which could be potentially used as fuel.

2.2.1 Process Overview

As described in 2.1.4.2.Outputs, Fischer-Tropsch reaction effluent is composed by a wide range of products, where the most valuable products for FFW purpose are hydrocarbons comprised between C11-C21+ (including waxes). Further wax cracking will be carried out after the different lighter hydrocarbons are separated.

FT products need to be separated in order to obtain different fractions of valuable products. The most valuable product following FFW project aim is diesel. Additionally, it is obtained naphtha fraction in the atmospheric column and off-gas fraction in both atmospheric and vacuum towers.

The designed section follows the same steps for a conventional refinery plant. There is a three phase separator, which removes the water made during FT reaction from part of the light hydrocarbons and other gases that will be sent to SNG section and the heavy hydrocarbons (C5+); an atmospheric distillation tower where different hydrocarbon cuts will be fractionated: off-gas, naphtha, diesel and an atmospheric residue will be treated in the last column of this section, a vacuum distillation tower, where light vacuum gas oil will be obtained and separated from a heavy vacuum gas oil that is the hydrocracking section feed.

The different cuts will require a later treatment in order to enhance their properties or at least, they should be blended in the same fraction pool.

2.2.2 Modelling Review

Hamelinck et al explained in the review about FT products for fuel and transportation the need of upgrading the FT reaction products through different ways to maximise the manufacture of FT liquid products. It is mention the separation C1-C4 from C5+. This light fraction or off-gas (C1-C4) is mentioned to be potentially recycled in order to maximise FT reaction or even to be sent to gasifier (previous reformer for cleaning). For FFW project, this stream will be sent to SNG production and it is the first stream (gas) separated within three phase vessel.

If the idea is not maximised fuel production and is the production of electricity and fuel, the recycle shall not be considered and it should be used a “once through” reactor.

It is mentioned the hydrocarbon recovery in different fractions, such as naphtha, diesel and waxes through the separation of C5-C9 hydrocarbons (naphtha fraction) from C10+ which will be later hydrocracked and isomerised.

In opposition to this study, different distillation columns have been simulated before hydrocracking section with the aim of fractionating more products and maximise the production of diesel before hydrocracking (atmospheric and vacuum). (19)

2.2.3 FFW Process Fischer-Tropsch Product Separation Design

The separation system designed for FT process in FFW project is based on:

- A three phase separation vessel. This equipment is used in order to separate different fractions obtained from FT reactor. Previous to 3 phase separator, the effluent from FT reaction is cooled to 35 ºC.
    - Water: An important amount of water is generated along the reactor according to the used kinetic (see above)
    - Gases: Syngas non-reacted, CO_2, a small quantity of light gases (paraffinic, olefinic, and alcohol) together with a small flow of water is removed in this stream.
    - FT products: Paraffins, Olefins, alcohols and waxes are together in this stream.
- Atmospheric distillation tower: In this column, FT products are separated into different fractions: off-gas, naphtha, diesel and a heavy atmospheric residue.
- Vacuum distillation tower: This column enables to separate the heavy atmospheric residue into a light fraction with some alcohols and occluded light gases, a light vacuum gas oil fraction and a heavy vacuum gas oil fraction that will be sent to the hydrocracking section.

The specifications for the columns have been the cuts into different fractions based on the upper and lower hydrocarbon lenght limits regarding the hydrocarbon recovery, e.g. diesel stream: 50 % C22 recovery, taking into account diesel hydrocarbon range is between C11-C22. The recovery specifications have been done taking into account the freedom degrees for each column. The maximum obtaining of diesel has been the main considered point for both columns.

Due to the diesel production target and as an strategy to obtain the maximum amount of it, the vacuum distillation tower has been placed after the atmospheric distillation tower and before the hydrocracking. This column allows to obtain two diesel fractions, one light vacuum gas oil, which can be treated as a product later on, and a heavy vacuum gas oil, which is sent to hydrocracking section. Additionaly, there is a stream with some gases and alcohols that have not been separated in previous stages.

Both columns need to introduce the feed at vapor conditions (near the bottom), which requires a previous furnace.

2.2.3.1 Assumptions

No further assumptions have been made for this section of FFW products. This section has been designed as a petroleum refinery distillation section due to the hydrocarbon nature. The main assumptions have been made regarding product cuts, which have been:

- Tail gas and LPG (off-gas): C1-C4
- Naphtha: C5-C10
- Diesel: C11-C22
- Waxes/residue: >C22

2.2.3.2 Pressure Drop

Pressure drop in each column section has been calculated through aspen HYSYS Tray Sizing tool, which sizes each column from the basis parameters of it (tray or packaging and kind of it). Pressure drop results are shown within output section for atmospheric and vacuum towers.

2.2.4 Unit Specification and Analysis

The Separation section is represented in Figure 7 and Figure 8.

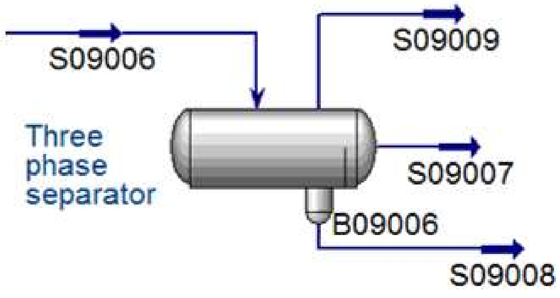


Figure 7. FT Separation section – Three phase separation vessel

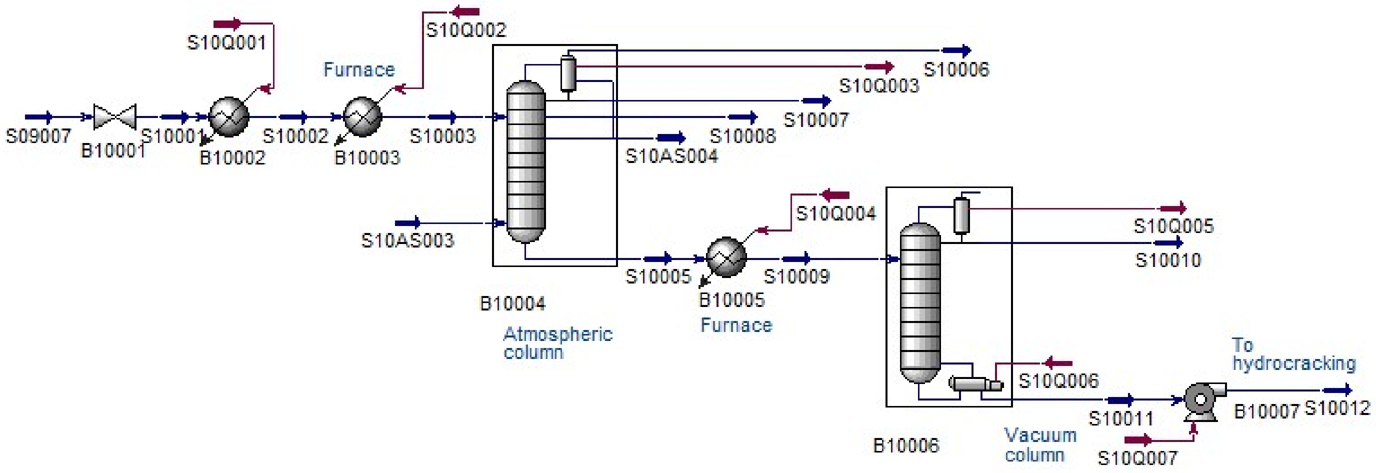


Figure 8. FT Separation section

2.2.4.1 Inputs

As part of FT process, the separation section is included (before hydrocracking). This section is made up of a three phase separator, an atmospheric distillation tower and a vacuum distillation tower. Inputs are shown in the table below and the outlet stream temperature for the three streams is in accordance with the three phase separation vessel specification. This temperature has been specified at 15 ºC and is obtained through a heat exchanger after FT reactor and the pressure is 32.7 bar.

In the Table 8 and Table 9, the inputs for the atmospheric tower and the vacuum column, respectively, are shown.

Table 8. Atmospheric distillation tower inputs (B10004)

Input	**Value**
Number of stages	20
Column type	Packed
Condenser type	Partial
Reboiler type	N/A
Top pressure, bar	1.5

Input	Value
Bottom pressure, bar	1.9
Water steam amount, kg/h	100
Feed, kg/h	812
Reflux ratio	3.3
n-pentane recovery off gas stream (S10006)	0.1
n-C11 recovery naphtha stream (S10007)	0.2
n-C22 recovery diesel stream (S10008)	0.5
Feed stage	19
Off gas stage (S10006)	Condenser
Naphtha stage (10007)	Condenser
Diesel stage (10008)	17
Atmospheric residue stage (S10005)	Bottom, 20
Feed temperature, ºC	370.4

Table 9. Vacuum distillation tower inputs (B10006)

Input	Value
Stage number	9
Column type	Packed
Condenser type	Total
Reboiler type	HYSYS regular
Top pressure, bar	0.11
Bottom pressure, bar	0.13
Water steam amount, kg/h	N/A
Feed, kg/h	193.8
Reflux ratio	Calculated, no specified: 3,04
n-C22 recovery LVGO (S10010)	0.72
n-C23 recovery HVGO(S10012)	0.78
Feed stage	8
LVGO stage (S10010)	Condenser
Water outlet stage (S10011)	Condenser
HVGO (S10012)	9
Feed temperature, ºC	360.7

2.2.4.2 Outputs

Three phase separator generates three streams:

- Stream S09009. This stream is mainly composed by light gases and a small quantity of water
- Stream S09007. A small amount of gases remains in this stream. It is composed by FT products (alkenes, olefins and alcohols) to FT separation and hydrocracking.

- Stream S09008. This is the aqueous stream where water is separated from the others streams. Along with water, is removed small amounts of light alcohols, such as methanol and ethanol (high affinity to water).

This vessel is adiabatic (Q=0). The mass balance for this equipment appears in Table 10.

Table 10. Three phase separator mass balance (B09006)

Stream	S09006 (Feed)	S09007 FT products	S09006 Light gases	S09008 Aqueous phase
Vapour fraction	0.85	0	1	0
Temperature, ºC	15	15	15	15
Pressure, bar	32.70	32.70	32.70	32.70
Molar Flow, kmol/h	552.83	5.48	469.66	77.69
Mass Flow, kg/h	12,918	875	10,641	1,401

Initially, distillation columns were designed as bubble-cap column towers (as petroleum atmospheric refining columns), but the diameter of both columns is small (<1 m), which means that the use of trays is not recommendable. Finally, these columns have been designed as packed columns (Rasching rings, random packing 1 inch). In Table 11 and Table 12 are represented the results of the design of the atmospheric tower and the outlet mass flows.

Table 11. Atmospheric distillation column (B10004) outputs

Output	Value
Diameter, m	0.45
Height, m	8.76
Section delta P, bar	2.78E-02
Condenser heat S10Q003, kJ/h	- 959,012

Table 12. Atmospheric distillation column (B10004) mass balance output

Component	S10006 (Off gas)	S10007 (Naphtha)	S10AS004 (steam water output)	S10008 (Diesel)	S10005 (Atm. residue)
Flow Rate (kg/h)	20.54	251.24	99.95	405.96	198
$H_2$0	0.21	0.04	99.57	0.13	0.09
H_2	0.03	0	0	0	0
CO	1.02	0.01	0	0	0
CO_2	7.84	0.80	0.01	0.01	0
N_2	4.77	0.05	0	0	0
C1OH	0.16	2.76	0.35	0.02	0
C2OH	0.05	1.76	0.02	0.01	0
C3OH	0.01	1.21	0	0.01	0

Component	**S10006 (Off gas)**	**S10007 (Naphtha)**	**S10AS004 (steam water output)**	**S10008 (Diesel)**	**S10005 (Atm. residue)**
C4OH	0	1.32	0	0.02	0
C5OH-C10OH	0	27.39	0	10.75	0.01
C11OH-C15OH	0	0	0	17.07	0.15
C1	0.47	0.01	0	0	0
C2	0.09	0.02	0	0	0
C3	0.31	0.22	0	0	0
C4	0.73	1.97	0	0.01	0
C5-C10	1.77	148.59	0	6.07	0.01
C11-C20	0	6.59	0	299.30	10.80
C21+	0	0	0	39.37	180.69
C2=	0.01	0	0	0	0
C3=	0.59	0.37	0	0	0
C4=	0.98	2.18	0	0.01	0
C5= - C10=	1.50	54.22	0	1.48	0
C11= - C20=	0	1.72	0	29.64	0.74
C21= +	0	0	0	2.06	5.52

The results show a good separation into different fractions. The steam water stream aims to remove small amounts of gases that have not been removed in three phase vessel. Naphtha stream maximizes the amount of the fraction comprised between C5-C10 hydrocarbons, included alkenes and alcohols which single boiling point of each compound is in the same range. Some small quantities of waxes are lost in this stream. Diesel stream has been maximised as a target of this project (C11-C20), a post treatment is suggested to remove the alcohols and reduce the quantity of olefins. Finally, 198 kg/h waxes are obtained, which are sent to vacuum distillation to obtain more diesel and separate all the waxes that will be treated in HCR process.

On the other hand, an analysis of the main fuel properties related with these streams have been carried out. The results are shown as follows:

Table 13. Properties for the FT fuels in atmospheric column

Property	**S10007 (Naphtha)**	**S10008 (Diesel)**	**S10005 (Atm. residue)**
Density @20 ºC, kg/m^3	712.22	774.7	892.01
Viscosity @ outlet temperature, cSt	0.71	2.81	8.77
Flash point, ºC	-21.47	87.59	150
Aromatic content, %	<1 %	<1 %	<1 %
Cetane number	-	77.01	-

Property	**S10007 (Naphtha)**	**S10008 (Diesel)**	**S10005 (Atm. residue)**
HHV, kJ/kg	47,844	32,581	17,889
LHV, kJ/kg	44,362	30,250	16,609

In Table 14 and Table 15, the design and the mass outputs for the vacuum distillation tower are represented.

Table 14. Vacuum distillation tower (B10006) design outputs

Output	**Value**
Diameter, m	0.30
Height, m	4.2
Section delta P, bar	9.60e-003
Condenser heat S10Q005, kJ/h	- 109,315
Reboiler heat S10Q006, kJ/h	17,520

Table 15. Vacuum distillation tower output mass balance

Component	**S10010 (LVGO)**	**S10011 (HVGO)**	**S10013 (WATER)**
Flow Rate (kg/h)	30.09	167.63	0.23
H_20	0	0	1
H_2	0	0	0
CO	0	0	0
CO_2	0	0	0
N_2	0	0	0
C1OH	0	0	0
C2OH	0	0	0
C3OH	0	0	0
C4OH	0	0	0
C5OH-C10OH	0.01	0	0
C11OH-C15OH	0.15	0	0
C1	0	0	0
C2	0	0	0
C3	0	0	0
C4	0	0	0
C5-C10	0.01	0	0
C11-C20	10.55	0.25	0
C21+	18.06	162.63	0

Component	**S10010 (LVGO)**	**S10011 (HVGO)**	**S10013 (WATER)**
C2=	0	0	0
C3=	0	0	0
C4=	0	0	0
C5= - C10=	0	0	0
C11= - C20=	0.72	0.02	0
C21= +	0.77	4.74	0

This column achieves a clear separation of light diesel fraction and the heavy vacuum residue (to be cracked in hydrocracking (HCR section). The stream sent to hydrocracker is made up of heavy components only, mainly paraffins together with some heavy olefins. In order to achieve the hydrocracking conditions, this stream is pumped up to 70 bar to operate within hydrocracker conditions.

The properties for the vacuum gas-oil and the hydrocracking feed are shown in Figure 16.

Table 16. Properties of the vacuum diesel.

Property	**S10010 (LVGO)**	**S10011 (HVGO)**
Density @20 ºC, kg/m^3	792.73	892.01
Viscosity @ outlet temperature, cSt	5.17	8.77
Flash point, ºC	134.36	150
Aromatic content, %	<1 %	<1 %
Cetane number	78.03	68.24
HHV, kJ/kg	23,701	17,889
LHV, kJ/kg	22,006	16,609

Additionally, there are two furnaces in order to vaporise the feed for both columns since to obtain clear cut fractions, petroleum refinery columns have modelled as analogy to this process. Within these processes, the feed is vaporised and introduced close the bottom stages. The values for these furnaces are shown in Table 17 and Table 18.

Table 17. Furnace B10003 (to atmospheric tower)

Parameter	**Value**
Input temperature, ºC	230
Output temperature, ºC	370.4
Heat, kJ/h	466,139

Table 18. Furnace B10005 (to vacuum tower)

Parameter	Value
Input temperature, ºC	303.6
Output temperature, ºC	360.7
Heat, kJ/h	78,090

2.3 Hydrocracking

Hydrocracking section is designed in order to break the waxes (long-chain) into short chains with the purpose of obtaining diesel. Hydrocracking section is composed by a hydrocracking reactor along with a high pressure separator and a distillation column.

2.3.1 Process Overview

As a refining process for the FT products, hydrocracking is used to obtain mainly distillate products for diesel fuel blending, as well as gasoline motor and jet fuel products. Heavy FT fractions (waxes) are solid at ambient conditions, are able to be converted into lighter products. The use of hydrocracking enables the production of blending materials for transportation fuel applications, even for lubricant base oil.

LTFT process, utilises either Fe or Co-based catalyst. Both give a mixture of different hydrocarbons, usually high molecular weight hydrocarbons (an important fraction of them has the boiling point >370 ºC), whilst the distillate quantity is limited. The products are usually made up of mainly linear paraffins, along with olefins and oxygenates, such as alcohols. Since there is a high fraction of linear paraffins, the middle distillate fraction has a high cetane number; however it presents poor cold flow properties. These properties are enhanced through the hydrocracking treatment. Thus, the hydrocracking process aims to maximize middle distillate yield and improve the cold flow properties of this fraction (20) (21).

One of the advantages of FT products is the absence of sulphur and nitrogen compounds and the high chemical reactivity of heavy paraffin molecules that enables a high conversion of the FT products at mild hydrocracker conditions. (22)

The implementation of hydrocracking for FT waxes was carried out by Shell in their FT plant in Malaysia during the 1990s. Years later, Exxon offers a process for hydrocracking/hydroisomerization FT wax to liquids. Currently, the Sasol/Chevron plant is being constructed in Nigeria and takes into account the maximum obtaining of diesel. The diesel fuel produced from hydrocracker has a cetane number >70. (23) (24) (25) (26)

In Table 19 different process conditions for hydrocracking are detailed (22) (27) (28) (29). The table shows that FT Hydrocracking conditions are similar to mild-hydrocracking.

Table 19. Process conditions for hydrocracking processes and catalyst

Operating Conditions	Conventional Hydrocracking	Mild Hydrocracking	FT Hydrocracking
Wax conversion, %	20-70	70-100	20-100
Total Pressure, bar	100-200	50-80	35-70
H_2 pressure, bar	85-140	35-70	10-50
Temperature, ºC	350-450	350-440	325-375

Operating Conditions	**Conventional Hydrocracking**	**Mild Hydrocracking**	**FT Hydrocracking**
H_2/feed ration, m^3/m^3	800-2000	400-800	500-1,800
LHSV, h^{-1}	0.5-2	0.3-1.5	0.5-3
Catalyst			
Hydrogen Transfer (metal)	Ni/Mo NI/W Pd	Ni/Mo Co/Mo	Ni/W Ni/Mo Pt Pd
Support (Acid)	Si-Al Zeolite	Alumina Si-Al	Si-Al Zeolite

According to Pellegrini *et al* and their approach and taking into account the feedstock of the hydrocracker is mainly made up of paraffins and olefins, usually it is considered that the olefin fraction will be converted into n-paraffins after introduction into reactor in an instantaneous way as is shown below (30):

$$O_n + H_2 \rightarrow P_n$$

The paraffins cracking is carried out according to (31):

$$Pn + H_2 \rightarrow P_s + P_r$$

Where n=r+s

It is assumed that two hydrocarbons are generated with the same number of carbon atoms during the cracking, being s=r=n/2 when the n is an even number and s=r+1=(n/2+0.5) when n is an odd number (32).

2.3.1.1 Possible configuration

There are two main categories of configurations for hydrocracker process: single stage or two stage configuration (27). Hydrocracking process for FT waxes is single stage configuration.

2.3.1.1.1 Single-stage configuration

Single-stage is the simplest configuration, based on the use of a single reactor or two reactors (in series). When the target of the process is maximize the diesel production, this configuration is usually the most used. This configuration is represented in Figure 9. The process consists of the mixture of fresh feed along with unconverted hydrocarbons. Stream then passes throughout the catalyst bed in the presence of hydrogen. The output reactor effluent is introduced into different high and low pressure separator vessels in order to recover the hydrogen. Through a final distillation column, different final products are fractionated, obtaining: light (C5-80 ºC) and heavy (150-290 ºC) naphtha, which will be converted into high octane gasoline or will be transformed into petrochemicals; jet fuel/kerosene (150-290 ºC), for turbine engines; and diesel fuel (290-370 ºC). Non-converted hydrocarbons are obtained as the fractionation bottom product, which is usually recycled to the reactor.

The main advantages products obtained are:

- Naphtha: high octane rating, aromatic content and specific gravity
- Diesel: advantages low pour point, low cloud point, flash point, high cetane number and specific gravity.

There is a variation of this single-stage configuration, denominated as “once-through”. The difference is that there is no recycling of the unconverted oil from the first pass. The fractionation bottom products are used as steam cracker feed, FCC feed or lube base oil.

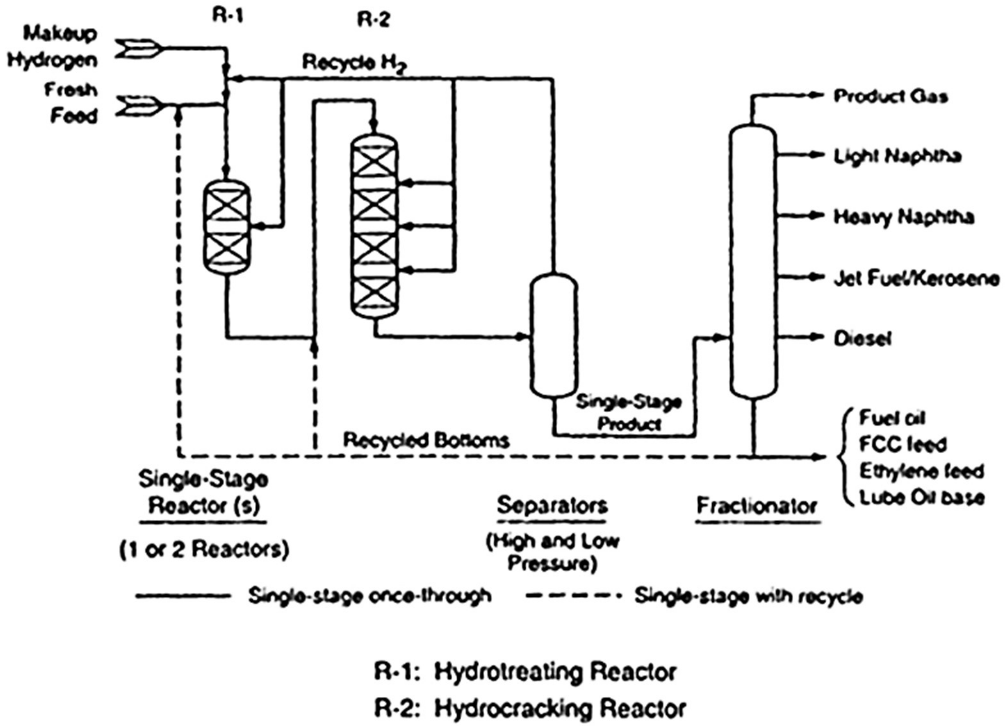


Figure 9. Single-stage configuration hydrocracking scheme with and without recycle ("once through") (27)

The configuration chosen for the hydrocracker developed in FFW project with Aspen HYSYS software is a single-stage configuration hydrocracker. The main objective in this section is increase the yield of the waxes to diesel. Reference texts often utilise of the single-stage hydrocracker after a vacuum distillation (when products are from LTFT) stage in the FT process. (4) (24).

2.3.2 FFW hydrocracking process design

The hydrocracking unit incorporated in Aspen HYSYS allows a choice between single stage and two stages configuration. As mentioned previously, the configuration for FFW hydrocracker is single stage, focusing on the production of diesel. The next option is the selection of the number of beds. In order to design a hydrocracking section with the minimum capital expenses (because small scale of process means CAPEX dominates the process costs), one reactor with two beds is considered. When the desirable product is naphtha, up to 6 beds are used; whilst where the desirable product is diesel, the quantity of beds is up to 4. (27)

Aspen HYSYS HCR includes a high pressure separator (to separate the hydrogen from the rest of the products) and amine scrubber. Amine scrubber has not been selected since is out of the scope of this equipment (there is no nitrogen compounds).

The final operation is the fractionator. The different cuts of the fractionator are: light ends, naphtha, distillate and bottom. HYSYS enables the selection of up to 3 cuts for naphtha and distillate fractions. For this study, one cut for each is selected. Bottom recycle to feed has been selected as well (single stage with recycle option), in order to recirculate unconverted waxes at the beginning of the reactor.

For hydrocracker design in Aspen HYSYS a template of the model that will be added to the simulation flowsheet is required. In order to create this template, the *feed type library* needs to be utilised. The hydrocracking section feed comes from a vacuum distillation tower, which means that is able to be charged as *“hvgo”* feed or “heavy vacuum gas oil”. The feed type has to been selected in order to create the most similar HCR model to the actual model, HYSYS counts on different predefined feed libraries according to the feed, such as FCC (fluid catalytic cracking), lvgo (light vacuum gas oil), heavy residue, etc. among others. The properties from the feed are obtained from the HYSYS tool *stream analysis-petroleum assay.*

The simulation of the model requires a change in the fluid package and the property model and component list – since the HCR is a petroleum refining model, the component lists have to be based on hypocomponents or assay, and hydrocracker model works with its own component list (HCRSRK). Hypocomponents are created through a new list based on boiling point ranges or this list can be charged from the HYSYS library regarding the model used (for this case, HCR). Assays can be created from several paths, using the oil manager or from the stream and it is necessary that the component list used in the stream is based on, at least partially, hypocomponents, as well as having knowledge about some properties of the blend, such as the distillation curve that can be checked in petroleum assay tool. The component list that HYSYS uses is based on its own components and it is necessary a hydrocracking transition to convert the products into other component list. Some of the components used by HCRSRK are: C4, C9A, HN1, etc. Each component has a legend that enables to decode it. Therefore, some changes in the simulation feed to hydrocracker are needed in order to solve the created model.

The hydrogen quantity required for the hydrocracker working is calculated from the inputs by the model.

Figure 10 and Figure 11 represent HYSYS hydrocracking flowsheet applied in FFW process.

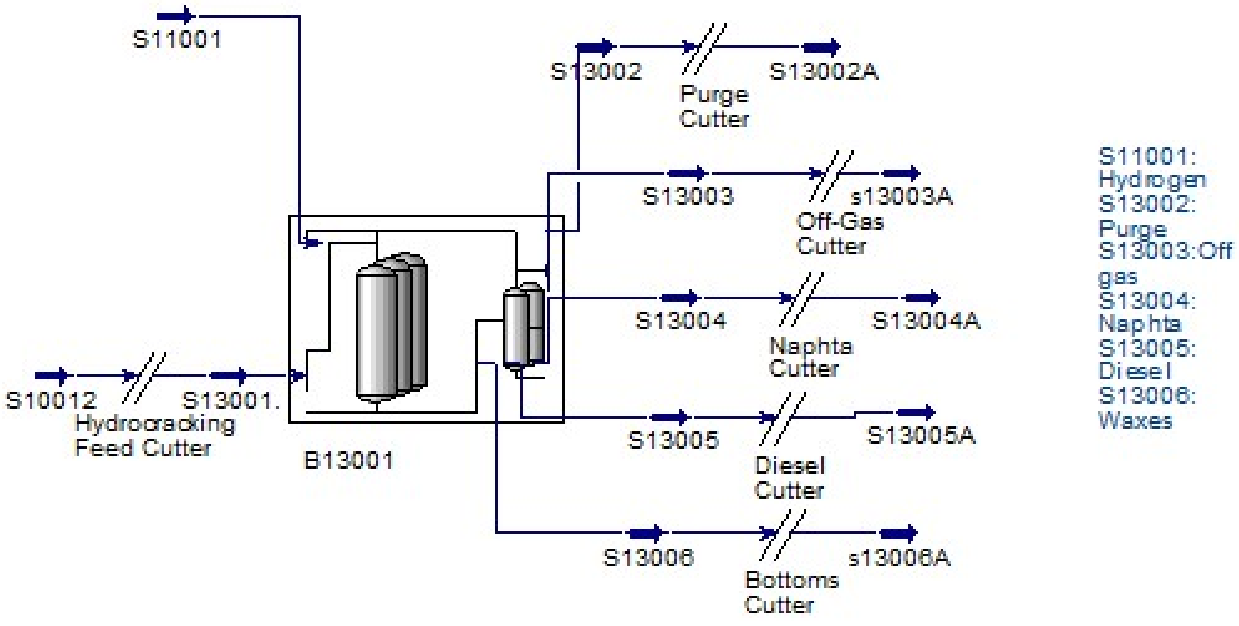


Figure 10. Hydrocracking section overview

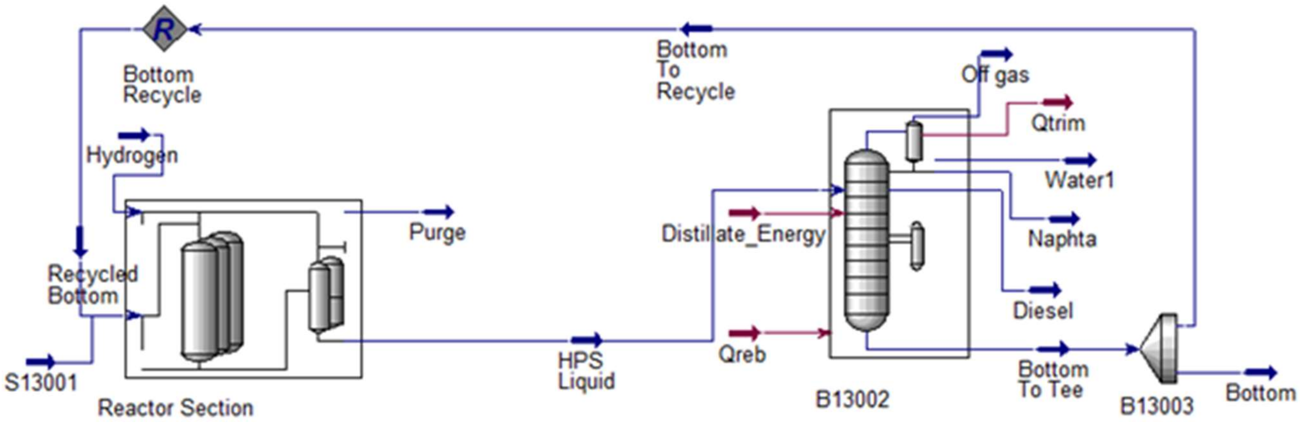


Figure 11. Hydrocracking whole section

The reactor model used by Aspen HYSYS is based on rigorous kinetics models (97 lump reaction kinetics). HCR model in HYSYS has 97 components in the reaction network, which belong to six groups: light gases, paraffin, naphthene, aromatics, sulphur compound and nitrogen compound (two last compounds are not within FFW post-gasification compounds); and 177 reaction pathways, which are the typical within hydrocracking reactions. The 97 model compounds are consistent with previous publications (33) .

The Fractional distillation column to separate the HCR reactor effluent into the different fuel cuts is modelled according to the petroleum distillation column module included in Aspen HYSYS, which enables a clear separation based on temperatures or molar flows.

2.3.2.1 Assumptions

Assumptions made for the hydrocracking process include:

- Consideration of pure hydrogen for the fresh hydrogen stream (hydrogen make-up).
- Steady state
- Feed is a heavy vacuum gasoil product.
- Intra-particle mass and heat transfer resistances are negligible.

2.3.2.2 Pressure drop

Pressure drop is calculated using HYSYS HRC model both for hydrocracking reaction and hydrogen stream. The results are shown after running the simulation. See section 2.2.4.1.

2.3.3 Unit Specification and Analysis

Prior to running the hydrocracker as a final simulation, several configurations were tested in order to shorten the range of some parameters, such as temperature and catalyst loading.

Results are represented in Figure 12 and Figure 13.

Both the temperature and the catalyst amount increase the overall conversion referred to C22+ (wt %). However, the increase of the temperature is not good for the middle distillate yield. High temperatures within the FT hydrocracking range (represented in Table 19) are more favourable to the naphtha yield in comparison to diesel, which is the desirable fraction.

Low temperatures (between 325 ºC (min.) and 350 ºC) are not favourable towards an acceptable conversion value, even considering an increase in the catalyst loading.

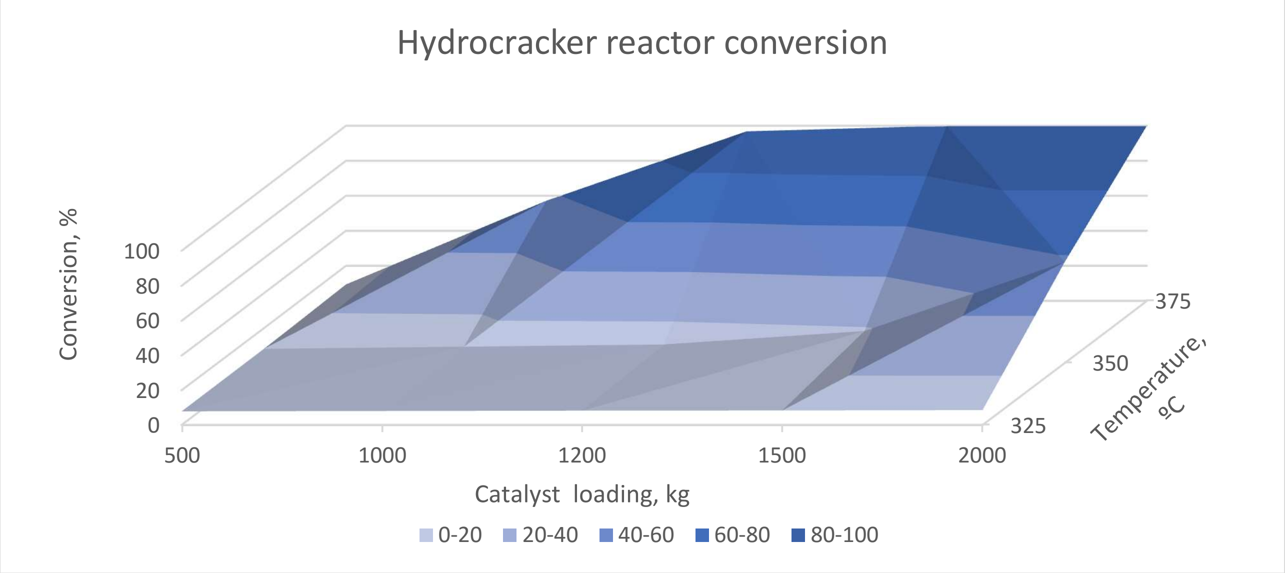


Figure 12. Hydrocracking conversion as a function of temperature and catalyst loading

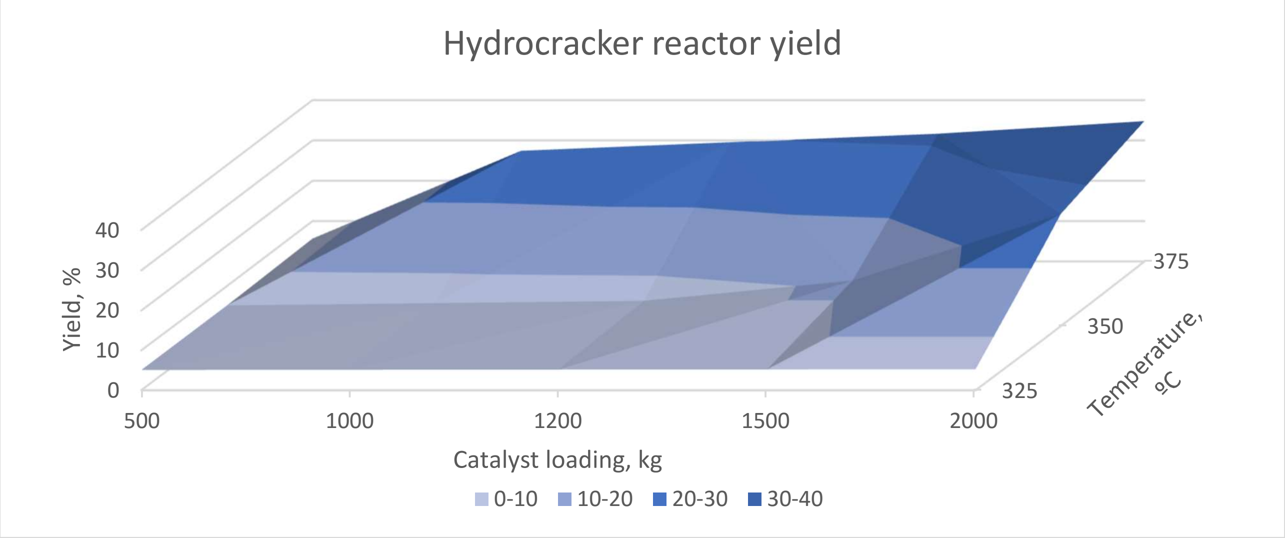


Figure 13. Hydrocracking middle distillate yield as a function of temperature and catalyst loading

The optimisation of conditions for the hydrocracking design, shown below, has been done for inlet temperatures in each bed between 325 and 375 ºC. The best case has been at 357 and 358 ºC (bed 1 and 2), where a compromise between a relatively low temperature and the best yield for middle distillates has been achieved. According to D4.2, hydrocracking conditions were 330 ºC at lab scale. Catalyst loading (WHSV) and temperature were then modified at steady state in order to achieve conversions between 5-99 % (D4.2) as well as were done in the simulations in HYSYS, where the system has been designed and optimised for the highest conversion of waxes (≈90 %) for the conditions listed in Table 20 (after an iterative process where these conditions have been varied).

2.3.3.1 Design Inputs

The design of hydrocracking section has been developed in Aspen HYSYS from the previous scale-up products obtained from FT reaction and later, FT separation. The catalyst used as reference has been platinum supported on silica-alumina (Pt/S40). In Table 20, the main inputs for hydrocracking section design appear. The inputs are the same as those in the base case.

Table 20. Inputs for hydrocracking section

Input	Value
Bed 1 diameter, m	1
Bed 2 diameter, m	1
Catalyst loading per bed, kg	900/1,200
Bed voidage (supposed)	0.5
Hydrocracker configuration	Single stage with recycle
Feed type	HVGO (Heavy Vacuum Gas Oil)
Feed mass flow, kg/h	167.6
Recycle mass flow, kg/h	51
Bed 1 inlet temperature, ºC	358
Bed 2 inlet temperature, ºC	359
H_2 temperature, ºC	50
H_2 pressure, bar	60
Purge fraction	0.1
Gas to oil ratio, m^3/m^3	1,500
Fractionator pressure (B13002), bar	10
Fractionator stage number (B13002)	9

Aspen HYSYS HCR model uses its own component list and thermodynamic model, which is denominated HCRSRK. The feed has to be utilised with a petroleum model. In this case, a petroleum transition into hypos (boiling point ranges) from the original component list (based on real components and with PRSV thermodynamic model) is utilised.

Hydrocracker design inputs are based on an iterative process according to the results obtained. The main inputs, such as temperature, hydrogen conditions and gas to oil ratio are based on literature.

In order to define the feed characteristics, a stream analysis of the feed that was readjusted after the template model was introduce in the flowsheet. It was undertaken as a first step in the calibration of the hydrocracker model. The feed stream characteristics are shown in Table 21.

Table 21. Hydrocracking feed characteristics

Parameter	Value
API Gravity	43.07
Specific Gravity, 60F/60F	0.81
Distillation Type	D2887
0% Point, ºC	352.07
5% Point, ºC	364.37

Parameter	Value
10% Point, ºC	376.67
30% Point, ºC	410.11
50% Point, ºC	434.49
70% Point, ºC	468.52
90% Point, ºC	495.14
95% Point, ºC	498.85
100% Point, ºC	503.21

The petroleum assay for this stream has been set by using the values shown in Table 22. The petroleum assay tool will estimate the petroleum properties and the composition of the hypocomponent list in order to generate the most proper results in the hydrocracking simulations. The assay inputs were obtained checking the petroleum properties of the HVGO stream.

Table 22. Hydrocracking feed. Petroleum properties

Property, value	Whole Crude	Cut 1	Cut 2	Cut 3	Cut 4	Cut 5	Cut 6	Cut 7	Cut 8
Initial Temp., ºC	IBP	IBP	364.4	376.7	410.1	434.5	468.5	495.1	498.9
Final Temp, ºC	FBP	364.4	376.7	410.1	434.5	468.5	495.1	498.9	FBP
Cut Yield By Wt, %	100	5	5	20	20	20	20	5	5
Std Liquid Density, kg/m^3		798	799	803	806	815	816	817	817
Sulphur By Wt, %	0	0	0	0	0	0	0	0	0
Naphthenes. %	0	0	0	0	0	0	0	0	0
Arom. By Vol. %	0	0	0	0	0	0	0	0	0
Pour Point, ºC	102.1	102.1	102.1	102.1	102.1	102.1	102.1	102.1	102.1
Freeze Point, ºC	102.1	102.1	102.1	102.1	102.1	102.1	102.1	102.1	102.1
Cloud Point, ºC	44.8	44.8	44.8	44.8	44.8	44.8	44.8	44.8	44.8
RON	42.4	42.4	42.4	42.4	42.4	42.4	42.4	42.4	42.4
MON	46.4	46.4	46.4	46.4	46.4	46.4	46.4	46.4	46.4

2.3.3.2 Outputs

The main outputs from the simulation of the HCR reactor are indicated in Table 23.

Table 23. HC outputs

Output	Value
Delta T-Rise in each bed, ºC	14.42
Conversion (C22+)	89.30
Pressure drop bed 1, bar	5.06e-007
Pressure drop bed 2, bar	7.15e-007
Hydrogen in bed 1 Consumption, m^3/h	396
Hydrogen in bed 2 Consumption, m^3/h	224

Output	Value
Hydrogen feed S11002, kg/h	12.03

Pressure drop in the HCR reactor is calculated by HYSYS and the results show small values for this parameter in both beds. The overall conversion obtained from the specified inputs is high (near 90 %), with a high recycle mass flow (51 kg/h) of waxes. There is an increase of the temperature in each bed, which has been calculated using the software. This increase is not in agreement with the literature, which indicates that FT hydrocracker operates in isothermal conditions.

The mass balance for the fractionator column is represented in Table 24.

Table 24. Fractionator column mass balance (hydrocracking section)

Parameter	Reactor output (hydrogen separator)	Off gas 13003	Naphtha 13004	Steam Water (Column)	Bottom To Tee	Diesel 13005
Temperature, º C	50.00	49.66	184.47	179.99	542.85	391.43
Pressure, bar	60	10	10	10	10	10
Molar Flow, kmol/h	1.60	0.30	0.66	0	0.22	0.43
Mass Flow, kg/h	219.32	12.09	66.86	0	61.84	78.53

As appeared in Table 24, the consumption of steam for distillation is almost null. The energy balance for this column is shown below in Table 25.This balance shows a distillate reboiler energy, and due to the amount of steam water in its stream, it is suggested that the own process gases which are present along this column are able to drag the vapours up to the top of the column, achieving the cuts desired similar to a classical reboiled stripper operation where the gases are used as stripper fluid.

Table 25. Energy consumption in hydrocracking separation section

Energy source	Value, kJ/h	Type
Condenser	2.38E+07	3 Phase Condenser
Distillate (steam)	2.39E+08	Energy Stream

Final products and their properties are represented in Table 26 and Table 27.

Table 26. Hydrocracking final cuts

Cut	Volume flow, m^3/h	Mass flow, kg/h	Volume, %	Weigh, %
Naphtha	9.27e-002	66.85	44.86	39.88
Distillate	8.49e-002	78.53	41.08	46.84
Bottom	1.16e-002	10.83	5.65	6.46

Table 27. Characteristics of hydrocracking final products

Property	Naphtha	Distillate	Bottom
API Gravity	54.23	39.07	21.09
Specific Gravity	0.76	0.83	0.92
Sulfur, %	-	-	-
Total Nitrogen, ppm wt%	-	-	-
Basic Nitrogen, ppm wt%	-	-	-
Paraffins, %	56.81	36.58	70.62
Aromatics, %	5.59	3.93	1.82
RON	53.80	15.20	-
MON	51.52	13.44	-
Smoke Point, mm	22.95	18.16	17.50
Freeze Point, ºC	-82.49	-25.36	-10.19
Flash Point, ºC	15.46	91.91	149.79
Cetane Index	28.47	60.74	35.55
Pour Point, ºC	-62.30	-15.62	1.57
Watson K	11.89	12.16	13.05
Viscosity, ºC	0.23	0.08	0.09
Density, kg/m^3	762.7	828.7	-

The diesel production has been maximized up to the quantity of 78 kg/h. However, naphtha quantity obtained is still elevated (66.85 kg/h). The results shown above are a compromise between the quantity of waxes obtained at the bottoms, the maximum production of diesel and the maximum conversion and yield to diesel. HCR model is very sensitive to small changes and to obtain the compromise between the listed factors it is necessary to make simultaneous changes in some specifications, such as bed temperature (according to published literature it should be in mild conditions), catalyst loading, hydrogen feed configuration, etc. Small changes in the system can increase the conversion, for which a high value has been achieved, but the yield is usually toward naphtha. This can be used to valorise this cut as a valuable product. Improvements can be made in the system with a post-treatment or a previous hydrotreatment together with hydrocracking as some authors suggest. Other treatment proposed for FT products refining is the olefin dimerization and oligomerisation as a classic thermal treatment. (34)

Cetane index is higher than commercial cetane index for diesel (50), although is not as higher as cetane index for the diesel in the upgrading sections (distillation) but is acceptable according the current standards (Table 28) and the density of the fuel is higher than the minimum (820 kg/m^3), therefore the hydrocracking diesel complies with some of the major requests. In Table 28, the different properties for middle distillates in actual FT plants are represented and the values for these parameters regulated by EN-590:2004. Although these results show very positive outcomes for the FFW scale-up, hydrocracking results are not reliable at all, since the right hydrocracker should be simulated taking into consideration a calibration of the model with actual parameters obtained during the lab experiments (curves ASTM of the products, distribution, etc), which have not been possible to be included at this stage of the simulations. As a first approach of the hydrocracking section, the results of the simulations are accepted and the different assumptions are taken as valid.

Table 28. FT diesel duel properties for different plants and European regulation (34)

Diesel property	PetroSA GTL diesel (HTFT)	Sasol Synfuels CTL diesel (HTFT)	Oryx GTL distillate (LTRFT)	South African SANS 342	European EN590:2004
Cetane number	52	55	87	45 min	51 min
Density @20 ºC, kg/m^3	815	829	771	800 min	820-845
Viscosity @ 40 ºC, cSt	2.5	2.2	2.4	2.2-5.3	2.0-4.5
Flash point, ºC	83	77	65	62 min	55 min
Cold filter plugging point, ºC	-4	-6	-7	-4 max	Regulated (by region and season)
Aromatic content, mass %	15	25	<1	Not regulated	Not regulated
Polynuclear aromatics, mass %	<1	<1	<1	Not regulated	11 max

A small amount of waxes is obtained as well. This outlet stream has been minimised and the maximum amount allowable of waxes are recycled through. These waxes can be used as a by-product, where a potential option can be their revalorisation through the production of lube oil or lubricant oils, similar to conventional refineries.

2.3.3.3 Validation

Hydrocracking of HTFT and LTFT is significantly different, due to the nature of both waxes at 360 ºC is different. Whilst HTFT contains around 25 % of aromatics, LTFT is mainly n-alkanes. In the same context, the products from FT wax hydrocracking are not the best for motor based on gasoline, they are more suitable for distillates and lubricant base production.

Taking into account the catalysts, Sasol uses sulphide base metal catalysts that are cheaper but less selective. However, Shell plant uses unsulfured noble-metal-promoted catalyst, e.g based on Pt/Alumina. (35)

There are not many published reports about real data of hydrocracker behaviour for FT process and currently, no FT biomass plant is operating at large scale mainly due to logistical problems and higher cost of the feedstock. During the 1970s, Sasol developed studies about real FT wax hydrocracking to produce transportation fuel. UOP has looked into the hydrocracking of Arge reactor based on Fe-LTFT wax with two kind of catalyst (unknown catalysts, likely silica-alumina and zeolite supports). Using a recycling mode, the maximum yield was around 80 % within 149-371 ºC cut. At this moment, there is a significant interest in the hydrocracking of FT waxes to convert into distillate fuels (36) (37)

Calemma et al studied the use of noble metal supported on amorphous silica-alumina as catalyst for the hydrocracking of LTFT wax. Middle distillate yields were obtained with a conversion up to 85-90 %, being the maximum yield around 82-87 %. (38). Calemma et al studies suggested that Co-LTFT is subjected to hydrocracking in the range of 319-351 ºC at H_2 pressure between 35-60 atm.

2.4 Methanation

2.4.1 Process Overview

The methanation process involves the production of methane, usually via the hydrogenation of carbon oxides as shown in the following equations (39):

$$3H_2 + CO \leftrightarrow CH_4 + H_2O \qquad -206 \text{ kJ/mol}$$

$$H_2O + CO_2 \leftrightarrow CO + H_2 \qquad 42\text{kJ/mol}$$

The process can take place at high or low temperature but as expected, the reactions are favoured by low temperatures and high pressures. As shown by the reactions, the process is highly exothermic and so the heat evolved during the reaction is usually recovered by the generation of high-pressure steam.

The process steps upstream of the methanation unit are designed to provide a near stoichiometric ratio of hydrogen to carbon oxides in the gas according to the methanation reactions. Downstream, usually some kind of fuel upgrading will be required to meet specifications. Often this includes the removal of water and carbon dioxide (39) and in this case, the N_2.

With the aim of producing synthetic natural gas it is important to note the composition of natural gas. For natural gas for the European market according to ISO 13686:2013 (40) the following table collects the specified composition (Table 29).

Table 29. European natural gas composition ***(Source: ISO 13686:2013)***

Component	Minimum % by weight	Maximum % by weight
Methane	70	98
Ethane	0.3	18
Propane	-	8.0
Butane	-	2.0
Pentane	-	0.2
Nitrogen	-	30.0
Carbon Dioxide	-	15.0
Each other component	-	0.1

2.4.1.1 Reactors

Methanation is usually either carried out in a series of adiabatic fixed bed reactors with inter-cooling and optional product recycle (e.g. TREMP or Lurgi methanation), or in a single fluidised bed reactor at isothermal conditions (e.g. COMFLUX methanation) (41). A reactor based on TREMP technology (Figure 14) (42) is used in the FFW project because it has the following advantages:

- Most efficient heat recovery - through production high pressure steam,
- A large temperature rises over catalyst results in high conversion and where used, a very low recycle ratio with corresponding energy savings and reduced equipment cost.
- It is very easy to implement and scale up compared to fluidized reactors or other cooled/isothermal concepts.

- It requires very little control during operation since the reactor is overloaded with catalyst to respond itself against deactivation.
- No attrition problems with the catalyst.

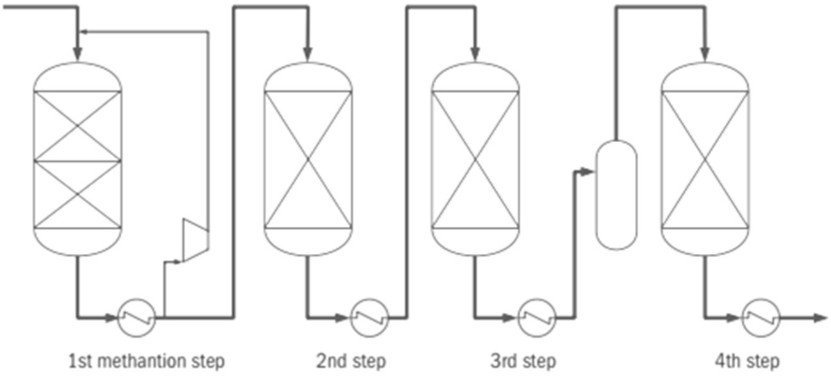


Figure 14: TREMP Methanation Train of Reactors

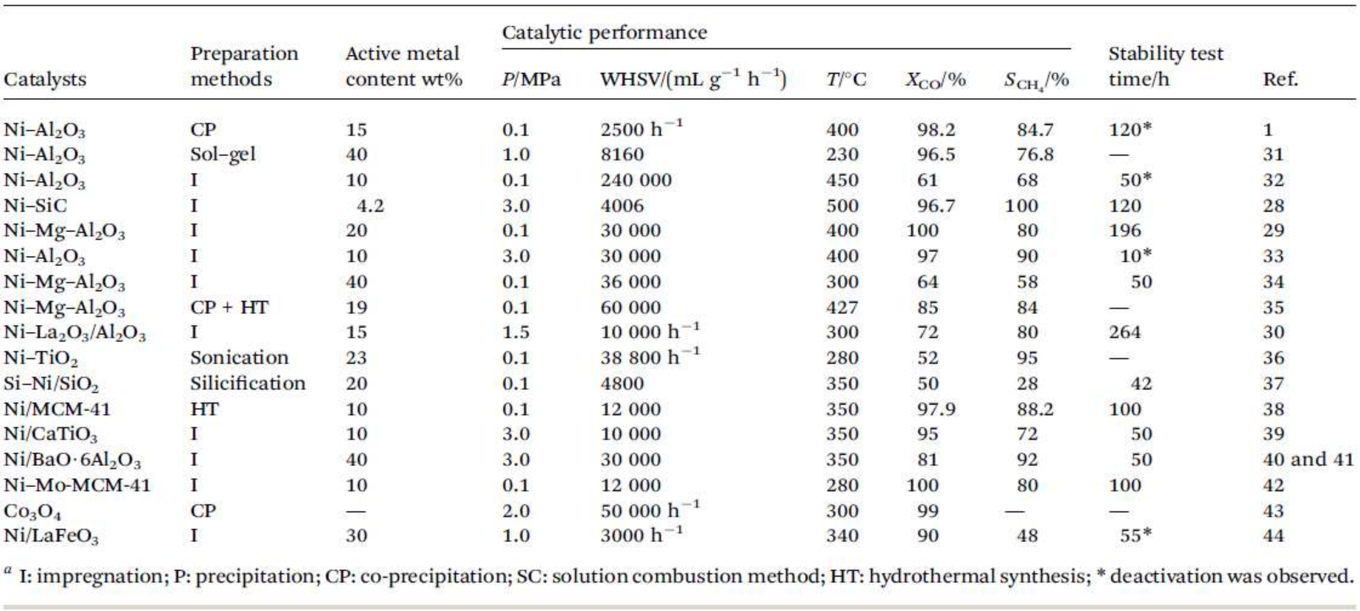
The reactions take place in the adiabatic fixed bed reactors. The heat of the reaction results in a high temperature increase, and usually a recycle is used to control the temperature rise in the first methanation reactor. The exit gas from the first reactor is cooled by production of superheated high pressure steam. Where utilised, the gas then enters the subsequent methanation stages. The number of reactors and the configuration of the process depend on the specific application.

2.4.1.2 Catalysts

Methanation catalysts are typically composed of active metal particles dispersed on metal oxide supports. So far, a number of active metals including Ni, Fe, Co, Ru, Rh, Pt, Pd, W, Mo and various oxide supports (Al_2O_3, SiO_2, TiO_2, SiC, ZrO_2, CeO_2, Cex $Zr_{1-x}O_2$) have been carefully investigated in carbon monoxide methanation reactions for SNG production.

Table 30 (43) lists some methanation catalysts studied in recent years. It should be noted that it is difficult to directly compare the performance of these catalysts because different reaction conditions were used. However, some general results can be summarized. Ni with loading amounts of 10–40 wt% is the main active metal for carbon monoxide methanation. Nearly 100% conversion of carbon monoxide and about 90–100% selectivity of methane could be obtained over optimized Ni catalysts at 3.0 MPa with H_2:CO feed ratio of 3.

Table 30 Summary of the carbon monoxide methanation catalysts developed in recent years (43)



Catalysts	Preparation methods	Active metal content wt%	Catalytic performance					Stability test time/h	Ref.
			P/MPa	WHSV/(mL g^{-1} h^{-1})	T/°C	X_{CO}/%	S_{CH_4}/%		
$Ni–Al_2O_3$	CP	15	0.1	2500 h^{-1}	400	98.2	84.7	120*	1
$Ni–Al_2O_3$	Sol–gel	40	1.0	8160	230	96.5	76.8	—	31
$Ni–Al_2O_3$	I	10	0.1	240 000	450	61	68	50*	32
Ni–SiC	I	4.2	3.0	4006	500	96.7	100	120	28
$Ni–Mg–Al_2O_3$	I	20	0.1	30 000	400	100	80	196	29
$Ni–Al_2O_3$	I	10	3.0	30 000	400	97	90	10*	33
$Ni–Mg–Al_2O_3$	I	40	0.1	36 000	300	64	58	50	34
$Ni–Mg–Al_2O_3$	CP + HT	19	0.1	60 000	427	85	84	—	35
$Ni–La_2O_3/Al_2O_3$	I	15	1.5	10 000 h^{-1}	300	72	80	264	30
$Ni–TiO_2$	Sonication	23	0.1	38 800 h^{-1}	280	52	95	—	36
$Si–Ni/SiO_2$	Silicification	20	0.1	4800	350	50	28	42	37
Ni/MCM-41	HT	10	0.1	12 000	350	97.9	88.2	100	38
$Ni/CaTiO_3$	I	10	3.0	10 000	350	95	72	50	39
$Ni/BaO\cdot 6Al_2O_3$	I	40	3.0	30 000	350	81	92	50	40 and 41
Ni–Mo-MCM-41	I	10	0.1	12 000	280	100	80	100	42
Co_3O_4	CP	—	2.0	50 000 h^{-1}	300	99	—	—	43
$Ni/LaFeO_3$	I	30	1.0	3000 h^{-1}	340	90	48	55*	44

[a] I: impregnation; P: precipitation; CP: co-precipitation; SC: solution combustion method; HT: hydrothermal synthesis; * deactivation was observed.

Although Ni catalysts are preferred in catalytic methanation reaction, some problems still exist, such as carbon deposition, sintering, $Ni(CO)_4$ formation, and sulphur poisoning during SNG production. Therefore, the stability of methanation catalyst is of great importance besides the activity and selectivity. It is well known that the deactivation of supported metal catalysts by carbon or coke formation is a serious problem in methanation process. The typical causes are: (1) polluting the active metal surface, (2) blocking the voids and pores of catalysts, (3) physical disintegration of the catalyst support.

2.4.2 FFW methanation process design

The gas stream from the three phase separator in Fischer-Tropsch, mainly composed by N_2, H_2, CO and CO_2, is mixed with a part of the H_2 generated in WGS process in order to get a flow rate control for H_2:CO of 3:1 in mole. Then the stream is ready to enter in the methanation process.

The developed methanation process is shown in the Figure 15. It is formed by three Equilibrium Reactors in serial with intermediate cooling and a water vessel separator at the end. The reactions added are the CO methanation and the reverse WGS reaction, described above. H_2:CO ratio is 3 in the feed (S12001), as well as TREMP process. A heat exchanger is incorporated after each reactor to lower the temperature to 300 ºC. For the first reactor, product recycling is used in order to avoid higher temperatures than 600 ºC in the outlet stream which needs to be compressed but not cooled since the feed comes with a low temperature.

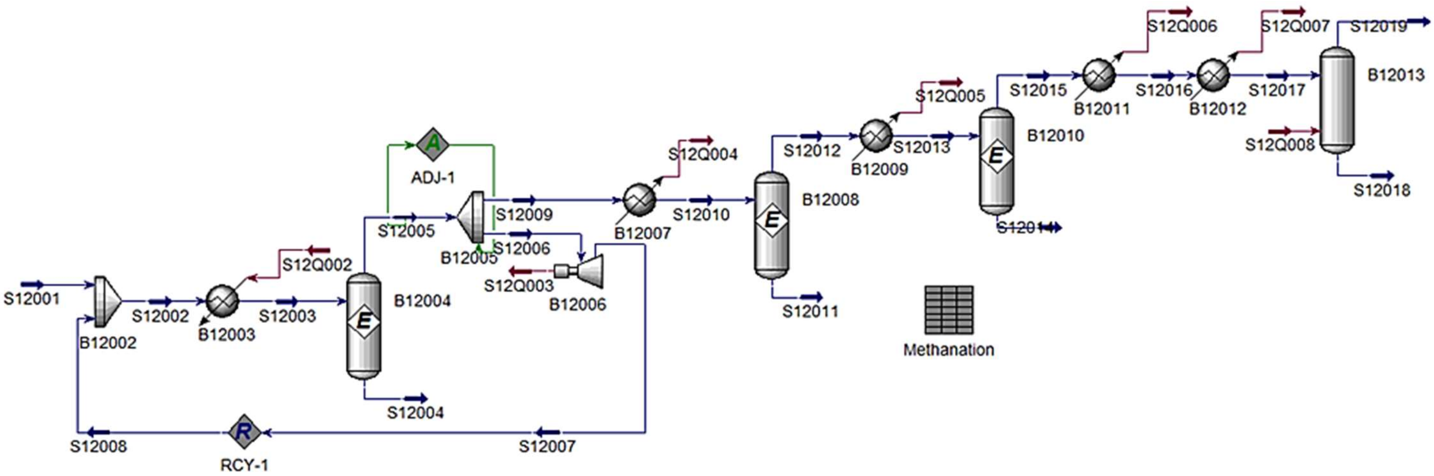


Figure 15. Methanation Process

The determination of the reactor volume (catalyst loading) in adiabatic fixed bed reactors is not based on kinetics (likewise in FT). It is based on the so-called “resistance number” (44). (This is information that will be provided after the activities in WP5).

Selectivity has also been obtained towards other longer carbon chains and CO_2 and at high temperatures, sub-products were not detected. In Table 31 is shown the stoichiometry inserted in Aspen HYSYS.

Table 31. Methanation stoichiometry coefficients

Component	Value	
	Reaction 1	Reaction 2
CO	-1	1
Hydrogen	-3	1
Methane	1	0
H_2O	1	-1
CO_2	0	-1

2.4.2.1 *Assumptions*

It is assumed that product distribution follows the selectivity obtained by KTH, as shown in the Figure 16, and that, at 600 ºC, sub-products (SC2, SC3, SC4) selectivity are negligible.

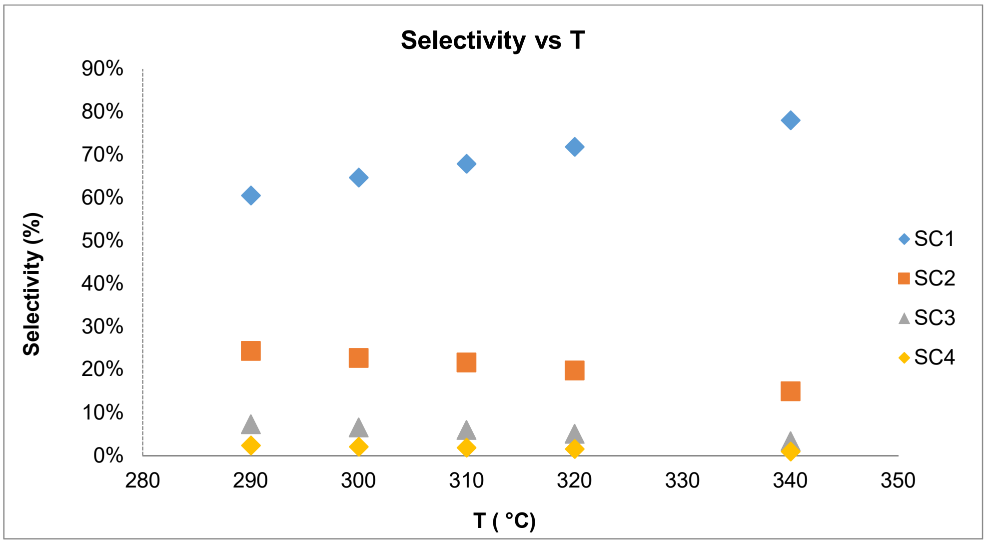


Figure 16. Methanation reaction selectivity versus temperature

Other assumptions:

- Equilibrium reactor (technology very close to equilibrium in reality) (39)
- Heat losses are 0 kW in each reactor.
- Process is under steady-state conditions.
- Input flow rate of reactive is constant.
- Catalyst deactivation are negligible.
- Intra-particle mass and heat transfer resistances are neglected.
- Temperature gradients inside the reactor are not assumed.

2.4.2.2 Pressure Drop

The pressure is estimated, rules of thumb establish that in adiabatic fixed bed reactor, it would be between 1-10 % of the inlet pressure (45), i.e. 0.3-3 bar in this case. Pressure Drop is fixed in 0.5 bar as assumed Heyne S. *et al.* (2010) (46).

2.4.3 Unit Specification and Analysis

2.4.3.1 Inputs

For the base model, the inputs in Table 32 are made. The sizing of the reactor is determined by the maximum outlet temperature (600 ºC), the adiabatic condition in the reactors and the reasonable drop pressure.

Table 32 Methanation model inputs

Input	**Value**		
Reactor	**1**	**2**	**3**
Inlet temperature, ºC	300	300	300
Outlet temperature, ºC	600	-	-
Heat Flow, kJ/h	0	0	0
Recycle Ratio	0.47	0	0
Pressure Drop, bar	0.5	0.5	0.5

The inlet streams (fresh feed, recycle and its combination heated) condition and flows are shown in the Table 33.

Table 33 Methanation inlet stream

Stream Name	S12001 (Feed)	S12002 (Recycle)	S12003 (Reactor Feed)
Vapour Fraction	1	1	1
Temperature, ºC	14.6	604.5	300 (Heated from 293)
Pressure, bar	32.7	30	30
Molar Flow, kmol/h	517.5	382.6	900.1
Mass Flow, kg/h	10,830	9,608	20,440
Mass fraction			
H_2O	0.0006	0.0699	0.0332
H_2	0.0295	0.0057	0.0183
CO	0.1406	0.0254	0.0864
CO_2	0.1434	0.1496	0.1463
Nitrogen	0.6437	0.6434	0.6435
Methane	0.0246	0.0884	0.0546
C2+	0.0080	0.0080	0.0080
C1=+	0.0091	0.0091	0.0091

2.4.3.2 *Outputs*

Methanation conversion is shown in the Table 34, both WGS inverse conversion and methanation reaction. In the first reactor, the reactive concentration is decreased, and then the reaction rate, using recycling in order to control the outlet temperature.

Table 34. Methanation process conversion and recycling

Conversion	Reactor 1	Reactor 2	Reactor 3	
WGS Inverse Reaction	2.27	10.15	0	
Methanation Reaction	68.38	85.13	91.69	**Total**
Total CO conversion	81.95	95.28	91.69	99.93
Outlet Temperature, ºC	600	417	316	

The sizing of the reactors is made using the GHSV used by the KTH for this conditions, 8000 Nl/L·h and the catalyst properties. The Length/Diameter relation is fixed as 4. The total amount of catalyst for this GHSV is 19,582 kg.

Table 35. Methanation reactor sizing

Parameter	Reactor 1	Reactor 2	Reactor 3
Volumetric Flow, NL/h	21,283,121	10,199,179	9,742,903

Parameter	Reactor 1	Reactor 2	Reactor 3
GHSV, L/h L	8,000	8,000	8,000
Catalyst Volume, L	2,660.39	1,274.90	1,217.86
Catalyst amount, kg	10,109	4,845	4,628
Catalyst Porosity	0.51	0.51	0.51
Bed Porosity	0.39	0.39	0.39
Reactor Volume, m3	8.901	4.265	4.074
Length, m	5.70	4.45	4.35
Diameter, m	1.41	1.10	1.09
L/D	4.0	4.0	4.0

Outlet stream composition from the third reactor and the two streams separated in the vessel are shown in the Table 36, as mentioned above, carbon dioxide, water and nitrogen have to be removed. Water is taken out using a pressure vessel at 15 ºC but the ways of removing nitrogen and carbon dioxide have to be studied at this point.

Table 36. Methanation process products

Stream	**Out from Reactor 3 (S12017)**	**Water (S12018)**	**Gas (S12019)**
Mass flow	**10,830**	**827.3**	**9,904**
Mass fraction			
H_2O	0.0858	0.9976	0.0004
H_2	0.0003	0	0.0004
CO	0.0001	0	0.0001
CO_2	0.1499	0.0005	0.1639
Nitrogen	0.6435	0	0.7038
Methane	0.1027	0	0.1123
C2+	0.0080	0	0.0088
C1=+	0.0091	0	0.0100

As an exothermic process, heat is released and it will be recovered in heat exchanger as water steam after each reactor. A high flow of HP steam is produced whilst a lower amount of LP steam is recovered to cool the main stream before it is introduced into the separator vessel (Table 37).

Table 37. Methanation services

Heat Exchanger	**T inlet, ºC**	**T outlet, ºC**	**Service**	**T inlet service, ºC**	**T outlet service, ºC**	**Mass flow service, kg/h**
B12003	293.2	300	Dowtherm	385	350	1,999
B12007	600	300	HP Steam Generation	250	251	2,941
B12009	416.8	300	HP Steam Generation	250	251	1,092
B12011	316	270	HP Steam Generation	250	251	417

Heat Exchanger	T inlet, ºC	T outlet, ºC	Service	T inlet service, ºC	T outlet service, ºC	Mass flow service, kg/h
B12012	270	140	LP Steam Generation	140	141	884
B12013 (Vessel)	140	15	Chilled Water	5	20	67,655

2.4.3.3 Validation

The results are compared to two references, TREMP process and the literature reviewed. Conversion is near 100 %, which is a reasonable value for a methanation process at 24 bar. At 30 bar, conversion is between 81 and 96.7 for one isothermal reactor in the research literature and almost 100 % in the adiabatic TREMP process at 30 bar. Comparison is in Table 38.

Table 38. Methanation processes comparison

	TREMP (47)	**Literature** (43)	**FFW methanation process**
Number of Reactors	4	1	3
Operation	Adiabatic	Isothermal	Adiabatic
Temperature, ºC	300 (In)	300 – 500	300 (In)
Pressure, bar	30	20-30	24
Conversion, %	99.9	81 – 96.7	99.9 (Total) First reactor: 82

2.5 Methane Upgrading

Due to the high content in nitrogen in the outlet methanation stream, advanced separation options should be considered. A case study has been done to know the composition in function of FT reactor conversion in case of a reduction of the nitrogen fraction could be achieved. In the Figure 17, the composition of the stream versus the conversion is shown.

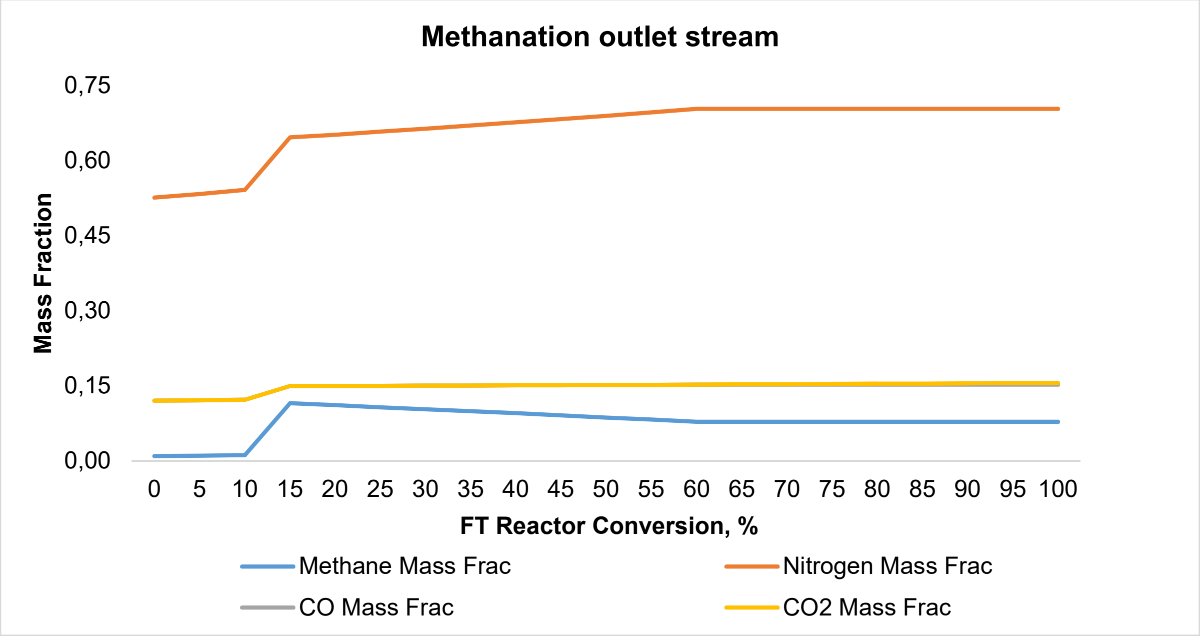


Figure 17 Fischer-Tropsch reaction conversion versus methanation outlet composition

CO_2 amount is also too high and does not meet the current European legislation. First, it is necessary to perform the nitrogen removal from the SNG product stream since the N_2 concentration is the highest. After N_2 has been removal, CO_2 removal will be performed in a similar system to the CO_2 cleaning for post-gasification, as designed in D3.4.

2.5.1 SNG N_2 Removal

Nitrogen removal from natural gas is a quite difficult task. Both pipeline and requirements specifications for natural gas limit the nitrogen content, which means that this component has to be removed. Currently, cryogenic distillation is the most well-known system for this operation. However, cryogenic distillation is expensive for small applications. Other path for nitrogen removal is pressure swing adsorption processes that have been applied in some limited cases. At this moment, membranes are in development for this purpose.

Due to the non-combustible nature of some components presented both in natural gas and synthetic natural gas, such as carbon dioxide and nitrogen, the legislation demands to remove from this product before to be sold. Although some processes are well-known and implanted to remove these contaminants in order to obtain high quantities of natural gas, it is not possible to apply in small systems due to the non-applicable scale economies (48).

Separation methods for natural gas can be based on thermodynamic and/or transport properties: vapour pressure, boiling points, solubility, adsorption capacity and diffusivity. The operations available are: (49)

- Heat transfer to create a new phase
- Absorption
- Adsorption
- Permeation by means of a membrane
- Chemical conversion to another product

The most important are absorption, adsorption and membrane technology.

a) **Absorption.** The main processes for natural gas cleaning using absorption are used to remove carbon dioxide and sometimes nitrogen through the selective absorption of methane. Nitrogen removal is not a common practice using absorption technology for natural gas cleaning purpose.

Currently, there are some commercial nitrogen removal processes, which operate as physical absorption of methane into a hydrocarbon oil for a gas feed rate between 2-30 MMscfd. The cost of this kind of solvent compression is not affordable for high scales.(50)

b) **Cryogenic distillation.** Due to the differences between the methane boiling point (-94.7 ºC) and nitrogen (-148.7 ºC). This difference between boiling points enables, through the study of the vapour-liquid curve, the separation of the two compounds using cryogenic distillation. It is easily designed using the McCabe-Thiele method for distillation, which will allow to obtain the ideal stages number for the column (the actual number of stages will be higher).

Nowadays, cryogenic distillation is the only demonstrated technology that can produce high recovery rates of methane at high purity (nitrogen content <3 %). Several companies have implanted this technology, such as Linde, Constain, Praxair, ConocoPhillips and APCI.

As main disadvantage, it is highlighted its high cost. (51)

The cost of cryogenic is high and can be sensitive to the plant dimensions. (52)

c) **Adsorption.** For gas natural industry, adsorption is used to clean the methane from other impurities: water, sulphur, mercury and heavy hydrocarbons. Adsorption processes are also used to remove carbon dioxide and nitrogen from natural gas obtained from different sources.

One of the most important parameters to assure the adsorption success is the right solvent selection, which is chosen based on the components separation desired.

Similar to absorption, separation can be carried out through an adsorption cycle and a regeneration stage using thermal-swing adsorption (TSA) and pressure-swing adsorption (PSA).

There is a wide range of solvents capable to separate methane and nitrogen at atmospheric conditions. Selected activated carbons are used for this purpose as American Energies Corporation, TGPE, and IACX, among others, describe.

d) **Membranes.** This technology offers some attractive advantages over other operations explained above such as absorption, adsorption and distillation (cryogenic). The main advantage is to work without the necessity of phase change and the low energy requirements along with a simple process and start up and shutdown procedures.

Membranes were implanted in natural gas industry during the 1980s and CO_2 capture is the most competitive application for membrane in natural gas area.

The selected technology is separation by means of a membrane. Membranes technology for separation of gases are sorted in different categories according to the manufacture materials: polymeric, inorganics and mixed matrix, although the classification also can be according to the separation mechanism: molecular diffusion or permeation. Polymeric membranes are classified as rubbery or glassy polymers. The selectivity of the membrane is function of the material.

The main development for membranes in natural gas has been focused on CO_2 removal. Due to the similar kinetic diameter between N_2 and CH_4, the separation by diffusion and the selectivity are not very good for polymer membranes. These parameters can be enhanced through the addition of inorganic fillers in order to synthetize mixed matrix membranes. Literature describes polymer membranes (in general terms) as a mediocre way to separate natural gas/nitrogen. (53)

However, inorganic membranes have shown better results for nitrogen/natural gas separation, achieving more than 10 of selectivity value through the use of silica based membranes and 2 magnitude order bigger values for permeances in comparison with polymeric membranes. (53)

There are two kind of membranes for this purpose: CH_4 selective membranes, where methane is more permeable than N_2, and it will be compressed after the membrane due to it will be out by the low-pressure side (permeate) and N_2-selective membranes, where methane will be separated in the retentate side. These configurations are shown in Figure 18.

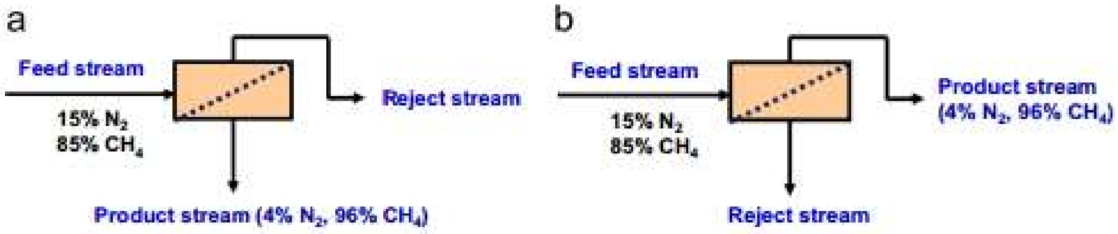


Figure 18. Membrane configurations for N_2 and CH_4 separation (53)

So far, the best results for N_2/CH_4 separation using inorganic membranes, such as SAPO-34 membranes, are provided in natural gas separation. SAPO-34 membranes are zeolite membranes (based on alumina), used for the separation of CO_2/CH_4, CO_2/N_2, CH_4/N_2, H_2/CO_2 and H_2/N_2 mixtures. (54) (55)

An ideal membrane to upgrade the SNG would preferentially permeate nitrogen and leave methane as a high-pressure product. Unfortunately, separation of nitrogen from methane is very difficult for polymer membranes. Most polymer have nearly equal permeation rates for nitrogen and methane, whilst some rubbery polymers are even slightly ‘methane-selective’. The polymers with highest combination of N_2/CH_4 selectivity and nitrogen permeability are perfluoropolymers but the data obtained have not been good enough. The nitrogen/methane ratio is such a difficult membrane separation is related to the molecular properties of the gases and the nature of the permeation process. (56)

Although the good results for inorganic zeolite-based membranes, the future for nitrogen removal from natural gas is expected for the polymeric membranes and at this moment is the commercial market for this technology. MTR has the NitroSep™ technology that is able to separate N_2 from CH_4 up to 4 % N_2 in the product gas stream. This membrane is a polymeric material with a spiral wound module type. The specifications for the membrane design (NitroSep) are in the Table 39.

Table 39. Design specifications for CH_4/N_2 separation membrane

Parameter	**Value**
Working pressure, bar	27-41
Working temperature, ºC	-9 up to +10 (57 max)
Permeation rate α	3-4
N_2 permeability, mol/MPa/m^2/s	0.03
Permeate pressure, bar	10,13
Feed pressure, bar	68

Parameter	Value
Feed temperature, ºC	10
Thickness, μm	1-5
Glassy membranes	
Fast gas	Nitrogen
Separation CH_4/N_2	200
Rubbery membranes	
Fast gas	Methane
Separation CH_4/N_2	100

2.5.1.1 Design

The separation mechanism and the design follow the same strategy explained in D3.4 (Chemical pretreatment) for nitrogen removal (from hydrogen) placed in base case.

2.5.2 Process Specs and Analysis

2.5.2.1 Inputs

As mentioned earlier, the components to separate are methane and nitrogen, the first one will have higher permeability and will pass further through the membrane.

Table 40. Membrane inputs

Parameter	Value
Compound A	Methane
Compound B	Nitrogen
Feed molar fraction (A)	0.158[2]
Feed molar fraction (B)	0.842
P_F, bar	28.5
T_F, ºC	4.6
l_m, μm	1
P_p, bar	4.5
Flow rate, mol/s	99.2
P_{MA}, mol/m^2·s·bar	$1.2\cdot10^{-8}$
P_{MB}, mol/m^2·s·bar	$3\cdot10^{-9}$
α*	3.9
r	0.158

---

[2] Molar fractions of H_2 and N_2 has been normalised to consider a binary feed.

2.5.2.2 Outputs

The design outputs are represented in Table 41.

Table 41.Design of hollow-fiber membrane for separation of N_2/CH_4

Parameter	Value
Molar fraction A (residue)	0.95
Molar fraction A (permeate)	0.07
θ (cut)	0.845
Permeate flow rate, mol/s	115.8
Residue flow rate, mol/s	241.1
Area, m^2	7,500

2.5.3 SNG CO_2 Removal

In order to comply with current European legislation and regulated normative, SNG produced in the FFW base case needs to be treated and its content in carbon dioxide should be decreased. Taking advantage of the CO_2 removal system used in post-gasification section through DEPG (design and explanation take place in D.3.4 Chemical Pre-treatment), the same system has been proposed for this purpose and will be shared the regeneration section both purposes.

As shown in Figure 19, the CO_2 removal is made up of a cooler, which reduces the temperature from post-N_2 removal, compression and an absorption column (absorber model), where the product to purify is introduced at the bottom of the tower and the regenerated solvent is introduced into the top of the column. The purified gas product stream will leave at the top of the tower, whilst the solvent containing the CO_2 and other potential co-products in small quantity, leaves at the bottom and is sent to the regeneration section common for hydrogen purification and methanation upgrading (see D3.4).

DEPG is widely used for CO_2 removal from natural or synthetic gas purposed. Aside from the CO_2 removal, DEPG or Selexol® solvent has a higher selectivity for other components such as linear or ramified hydrocarbons heavier than methane, which is an advantage in terms of decreasing the concentration of hydrocarbons, such as propane, in order to comply the current restrictions for SNG.

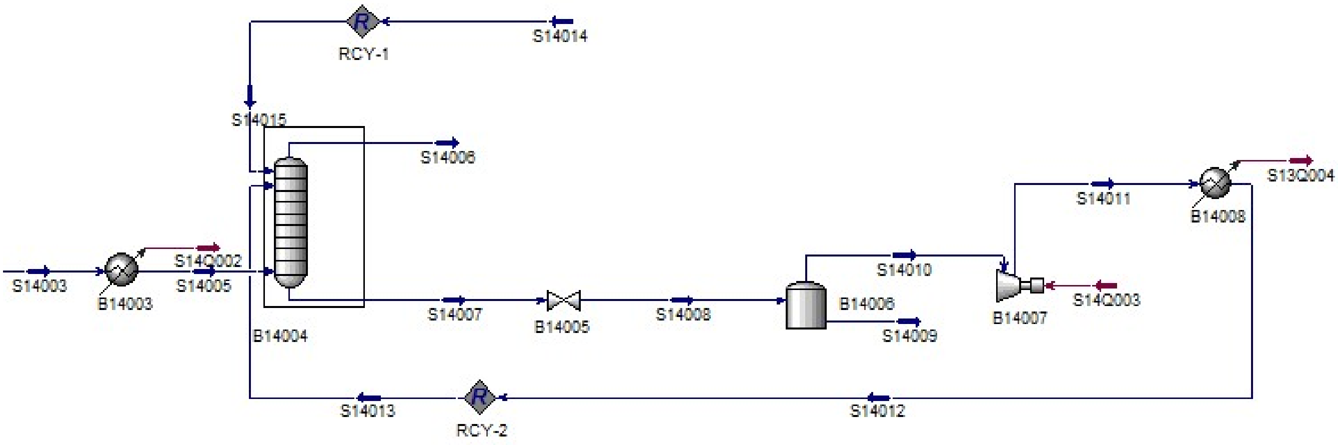
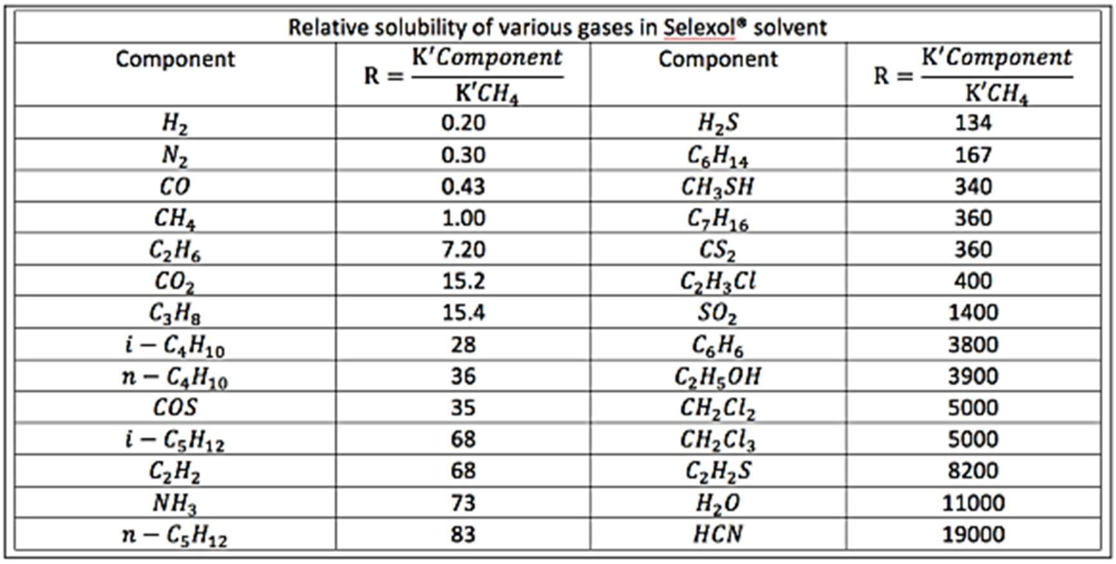


Figure 19. CO_2 removal system for methane upgrading

The solubility of the main gases in Selexol is represented in Table 42

Table 42. Solubility of gases in DEPG (57)



Relative solubility of various gases in Selexol® solvent			
Component	$R = \frac{K'Component}{K'CH_4}$	Component	$R = \frac{K'Component}{K'CH_4}$
H_2	0.20	H_2S	134
N_2	0.30	C_6H_{14}	167
CO	0.43	CH_3SH	340
CH_4	1.00	C_7H_{16}	360
C_2H_6	7.20	CS_2	360
CO_2	15.2	C_2H_3Cl	400
C_3H_8	15.4	SO_2	1400
$i - C_4H_{10}$	28	C_6H_6	3800
$n - C_4H_{10}$	36	C_2H_5OH	3900
COS	35	CH_2Cl_2	5000
$i - C_5H_{12}$	68	CH_2Cl_3	5000
C_2H_2	68	C_2H_2S	8200
NH_3	73	H_2O	11000
$n - C_5H_{12}$	83	HCN	19000

To build this simulation, Acid Gas fluid package has been imported into the Aspen HYSYS properties. This model is based on the PC-SAFT equation, where the properties have been validated through both literature and experimental data by Aspen Technology. This model assures a good prediction of the property behaviour for this absorption operation.

The assumptions made for this operation have been:

- All the nitrogen has been removed through the membrane before this CO_2 removal.
- Part of the other hydrocarbons has been previously removed. Any remaining compound will be removed in this system (in terms of propane, ethane, etc). Within the used component list for acid gas these components are not specified.

The mass composition for the SNG in the absorption column is shown in Table 43.

Table 43. SNG composition in CO_2 removal inlet

Compound	**Composition**
DEPG	-
CO	0.0004
CO_2	0.55
Hydrogen	0.001
H_2O	0.001
Nitrogen	0.07
Argon	-
Methane	0.37

The product stream (methane gas) obtained after the DEPG absorption column complies with the European standards as shown in Table 29. The mass composition and the SNG mass flow as final product is represented in Table 44.

Table 44. SNG final product composition

Component	Value
DEPG	-
CO	0.001
CO_2	0.124
Hydrogen	0.003
H_2O	0.000
Nitrogen	0.154
Methane	0.719
SNG total mass flow, kg/h	1,319

The absorbent is prior sent to a flash drum, and then to a stripper or regenerator column in order to remove the CO_2 and clean the absorbent. The regeneration is carried out in other section of the process. In this way the absorbents used for hydrogen CO_2 removal and methane upgrading are cleaned in the same equipment and it is not necessary the investment for another stripping column.

The absorption column has been designed as well. This type of columns can use either trays or packing. For absorption operations is recommended the use of packaging due to the high capacity, lower pressure drop and better options for construction materials (to avoid rust problems potentially generated by acid gas throughout the equipment). (57)

Physical solvents as Selexol® operate in a similar way to chemical absorption, showing some advantages as the energy savings due to the absence of chemical reaction and the heat associated to this operation. These similarities to chemical absorption suggest to use random packaging such as IMTP rings. (58)

Absorption column design inputs and outputs are represented in Table 45.

Table 45. CO_2 removal column design for methane upgrading

Parameter	Value
Absorption	Physical
Number of stages	10
Top pressure	51.70
Bottom pressure	51.80
Column diameter, m	0.30
Column height, m	5
Packing	Metal IMTP
Regenerated DEPG mass flow, kg/h (from section 5)	38,711

Other equipment is used to reach the specifications of the process, such as the vessel drum, heat exchangers and compressor. Specifications and energy balance are shown below

Table 46. Auxiliary equipment in methane upgrade section (CO_2 removal)

Equipment	Inlet temperature, ºC	Outlet temperature, ºC	Inlet pressure, bar	Outlet pressure, bar	Q, kJ/h	Efficiency, %
B14003 (cooler)	166	20.01	52	52	725049	100
B14005 (pressure valve)	13.97	14.24	51.8	34.8	-	0.7
B14006 (vessel drum)	14.24	14.24	34.8	34.8	N/A (Tank)	N/A
B14007 (compressor)	14.24	54.16	34.8	52	5357	75
B14008 (cooler)	52.16	20.01	52	32	5907	100

2.6 FFW Base Case Energy Integration

FFW base case has been energetically integrated in order to reduce the energy consumption and to calculate the energy savings for the scale-up of the whole process (described along this deliverable and D.3.4) which included, aside from the FT reaction and product upgrading and SNG, CO_2 removal and WGS. Gasification, Gas cleaning, Hydrocracking could not have been included since they are in separated simulations and are themselves integrated. The used tool for this aim has been *Aspen Energy Analyzer*, included within Aspen HYSYS 8.8 as an integer tool (older versions did not incorporate this tool in HYSYS).

2.6.1 Energy Integration Overview

FFW project includes some sections which are exothermic and generate an excess of energy (such as Fischer-Tropsch and methanation). On the other hand, especially when products need to be treated, there are some points in the process that need to be chilled or cooled in order to carry out the operations in a right way. Either way, there are several streams along the process that need to be cooled or heated, depending on the unit operation performed. Sometimes the process equipment is which needs a heat exchange due to the specifications and conditions (e.g. to maintain the isothermicity within FT reactor). These streams could be combined in order to reduce the required services and achieve important energy savings for the process.

2.6.2 FFW Energy Integration Design

Energy integration is modelled through Activated Energy Analysis in HYSYS v8.8. This tool enables to calculate the potential energy savings throughout several scenarios and the calculation of GHG emissions. The entire analysis is carried out within the current simulation and it is possible to add other streams to the process. This last point has been very important since not all the parts of the process have been able to be included in the same flowsheet in HYSYS (gasification is simulated by Aspen

Plus due to the solid modelling is better performed using this AspenTech software and hydrocracking has been carried out in other HYSYS flowsheet).

Activated Energy analysis assesses each heat exchanger of the process and determines a target value of energy saving and the utilities.

Besides, Aspen Energy Analyzer software allows performing the composite curves and the pinch analysis for the system so that it would be possible to determine which configuration would be the economic optimum.

2.6.3 Unit Specification and Analysis

The targets set by Activated Energy Analysis are displayed in the Figure 20. For each of total utilities, heating utilities, cooling utilities, and carbon emissions, the current value and target value are shown. Energy targets are the minimum amount of utilities needed to satisfy the process stream requirements (59). The energy target values are calculated depending on the Utility Load Allocation Method and pinch temperature.

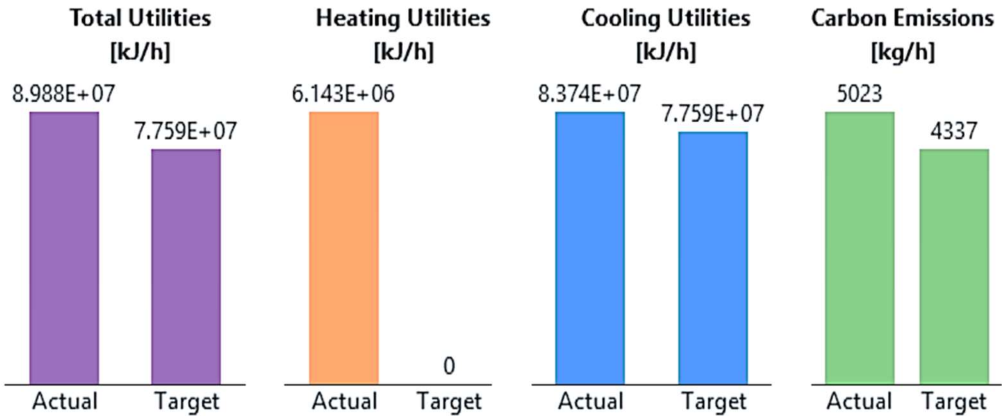


Figure 20. Targets set by Aspen Energy Analyser

Once the target is calculated, Aspen Energy Analyzer will plot the Composite Curves (Figure 21). This software includes The Recommend Near-optimal Designs (RND) that generate near optimal heat exchanger network designs. 10 possible configurations were created, as below

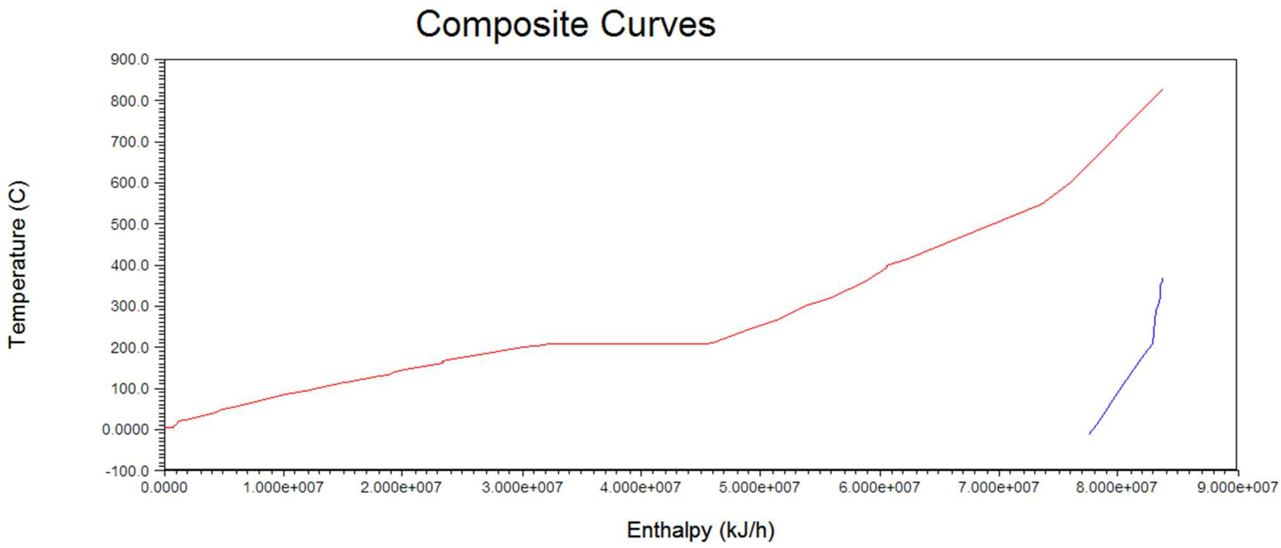


Figure 21. Composite curves

Table 47. Recommend Near-optimal Designs

Design	Total Cost Index, Cost/s	Area, m^2	Units	Shells	CAPEX, Cost	Heating, kJ/h	Cooling, kJ/h	OPEX, Cost/s
Simulation Base Case	-1.80E-02	2,776	27	45	1,349,674	6,143,375	83,737,727	-3.18E-02
Design1	-2.15E-02	2,746	42	62	1,319,419	95,391	77,689,744	-3.50E-02
Design2	-2.16E-02	2,753	42	61	1,326,029	95,391	77,689,744	-3.52E-02
Design3	-2.17E-02	2,710	44	71	1,338,561	95,391	77,689,744	-3.53E-02
Design4	-2.17E-02	2,692	39	70	1,293,036	95,391	77,689,744	-3.49E-02
Design5	-2.17E-02	2,587	43	70	1,283,265	95,391	77,689,744	-3.48E-02
Design6	-2.17E-02	2,587	43	70	1,283,265	95,391	77,689,744	-3.48E-02
Design7	-2.18E-02	2,662	42	71	1,299,520	95,391	77,689,744	-3.51E-02
Design8	-2.20E-02	2,647	41	61	1,278,760	95,391	77,689,744	-3.51E-02
Design9	-2.27E-02	2,616	37	57	1,217,720	95,391	77,689,744	-3.51E-02
Design10	-2.77E-02	2,557	34	57	1,166,683	95,391	77,689,744	-3.49E-02

The optimum chosen design is highlighted in blue colour, which is the design with lowest CAPEX and the maximum total index cost for a supposed project life of 10 years. This value is negative because Aspen considers the remaining generation of high energy container services such as High Pressure Steam that can be used for the production of self-electricity, for example.

The heat exchanger net is described in the Table 48.

Table 48. RND developed

Heat Ex.	Type	Load, kJ/h	Cost Index, Cost	Area, m^2	Shells	LMTD, C	Overall U, kJ/h·m^2·C	F Factor	Hot Stream	Hot T in , C	Hot T out, C	Cold Stream	Cold T in, ºC	Cold T out, ºC	dT Min Hot, ºC	dT Min Cold, ºC
E-001	Cooler	3,984,092	30,935	59.2	1	136	494	1.00	S12009 To S12010	539	300	HP Steam Generation	250	250	289	50
E-002	Cooler	6,028,273	27,671	40.3	2	47	6,127	0.99	S03006 To S03007	323	181	MP Steam Generation	174	175	148	7
E-003	Cooler	2,434,468	15,618	11.4	1	40	5,236	1.00	S03006 To S03007	181	150	LP Steam Generation	124	124	57	26
E-004	Cooler	129,056	10,560	0.6	1	248	814	1.00	S04003 To S04005	270	265	Chilled Water	15	25	245	250
E-005	Cooler	13,028,037	69,754	219.6	1	85	697	1.00	S09Q003	210	210	LP Steam Generation	124	125	85	85
E-006	Cooler	3,294,811	49,959	111.7	2	35	833	1.00	S04003 To S04005	265	127	LP Steam Generation	124	124	141	3
E-007	Cooler	2,179,950	23,253	28.1	2	31	2,001	0.98	S09005 To S09006	129	15	Chilled Water	12	15	114	3
E-008	Cooler	1,648	10,022	0.0	1	147	1,116	0.99	S09005 To S09006	210	129	Chilled Water	15	25	185	114
E-009	Cooler	5,970	10,674	0.7	2	13	766	0.85	S14011 To S14013	52	20	Chilled Water	15	25	27	5
E-010	Cooler	4,235,411	66,411	171.8	2	38	684	0.95	S03Q005	150	20	Chilled Water	15	25	125	5
E-011	Cooler	5,056,671	74,243	202.1	2	95	263	1.00	S04001 To S04002	362	150	LP Steam Generation	124	125	237	26
E-012	Cooler	2,686,458	45,445	96.1	2	28	1,468	0.99	S09005 To S09006	210	129	LP Steam Generation	124	125	85	5
E-013	Cooler	2,802	10,288	0.2	2	13	1,110	0.85	S06007 To S06002	50	20	Chilled Water	15	25	25	5
E-014	Cooler	959,080	13,676	5.7	2	42	3,181	0.94	To Condenser To S10AS004	137	25	Chilled Water	15	25	112	10
E-015	Cooler	1,990,358	23,619	34.6	1	86	684	0.98	S12Q008	140	76	Chilled Water	15	25	115	62
E-016	Cooler	1,859,459	25,619	41.0	1	98	464	1.00	S12012 To S12013	417	300	HP Steam Generation	249	250	167	51
E-017	Cooler	2,068,962	57,771	139.6	2	23	684	0.93	S12Q008	76	10	Chilled Water	5	12	64	5
E-018	Cooler	2,785,537	69,639	219.1	1	295	43	1.00	S02001 To S02002	551	400	MP Steam Generation	174	175	376	226
E-019	Cooler	2,651,985	41,227	82.0	2	70	461	1.00	S12015 To S12017	316	140	LP Steam Generation	124	125	191	16

Heat Ex.	Type	Load, kJ/h	Cost Index, Cost	Area, m^2	Shells	LMTD, C	Overall U, $kJ/h \cdot m^2 \cdot C$	F Factor	Hot Stream	Hot T in , C	Hot T out, C	Cold Stream	Cold T in, ºC	Cold T out, ºC	dT Min Hot, ºC	dT Min Cold, ºC
E-020	Cooler	3,242,473	56,252	134.1	2	91	266	1.00	S03004 To S03005	397	200	MP Steam Generation	174	175	222	26
E-021	Cooler	725,050	21,446	23.4	2	42	783	0.95	S14003 To S14005	166	20	Chilled Water	15	25	141	5
E-022	Cooler	3,291,509	46,593	100.0	2	49	685	0.96	S04003 To S04005	127	20	Chilled Water	5	12	115	15
E-023	Cooler	14,256,866	116,791	453.7	1	318	99	1.00	S02003 To S02004	827	400	HP Steam Generation	249	250	577	151
E-024	Cooler	790,818	16,957	14.9	1	32	1,642	1.00	S07012 To S07014	8	7	Refrigerant 1	- 25	- 24	32	32
E-025	Heater	54,951	12,452	4.1	1	25	752	0.87	Dowtherm	385	365	S10005 To S10009	340	361	24	25
E-026	Heater	23,140	10,850	1.1	1	37	603	0.96	Dowtherm	365	356	S10005 To S10009	304	340	25	53
E-027	Heater	17,300	10,814	1.0	1	27	631	0.99	Dowtherm	356	350	To Reboiler TO S0012	322	330	26	28
E-028	Exchanger	21,818	11,285	1.4	3	40	495	0.81	To Condenser TO S10010	125	56	S09003 To S09004	- 13	105	20	69
E-029	Exchanger	2,194,500	59,737	174.6	1	318	41	0.97	S02001 To S02002	551	400	S09003 To S09004	105	210	341	296
E-030	Exchanger	209,852	15,096	10.1	1	263	79	0.99	S02003 To S02004	827	400	S12002 To S12003	293	300	527	107
E-031	Exchanger	2,510,208	75,146	163.6	5	26	528	0.79	S09005 To S09006	129	15	S09003 To S09004	- 13	105	24	28
E-032	Exchanger	1,024,748	13,997	7.5	1	357	413	0.97	S12009 To S12010	600	539	S10001 To S10003	16	370	230	523
E-033	Exchanger	85,209	12,758	3.3	4	35	585	0.80	To Condenser TO S10010	265	125	S09003 To S09004	105	210	55	20
E-034	Exchanger	1,648	10,125	0.1	1	413	41	1.00	S02001 To S02002	400	400	S09003 To S09004	- 13	- 13	413	413

Utility	**Use**	**Cost Index, Cost/s**	**Load, kJ/h**	**Effective Cp, kJ/kg·C**	**Inlet T, ºC**	**Outlet, ºC**	**Flow, kg/h**
Chilled Water	Cooling	9.20E-04	15,589,796	3	5	25	259,830
LP Steam Generation	Cooling	-1.53E-02	29,152,430	2196	124	125	13,275
HP Steam Generation	Cooling	-1.39E-02	20,100,417	1981	249	250	10,147
MP Steam Generation	Cooling	-7.33E-03	12,056,283	1703	174	175	7079
Refrigerant 1	Cooling	6.02E-04	790,818	4	-25	-24	197,704
Dowtherm	Heating	9.27E-05	95,391	3	385	350	908
	Total	-3.49E-02					

For Gasification and Gas Cleaning, energy requirements have been estimated since it could not have been integrated with the rest of the process, whilst Hydrocracker has not heat exchangers because it is a model and they are included in it. The estimations are based on an 80% approach of the target explained before. Therefore, there will be heaters and coolers only and heat exchangers would have to be found in an accurate study.

Table 49. Gasification and gas cleaning heat exchanger net

Heat Ex	**Type**	**Load, kJ/h**
E-035	Heater	377,805
E-036	Heater	1,411,467
E-037	Heater	303,422
E-038	Heater	1,641,087
E-039	Cooler	2,857,699
E-040	Cooler	492,986
E-041	Cooler	2,785,537
E-042	Cooler	14,256,866
E-043	Cooler	47,60,400
E-044	Heater	941,880

2.7 Base case summary

FFW base case developed throughout this section explains the synthesis of different products, such as diesel and synthetic natural gas as target product and naphtha as secondary product, through the performance of different processes:

- Fischer-Tropsch reaction. Modelled through a slurry bed reactor using CSTR model, this section aims to obtain long chain paraffins. The main paraffin amounts are between C10 and C21+. Separation stages allow to obtain some final products before hydrocracking.
- Hydrocracking. This section breaks down the heavy vacuum gas oil, obtained from the last FT separation column, into different short chain paraffins. Several analysis have been carried out to maximise the diesel production. The different parameters taken into account have been the catalyst loading, the bed temperature, the middle distillate yield (to diesel) and the conversion.

High conversions enable high naphtha yields, whilst low temperatures make a low conversion. The compromise between parameters and the maximum diesel production has been found between 350 and 360 ºC as inlet temperature in each bed (the reactor is made up of two beds).

- Methanation. SNG is synthetized along methanation equilibrium reactors with cooling systems. Due to the high nitrogen concentration in the feed, is it is necessary the consideration of a membrane and an absorption system that will be able to remove this amount in order to meet the European requirements for this gas. Therefore, a methane upgrading section has been designed for this purpose.
- According to the decisions and conclusions in D.4.1, it is more feasible an increase in the ratio SNG/diesel. The results obtained at this point reported a ratio of 0.142 kg/diesel/Nm^3 of SNG. The production ratio achieved during the base case simulation is 0.30 kg diesel/Nm^3 SNG[3].

The total mass flows of the process products and by-products are represented in the Figure 22. Energy flows are represented in the Figure 23 and equipment list appears in Table 51.The efficiency of this part of the up-scaling of FFW project (excluding chemical pre-treatment explained along D.3.4) is a 72 %.

Table 50 and Table 51 show in more detail the M&E balance for the base case processes developed along this section, where the inputs come from the processes detailed in D3.4 (see this deliverable for further information). The results also are shown per kg of biomass for the task 6.1 about the LCA.

Figure 26 shows a global vision of the entire FFW up-scaled process (base case).

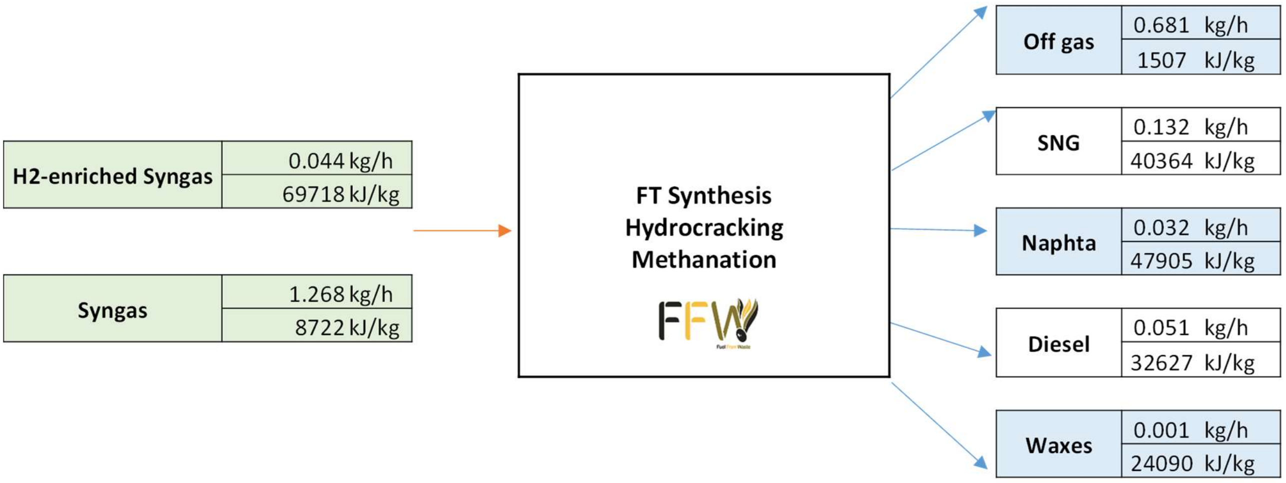


Figure 22. FFW Products (White) and By-Products (Blue) Mass Balance for base case

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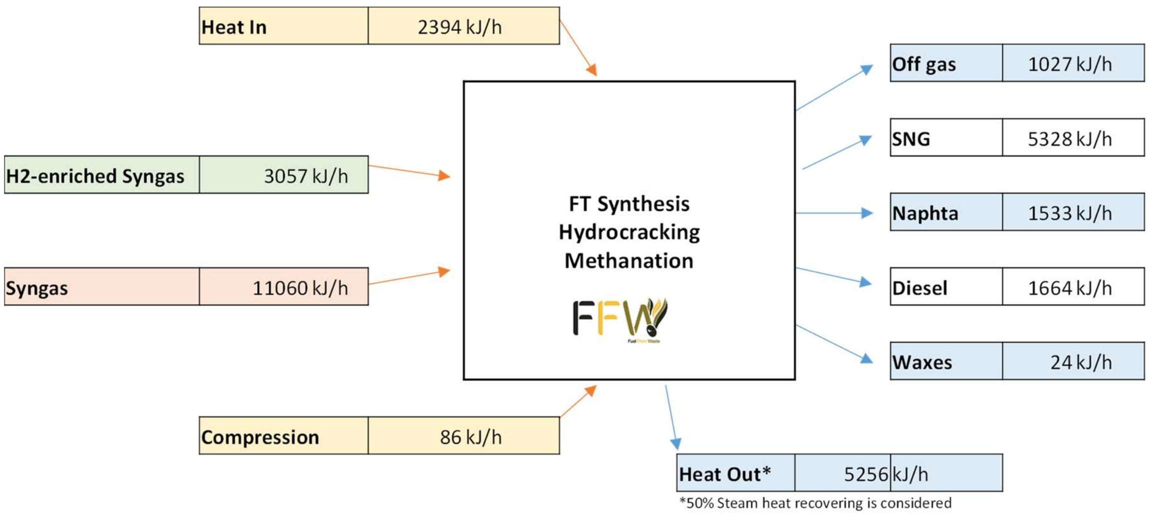
[3] kg of diesel are expressed as the addition of all diesel streams (atm. Column, vacuum column and hydrocracking) and Nm^3 is considered the volumetric flow of the SNG stream after upgrading.



$$\text{Process efficiency} = \frac{5328+1533+1664+24+2373}{3057+11060+2394+86} \qquad 72\%$$

Figure 23. FFW Energy Balance for base case

In Figure 24 and Figure 25, the yields to products obtained during FT and after hydrocracking stage are represented and compared with yields obtained by KTH at lab scale according to D.4.1 (in the same conditions T=210 ºC and 20 bar). The differences between before and after hydrocracking process remain the same for SNG and LPG, especially production of LPG shows similar results with experimental activities. However, the product distribution for naphtha, diesel and waxes is around a half that reported by experimental activities. This results are mainly due to the difference of syngas purity, which implies the presence of products (water, methane, CO_2) in the feed stream in FT process and the differences between the CO conversion, which has been fixed at 40 % for experimental activities at lab scale and 60 % for the scale up through simulations. Some differences can be also observed due to the thermodynamic model. Literature references collects in a high extension the use of RKS or PR. Nevertheless, due to the presence of alcohols (polar compounds), the use of these thermodynamic models is unfeasible with Aspen HYSYS, so the selected model according to conventional schemes has been PSRV in order to consider the prediction of alcohols.

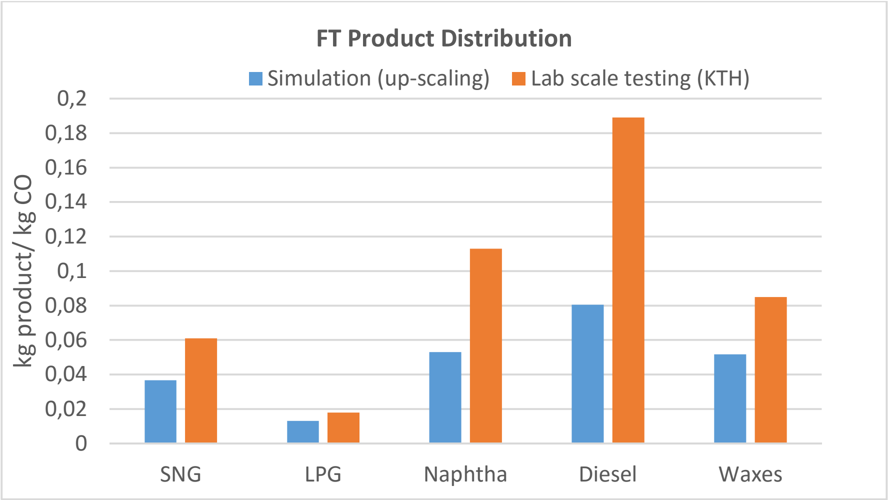


Figure 24. FT product distribution

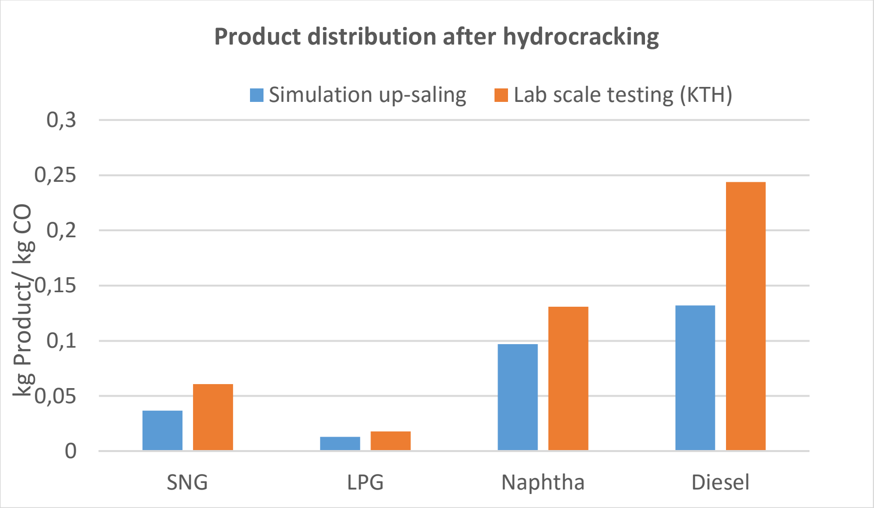


Figure 25. Product distribution after hydrocracking of waxes

After hydrocracking, the product distribution for naphtha and diesel have increased in comparison before this stage. Specially, naphtha production. Diesel yield is lower, which shows the throughput to naphtha in this operation. The conditions during the simulation have been a bit different, since the hydrocracking activities were developed with a conversion around 60 % (as D.5.3 details) in order to maximise diesel production, whilst the conversion during the simulations has been maximised up to near 90 % in order to obtain the minimum amount of waxes and always taking into account the production of diesel as target. Hydrocracking equipment should be calibrated according to the experimental distribution (ASTM curves of the different products, content for each product cut, etc.) in order to obtain more accurate results related to this stage of the process.

Table 50. FFW process mass balance-base case

Process	**Materials in/out**	**Amount in (kg/h)**	**Per 1kg of biomass (kg/h)**	**Comments**	**HHV, kJ/kg**
Fischer-Tropsch	CO-enriched	12,679.9	1.268		
	Hydrogen-enriched - 1	238.8	0.024	51.36 % of the Hydrogen-enriched stream	
	Gas to Methanation	-10,641.4	-1.064	H_2: 0.240; CO: 0.116; CO_2: 0.071; N_2: 0.530; CH_4: 0.030	
	HCs to separation	-875.7	-0.088	Liquid products from F-T reaction	
	Water	-1,401.6	-0.140	H_2O: 0.997; MetOH: 0.003	
F-T Product Separation	HCs from F-T	875.7	0.088		
	Stripping Steam inlet	100.0	0.010	Water	
	Stripping Steam outlet	-100.0	-0.010	Water	
	Off Gas	-20.5	-0.002	H_2: 0.002; CO: 0.005; CO_2: 382; N_2: 0.232; Light HC: Rest	16595

Process	**Materials in/out**	**Amount in (kg/h)**	**Per 1kg of biomass (kg/h)**	**Comments**	**HHV, kJ/kg**
	Naphtha	**-251.2**	**-0.025**	From C5 to C11	47844
	Diesel ATM	**-406.0**	**-0.041**	From C12 to C22	32,582
	Bottom/Feed VACUUM Column	-198.0	-0.020	From C23; Outlet from atmospheric column	
	Bottom/Feed VACUUM Column	198.0	0.020	Inlet to vacuum column	
	Water	-0.2	0.000		
	Diesel VAC	**-30.1**	**-0.003**	From C12 to C22	23,702
	Waxes to Hydrocracking	-167.6	-0.017		
Hydrocracking	Waxes from F-T	167.6	0.017		
	Hydrogen-enriched - 3	12.0	0.001		
	Purge	-9.9	-0.001	H_2: 0.929; Light HC: Rest	88,440
	Off Gas	-12.1	-0.001	H_2: 0.192; Ethane: 0.100; Propane: 0.157; Butane: 0.400; Other Light HC: Rest	49,146
	Naphtha	**-66.9**	**-0.007**		48,135
	Diesel	**-78.5**	**-0.008**		36,280
	Waxes	-10.8	-0.001		24,090
Methanation	Gas from F-T	10,641.4	1.064		
	Hydrogen-enriched - 2	187.7	0.019	40.37 % of the Hydrogen-enriched stream	
	Product to methane upgrading	-9,904.2	-0.990		
	Water	-927.3	-0.093	H_2O: 0.997; MetOH: 0.003	
Methane Upgrading	Product from methanation	9,715.3	0.972	Error by Fluid Package change 9904.2-9715.3	
	Nitrogen removed	-6,761.4	-0.676	Membrane: Polyperfluoroallyl vinyl ether (NitroSep)	
	DEPG clean to Methanation	38,725.0	3.873		
	DEPG dirty from Methanation	-40,346.7	-4.035		
	Methane Product	**-1,318.8**	**-0.132**		40,364
Hydrogen	H2 not used	**-9.1**	-0.001		69,718
Total		3.5	0.000		

Table 51. FFW process energy balance-base case[4]

Process	Energy Input/Output	Energy added (kJ/h)	Per 1kg of biomass (kJ/h)	Comments
Fischer-Tropsch	Blower	-397,938	-39.8	
	Reactor heat	-11,996,504	-1,199.7	LP Steam Generation
	Cooler	-2,961,265	-296.1	LP Steam Generation
	Cooler	-64,591	-6.5	Chilled Water
F-T Product Separation	Blower	78,091	7.8	Dowtherm
	Condenser ATM	-959,080	-95.9	Chilled Water
	Reboiler VACUUM	17,300	1.7	Dowtherm
	Pump	2,380	0.2	
Hydrocracking	Preheater	26,346	2.6	Dowtherm
	Quencher	-156,646	-15.7	HP Steam Generation
	Heater	23,900,600	2,390.1	HP Steam
	Cooler	-23,858,099	-2,385.8	LP Steam Generation
Methanation	Blower	62,828	6.3	
	Cooler	-3,984,092	-398.4	HP Steam Generation
	Product Heater	0	0.0	HP Steam Generation
	Cooler	-1,859,459	-185.9	HP Steam Generation
	Cooler	-2,651,985	-265.2	LP Steam Generation
	Vessel	-4,059,320	-405.9	Chilled Water
Methane Upgrading	Blower	685,132	68.5	
	Cooler	725,050	72.5	Chilled Water
	Blower	5,358	0.5	
	Cooler	5,970	0.6	Chilled Water
Hydrogen	Blower	26,275	2.6	
Total (Net)	Net	**-27,413,651**	**-2741.4**	kJ/h
	Net	**-27,414**	**-2.7**	Net MJ/hr energy added
	Compression	**1,147**	**0.1**	MJ/h

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[4] Blower energy efficiency is included in results

Table 52. Equipment list for base case (completed post-gasification section)

Equipment	Section	Unit Operation Model
B08002	8 (Mixing section)	Tee
S09001	9 (Fischer-Tropsch)	Expander
S09002	9 (Fischer-Tropsch)	Mixer
S09003	9 (Fischer-Tropsch)	Heat Exchanger
S09004	9 (Fischer-Tropsch)	CSTR Reactor
S09005	9 (Fischer-Tropsch)	Heat Exchanger
S09006	9 (Fischer-Tropsch)	Three phases separator
B10001	10 (Separation of FT products)	Valve
B10002	10 (Separation of FT products)	Heat Exchanger
B10003	10 (Separation of FT products)	Heater (Furnace)
B10004	10 (Separation of FT products)	Distillation Column
B10005	10 (Separation of FT products)	Heater (Furnace)
B10006	10 (Separation of FT products)	Distillation column
B10007	10 (Separation of FT products)	Pump
B11001	11 (Hydrogen compression)	Compressor
B12001	12 (Methanation)	Mixer
B12002	12 (Methanation)	Mixer
B12003	12 (Methanation)	Heat Exchanger
B12004	12 (Methanation)	Equilibrium Reactor
B12005	12 (Methanation)	Splitter
B12006	12 (Methanation)	Compressor
B12007	12 (Methanation)	Heat Exchanger
B12008	12 (Methanation)	Equilibrium Reactor
B12009	12 (Methanation)	Heat Exchanger
B12010	12 (Methanation)	Equilibrium Reactor
B12011	12 (Methanation)	Heat Exchanger
B12012	12 (Methanation)	Heat Exchanger
B12013	12 (Methanation)	Vessel separator
B13001	13 (Hydrocracking)	HCR Reactor
B13002	13 (Hydrocracking)	Petroleum Distillation Column
B14001	14 (Methane upgrading)	Component Splitter (membrane)
B14002	14 (Methane upgrading)	Compressor
B14003	14 (Methane upgrading)	Heat Exchanger
B14004	14 (Methane upgrading)	Absorber Column
B14005	14 (Methane upgrading)	Valve
B14006	14 (Methane upgrading)	Tanks

Equipment	**Section**	**Unit Operation Model**
B14007	14 (Methane upgrading)	Compressor
B14008	14 (Methane upgrading)	Heat Exchanger

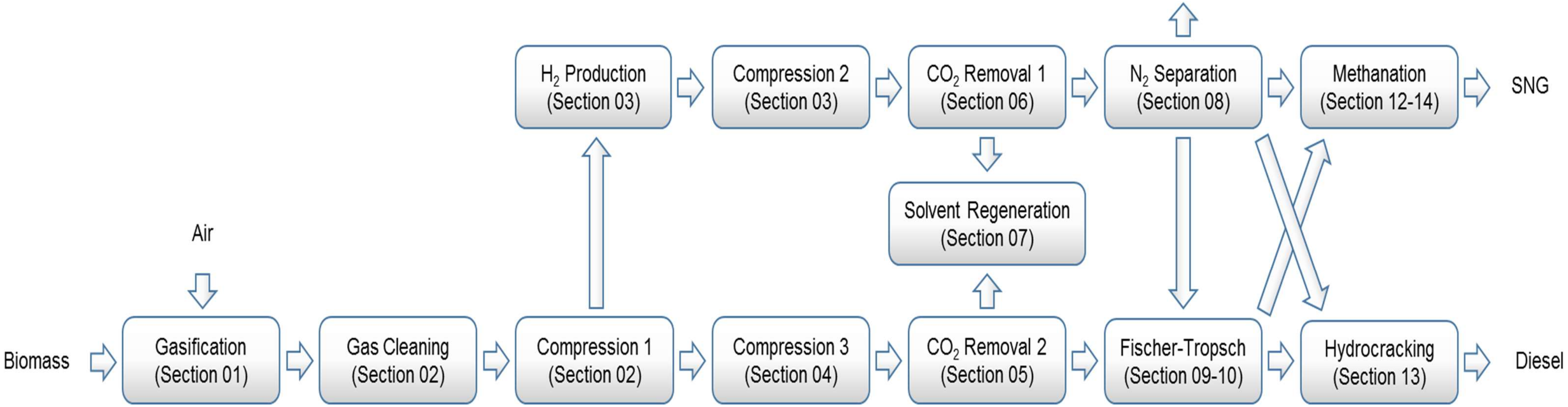

Figure 26: Block Flow Diagram for Base Case

3 Optimisation: Syngas from gasification with oxygen

This section describes an alternative process set up. In this scenario, syngas is produced from gasification with pure/concentrated O_2 (not air) as gasifiying agent which is produced on site using cryogenic distillation as is detailed in D3.4. As a result, the produced synthesis gas does not contain nitrogen (rather nitrogen appears in low concentrations) which gives greater flexibility in process design. WGS reactors are used to alter H_2:CO at 2 different stages in the process. H_2 generation is still required for hydrocracking and it is obtained through water gas shift reaction.

Note: initially, in addition to gasification with O_2, gasification with O_2/Steam was considered, however this results in higher concentrations of CH_4 – which has negative affect on purity of H_2 production (H_2 needed for hydrocracking). Methane reforming can be used for converting methane however methane reforming process are expensive and usually only economical at larger scale (don’t scale down well)

3.1 Fischer-Tropsch Synthesis

Fischer-Tropsch process takes place in the FFW process through one reactor only- The Fischer-Tropsch reactor along with the separation system which separates the FT products from other gases and water. This case shows the design of the reactor with a small amount of nitrogen.

3.1.1 Process Overview

The state-of-the-art regarding the catalysts and reactors for Fischer-Tropsch reaction process is explained along section 2.1.1 Process Overview, and the modelling review applies the same principles for this design. Due to the scale-up is made to be used by the catalysts developed by KTH, the reactor configuration is still slurry bed reactor (SBR).

3.1.2 Modelling Review

Modelling review is detailed in section 2.1.2 Modelling Review for FT reaction using simulation software.

3.1.3 FFW Process Fischer-Tropsch Design

The case study has been developed under the same principles than base case. The reactor type is CSTR in order to simulate a slurry bed reactor flux model and KTH kinetic and selectivity has been used for its modelling.

Both assumptions and pressure drop remain the same that in the base case.

3.1.4 Unit Specification and Analysis

The flowsheet for this section has the same streams and equipment used in base case. See Figure 5 to track down the streams mentioned along this section in the document.

3.1.4.1 Design Inputs

The design inputs introduced for FT reaction in Aspen HYSYS for case study are shown in Table 53. Long chain hydrocarbons are the objective for this reactor.

Table 53. Fischer-Tropsch Model Inputs – case study

Input	Value
CSTR Inlet temperature, ºC	210
CSTR outlet temperature, ºC	210
Pressure drop, bar	1
Inlet Pressure Reactor, bar	33.70
Activation energy of catalyst, kJ/kmol	103.9
Reaction Exponent - CO	0.5
Reaction Exponent – H_2	-0.25
Specified possible paraffin length	1-30. 32. 36.
Specified possible olefin length	2-20. 22. 24
Reactor volume, m^3	7.40
Reactor Length, m	7
Liquid Volume, % (m^3)	85 (6.29)
Catalyst particle Diameter, μm	53-90
Particle Sphericity	1
CO Mass Flow, kg/h	3,508
H_2 Mass Flow, kg/h	530
Total Feed Mass Flow (other components as CO2 included), kg/h	4,975

Reactor volume is 31 % lower in comparison with the Base Case, this would lead to a marked CAPEX reduction.

Peng Robinson-Stryjek and Vera (PRSV) or Enhanced Peng Robinson equation is used as the property model since it is useful in calculating VLE thermodynamic properties. Some references texts use Redlich-Kwong Soave (RKS), yet this equation is not valid for this system due to the presence of alcohols, and HYSYS is not able to use part of the component list (oxygenated compounds) if this model is applied.

Paraffins and olefins available on Aspen HYSYS are limited so paraffins of carbon chain length 31, 32 and 33 are all represented by C32H66, the amount of which is dependent on the number of mols of carbon atoms present in total by the 3 carbon chain lengths. Paraffins with carbon chain length 34-39 are all represented by C36H74, the amount of which is dependent on the number of mols of carbon atoms present in total by the 6 carbon chain lengths. The distribution used for olefins shows no olefins with a carbon chain length over C24.

3.1.4.2 Outputs

The different outputs in the FT reactor design along with the mass balance are shown in

Table 54.

Table 54. FT reactor design outputs – case study

Output	Value
Conversion-CO, %	60
Diameter, m	1.16
Catalyst loading, kg	4,094
Productivity, kg HC/kg catalyst·h	0.27
MP steam generation, kg/h	6,055
Heat flow, kJ/h	-1.2E+07

It is noted the reduction of the catalyst amount in a 36%, what would be a reduction of the CAPEX. Besides, the productivity[5] is 29% higher with respect to the Base Case but an 8% lower flow of MP Steam is obtained.

Table 55. FT reactor mass fraction outputs – case study

Component	Mass flow, kg/h
H_2O	1,292.21
H_2	209.63
CO	1,403.30
CO_2	790.77
N_2	98.60
C1OH	9.47
C2OH	2.87
C3OH	1.39
C4OH	1.32
C5OH-C10OH	35.21
C11OH-C15OH	15.85
C1	210.14
C2	10.32
C3	14.16
C4	21.84
C5-C10	180.61
C11-C20	291.64
C21+	202.59
C2=	0.93
C3=	30.62
C4=	30.66

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[5] Where productivity, in terms of hydrocarbon produced per used catalyst, is expressed as paraffins, olefins, waxes and alcohols as HC products

Component	Mass flow, kg/h
C5= - C10=	85.12
C11= - C20=	29.56
C21= +	6.98

Some heat exchangers are modelled for this section of the process. They are necessary to heat the FT feed and to chill the effluent before the three phase separator. The first approach of these heat exchangers (without any energetic integration) is represented in Table 56.

Table 56. Heat exchanger designs for FT reaction section – case study

Heat Exchanger	T inlet, ºC	T outlet, ºC	Service	Mass flow service, kg/h
B09003	-17.37	210	HP Steam	1,638
B09005	210	35	Cooling Water	51,033

3.1.4.3 Validation

Validation has been detailed in base case according to different authors.

Following the Figure 6 represented in section 2.1.4.3.Validation, the designed reactor is within the same range than base case (pilot plant scale).

3.2 Fischer-Tropsch Product Separation

3.2.1 Process Overview

FT products, as in base case, need to be fractionated so as to obtain different valuable product fractions (fuel), and taking into account that diesel is the main project objective. As in the base case, the product separation is composed by a three phase separator and two distillation columns (atmospheric and vacuum).

3.2.2 FFW Process Fischer-Tropsch Product Separation Design

FT products separation section has been designed as base case section. This unit is similar to a refinery section, where a fractional distillation tower appears (atmospheric) together with a vacuum distillation to increase the diesel production and send to hydrocracking section the heaviest products (waxes).

3.2.3 Unit Specification and Analysis

In Figure 8 (base case) is represented the Separation section. The section is the same as in the base case (equipment) although will appear some differences in terms of the obtained products.

3.2.3.1 Inputs

This section, as in the base case, is made up of a three phase separator, an atmospheric distillation tower and a vacuum distillation tower. The heaviest products obtained at the end of the separation process (vacuum column) will be sent to hydrocracking section as a heavy vacuum gas oil product. Inputs are shown in the table below and the outlet stream temperature for the three streams is in accordance with the three phase separation vessel specification. This temperature has been specified at 15 ºC and is obtained through a heat exchanger after FT reactor (cooler).

Table 57. Atmospheric distillation tower inputs (B10004) – case study

Input	Value
Number of stages	20
Column type	Packed
Condenser type	Partial
Reboiler type	N/A
Top pressure, bar	1.5
Bottom pressure, bar	1.9
Water steam amount, kg/h	100
Feed, kg/h	851.5
Reflux ratio	2.62
n-pentane recovery off gas stream (S10006)	0.09
n-C11 recovery naphtha stream (S10007)	0.2
n-C22 recovery diesel stream (S10008)	0.5
Feed stage	19
Off gas stage (S10006)	Condenser
Naphtha stage (10007)	Condenser
Diesel stage (10008)	17
Atmospheric residue stage (S10005)	Bottom, 20
Feed temperature, ºC	365.8

Table 58. Vacuum distillation tower inputs (B10006) – case study

Input	Value
Stage number	9
Column type	Packed
Condenser type	Total
Reboiler type	HYSYS regular
Top pressure, bar	0.11
Bottom pressure, bar	0.13
Water steam amount, kg/h	N/A
Feed, kg/h	182
Reflux ratio	Calculated, no specified: 3.04
n-C22 recovery LVGO (S10010)	0.72
n-C23 recovery HVGO(S10012)	0.78
Feed stage	8
LVGO stage (S10010)	Condenser
Water outlet stage (S10011)	Condenser
HVGO (S10012)	9

Input	Value
Feed temperature, ºC	360.8

Both columns remain similar to the base case columns in the same sections, although there are minor differences in some parameters, such as the feed temperature and the reflux ratio, due to the small variance in the inlet mass flow from FT reaction in comparison with base case.

3.2.3.2 Outputs

Three phase separator generates three streams:

- Stream S09009. This stream is mainly composed by light gases and a small quantity of water
- Stream S09007. A small amount of gases remains in this stream. It is composed by FT products (alkenes, olefins and alcohols) to FT separation and hydrocracking.
- Stream S09008. This is the aqueous stream where water is separated from the others streams. Along with water, is removed small amounts of light alcohols, such as methanol and ethanol (high affinity to water).

This vessel is adiabatic (Q=0). The mass balance for this equipment appears in Table 10.

Table 59. Three phase separation mass balance (B09006) – case study

Stream	S09006 (Feed)	S09007 FT products	S09009 Light gases	S09008 Aqueous phase
Vapour fraction	0.71	0.00	1.00	0.00
Temperature, ºC	15.00	15.00	15.00	15.00
Pressure, bar	32.70	32.70	32.70	32.70
Molar Flow, kmol/h	268.34	5.72	190.88	71.74
Mass Flow, kg/h	4,975.79	851.45	2,829.75	1,294.58

Initially, distillation columns were designed as bubble-cap column towers (as petroleum atmospheric refining columns), but the diameter of both columns is small (<1 m), which means use of trays is not recommendable. Finally, these columns have been designed as packed columns (Ballast rings metal, random packing 1 inch). Table 60 and Table 61 are represented the results of the design of the atmospheric tower and the outlet mass flows.

Table 60. Atmospheric distillation column (B10004) outputs – case study

Output	Value
Diameter, m	0.46
Height, m	8.77
Section delta P, bar	2.65E-02
Condenser heat S10Q003, kJ/h	-945,600

Table 61. Atmospheric distillation column (B10004) mass balance output – case study

Component	S10006 (Off gas)	S10007 (Naphtha)	S10AS004 (steam output)	S10008 (Diesel)	S10005 (Atm. residue)
Flow Rate (kg/h)	27.39	267.99	99.95	374.12	181.98
$H_2$0	0.27	0.04	99.53	0.12	0.08
H_2	0.07	0	0	0	0
CO	2.41	0.02	0	0	0
CO_2	11.28	1.04	0.01	0.01	0
N_2	0.17	0	0	0	0
C1OH	0.23	3.52	0.40	0.02	0
C2OH	0.07	2.14	0.02	0.01	0
C3OH	0.01	1.26	0	0.01	0
C4OH	0	1.27	0	0.02	0
C5OH-C10OH	0	25.27	0	9.89	0.01
C11OH-C15OH	0	0	0	15.72	0.13
C1	0.97	0.03	0	0	0
C2	0.23	0.04	0	0	0
C3	0.76	0.51	0	0	0
C4	1.70	4.11	0	0.02	0
C5-C10	2.77	153.36	0	5.50	0.01
C11-C20	0	6.09	0	275.92	9.61
C21+	0	0	0	36.19	166.40
C2=	0.01	0	0	0	0
C3=	1.49	0.83	0	0.01	0
C4=	2.32	4.66	0	0.03	0
C5= - C10=	2.59	62.25	0	1.41	0
C11= - C20=	0	1.57	0	27.33	0.66
C21= +	0	0	0	1.89	5.08

A small decrease in the amount of fractionated products, mainly diesel and residue, is observed (taking as reference base case).

The properties for the fuels obtained along the atmospheric column are shown in Table 62.

Table 62. Properties for the FT fuels in atmospheric column

Property	S10007 (Naphtha)	S10008 (Diesel)	S10005 (Atm. residue)
Density @20 ºC, kg/m^3	713.30	774.66	807.21
Viscosity @ outlet temperature, cSt	0.63	2.80	8.7
Flash point, ºC	-	87.47	150.2
Aromatic content, %	<1 %	<1 %	<1 %
Cetane number	-	77.05	68.20

HHV, kJ/kg	47,843	32,582	17,867
LHV, kJ/kg	44,360	30,250	16,588

In Table 63 and Table 64 the design and the mass outputs for the vacuum distillation tower are represented.

Table 63. Vacuum distillation tower (B10006) design outputs – case study

Output	Value
Diameter, m	0.30
Height, m	4.11
Section delta P, bar	0.007
Condenser heat S10Q005, kJ/h	-99,841
Reboiler heat S10Q006, kJ/h	16,155

The dimensions and heat exchangers (condensers and reboiler) energy obtained from the two columns are similar to the columns of the Base Case.

Table 64. Vacuum distillation tower output mass balance – case study

Component	S10010 (LVGO)	S10011 (HVGO)
Flow Rate (kg/h)	27.48	154.49
H_20	0.08	0
H_2	0	0
CO	0	0
CO_2	0	0
N_2	0	0
C1OH	0	0
C2OH	0	0
C3OH	0	0
C4OH	0	0
C5OH-C10OH	0.01	0
C11OH-C15OH	0.13	0
C1	0	0
C2	0	0
C3	0	0
C4	0	0
C5-C10	0.01	0
C11-C20	9.38	0.22
C21+	16.52	149.88
C2=	0	0
C3=	0	0

Component	S10010 (LVGO)	S10011 (HVGO)
C4=	0	0
C5= - C10=	0	0
C11= - C20=	0.64	0.02
C21= +	0.71	4.38

The properties of the vacuum gas-oil are shown below:

Table 65. Properties of the vacuum diesel.

Property	S10010 (LVGO)	S10011 (HVGO)
Density @20 ºC, kg/m^3	793.34	809.73
Viscosity @ outlet temperature, cSt	5.2	10.02
Flash point, ºC	134.9	155.1
Aromatic content, %	<1 %	<1 %
Cetane number	77.74	65.78
HHV, kJ/kg	23,579	16,851
LHV, kJ/kg	21,886	15,646

Additionally, there are two furnaces in order to vaporise the feed for both columns since to obtain clear cut fractions, petroleum refinery columns have modelled as analogy to this process. Within this process, the feed is vaporised and introduced close the bottom stages. The values for these furnaces are shown in Table 66 and Table 67.

Table 66. Furnace B10003 (to atmospheric tower) – case study

Parameter	Value
Input temperature, ºC	230
Output temperature, ºC	365.8
Heat, kJ/h	427,569

Table 67. Furnace B10005 (to vacuum tower) – case study

Parameter	Value
Input temperature, ºC	301.6
Output temperature, ºC	360.8
Heat, kJ/h	73,000

3.3 Hydrocracking

Hydrocracking section is designed in order to break down the waxes (long-chain) into short chains with the purpose of obtaining diesel. Hydrocracking section is composed by a hydrocracking reactor along with a high pressure separator and a distillation column.

3.3.1 Process Overview

Hydrocracking section is quite similar to base case due to the same nature of the feed. The hydrocarbon blend does not show big differences respect to the feed introduced into base case hydrocracker.

3.3.2 FFW hydrocracking process design

Hydrocracking section design follows the same steps detailed along the hydrocracking in base case. No larger modifications have been done and hydrocracker has been designed using the same template that was created for base case feed.

3.3.2.1 Assumptions

Assumptions made for the hydrocracking process include:

- Consideration of pure hydrogen for the fresh hydrogen stream (hydrogen make-up).
- Steady state
- Feed is a heavy vacuum gasoil product.
- Intra-particle mass and heat transfer resistances are negligible.

3.3.2.2 Pressure drop

Pressure drop is calculated using HYSYS HRC model both for hydrocracking reaction and hydrogen stream. The results are shown after running the simulation.

3.3.3 Unit Specification and Analysis

The case study hydrocracking is designed according to the same schemes shown in Figure 10 and Figure 11 in base case. The streams explained along this section (case study) are mentioned according to these both schemes.

3.3.3.1 Design Inputs

The design of hydrocracking section has been developed in Aspen HYSYS from the previous products obtained from FT reaction and later, FT separation. The catalyst used as reference has been platinum supported on silica-alumina (Pt/S40). In Table 68, the main inputs for hydrocracking section design in case study appear.

Table 68. Inputs for hydrocracking section – case study

Input	**Value**
Bed 1 diameter, m	1
Bed 2 diameter, m	1
Catalyst loading per bed, kg	900/1200
Bed voidage (supposed)	0.5
Hydrocracker configuration	Single stage
Feed type	HVGO (Heavy Vacuum Gas Oil)
Feed mass flow, kg/h	154.5
Recycle mass flow, kg/h	45

Input	Value
Bed 1 inlet temperature, ºC	355
Bed 2 inlet temperature, ºC	358
H_2 temperature, ºC	50
H_2 pressure, bar	60
Purge fraction	0.1
Gas to oil ratio, m^3/m^3	1,500
Fractionator pressure (B13002), bar	10
Fractionator stage number (B13002)	9

To define the waxes recycle rate, some parameters have been fixed taking into account the results obtained in base case and the product distribution has been evaluated as appears in Figure 27.

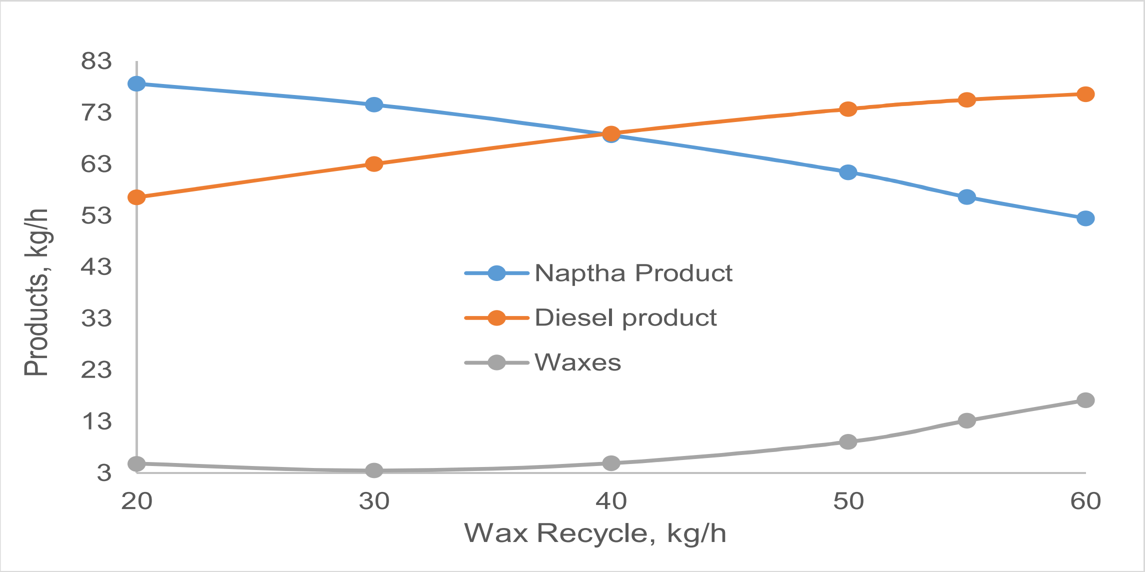

Figure 27. Hydrocracking product composition according to wax recycle rate for case study – case study

A compromise between diesel production and a reasonable amount of naphtha and waxes have been evaluated. An increase in the recycle to hydrocracker reactor makes a rise in the diesel production. However, this situation also makes that naphtha decreases and waxes increase. Waxes are not desirable within FFW project, although it is possible to find out a revalorisation for other purposes out of the scope of this project. With a recycling rate of 50 kg/h onwards, the increase in diesel production is slow in comparison with the decrease in naphtha and the rise in wax production. Therefore, the chosen recycling rate has been 45 kg/h due to naphtha is more valuable as sub-product than waxes.

The feed stream is the heavy vacuum gas oil obtained in Fischer-Tropsch products upgrading and its characteristics are shown in Table 69. No larger differences are found between this feed stream and base case feed stream in terms of API properties and distillation curve, although this curve shows minor temperature values in each point.

Table 69. Hydrocracking feed characteristics – case study

Parameter	Value
API Gravity	41.25
Specific Gravity, 60F/60F	0.81
Distillation Type	ASTM D86
0% Point, ºC	371.23
5% Point, ºC	392.77
10% Point, ºC	395.49
30% Point, ºC	405.40
50% Point, ºC	424.37
70% Point, ºC	436.84
90% Point, ºC	444.36
95% Point, ºC	449.54
100% Point, ºC	466.40

3.3.3.2 Outputs

The main outputs from the simulation of the HCR reactor are indicated in Table 70.

Table 70. HC outputs – case study

Output	Value
Delta T-Rise in each bed, ºC	16.10
Conversion	90.67
Pressure drop bed 1, bar	4.78e-007
Pressure drop bed 2, bar	6.76e-007
Hydrogen in bed 1 Consumption, m^3/h	362
Hydrogen in bed 2 Consumption, m^3/h	205
Hydrogen feed S11002, kg/h	11.13

Pressure drop in the HCR reactor is calculated by HYSYS and the results show small values for this parameter in both beds. The overall conversion obtained from the specified inputs is high (near 91 %) and shows a bit increase respect to base case (89 %) for lower inlet bed temperatures and it needs 7% lower of hydrogen flow.

The mass balance for the fractionator column is represented in Table 71.

Table 71. Fractionator column mass balance (hydrocracking section) – case study

Parameter	Reactor output (hydrogen separator)	Off gas 13003	Naphtha 13004	Steam Water (Column)	Bottom To Tee	Diesel 13005
Temperature, ° C	50	49.78	184.61	179.98	541.62	389.71
Pressure, bar	60	10	10	10	10	10
Molar Flow, kmol/h	1.49	0.28	0.62	0.00	0.19	0.40
Mass Flow, kg/h	200.14	11.47	63.62	0.00	53.01	72.04

As shown in base case, the water consumption for the distillation column calculated by HCR model is null. In Table 72 the required energy for this column is represented (calculated by HYSYS) and this balance remains very similar to base case hydrocracking distillation column.

Table 72. Energy consumption in hydrocracking separation section – case study

Energy source	Value, kJ/h	Type
Condenser	23862731	3 Phase Condenser
Distillate (steam)	23900600	Energy Stream

Final products and their properties are represented in Table 73 and their characteristics in Table 74.

Table 73. Hydrocracking final cuts – case study

Cut	Volume flow, m^3/h	Mass flow, kg/h	Volume, %	Weigh, %
Naphtha	0.09	63.62	46.27	41.18
Distillate	0.08	72.04	40.89	46.63
Bottom	0.01	8.01	4.55	5.18

Table 74. Characteristics of hydrocracking final products – case study

Property	Naphtha	Distillate	Bottom
API Gravity	54.24	38.67	21.50
Specific Gravity	0.76	0.83	0.92
Sulfur, %	-	-	-
Total Nitrogen, ppm wt%	-	-	-
Basic Nitrogen, ppm wt%	-	-	-
Paraffins, %	58.33	35.12	70.72
Aromatics, %	6.83	5.17	2.43
RON	53.87	13.92	0.00
MON	51.26	12.26	0.00
Smoke Point, mm	22.79	18.20	17.49
Freeze Point, °C	-82.21	27.32	-7

Property	Naphtha	Distillate	Bottom
Flash Point, ºC	15.55	93.80	149.79
Cetane Index	28.84	60.09	36
Pour Point, ºC	-62.13	-14.64	1.85
Watson K	11.89	12.16	13.05
Viscosity, ºC	0.23	0.08	0.02
Density, kg/m^3	762.6	826.9	-

Results show similar characteristics to base case hydrocracking products. This resemblance is due to the hydrocracking feed, which is almost the same for both cases, showing small differences in the mass flow only.

The bed inlet temperature has been possible to decrease for this hydrocracking section, at least the first bed up to 355 ºC (base case is higher).

The cetane index comply with the current standards (>50) and the density comply with the European minimum (820 kg/m^3). These results needs a more accurate approach comparison that would be done through the calibration of the model with experimental data of the lab hydrocracker.

3.3.3.3 Validation

Hydrocracking validation is mentioned in the corresponding section in base case. The final results are similar to the base case for this section of the FFW project scaling-up, accordingly the validation is the same for two both scenarios represented along this deliverable.

3.4 Methanation

3.4.1 Process Overview

Methanation process review is explained in base case. Details about the reactors and catalyst configuration appear in 2.4.1.Process Overview section. The design procedure has been the same although the obtained results are different. The absence of nitrogen enhances the process, removing some operations such as membrane for nitrogen removal (or any operation that could be considered for this purpose).

3.4.2 FFW methanation process design

The gas stream from the three phase separator in Fischer-Tropsch (S09006), mainly composed in this case by H_2, CO and CO_2, is mixed with a part of the H_2 generated in WGS process once it is reduced the pressure to 30 bar (S08003) in order to get a flow rate control for H_2:CO of 3:1 in mole. Then the stream enters into the methanation process.

The developed methanation process is shown in the Figure 28, it is the same as in base case except that the heat exchanger, a cooler in this case, is in the recycle since it is going to be larger and the temperature of the mix would be higher than 300 ºC.

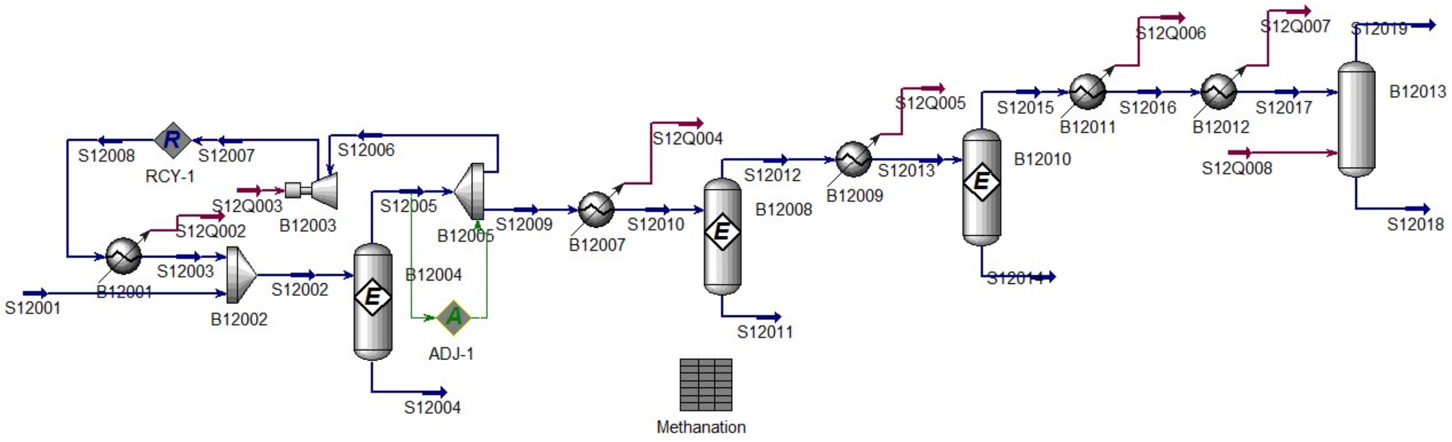

Figure 28 Methanation Process – case study

3.4.2.1 *Assumptions*

Same assumptions are done with regards to base case.

3.4.2.2 *Pressure Drop*

Pressure Drop has been estimated in 0.5 bar for this system (as per base case).

3.4.3 Unit Specification and Analysis

3.4.3.1 Inputs

For the base case model, the inputs are collected in Table 75. The sizing of the reactor is determined by the maximum outlet temperature (600 ºC), the adiabatic condition in the reactors and the reasonable drop pressure.

Table 75 Methanation model inputs – case study

Input	**Value**		
Reactor	1	2	3
Inlet temperature, ºC	300	300	300
Outlet temperature, ºC	600	-	-
Heat Flow, kJ/h	0	0	0
Recycle	0.78	0	0
Pressure Drop, bar	0.5	0.5	0.5

The inlet stream condition and flows are shown in the Table 76.

Table 76 Methanation inlet stream – case study

Stream Name	**S12001 (Feed)**	**S12002 (Recycle)**	**S12003 (Reactor Feed)**
Vapour Fraction	1	1	1
Temperature, ºC	9	391 (cooled from 600 ºC)	300
Pressure, bar	32.7	30 (expanded from 29.5)	30
Molar Flow, kmol/h	233.6	522.4	756
Mass Flow, kg/h	3,021	10,700	13,720
Mass fraction			

Stream Name	S12001 (Feed)	S12002 (Recycle)	S12003 (Reactor Feed)
H_2O	0.0007	0.2350	0.1834
H_2	0.0958	0.0121	0.0305
CO	0.4735	0.0344	0.1311
CO_2	0.2808	0.3384	0.3257
Nitrogen	0.0356	0.0357	0.0357
Methane	0.0699	0.3006	0.2498
C2+	0.0192	0.0192	0.192
C1=+	0.0237	0.0238	0.0238

3.4.3.2 Outputs

CO conversion is shown in the Table 77. In the first reactor, the reactive concentration is high so the reaction is really fast and it reaches the maximum temperature (600 ºC) with a low conversion that is modify using the product recycle. As the CO concentration is lower in the second reactor, the heat flow is more dispersed in the stream. That permits a larger reactor which will reach a higher conversion.

Table 77. Methanation process conversion and recycling – case study

Conversion	Reactor 1	Reactor 2	Reactor 3	
WGS Inverse Reaction	6.4	0	0	
Methanation Reaction	67.3	93.27	91.84	**Total**
Total CO conversion	92.73	93.27	91.84	99.96
Outlet Temperature, ºC	593	431	326	

Reactor volume has been calculated by the same GHSV (NL/L·h) as per base case (it may be different because of the different composition in the inlet stream). The same L/D relation has been used. It is needed 11,706 kg of catalyst, a 40% lower, and the same reduction for the reactor volume is obtained, what would reduce the CAPEX.

Table 78. Methanation reactor sizing – case study

Parameter	Reactor 1	Reactor 2	Reactor 3
Standard Volumetric Flow, NL/h	17,876,156	3,482,980	3,284,063
GHSV, NL/h·L	16,000	8,000	8,000
Catalyst Volume, L	1,117.26	435.37	410.51
Catalyst amount, kg	8,491	1,654	1,560
Catalyst Porosity	0.51	0.51	0.51
Bed Porosity	0.39	0.39	0.39
Reactor Volume, m^3	3.738	1.457	1.373
Length, m	4.25	3.10	3.05
Diameter, m	1.06	0.77	0.76
L/D	4.0	4.0	4.0

Outlet composition from the third reactor is shown in the Table 79. As mentioned before, carbon dioxide and water have to be removed. Water is taken out using a pressure vessel at 15 ºC and carbon dioxide ways of removal have been studied and it is used the absorption with DEPG.

Table 79 Methanation process products – case study

Stream	Out from Reactor 3 (S12017)	Water (S12018)	Gas (S12019)
Mass flow, kg/h	3,018	827.3	2,191
Mass fraction			
H_2O	0.2738	0.9974	0.0006
H_2	0.0009	0	0.0012
CO	0.0002	0	0.0003
CO_2	0.3182	0.0013	0.4379
Nitrogen	0.0357	0	0.0492
Methane	0.3275	0	0.4512
C2+	0.0192	0	0.0264
C1=+	0.0238	0	0.0327

The product (S12019) does not comply the standard, therefore, it needs to be treated. In this case, N_2 is not a problem but a high level of CO_2 still remains.

A high flow of HP steam is produced whilst a lower amount of LP steam is recovered to cool the main stream before it is introduced to the separator vessel (Table 80). Unlike the base case, it is needed to heat the recycle and is not to cool the feed.

Table 80 Methanation services – case study

Heat Exchanger	T inlet, ºC	T outlet, ºC	Service	T inlet service, ºC	T outlet service, ºC	Mass flow service, kg/h
B12001	600	391	HP Steam Generation	385	350	3,156
B12007	600	300	HP Steam Generation	250	251	1,239
B12009	431	300	HP Steam Generation	250	251	523
B12011	326	270	HP Steam Generation	250	251	213
B12012	270	140	LP Steam Generation	140	141	896
B12013	140	15	Chilled water	5	25	24,497

3.4.3.3 Validation

The results are compared to the same references as in the base case: TREMP process and the literature reviewed. Conclusions are similar to base case due to the likeness of the results. Comparison is in Table 81.

Table 81. Methanation processes comparison – case study

	TREMP (47)	**Literature** (43)	**FFW methanation process case study**
Number of Reactors	4	1	3
Operation	Adiabatic	Isothermal	Adiabatic
Temperature, ºC	300 (In)	300 – 500	300 (In)
Pressure, bar	30	20-30	24
Conversion, %	99.9	81 – 96.7	99.9 (Total) First reactor: 81

3.5 Methane Upgrading

3.5.1 Process Overview

Methane upgrading for case study does not include a membrane use due to the low concentration of nitrogen inside the system. The system is composed by the same absorption using Selexol as in the base case.

3.5.2 FFW process design /modelling

The process is designed according the base case methane upgrading (CO_2 removal). Figure 29 represents the equipment and streams for this section.

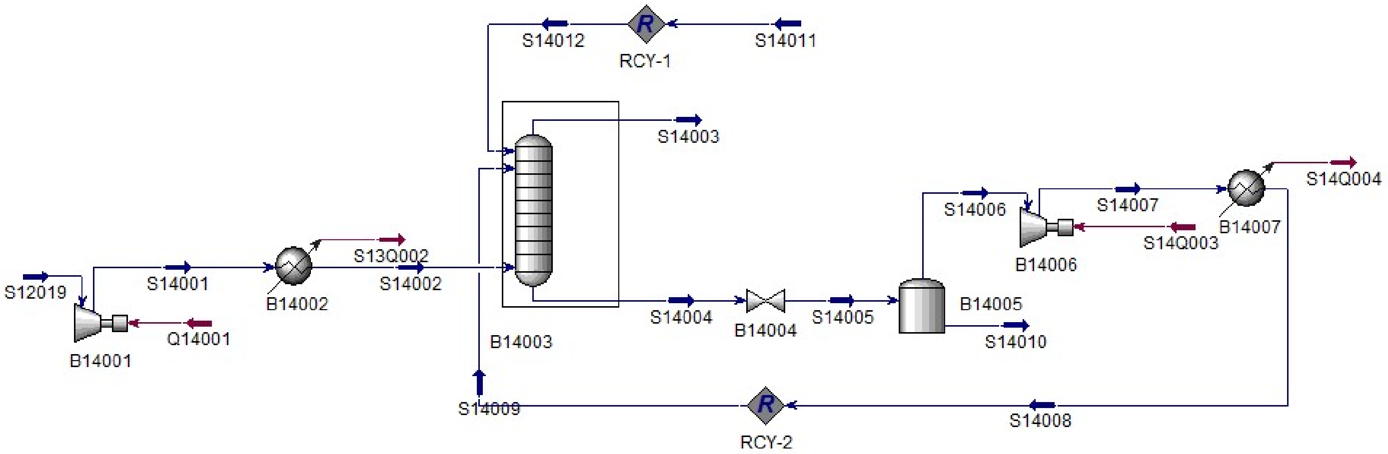

Figure 29. Methane upgrading for case study

3.5.3 Process Specs and Analysis

The mass composition for the SNG in the absorption column is shown in Table 82.

Table 82. SNG composition in CO2 removal inlet – case study

Component	Mass Fraction
DEPG	-
CO	0.0003
CO_2	0.47

Component	Mass Fraction
Hydrogen	0.001
H_2O	0.001
Nitrogen	0.05
Argon	-
Methane	0.48
Total Mass Flow, kg/h	2,057

The product stream (methane gas) obtained after the DEPG absorption column complies with the European standards as was shown in Table 29. The mass composition and the SNG mass flow as final product is represented in Table 83.

Table 83. SNG final product composition – case study

Component	Mass Fraction
DEPG	-
CO	0.0005
CO_2	0.148
Hydrogen	0.002
H_2O	0.000
Nitrogen	0.09
Methane	0.76
SNG total mass flow, kg/h	1,203

Absorption column design inputs and outputs are represented in Table 84.

Table 84. CO2 removal column design for methane upgrade – case study

Parameter	Value
Absorption	Physical
Number of stages	10
Top pressure	51.70
Bottom pressure	51.80
Column diameter, m	0.24
Column height, m	5
Packing	Metal IMTP
Regenerated DEPG mass flow, kg/h (from section 5)	16,931

Column diameter is smaller than base case and the DEPG consumption has decreased up to near a half. The mass flow treated is similar in both cases (the difference is a bit more of mass flow in base case) and it is observed some savings for case study in comparison to base case.

Other equipment is used to achieve the specifications of the process, such as the vessel drum, heat exchangers and compressor. Specifications and energy balance are shown in Table 85.

Table 85. Auxiliary equipment in methane upgrading section (CO2 removal) – case study

Equipment	Inlet temperature, ºC	Outlet temperature, ºC	Inlet pressure, bar	Outlet pressure, bar	Q, kJ/h
B14001 (compressor)	-10	44.10	28.50	52	150,620
B14002 (cooler)	44.10	20.09	52	52	-90,585
B14004 (valve)	15.65	15.77	51.80	34.80	-
B14005 (flash drum)	15.77	15.77	34.80	34.80	-
B14006 (compressor)	15.77	53.59	34.80	52	3,434
B14007 (cooler)	34.80	20.01	52	52	-4,016

3.6 FFW case study energy integration

FFW study case has been energetically integrated in order to reduce the energy consumption in the same way as per the Base Case. Aspen Energy Analyser has been the tool for this aim. ASU, Gasification, Gas Cleaning (D.3.4) and Hydrocracking are not included since they are in separated simulations and are integrated themselves.

3.6.1 Energy Integration Overview

This section is explained in the Base Case.

3.6.2 FFW Energy Integration Design

This section is explained in the Base Case.

3.6.3 Unit Specification and Analysis

The targets set by Aspen Energy Analyser is displayed in the Figure 30. For each of total utilities, heating utilities, cooling utilities, and carbon emissions, the current value and target value are shown.

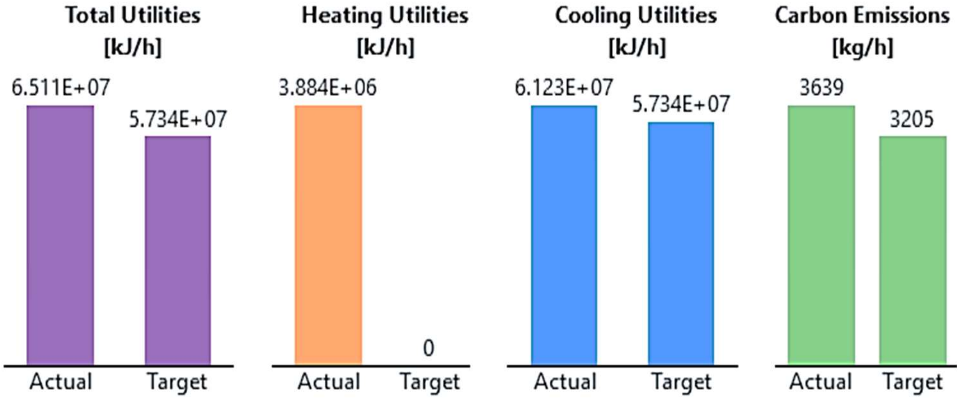

Figure 30. Targets set by Aspen Energy Analyser – case study

Aspen Energy Analyzer will plot the Composite Curves (Figure 31).

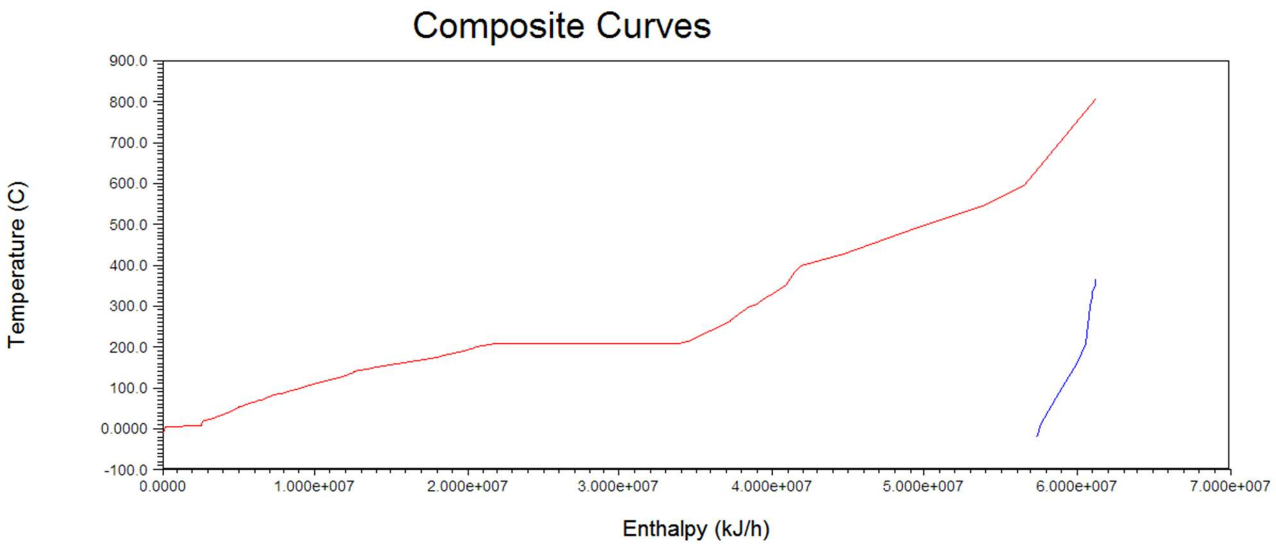

Figure 31. Composite curves – case study

Table 86. Design results – case study

Design	**Total Cost Index, Cost/s**	**Area, m²**	**Units**	**Shells**	**CAPEX, Cost**	**Heating, kJ/h**	**Cooling, kJ/h**	**OPEX, Cost/s**
Simulation	-1.25E-02	1,232	28	43	919,920	3,884,474	61,226,236	-2.19E-02
Base Case	-1.65E-02	1,274	43	90	932,506	89,165	57,430,927	-2.60E-02
Design1	-1.68E-02	1,188	41	84	881,063	89,165	57,430,927	-2.58E-02
Design2	-1.69E-02	1,195	42	89	892,591	89,165	57,430,927	-2.61E-02
Design3	-1.70E-02	1,157	43	77	883,009	89,165	57,430,927	-2.60E-02
Design4	-1.71E-02	1,233	38	66	860,986	89,165	57,430,927	-2.59E-02

The optimum design chosen is marked in blue: the design with lowest CAPEX, which is 26% lower, and the maximum total index cost for a supposed project life of 10 years, which is 38% lower as well.

Heat Ex.	Type	Load, kJ/h	Cost Index, Cost	Area, m^2	Shells	Overall U, kJ/h·m^2·ºC	F Factor	Hot Stream	Hot T in, ºC	Hot T out, ºC	Cold Stream	Cold T in, ºC	Cold T out, ºC	dT Min Hot, ºC	dT Min Cold, ºC
E-001	Cooler	1,934	10,181	0.1	13	1,273	0.88	S06007 To S06002	57	20	Chilled Water	16	25	32	4
E-002	Cooler	11,356	10,704	0.7	18	1,000	0.90	S05005 To S05008	73	20	Chilled Water	16	25	48	4
E-003	Cooler	90,585	17,881	14.7	10	767	0.84	S14001 To S14002	44	20	Chilled Water	16	25	19	4
E-004	Cooler	945,597	13,847	6.0	40	3,190	0.94	To Condenser@COL3 To S10AS004	132	26	Chilled Water	16	25	107	9
E-005	Cooler	4,383	10,544	0.5	12	785	0.87	S14007 To S14009	54	20	Chilled Water	16	25	29	4
E-006	Cooler	691,089	15,842	12.0	85	684	0.99	S12Q008	140	77	Chilled Water	16	25	115	61
E-007	Cooler	1,570,028	39,498	69.0	35	684	0.95	S03Q005	150	20	Chilled Water	16	25	125	4
E-008	Cooler	147,260	10,746	0.9	168	964	0.99	S04003 To S04005	267	127	Chilled Water	16	25	242	111
E-009	Cooler	64,591	10,177	0.2	144	3,147	0.99	S09005 To S09006	210	126	Chilled Water	16	25	185	110
E-010	Cooler	11,996,504	65,911	202.1	85	697	1.00	S09Q003	210	210	LP Steam Generation	124	125	85	85
E-011	Cooler	116,125	10,399	0.4	109	3,452	1.00	S03006 To S03007	320	177	LP Steam Generation	124	125	195	53
E-012	Cooler	2,328,926	22,878	27.1	73	1,939	1.00	S12015 To S12017	326	140	LP Steam Generation	124	125	201	16
E-013	Cooler	1,157,959	26,282	32.8	35	996	0.99	S04003 To S04005	267	127	LP Steam Generation	124	125	142	3
E-014	Cooler	2,961,265	26,047	35.7	22	4,145	0.99	S09005 To S09006	210	126	LP Steam Generation	124	125	85	2
E-015	Cooler	2,110,684	19,237	21.3	152	637	1.00	S12009 To S12010	592	300	HP Steam Generation	250	250	342	50
E-016	Cooler	2,481,772	25,188	39.6	94	666	1.00	S04001 To S04002	353	216	MP Steam Generation	174	175	178	42
E-017	Cooler	2,686,506	24,334	28.0	36	4,797	0.99	S03006 To S03007	320	177	MP Steam Generation	174	175	145	3
E-018	Cooler	1,212,068	20,991	22.2	91	602	1.00	S03004 To S03005	395	200	MP Steam Generation	174	175	220	26

Heat Ex.	Type	Load, kJ/h	Cost Index, Cost	Area, m²	Shells	Overall U, kJ/h·m²·ºC	F Factor	Hot Stream	Hot T in, ºC	Hot T out, ºC	Cold Stream	Cold T in, ºC	Cold T out, ºC	dT Min Hot, ºC	dT Min Cold, ºC
E-019	Cooler	75,952	11,383	2.0	61	624	1.00	S12Q008	77	8	Refrigerant 1	-25	-25	102	33
E-020	Cooler	689,845	35,253	56.9	20	684	0.91	S12Q008	77	8	Chilled Water	5	16	61	3
E-021	Cooler	1,492,416	19,438	18.4	48	1,616	0.93	S04003 To S04005	127	20	Chilled Water	5	16	111	15
E-022	Cooler	2,310,957	17,014	12.7	42	3,976	0.93	S09006 To S09006	126	15	Chilled Water	5	16	110	10
E-023	Cooler	1,204,215	23,629	34.6	52	666	1.00	S04001 To S04002	216	150	LP Steam Generation	124	124	92	26
E-024	Cooler	717,374	11,575	2.3	38	8,153	1.00	S03006 To S03007	177	150	LP Steam Generation	124	124	53	26
E-025	Cooler	200,717	16,871	14.7	22	624	1.00	S12Q008	8	-10	Chilled Water	-24	-24	32	14
E-026	Cooler	2,331,380	26,033	42.4	33	1,649	1.00	S07012 To S07014	10	7	Chilled Water	-25	-24	35	32
E-027	Cooler	3,308,283	51,836	140.6	217	108	1.00	S02001 To S02002	551	400	HP Steam Generation	249	250	301	151
E-028	Cooler	5,343,697	23,899	35.5	229	658	1.00	S12007 To S12003	595	391	HP Steam Generation	249	250	345	142
E-029	Cooler	8,287,289	43,716	107.4	298	259	1.00	S02003 To S02004	768	400	HP Steam Generation	249	250	518	151
E-030	Cooler	890,172	16,817	14.6	103	596	1.00	S12012 To S12013	431	300	HP Steam Generation	249	250	181	51
E-031	Heater	51,002	12,290	3.7	25	751	0.87	Dowtherm	385	365	S10005 To S10009	339	361	24	26
E-032	Heater	22,003	10,712	0.9	38	690	0.96	Dowtherm	365	356	S10005 To S10009	302	339	26	55
E-033	Heater	16,160	10,689	0.8	27	729	0.99	Dowtherm	356	350	To Reboiler@COL4 To S0012	322	330	26	28
E-034	Heat Exchanger	833,411	13,579	6.5	552	235	0.99	S02003 To S02004	807	770	S10001 To S10003	89	366	441	681
E-035	Heat Exchanger	1,217,961	53,933	105.7	32	450	0.80	S04003 To S04005	267	127	S09003 To S09004	111	210	57	15

Heat Ex.	**Type**	**Load, kJ/h**	**Cost Index, Cost**	**Area, m^2**	**Shells**	**Overall U, $kJ/h \cdot m^2 \cdot ^\circ C$**	**F Factor**	**Hot Stream**	**Hot T in, ºC**	**Hot T out, ºC**	**Cold Stream**	**Cold T in, ºC**	**Cold T out, ºC**	**dT Min Hot, ºC**	**dT Min Cold, ºC**
E-036	Heat Exchanger	52,055	10,311	0.3	716	237	1.00	S02003 To S02004	770	768	S10001 To S10003	15	89	681	753
E-037	Heat Exchanger	1,591,718	60,160	118.0	25	553	0.80	S04003 To S04005	127	20	S09003 To S09004	-17	111	15	37
E-038	Heat Exchanger	100,164	11,162	1.1	52	1,406	0.86	To Condenser@COL4 To S10011	264	22	S10001 To S10003	15	89	176	7

Utility	Use	Cost Index, Cost/s	Load, kJ/h	Effective Cp, kJ/kg·C	Inlet T, C	Outlet, C	Flow, kg/h	Load/Cost save from the Base Case
Chilled Water	Cooling	6.22E-04	10,552,138	3	5	25	175,869	49
LP Steam Generation	Cooling	-1.08E-02	20,482,368	2196	124	125	9,327	30
HP Steam Generation	Cooling	-1.38E-02	19,940,125	1981	249	250	10,066	1
MP Steam Generation	Cooling	-3.88E-03	6,380,345	1703	174	175	3,747	47
Refrigerant 1	Cooling	5.77E-05	75,951	4	-25	-24	18,988	90
Dowtherm	Heating	8.67E-05	89,165	3	385	350	849	6
	Total	-2.77E-02					Total	21%

For Gasification and Gas Cleaning, energy requirements have been estimated as per the base case.

Table 87. Gasification and gas cleaning heat exchanger net – case study

Heat Ex	Type	Load, kJ/h
E-039	Cooler	10,860,000
E-040	Heater	377,805
E-041	Heater	1,411,467
E-042	Heater	303,422
E-043	Heater	1,641,087
E-044	Cooler	2,857,699
E-045	Cooler	492,986
E-046	Cooler	3,308,283
E-047	Cooler	8,287,289
E-048	Cooler	11,622,000
E-049	Heater	4,384,800

3.7 Case study summary

Case study design shows similar results in regards with the valuable products obtained throughout the processes explained along this deliverable in comparison with base case products.

Sections are similar to base case. However, small differences are noted. The main differences are detailed in the coming up points:

- Lower nitrogen concentrations in case study are favourable in terms of equipment size. The equipment are smaller than base case equipment.
- Simpler methane upgrading for SNG obtaining. Due to the low nitrogen concentration, a membrane use is not necessary for achieving SNG European Standards. However, CO_2 removal is still necessary since carbon dioxide concentration remains above the standard threshold.
- Slightly higher productivity of valuable hydrocarbons of Fischer-Tropsch is reported for the case study. (0.21 in base case vs. 0.27 in case study).
- A small increase in the conversion is obtained in hydrocracking reactor for C22+ (89 % in base case vs. 91 % in case study).

- The ratio diesel/SNG is as base case, 0.30 kg diesel/Nm^3 SNG[6].

The total mass flows of the process products and by-products are represented in the Figure 32. Energy flows are represented in the Figure 33 (again and as per base case, these inputs are obtained in D3.4. *Simulation of the Chemical Pretreatment*) and equipment list appears in Table 90. Table 88 and Table 89 summarised the M&E balance in more detail for all the sections described throughout this deliverable and results are shown per kg of biomass in order to use these numbers for the LCA.

The energy efficiency reported in case study is slightly lower than base case efficiency for the section explained along the current deliverable (65 %).

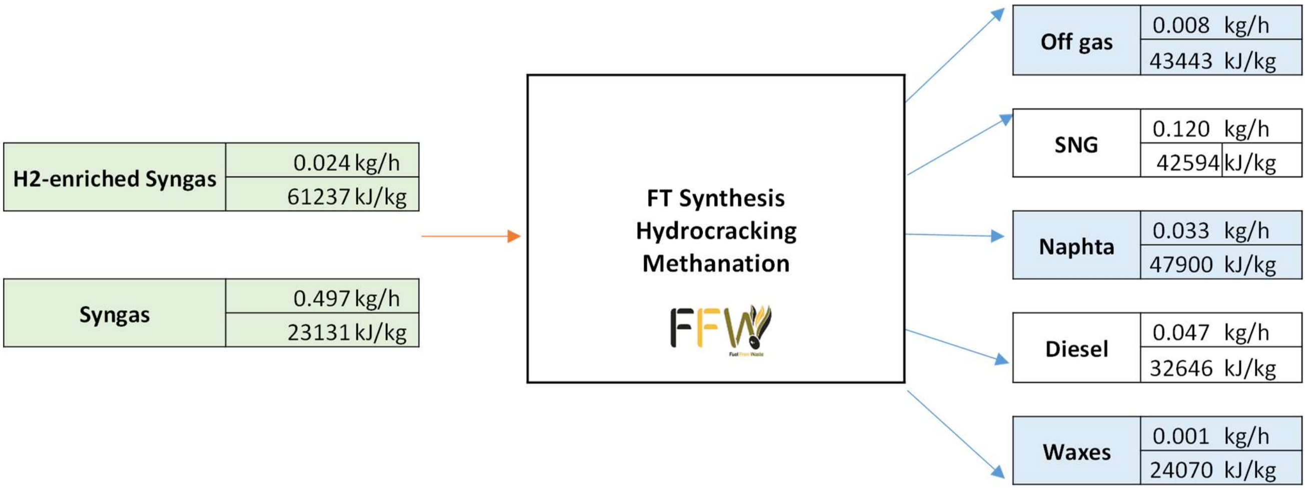

Figure 32. FFW Products (White) and By-Products (Blue) Mass Balance - case study

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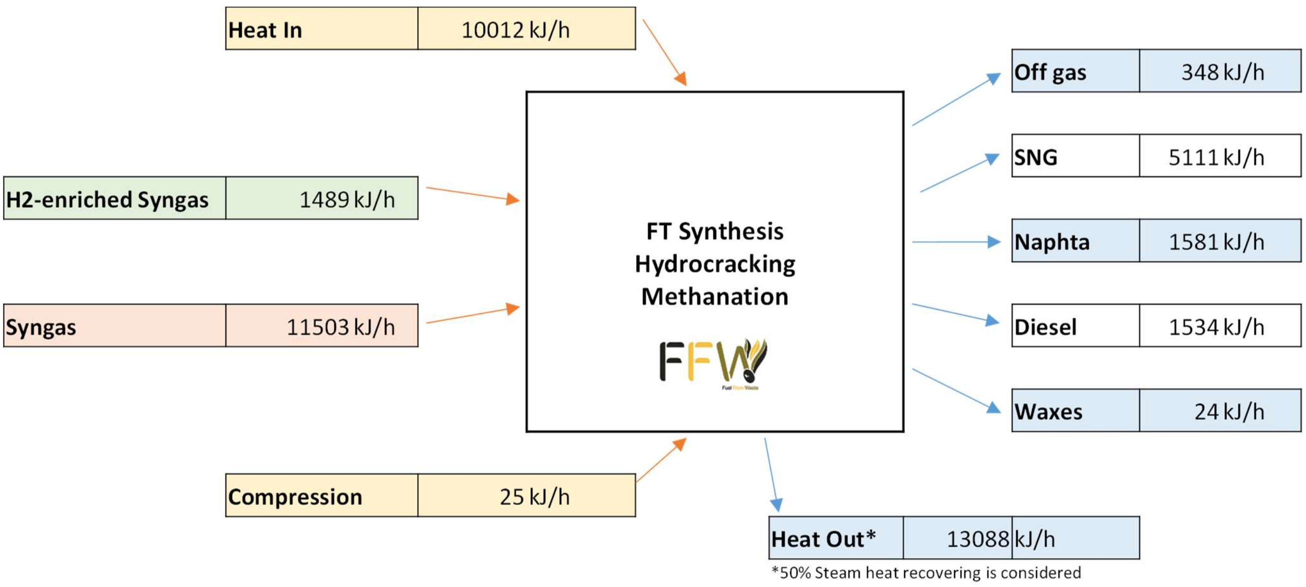
[6] kg of diesel are expressed as the addition of all diesel streams (atm. Column, vacuum column and hydrocracking) and Nm^3 is considered the volumetric flow of the SNG stream after upgrading.



$$\text{Process efficiency} = \frac{348+5111+1581+1534+24+6281}{1489+11503+10012+25} \quad 65\%$$

Figure 33. FFW Energy Balance for case study – case study

Figure 34 and Figure 35, as shown in base case, represent the different product distribution before and after hydrocracking. The trends are quite similar to base case, since the syngas composition is similar with a lower content in inert (nitrogen) which has not influence on the system, it does on the equipment sizing though.

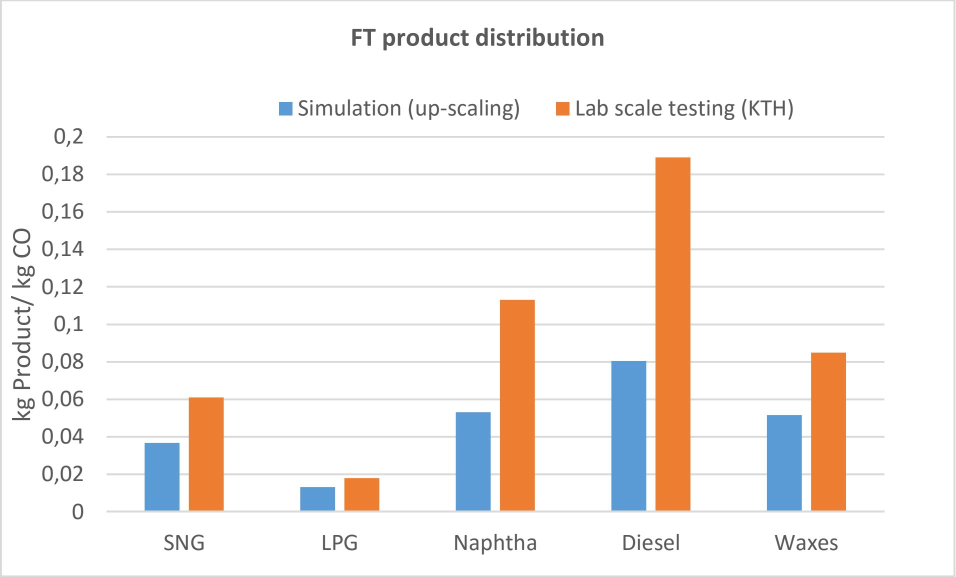


Figure 34. FT Product distribution - case study

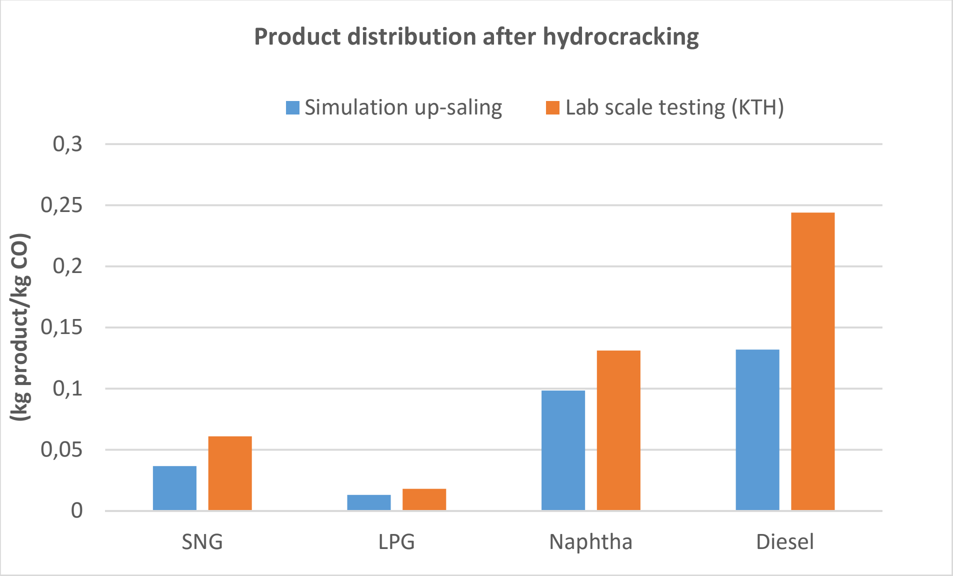


Figure 35. Product distribution after hydrocracking – case study

Table 88. FFW process mass balance-case study

Process	Materials in/out	Amount in (kg/h)	Per 1kg of biomass (kg/h)	Comments	HHV, kJ/kg
Fischer-Tropsch	CO-enriched	4,973.2	0.497		
	Hydrogen-enriched - 1	2.6	0.000	1.1 % of the Hydrogen-enriched stream	
	Gas to Methanation	-2,829.7	-0.283	H_2: 0.074; CO: 0.495; CO_2: 0.2748; N_2: 0.035; CH_4: 0.074	
	HCs to separation	-851.5	-0.085	Liquid products from F-T reaction	
	Water	-1,294.6	-0.129	H_2O: 0.997; MetOH: 0.003	
F-T Product Separation	HCs from F-T	851.5	0.085		
	Stripping Steam inlet	100.0	0.010	Water	
	Stripping Steam outlet	-100.0	-0.010	Water	
	Off Gas	-27.4	-0.003	H_2: 0.003; CO: 0.005; CO_2: 0.412; N_2: 0.006; Light HC: Rest	16,595
	Naphtha	**-268.0**	**-0.027**	From C5 to C11	47,844
	Diesel ATM	**-374.1**	**-0.037**	From C12 to C22	32,582
	Bottom/Feed VACUUM Column	-182.0	-0.018	Out from atmospheric column	
	Bottom/Feed VACUUM Column	182.0	0.018	Inlet vacuum column	
	Diesel VAC	**-27.5**	**-0.003**	From C12 to C22	23,579

Process	**Materials in/out**	**Amount in (kg/h)**	**Per 1kg of biomass (kg/h)**	**Comments**	**HHV, kJ/kg**
	Waxes to Hydrocracking	-154.5	-0.015		
Hydrocracking	Waxes from F-T	154.5	0.015		
	Hydrogen-enriched - 3	11.1	0.001		
	Purge	-9.1	-0.001	H_2: 0.927; Light HC: Rest	87,889
	Off Gas	-11.5	-0.001	H_2: 0.009; Ethane: 0.074; Propane: 0.170; Butane: 0.576; Other Light HC: Rest	49,167
	Naphtha	**-63.6**	**-0.006**		48,134
	Diesel	**-72.0**	**-0.007**		36,435
	Waxes	-8.0	-0.001		24,070
Methanation	Gas from F-T	2,829.7	0.283	78.9 % of the Hydrogen-enriched stream	
	Hydrogen-enriched - 2	191.7	0.019		
	Product to methane upgrading	-2,173.5	-0.217		
	Water	-845.3	-0.085	H_2O: 0.997; MetOH: 0.003	
Methane Upgrading	Product from methanation	2,060.3	0.206		
	DEPG clean from Methanation	16,927.9	1.693		
	DEPG dirty to Methanation	-17,786.2	-1.779		
	Methane Product	**-1,203.0**	**-0.120**		42,594
Hydrogen	H2 not used	**-37.6**	-0.004		61,237
Total		-34.5	-0.003		

Table 89. FFW process energy balance-case study

Process	**Energy Input/Output**	**Energy added (kJ/h)**	**Per 1kg of biomass (kJ/h)**	**Comments**
Hydrogen-enriched	Expander	-31,311	-3.13	
Fischer-Tropsch	Expander	-297,775	-29.78	
	Reactor heat	-11,996,504	-1,199.65	LP Steam Generation
	Cooler	-2,961,265	-296.13	LP Steam Generation
	Cooler	-2,375,548	-237.55	Chilled Water

Process	Energy Input/Output	Energy added (kJ/h)	Per 1kg of biomass (kJ/h)	Comments
F-T Product Separation	Condenser ATM	-945,597	-94.56	Chilled Water
	Heater	73,005	7.30	Dowtherm
	Reboiler VACUUM	16,160	1.62	Dowtherm
	Pump	2,170	0.22	
Hydrocracking	Preheater	26,346	2.63	Dowtherm
	Quencher	-156,646	-15.66	HP Steam Generation
	Product Heater	0	0.00	HP Steam Generation
	Heater	10,0000,000	10,000.00	HP Steam
	Cooler	-99,841,557	-9,984.16	LP Steam Generation
Methanation	Blower	84,600	8.46	
	Cooler	-5,343,697	-534.37	HP Steam Generation
	Product Cooler	-2,110,684	-211.07	HP Steam Generation
	Product Cooler	-890,172	-89.02	LP Steam Generation
	Product Cooler	-2,328,926	-232.89	LP Steam Generation
	Vessel Cooler	-1,506,546	-150.65	Chilled Water
Methane Upgrading	Blower	166,083	16.61	
	Cooler	-90,585	-9.06	Chilled Water
	Blower	3,437	0.34	
	Cooler	4,383	0.44	Chilled Water
Hydrogen	Blower	5,318	0.53	
Total	Net	**-30,464,001**	**-3046.40**	kJ/h
	Net	**-30,464**	**-3.05**	Net MJ/hr energy added
	Compression	**259**	**0.03**	Net MJ/hr energy added

Table 90. Equipment list for case study (completed post-gasification section) – case study

Equipment	Section	Unit Operation Model
B08001	8 (Mixing section)	Tee
B08002	8 (mixing section)	Expander
S09001	9 (Fischer-Tropsch)	Expander
S09002	9 (Fischer-Tropsch)	Mixer
S09003	9 (Fischer-Tropsch)	Heat Exchanger
S09004	9 (Fischer-Tropsch)	CSTR Reactor
S09005	9 (Fischer-Tropsch)	Heat Exchanger
S09006	9 (Fischer-Tropsch)	Three phases separator

Equipment	**Section**	**Unit Operation Model**
B10001	10 (Separation of FT products)	Valve
B10002	10 (Separation of FT products)	Heat Exchanger
B10003	10 (Separation of FT products)	Heater (Furnace)
B10004	10 (Separation of FT products)	Distillation Column
B10005	10 (Separation of FT products)	Heater (Furnace)
B10006	10 (Separation of FT products)	Distillation column
B10007	10 (Separation of FT products)	Pump
B11001	11 (Hydrogen compression)	Compressor
B12001	12 (Methanation)	Mixer
B12002	12 (Methanation)	Mixer
B12003	12 (Methanation)	Heat Exchanger
B12004	12 (Methanation)	Equilibrium Reactor
B12005	12 (Methanation)	Splitter
B12006	12 (Methanation)	Compressor
B12007	12 (Methanation)	Heat Exchanger
B12008	12 (Methanation)	Equilibrium Reactor
B12009	12 (Methanation)	Heat Exchanger
B12010	12 (Methanation)	Equilibrium Reactor
B12011	12 (Methanation)	Heat Exchanger
B12012	12 (Methanation)	Heat Exchanger
B12013	12 (Methanation)	Vessel separator
B13001	13 (Hydrocracking)	HCR Reactor
B13002	13 (Hydrocracking)	Petroleum Distillation Column
B14001	14 (Methane upgrading)	Compressor
B14002	14 (Methane upgrading)	Heat Exchanger
B14003	14 (Methane upgrading)	Absorber Column
B14004	14 (Methane upgrading)	Valve
B14005	14 (Methane upgrading)	Tanks
B14006	14 (Methane upgrading)	Compressor
B14007	14 (Methane upgrading)	Heat Exchanger

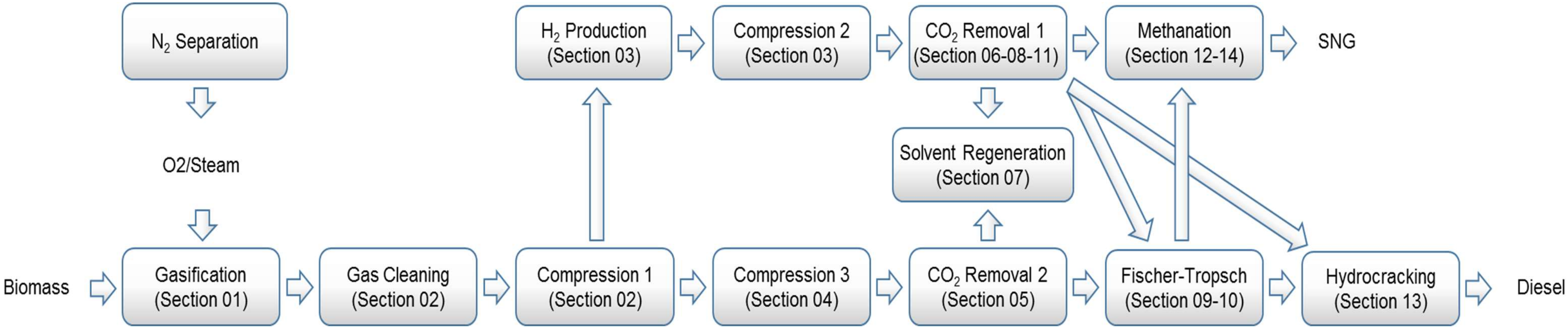


Figure 36: Block Flow Diagram for case study – case study

4 Discussion

Base case and case study have been designed and optimised in order to select the best configuration for the FFW project scale-up. Nitrogen presence is not good within the process, it is required an extra equipment, membranes have been chosen for this case, and high concentrations, as this deliverable shows, do not meet the European standardised parameters for the SNG which increase the capital expenses. Considering the base case, the main findings are as follows:

- FT process enables to obtain the maximum amount of hydrocarbons between C10-C21+, using a slurry bed reactor. This configuration has been designed using continuous stirred tank reactor configuration in HYSYS. The conversion has been fixed in 60 % to obtain the maximum amount of product without compromising the nitrogen concentration as output.
- FT products can be fractionated into hydrocarbon cuts and separated from the light gases by means of similar operations carried out in a petroleum refinery, which include distillation and cracking (with hydrogen).
- Hydrocracking model is favoured to middle distillates yields at low conversions (near 10 %). These results are not good because of the high amount of waxes that are still remaining as output. The model has been optimised at low inlet bed temperatures, near 360 ºC, achieving high conversion (around 90 %) and a reasonable yield for diesel fraction in comparison to naphtha, taking into account the conditions. However, the hydrocracking model created in the simulations should be calibrated with information of the experimental hydrocracker, including product distribution and experimental ASTM curves.
- SNG product contains a high amount of nitrogen and other components limited by the current legislation. This stream needs to be cleaned up, the best option is a membrane and an absorption operation, at least to remove the main concentration of nitrogen and carbon dioxide (taking into account the scale of the process).
- The heat integration of the process will produce a saving of energy: 98% for the heating and 7% for the cooling. This saving for the heating will produce a great reduction in the OPEX and CAPEX since the furnaces are not needed anymore. Besides, a large quantity of steam is produced in the cooling which might be used with other objectives such as electricity production in steam turbines. Due to the smaller flows to heat/cool in the Case Study, there is a 21% lower energetic requirement.
- The process equipment are smaller in the case study in the parts where there are gases such as FT section and methanation section and, moreover, in these reactors the catalyst amount will be reduced, i.e. in F-T is 36% lower. That will lead to a considerable reduction of the CAPEX.
- The process efficiency varies in both cases; the base case is a 7% more energy efficient than the case study. This data is not relevant due to the low precision of a basic engineering design.

Gasification is usually performed in absence of nitrogen or with low amounts of this compound, which reduces the compression energy and equipment dimensions.

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