Simulation of the Chemical Pre-treatment Process

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Lead Author	*Exergy*
Contributors	*Fraunhofer, KTH, Eifer*
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Disclaimer

Summary

The FFW project investigates co-production of fuels from olive oil industry waste: diesel and synthetic natural gas (SNG). The project work covers several technical project phases including research technology development, technology demonstration and industrial scale simulation. The entire FFW process requires several stages which can be broadly broken down into different stages: physical pre-treatment of biomass, chemical pre-treatment, and fuel synthesis stages. This document, details the simulation of the chemical pre-treatment process. The following steps have been undertaken:

- Building and validation of a gasifier model according to literature where (when available) similar gasifier, fuel, bed material and oxidising agent have been utilised.
- Scale up of model to dimensions of SOIL gasifier taking into account expected changes in reactor hydrodynamics and reaction conditions.
- Development of flow-sheet so other pre-treatment unit operations are included in the flow-sheet. This includes cyclones, heat exchangers, gas cleaning, water-gas-shift reactor, condenser, CO_2 removal and compressors. MSR and guard bed have been used during demo activities but due to the lack of current commercial viability, were discarded for the chemical pretreatment scale-up by simulation.
- Utilisation of FFW fuel in the scaled up model of the gasifier to undertake a sensitivity analysis to help determine process operating conditions, support equipment design and predict gas composition of the synthesis gas to be used in the downstream fuel synthesis stage of the FFW process
- Scale-up for industrial-scale process developed in deliverable 4.4.
- Additional simulation of case study (O_2/steam gasification). The main findings from undertaking work associated with this deliverable are as follows:
    - Efficiency of the gasifier increases with both temperature and equivalence ratio, however increased equivalence ratio significantly degrades the product gas which increases downstream processing costs. An equivalence ratio which allows for the highest safe operation of the gasifier , with maximum levels of heat recovery should be investigated for the demonstration activities. The simulation showed an ER of approximately 0.22 with maximum heat recovery would lead to a gasifier temperature of around 750 ºC (see D3.1 for further explanation) in order to avoid sintering problems in base case.
    - ER in case study has been set of 0.19. This value might be considered low, although it is justified due to the low operation temperature in the gasifier.
    - Gasification with steam does not fit the requirement of the syngas for FT process.
- Gas cleaning is an essential step that will ensure the right performance along the downstream process (Fischer-Tropsch and methanation processes). Although the presence of tar was not modelled throughout the gasification stage, the gas cleaning has been roughly designed from bibliographic information. Amongst several options, an oil scrubber was selected as the most suitable option. In D3.3, other options are detailed for scrubbing, such as RME oil (lower viscosity and pressure drop), although the environmental impact is quite higher as G1 biodiesel. Soybean oil was selected as oily absorbent and hot air as regeneration agent.
- Nitrogen needs to be removed along the base case process. A commercial membrane has been chosen as a feasible option for this operation (due to the scale of the process and the logistical limitations). Energy requirements for compression are higher along the base case due to the presence of nitrogen.

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1 Introduction

1.1 Purpose and Scope

This deliverable forms part of work package 3 (WP3) "*Chemical pretreatment technology*" of the FFW project and aims to report the information collected along the Task 3.4. The WP aims to investigate and optimise the gasification process and downstream gas-upgrading technologies of the FFW process. The main objective of the deliverable is to simulate the chemical pre-treatment processes on an industrial scale which will provide inputs into Task 4.4 'Optimisation and scale up of the system based on simulation', which in turn feeds information into Task 6.1 - 'Life cycle analysis of the FFW system' which will help to determine the viability of the industrial FFW process. At this stage, the simulations have helped support the overall process design for the chemical pre-treatment stage of the FFW pilot plant and the developed models will form a basis for industrial scale-up.

The simplified block flow diagram in Figure 2 shows the major steps required to produce synthesis gas for the synthesis stage of the base case FFW process from the physically treated biomass. The figure shows main stages:

- Gasification – Biomass is converted into a gaseous mixture of mainly carbon monoxide and hydrogen for use in the production of Fischer Tropsch and methanation reactor.
- Purification - Tar and other impurities are removed from the gas along with carbon dioxide and water.
- Compression - The pressure of the gas is increased in preparation for the synthesis section of the FFW process.
- Hydrogen Production - Some of the gasifier product gas is used for hydrogen production (using WGS reactors, CO_2 and N_2 removal).
    - Hydrogen rich gas is then used for altering the H_2:CO ratio before Fischer-Tropsch and methanation synthesis steps.
    - Hydrogen is used for cracking of Fischer Tropsch waxes in the hydrocracker.
- Carbon dioxide and water removal – Water content is reduced. Carbon dioxide is removed from the process gas by means of physical absorption with Selexol®.

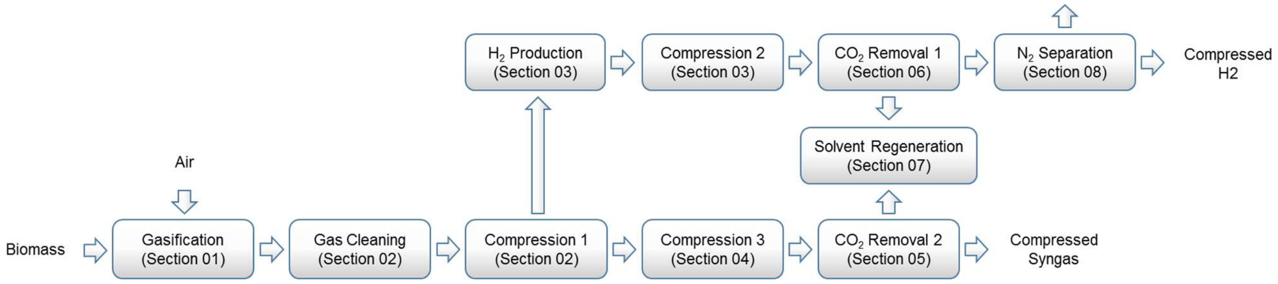

Figure 1. Simplified chemical pre-treatment block flow diagram

An additional process set-up is evaluated (case study). This set-up considers gasification with O_2/steam instead of air. The figure shows the main stages.

- Air Separation Unit (ASU) – Oxygen is separated from air through cryogenic distillation. Oxygen is then used as an oxidising agent in the gasifier.

- Gasification – Biomass is converted into a gaseous mixture of mainly carbon monoxide and hydrogen for use in the production of Fischer-Tropsch and methanation reactor.
- Purification - Tars and other impurities are removed from the gas along with carbon dioxide and water.
- Water gas shift - The composition of the gas is altered to reach the required hydrogen to carbon monoxide ratio
- Compression - The pressure of the gas is increased in preparation for the synthesis section of the FFW process. Compression stages are present in different sections along the entire process
- Hydrogen Production - Some of the WGS product gas is used for hydrogen production (using WGS reactors, CO_2 removal).
- Hydrogen is used for cracking of Fischer Tropsch waxes in the hydrocracking process (see D4.4).
- Water removal and carbon dioxide removal from product gas

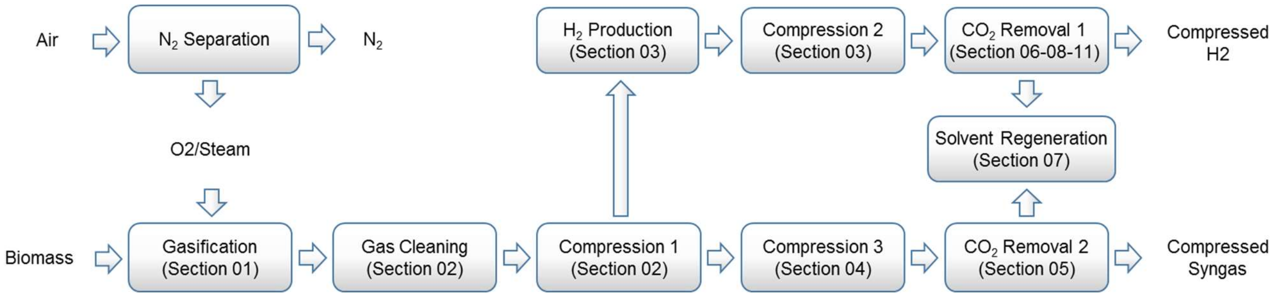

Figure 2. Simplified chemical pre-treatment block flow diagram

An overview of each one of the processes is provided within this document and where required a literature review of the modelling approaches is undertaken. Based on the literature review and the requirements of the project, each process is modelled, and where required optimised, using Aspen PLUS or Aspen HYSYS software. Required intermediate steps are added and discussed within each section. The modelled unit operations are used to help make develop pilot plant experiments.

Taking into consideration experimental results and requirements of the overall industrial scale system, alterations to the chemical pre-treatment individual unit operations can be made. The improved designs will further contribute to optimise the overall FFW industrial system as part of deliverable 4.4. which provides the input into the life cycle analysis.

1.2 Implementation

Flow-sheeting software Aspen PLUS and Aspen HYSYS are used to model the chemical pre-treatment process. To utilise both Aspen HYSYS and Aspen PLUS, unit operation models are placed onto a flow-sheet and these unit operations are connected with material and energy streams. When the flow-sheet is completed, the simulation can be run and (usually) mass and energy balances of each unit operation are solved sequentially. Where the unit operation models are not suitable to model the required process, several unit operations can be combined. Unit operations can also be supplemented by user sub-routines (usually written in Fortran code) or alternatively custom models can be built separately and utilised (within Aspen PLUS.)

The accuracy of the models is dependent on several factors however one very important factor is selection of the most appropriate property model along with the selection of the correct unit operations so as to reflect the process correctly.

1.2.1 Aspen PLUS

1.2.1.1 Property Models

Aspen Plus (1) provides both in-software written information and a property model selection tool to enable selection of the most appropriate property model. Information was accessed and the tool utilised to help determine the most appropriate property model. The following property models were considered for the majority of the chemical pre-treatment stage of the FFW process:

- Redlich-Kwong-Soave (RK-SOAVE)
- Peng Robinson (PENG-ROB)

Some information from Aspen PLUS has been included here to show the suitability of both of these property models. SRK has been utilised but moth models produced very similar results.

Both Redlich-Kwong-Soave and Peng Robinson were deemed unsuitable for simulation of the CO_2 removal process and for this section of the flow-sheet, the ACID-GAS property model was utilised (Aspen HYSYS).

1.2.1.1.1 Redlich-Kwong-Soave

The RK-SOAVE property method uses the Redlich-Kwong-Soave (RKS) cubic equation of state for all thermodynamic properties except liquid molar volume. For pseudo-components liquid molar volume is calculated using the American Petroleum Institute (API) method. The Aspen PLUS 'general model' is used to calculate liquid molar volume for real components.

This property method is comparable to the PENG-ROB property method. It is recommended for gas-processing, refinery, and petrochemical applications. Example applications include gas plants, crude towers, and ethylene plants.

Mixture Types

The RK-SOAVE property method can be used for nonpolar or mildly polar mixtures. Examples are hydrocarbons and light gases, such as carbon dioxide, hydrogen sulphide, and hydrogen. This property method is particularly suitable in the high temperature and high pressure regions, such as in hydrocarbon processing applications or supercritical extractions.

Range

Reasonable results can be expected at all temperatures and pressures. The RK-SOAVE property method is consistent in the critical region. Therefore, unlike the activity coefficient property methods, it does not exhibit anomalous behaviour. Results are least accurate in the region near the mixture critical point.

1.2.1.1.2 Peng-Robinson

The PENG-ROB property method uses the standard Peng-Robinson cubic equation of state for all thermodynamic properties except liquid molar volume. The API method is used to calculate liquid molar volume for pseudo-components and the 'Rackett model' is used for real components

This property method is comparable to the RK-SOAVE property method. It is recommended for gas-processing, refinery, and petrochemical applications. Sample applications include gas plants, crude towers, and ethylene plants.

Peng-Robinson state equation has been used in air separation unit (ASU) design. For nitrogen and oxygen system the Peng-Robinson state equation is usually used for calculation of equilibrium coefficient k_{ij} (2).

Mixture Types

The PENG-ROB property method can be used for nonpolar or mildly polar mixtures. Examples are hydrocarbons and light gases, such as carbon dioxide, hydrogen sulphide, and hydrogen.

This property method is particularly suitable in the high temperature and high pressure regions, such as in hydrocarbon processing applications or supercritical extractions.

This property method can be used for polar, non-ideal chemical mixtures, if appropriate alpha functions and mixing rules are used.

Range

Reasonable results are expected at all temperatures and pressures. The PENG-ROB property method is consistent in the critical region. Therefore, it does not exhibit anomalous behaviour, unlike the activity coefficient property methods. Results are least accurate in the region near the mixture critical point.

1.2.1.2 Unit Operation Models

Many unit operations models are used to model the chemical pre-treatment process. An overview of the models is given in Table 1 with information taken from Aspen PLUS (1).

Table 1. Aspen PLUS Unit Operation Models

Unit Operation Model	Description
RGIBBS	Rigorous reaction and/or multiphase equilibrium based on Gibbs free energy minimisation
RSTOIC	Stoichiometric reactor based on known fractional conversions or extents of reaction
RPLUG	Rigorous plug flow reactor with rate-controlled reactions based on known kinetics
RCSTR	Rigorous continuous stirred tank reactor with rate-controlled reactions based on known kinetics. Also allows for equilibrium reactions.
RYIELD	Nonstoichiometric reactor based on known yield distribution
HEATER	Thermal and phase state changer. Models heaters, coolers, condensers, and so forth.
HEATX	Two-stream heat exchanger. Models co-current and counter-current shell and tube heat exchangers. In rigorous mode, can also mode air-cooled and plate exchangers using Aspen Exchanger Design and Rating.
MIXER	Stream mixer. Combines material, heat, or work streams.
FSPLIT	Stream splitter. Divides feed based on splits specified for the outlet streams.
SPLIT	Sub-stream splitter. Divides feed based on splits specified for each sub-stream.
PUMP	Pump or hydraulic turbine

Unit Operation Model	Description
COMPR	Compressor/turbine. Models polytrophic or isentropic compressors, isentropic turbines, etc
FLASH2	Two-outlet flash. Models flash drums, evaporators, and so forth, using rigorous Vapour-Liquid or Vapour-Liquid-Liquid equilibrium.
SEP	Component separator. Separates components into multiple outlet streams based on specified flows or split fractions.
SEP2	Two outlet component separator. Separates components into two outlet streams based on specified flows, split fractions, or purities.
FLUIDBED	Models behaviour of fluidised bed units. Can now handle any reactions which could be specified for typical reactors like RCSTR
RADFRAC	Rigorous two- or three-phase fractionation for single columns. Models absorbers, strippers, reactive distillation, and so forth.
MCOMPR	Multistage compressor/turbine. Models multistage polytrophic or isentropic compressors, etc.

1.2.2 Aspen HYSYS

1.2.2.1 Aspen HYSYS Property Models

Aspen HYSYS (1) provides both in-software written information and a property model selection tool to enable selection of the most appropriate property model. Information was accessed and the tool utilised to help determine the most appropriate property model. The following property models were considered for the majority of the chemical pre-treatment stage of the FFW process:

- Peng-Robinson-Stryjek-Vera (PRSV)
- Perturbed Chain Statistical Association Fluid Theory (PC-SAFT)

Some information from Aspen PLUS has been included here to show the suitability of both of these property models. SRK has been utilised but moth models produced very similar results.

Both Redlich-Kwong-Soave and Peng Robinson were deemed unsuitable for simulation of the CO_2 removal process and for this section of the flow-sheet, the PC-SAFT property model was utilised (Acid gas model included in HYSYS).

1.2.2.1.1 Peng-Robinson-Sryjek-Vera

The PRSV model is a two-fold modification of the Peng-Robinson equation of state that extends the application of the original Peng-Robinson method for moderately non-ideal systems. This EoS is shown to match vapour pressures curves of pure components and mixtures more accurately than the PR method, especially at low vapour pressures. 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. (3)

Mixture Types

It has the potential to more accurately predict the phase behaviour of hydrocarbon systems, particularly for systems composed of dissimilar components and it can be extended to handle non-ideal systems with accuracies that rival traditional activity coefficient models.

Range

In the PSRV equation, the parameter fit is done in a particular temperature range which is usually below the critical temperature. Above the critical temperature, the PRSV alpha function tends to diverge and become arbitrarily large instead of tending towards 0. Because of this, alternate equations for alpha should be employed above the critical point. This is especially important for systems containing hydrogen which is often found at temperatures far above its critical point. Several alternate formulations have been proposed. Some well-known ones are by Twu et all or by Mathias and Copeman.

1.2.2.1.2 Perturbed Chain Statistical Association Fluid Theory

In Aspen HYSYS, the Acid Gas Cleaning functionality has been enhanced with a new property package, “Acid Gas - Physical Solvents”, based on the Perturbed Chain Statistical Association Fluid Theory (PC-SAFT) Equation Of State. It is used by the HYSYS acid gas cleaning workflow to simulate removal of acid gasses such as Carbon Dioxide and Hydrogen Sulfide from process streams.

Mixture Types

The equation of state gives good fits to these properties and agrees well with caloric properties. When applied to vapour-liquid equilibria of mixtures, the equation of state shows substantial predictive capabilities and good precision for correlating mixtures.

Range

Reasonable results are expected at all temperatures and pressures.

1.2.2.2 Aspen HYSYS Unit Operation Models

Many unit operations models are used to model the chemical pre-treatment process. An overview of the models is given in Table 1 with information taken from Aspen HYSYS (1).

Table 2. Aspen HYSYS Unit Operation Models

Unit Operation Model	Description
Mixer	Combines two or more inlet streams to produce a single outlet stream.
Tee	It 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
Heat Exchanger	It performs two-sided energy and material balance calculations.
Cooler/Heater	They 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.
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.
3-Phase 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.
Tank	Multiple feeds, one liquid and one vapor product stream. The Tank is generally used to simulate liquid surge vessels.
Absorber	The only unit operation contained in the Absorber is the Tray Section, and the only streams are the overhead vapour and bottom liquid products.
Refluxed Absorber	Tray section and an overhead condenser.

Unit Operation Model	**Description**
Distillation	Tray section with both a reboiler and condenser
Component Splitter	A material feed stream is separated into two component streams based on the parameters and split fractions that you specify
Tray Sections	Represents the series of equilibrium trays in a Column.
Pump	The Pump operation is used to increase the pressure of an inlet liquid 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.
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.
Equilibrium Reactor	It is a vessel which models equilibrium reactions. The outlet streams of the reactor are in a state of chemical and physical equilibrium.
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.
Recycle	The Recycle installs a theoretical block in the process stream. The stream conditions can be transferred either in a forward or backward direction between the inlet and outlet streams of this block. In terms of the solution, there are assumed values and calculated values for each of the variables in the inlet and outlet streams.
Stream Cutter	The stream cutter is an object that allows you to switch the fluid package of a stream anywhere in the flowsheet. This concept of changing fluid package is called fluid package transition.

2 Base Case

The flow-sheet used to model the FFW process is set-up. For the data presented in this document, the following general settings are adopted:

Table 3. Model Global Settings

Setting	Value
Aspen PLUS version	V8.8
Properties base method	SRK
Free water calculation method	STEAMNBS
Components database	APV86 PURE 32 APV86 AQUEOUS APV86 SOLIDS APV86 INORGANIC
In-put mode	Steady-state
Stream Class	MICINCPSD

It should be noted that the components database includes properties of conventional components only. For non-conventional components, like Biomass, additional data is added or calculated using correlations. The non-conventional components utilised in the FFW process are dealt with according the following table:

Table 4. Non-conventional components calculation methods

Input	Density Model	Enthalpy Model	Heat of Combustion Method	Heat of Formation Method	Heat Capacity Method	Enthalpy Basis
Non-conventional properties of biomass	DCOALIGT	HCOALGEN	6. User Input	1. Heat of Combustion correlation	1.Kirov Correlation	1.Elements in standard state at 298.15K and 1 atm
Non-conventional properties of ash	DCOALIGT	HCOALGEN	1.Boie correlation	1. Heat of Combustion correlation	1.Kirov Correlation	1.Elements in standard state at 298.15K and 1 atm

2.1 Gasification

The gasifier used in the demonstration activities is the one Soil Concept used for the CHP plant, the unit is already specified. The industrial scale base case considers an up-scaled version. The gasification stage additionally includes a blower, which increases pressure of the oxidising agent, a cyclone system to remove residual solids and a heat exchanger system for preheating of gasifying agent for the gasifier.

2.1.1 Gasification Overview

In the FFW process, a gasifier is used to convert biomass pellets and shredded material into gaseous products. In the process, partial thermal oxidation of biomass, results in a high proportion of gaseous products (carbon dioxide, water, carbon monoxide, hydrogen and other gaseous hydrocarbons), small quantities of char (solid product), ash, and some condensable compounds (tars and oils along with other impurities as listed in D3.3).

Different reactors can be used for gasification but the chemical processes that occur within the reactors largely remain the same. In all of the reactors, steam, air, oxygen, carbon dioxide or a mixture of is supplied to the reaction as an oxidising agent. The following generally accepted stages occur in all reactors (4):

- Drying. In this stage, the moisture content of the biomass is reduced. Drying occurs at any temperature above about 100 ºC.
- Devolatilisation (pyrolysis) - Essentially the thermal decomposition of the biomass in the absence of oxygen or air. In this process, the volatile matter in the biomass is released in the form of hydrocarbon gases. The biomass is reduced to solid charcoal (or char). At lower temperatures an increased number of hydrocarbon gases condense to generate liquid tars. It is generally accepted that most devolatisation occurs below 500 ºC and above that temperature additional gas formation is low.
- Oxidation (combustion). Solid biomass reacts with oxygen in the air (where utilised), resulting in formation of CO_2. Some CO is oxidised to form CO_2. Hydrogen present in the biomass is also oxidised to generate water. The reactions release a large amount of heat. Since oxygen is usually present in sub-stoichiometric quantities, carbon oxidation can become limited, some partial oxidation of carbon can occur, resulting in the generation of carbon monoxide.
- Gasification. In the absence (or sub-stoichiometric presence) of oxygen, several further reactions occur. CO_2 and H_2O react with carbon in the biomass to form CO and H_2.
- Volatiles will also react with each other including through various reaction -including the water-gas shift reaction.

Some of the key aspects which affect gasifier operation are now briefly discussed. The effect of some of the key differences can be seen in the varying results of different experimental studies.

2.1.1.1 Gasification Reactors

The most common gasifier reactor types are fixed bed (which can be updraft, down draft or cross draft), fluidised bed (which can be bubbling, circulating or twin bed) and entrained flow (5).

Despite carbon loss with ash, production of gas with moderate tar levels and high levels of particulates, a bubbling fluidised-bed gasifier is used for the FFW process. It has the following beneficial characteristics (6):

- Flexibility of operation at loads lower than design load.
- High fuel flexibility in terms of both size and type (entrained flow requires costly pre-treatment)
- Ease of operation.
- Good temperature control and high reaction rates.
- Good gas–solid contact and mixing.
- Possibility for In-bed catalytic processing
- High carbon conversion.
- High conversion efficiency.
- Good scale-up potential.

- Suitability for large-scale capacities – bubbling fluidised beds can be suitable up to 50MW and circulating fluidised beds as high as 500MW

In a bubbling fluidised bed gasifier, biomass, usually crushed to less than 10 mm, is fed into a bed of hot materials. These bed materials are fluidised with steam, air, or oxygen, or a combination of the above, depending on the choice of gasification medium. The ash generated from the fuel is usually removed from the bottom of the bed – although fly ash may escape with the gas. The bed temperature is normally kept below 900 ºC for biomass to avoid ash fusion and consequent agglomeration (6). Experiments undertaken by Fraunhofer (see D3.1) demonstrated that for olive waste, particularly 3 phase pomace, the softening temperature in the bed gasifier was much lower at 700 ºC. Very low sintering point is the biggest challenge in utilization of pomace residues at high-temperature process in addition to low and seasonal availability of the material.

2.1.1.2 Gasifier Bed Material

As mentioned earlier, use of a fluidised bed gasifier enables introduction of catalysts as the bed material for which the gasifying agent bubbles through. Various materials have been used for bed material in gasifiers. Alauddin *et al* (6) provide a good overview of fluidised bed gasification and the effect of different bed materials:

The bed materials act as heat transfer medium but they can also assist in tar cracking which can reduce requirements for downstream tar removal process. Additionally, the presence of catalyst as the bed material during biomass gasification promotes several chemical reactions which influences the composition and heating value of the producer gas (6) including the H_2:CO ratio.

Generally, three main groups of catalysts are utilised to remove tar from the producer gas: (1) natural catalysts such as dolomite and olivine; (2) alkali-based catalysts such as (Li, Na, K, Rb, Cs and Fr) and (3) metal-based catalyst such as nickel catalysts. All three groups were analysed by Alauddin (4):

Dolomite is the most commonly used catalyst which effectively removes heavy hydrocarbons from the gas stream. It also decreases agglomeration in fluidised bed which is particularly important when gasifying biomass with high alkali content. As olive pomace residues are, the undesired property of dolomite is its quick calcination in the gasifier which consequently results in a gas with high particulate. Olivine is reported to be less effective than dolomite but its resistance against attrition is more than that of dolomite. Alkali-based catalysts (Li, Na, K, Rb, Cs and Fr) are able to improve the gasification rate and reduce the tar content of the producer gas. However, difficulty in recovery, high cost and agglomeration at high temperatures are some of the disadvantages of the alkali-based catalysts. Metal-based catalysts are also highly effective in removing tar and improve the quality of the producer gas. The main problems associated with this type of catalysts are carbon deposition and nickel particle growth, which cause catalyst deactivation.

Many studies have been undertaken on the effects of different bed materials. Miccio *et al*. (7) concluded that the presence of a catalyst increased the hydrogen concentration in the producer gas and also the total gas yield was slightly improved. Another investigation conducted by Weerachanchai et al. (8) showed that calcined limestone and calcined concrete waste improved the H_2 and CO_2 content of the producer gas, whereas silica sand increased the CO content. Skoulou *et al* (9) concluded that although quartz sand is a cheap and abundant material, it caused severe de-fluidisation due to its tendency to enable tar formation at temperatures below 800 ºC. When Skoulou *et al* utilised olivine they observed that at low gasification temperature of 750 ºC and ER of 0.2, components of tar were thermally broken down and H_2 and CO was released, due to the catalytic effect of iron-based olivine.

Taking into account the studies which have taken place and the circumstances surrounding the SOIL Concept gasifier, olivine was selected as the most appropriate bed material for the industrial-scale base case study.

2.1.1.3 Gasifier Oxidising Agent

The purpose of the oxidising agent in the gasifier is two-fold.

1) to undergo combustion to provide energy for endothermic gasification reactions
2) to act as a fluidising agent to cause the gasifier bed to become fluidised and allow bed material to promote reactions occurring in the gasifier

Gasifying agents utilised include, air, oxygen, steam, nitrogen or a combination of different oxidising agents. Air is used in the SOIL gasifier, with the potential to add small amounts of steam. Benefits of using air as the oxidising agent:

- Should provide sufficient fluidisation velocity to fluidise the bed compared to pure oxygen in a gasifier with similar dimensions – use of oxygen necessitates recycle or gasifier of narrow diameter
- Does not increase moisture levels (compared to using steam) in the gasifier which for the Fraunhofer showed increased problem with agglomeration for FFW biomass (see D3.1).
- Does not increase levels of nitrogen in the system as much as using air nitrogen as the oxidising agent - which increases the size of downstream equipment
- Lessens temperature increases due to exothermic water-gas-shift, Fischer-Tropsch and methanation processes because the nitrogen acts as thermal ballast –
    - Presence of N_2 facilitates isothermal temperature control in the Fischer Tropsch reactor and forces Fischer Tropsch to be operated at higher pressures which offers a more homogeneous bubble regime if a slurry bed reactor is used (no longer considered).
    - Presence of N_2 offers the possibility of running the first fixed bed methantion reactor without recycling (or with a minor recycling) which can diminish the running costs of the plant.
- Cheap and available anywhere – cost of removing nitrogen from air is high.

Drawbacks of utilising air as a gasification agent include:

- Larger process equipment size requirements compared to using oxygen,
- Increased energy usage in downstream compression and heating
- Requirement for nitrogen removal downstream to produce standards compliant synthetic natural gas (SNG) in the downstream processes. Although, in practice, for commercial application, a solution is required to transport SNG from a FFW plant to different places. If grid injection is not available, probably the most practical solution is to liquefy the SNG, which can also serve to separate Nitrogen (BP:-196C) from SNG (BP: -162C). Membrane could also be used.
- Uncertainty regarding ability to achieve H_2:CO of 2:1 within the gasifier which means the FFW process has a requirement for a water gas shift reactor prior to the Fischer Tropsch process –increasing capital costs of the process.

Based on the positives and negatives of using air, and according to the circumstances of SOIL Concept, air is deemed the most appropriate choice of gasifying agent for the FFW demonstration activities and industrial scale base case study.

2.1.2 Modelling Review

2.1.2.1 Gasifier Modelling Approaches

There are numerous approaches to modelling gasifiers. The types of models are well summarised by Basu (5). An additional comprehensive review and detailed information regarding fluidised-bed biomass gasification modelling is given by Gomez-Barea and Leckener (10). Generally speaking, models can be classified as follows:

- Thermodynamic equilibrium – which predicts the maximum achievable yield of a desired product from a reacting system.
- Kinetic - predict the product from a gasifier. A kinetic model studies the progress of reactions in the reactor, giving the product compositions at different positions along the gasifier. It takes into account the reactor's geometry as well as hydrodynamics.
- Computational fluid dynamics (CFD) - CFD models solve a set of simultaneous equations for conservation of mass, momentum, energy, and species over a discrete region of the gasifier. Thus, they give distribution of temperature, concentration, and other parameters within the reactor.
- Artificial neural network - the neural network *learns* by itself from sample experimental data.

2.1.2.1.1 Aspen PLUS Modelling Approaches

A comprehensive review of Aspen PLUS gasification models is given in the review by Puig-Arnaat *et al* (4), which also details other modelling approaches. The developed Aspen PLUS models tend to be equilibrium models, kinetic models or combination of equilibrium and kinetic models

Equilibrium models tend to utilise an GIBBS reactor to simplify the gasification process. This method is used by Mathieu and Dubuisson (11) however this usually results in overestimate of char conversion and overestimates of the production of both hydrogen and carbon monoxide.

Several research groups, including Nikoo and Mahimpey (12) attempt to combine different reactor models to model the single unit gasifier. In their model an RGIBBS reactor predicts volatile reduction and hydrodynamics and kinetics are considered for the conversion of char by complementing two CSTR reactors with user sub-routines. The two CSTR reactors represent different distinct areas of the gasifier, the bed and the freeboard. The model shows good agreement with experimental data.

Other approaches to modelling gasifier in Aspen PLUS are semi-empirical, like work by Doherty *et al* (13). In their work adaptation of kinetics is adopted to enable improvement of the model.

2.1.3 FFW Gasification Process Model /Design

2.1.3.1 FFW Gasification Process Model Description

A combination of unit operation models and modelling approaches are used to model the FFW gasification process. The gasifier model is supplemented by the necessary additional unit operations (heat exchanger, cyclone) which enable the gasification process to be incorporated within the rest of the FFW. The overall gasification process can be seen in Figure 3

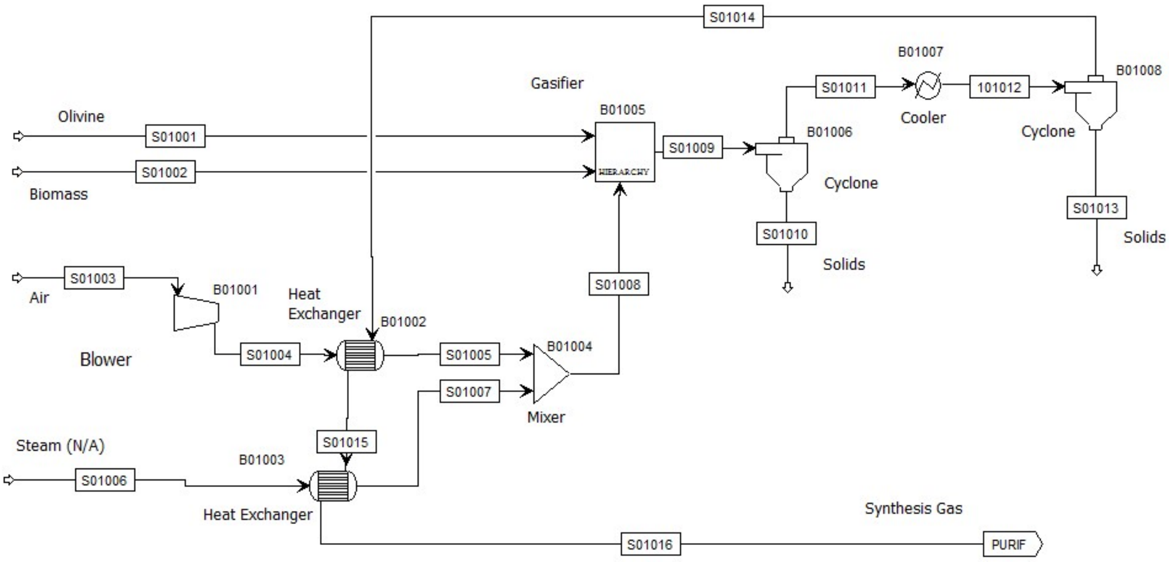

Figure 3. Gasifier Set-up

The flow-sheet of the FFW gasifier shows how physically treated biomass, along with small amounts of olivine, is added to the gasifier. The blower (modelled using a COMPR) increases the air pressure moderately. The air is preheated in a heat exchanger (HEATX) and is injected into the gasifier and acts to fluidise the bed. Devolatilisation, oxidation and gasification take place in the reactor (modelling detailed below). Produced gas enters the cyclones (CYCLONEs) where ash and char are removed leaving a mixture of gases with low levels of solids present. The gases pass through the air preheater (HEATX) before they are further processed as part of the purification stage. The majority of the solids (ash and some fractionated olivine) are collected at the bottom of the gasifier.

Figure 4 shows the unit operation models used to model the gasifier. Several models are used, which represent different stages and zones within the gasifier.

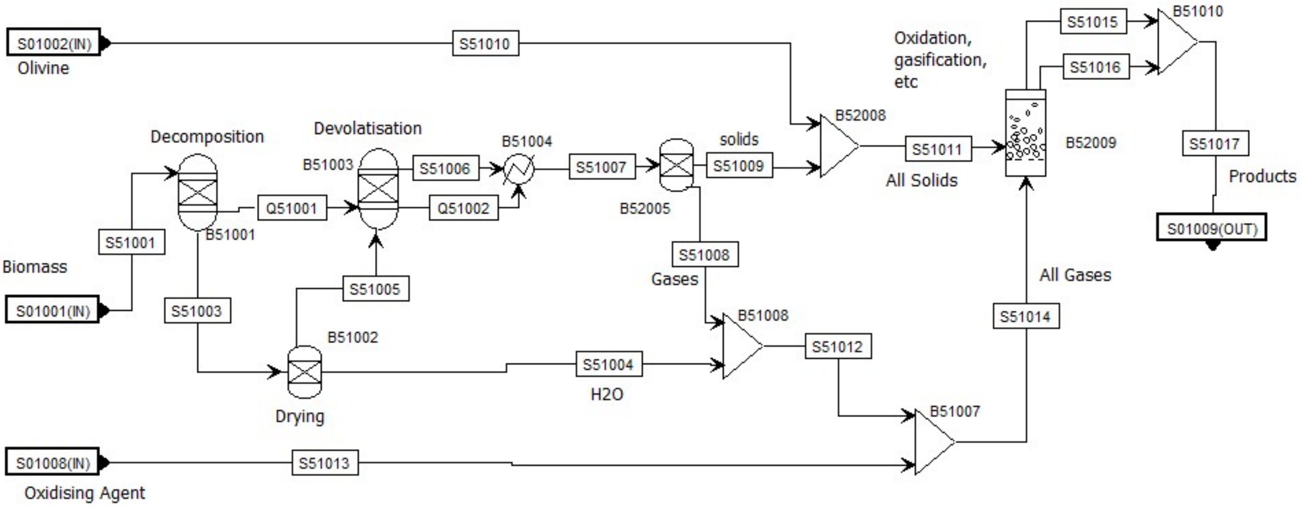

Figure 4. Modelling of the gasifier

2.1.3.2 Drying and Devolatilisation modelling:

On entering the gasifier bed and through exposure to heat, drying and devolatilisation of the biomass also takes place instantaneously – drying usually takes place below temperatures of 200 ºC, and devolatilisation takes place much faster than oxidation which takes place much faster than gasification (14). The drying devolatilisation is modelled using a combination of RYIELD and RGIBBS reactors and a Separator (SEP). The RYIELD breaks the biomass into its constituent components according to the ultimate analysis. The SEP unit separates out the water (drying). An energy stream connects the RYIELD reactor to an RGIBBS reactor.

The RGIBBS reactor models the devolatilisation of the biomass – which in the model occurs at a fixed temperature of 500 ºC. This temperature is maintained by taking energy from the produced gas/solid stream using a heater (B51004) which in the case of the FFW biomass lowers the temperature of the stream (since the temperature of the FLUIDBED unit is fixed and energy input/output of the unit is controlled to be 0, by changing the amount of air preheating, this should not affect the model). All of the volatiles leave the biomass with the product composition calculated according to the minimisation of the Gibbs equilibrium but limited to the major products of gasification (H_2, H_2O,CO, CO_2, S, O_2S, Cl_2, HCL, N_2, short chain alkanes and alkenes.) Tars are not modelled at this time. The effects of ignoring tars are deemed minimal – in fact EIFER show that destruction of tars in the MSR accounts for only a small increase in H_2 and CO (See D3.2 and D3.3). In the RGIBBS reactor, fixed carbon is specified (according to the analysis) as inert and does not take part in the reactions.

2.1.3.3 Volatiles reactions and char gasification modelling:

The non-instantaneous gasifying reactions are modelled using a ‘FLUIDBED’ unit – a unit that was recently added to Aspen PLUS - , and for the FFW model, replaced the combination of reactors, which was used to model these reactions in the gasifier. The fixed carbon, ash and small amounts of olivine are added to the reactor as ‘solids’. The volatiles, water vapour (previously separated from the biomass) and the oxidising agent (air) are added as the gas (or fluidising agent).

Detailed information regarding the fluidised bed model can be found within the Aspen PLUS help sections. Briefly, the model is divided into different vertical zones. At the bottom there is the dense fluidised bed also called the bottom zone, above which the freeboard or upper dilute zone is located. The transient region in between is denoted as the splash zone, where rising bubbles from the bottom bed explode and cause a more fuzzy transition between the bottom bed and upper dilute zone. The unit considers hydrodynamics and kinetics of a fluidised bed reactor.

For the FFW demonstration gasifier, the reactor dimensions and details of gas distributor are used – and the properties of the bed material and reactants are considered including the particle size distribution. For the base case industrial scale process, the dimensions of the gasifier are selected in order to maintain a gas velocity wish achieves fluidisation of the bed –without causing entrainment of the biomass (i.e. gas velocity <1m/s)

The kinetics for heterogeneous reactions are adopted from work by Gomez-Barea and Leckner (10). The kinetics for the gasification reactions are adopted from work by Nilsson *et al* (15) who investigated gasification kinetics of olive pruning residues. To describe the char conversion, a model is adopted whereby as the char reacts, the char particles shrink – known as ‘the shrinking particle’ model. The main reactions which have been considered are:

Table 5. FLUIDBED Reactions

Name	Reaction class	Stoichiometry
Water-gas-shift	POWERLAW	CO(MIXED) + H_2O(MIXED) → H_2(MIXED) + CO_2(MIXED)
Reverse Water-gas-shift	LHHW	CO_2(MIXED) + H_2(MIXED) → CO(MIXED) + H_2O(MIXED)
CO Oxidation	POWERLAW	CO(MIXED) + 0.5 O_2(MIXED) + 0 H_2O(MIXED) → CO_2(MIXED)
H_2 Oxidation	POWERLAW	H_2(MIXED) + 0.5 O_2(MIXED) → H_2O(MIXED)
CH_4 Oxidation	POWERLAW	CH_4(MIXED) + 2 O_2(MIXED) → CO_2(MIXED) + 2 H_2O(MIXED)
CH_4 Reforming	POWERLAW	CH_4(MIXED) + H_2O(MIXED) → CO(MIXED) + 3 H_2(MIXED)
Char Gasification (CO_2)	LHHW	CO_2(MIXED) + C(CIPSD) → 2 CO(MIXED)
Char Gasification (H_2O)	LHHW	C(CIPSD) + H_2O(MIXED) → CO(MIXED) + H_2(MIXED)

Direct char oxidation is omitted. Oxygen is consumed by volatiles only. This is not such an unreasonable assumption as highlighted Gomez-Barea and Leckner who state that it seems more reasonable that oxygen is mainly consumed by volatiles - because the oxidative reactions with H_2, CO and CH_4 are much faster than with char

2.1.3.4 Assumptions

Numerous assumptions were made in modelling of the gasifier. The main ones have been listed and justified here:

- Particle size distribution (PSD) of biomass is maintained when water and volatiles leave the solid.
- Ash is simply 'ASH' where constituents are deemed to be unreactive and density is assumed according to the 'BOIE' correlation.
- ASH separates from BIOMASS during decomposition of BIOMASS to fixed carbon and volatiles
- ASH PSD assumed to approximately follow that of report of Grammellis *et al* (16) – in a normal distribution
- Moisture does not take part in devolatilisation reactions (it is expelled from the biomass prior to this reaction step.
- Expelled volatiles and water vapour from biomass act with injected air to fluidise the bed from the level of air injection.
- Mass transfer limitations and diffusion effects are ignored within - temperatures are relatively high and the particles are relatively small –
- Temperature is constant throughout the fluid bed unit – oxidising agent reaches temperature of FLUIDBED instantaneously.

2.1.3.5 Model Validation

Validating of the gasifier model was deemed important since correct gasifier modelling would assist in determining best reaction conditions for the demonstration activities and also enable better downstream process design.

However, up-scaling from the experiments undertaken by Fraunhofer is challenging – since type of gasifier heavily influences the performance and direct comparison between fixed bed a fluid bed gasifiers is not particularly viable (D3.1). Thus, literature was searched for the most directly comparable gasification studies. Finding literature which fits well with the FFW gasification conditions has proven difficult since there are many conditions which have a heavy influence on the gasifier. The most important common aspects required are:

- Gasifier type (Fluid bed)

- Bed material (olivine)
- Feedstock (olive waste)
- Oxidising agent (air)
- Scale (10,000 kg/h of biomass)

The most suitable work was deemed to be that by Skoulou *et al* (9). However, this study was not perfect for validation. In common with the FFW process, a fluidised bed was used, and the bed material was olivine. Also, the oxidising agent used was air and the feedstock was olive kernels but it important to note the feed selected for the FFW process has significant levels of pruning residues which makes the results less comparable. Additionally, the scale is very small – the experiments having been undertaken at lab-scale and the gas distribution is different (the SOIL gasifier uses caps but the Skoulou gasifier uses a perforated plate). Finally, the information provided in the paper was not as conclusive, for instance, no information is given regarding amount of bed material used or the actual flow rate of biomass and gasifying agent and the results provided at different temperature ranges were very limited, thus it is difficult to determine how accurate the model is at different temperatures.

For the validation, the gasifier dimensions and gas distribution details were updated. The proximate and ultimate analysis and Higher Heating Value (HHV) of the olive kernels used in the study were added into the model. The biomass feed rate was reduced and the equivalence ratio was updated so it was in agreement with work the study. The particle size distribution (PSD) of the biomass and olivine was assumed. Temperature of the model gasifier was controlled by the amount of preheating of air – the amount of air preheating used in the study was not specified for experimental runs but the gasifier temperature was – this of course means that heat loss in the gasifier in the study could not be calculated since the carbon conversion was also not detailed.

Table 6. Comparison of product gas composition - Skoulou gasifier and Aspen Model

Setting / Result	**Aspen Model**	**Skoulou**
Temperature, °C	750	750
Equivalence Ratio	0.2	0.2
CO, v% dry	13.20	14.26
CH_4, v% dry	4.59	3.75
H_2, v% dry	24.60	23.98
CO_2,v% dry	19.70	19.42
C_2H_4	Trace	1.52
C_2H_6	Trace	0.29
Difference (Nitrogen)	37.93	38.59

As shown in the table, the Aspen model shows reasonable agreement with Skoulou. It moderately over-predicts carbon dioxide and methane which compensates slightly for the under-prediction of ethane and ethene. It should be noted that although the model is a useful tool, the difference in feed material (olive kernel vs 3 phase and pruning blend) and scale means there may be some noticeable difference in performance with the demonstration gasifier. It is possible that the over-prediction of Hydrogen will be more pronounced when compared to the demonstration gasifier since higher iron levels in the ash content in the olive kernel is suspected to promote the WGS reaction thus increasing hydrogen levels at the expense of carbon monoxide – this phenomenon is likely to be disguised since the moisture levels of FFW biomass are lower. Further analysis shows that the reactor is so small it is unlikely that the WGS reaction has neared equilibrium, hence why H_2 levels may be lower than predicted.

2.1.4 FFW Gasifier process specification and analysis

2.1.4.1 Inputs

Data provided by Fraunhofer and Soil Concept was utilised to provide input into the gasifier model as show D3.1 and 5.3. Where required, data is normalised or converted to the required input for Aspen PLUS. Note the Ultimate and Proximate analyses are inputted on a dry basis. The input for aspen for Heating value is for HHV – also on a dry basis. The following inputs were made with regards to Biomass characterisation. Biomass flow rate / gasifier dimensions are selected to give superficial gas velocity of between approximately 0.5 and 1 m/s thus ensuring bed is fluidised but particles do not become entrained in the gas.:

Table 7. FFW process biomass simulation inputs

Proximate Analysis	
Moisture	5.65
Fixed Carbon	17.83
Volatile Matter	78.71
Ash	3.46

Ultimate Analysis	
Ash	3.46
Carbon	47.24
Hydrogen	6.81
Nitrogen	1.24
Chlorine	0
Sulphur	0
Oxygen	41.25

Particle Size	
Size distribution	normal
D50, mm	2.5
Standard Deviation, mm	0.6

Heat of Combustion	
HHV (dry basis), MJ/kg	19.9

Up-scaled air blown gasifier specifications are as follows:

Table 8. Demonstration Gasifier simulation inputs

Gasifier Dimensions	
Bed pressure drop, mbar	178
Total height, m	14

Gasifier Dimensions	
Lowe tube length, m	2.34
Conical Adapter length, m	2.34
Upper tube length, m	9.32
Lower tube diameter, m	6
Upper tube diameter, m	8

Gas distribution	
Type	Bubble Caps
Number of caps	500
Number of cap orifices	5
Cap orifice diameter	6

Bed Material Data	
Material	Olivine
Bulk Density, kg/m^3	1900
Geldart Classification	Geldart B (sandlike)

Bed Material Particle size	
Size distribution	Normal
D50, mm	0.5
Standard Deviation, mm	0.1

2.1.4.2 Outputs

Several factors influence the optimal operation of the gasifier. The most important optimisation parameters include the equivalence ratio and the gasifier temperature – yet higher temperatures nearly always improve the process efficiency and the limiting factor is feasibility of operating the gasifier at higher temperatures which causes ash softening as shows D3.1, especially in pomace residues. Steam addition is not considered in the base case - experiments at Fraunhofer showed this would most likely result in bed agglomeration when temperature is above 700 ºC.

- The equivalence ratio can be altered by increasing the amount of air added to the gasifier. The temperature is maintained at a constant by controlling the level of air preheating.
- The temperature of the gasifier can be increased or decreased, again by changing the amount of preheating that the air is given whilst the equivalence ratio is maintained.

All optimisation is subject to limitations, one notable limitation being the minimum air pre-heating temperature level (25 ºC, and the maximum air preheating temperature level) subject to amount of energy and temperature of the gas produced in the gasifier. The maximum energy which can be used for this purpose is limited by the energy recovered by dropping the temperature of the product gas. The output of the optimisation is measured in terms of:

- Gas composition
- Quality of gaseous product
- Total Energy conserved – or overall process efficiency

Energy conservation considers the total energy entering the gasifier in the biomass (25 ºC, 1 atm) and the total energy leaving the gasifier (if cooled to 25 ºC and 1 atm).

It should be noted that some minor mass convergence problems with the FLUIDBED unit were apparent during simulations which resulted in a mass balance error (approximately 0.5 %). This causes some of the results to lose accuracy.

2.1.4.2.1 Equivalence Ratio in the Gasifier

Equivalence ratio refers to the ratio of actual oxidising agent-fuel ratio to the stoichiometric air-fuel ratio required for complete combustion of the fuel. The stoichiometric amount of biomass can be calculated by considering each individual element in the biomass and each elements requirement for oxygen for complete combustion. Here it is has been calculated according to the following equation (5):

$$\text{Air required (kg/kg dry fuel)} = 0.1153C+0.3434(H-O/8)+0.0434S$$

Where C, H, O, and S are the weight percentages of carbon, hydrogen, oxygen and sulphur of the biomass, respectively, on a dry basis.

For the simulations, the temperature is kept constant at 750 ºC, the inlet pressure in the gasifier is kept constant at approximately 1.3 atm, gasifier pressure drop is constant at 178 mbar, and all other gasifier specifications are kept constant. These values are similar to Fraunhofer's system although sintering increases pressure loss in the fixed bed reactor and causes high volatility in values.

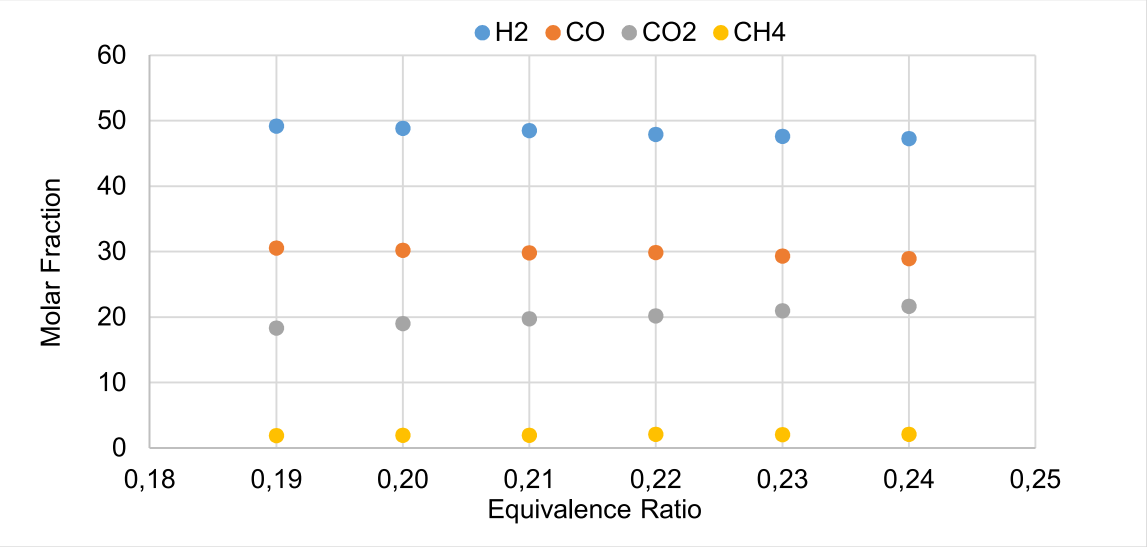

Figure 5. Effect of change in ER on product composition – base case

Figure 5 shows how as equivalence ratio is increased, H_2 and CO fraction decreases and CO_2 content of the gas increases. Effect on CH_4 content of the gas is negligible. This outcome would be expected since higher levels of O_2 increase combustion of CO and H_2 to increase levels of CO_2 and H_2O

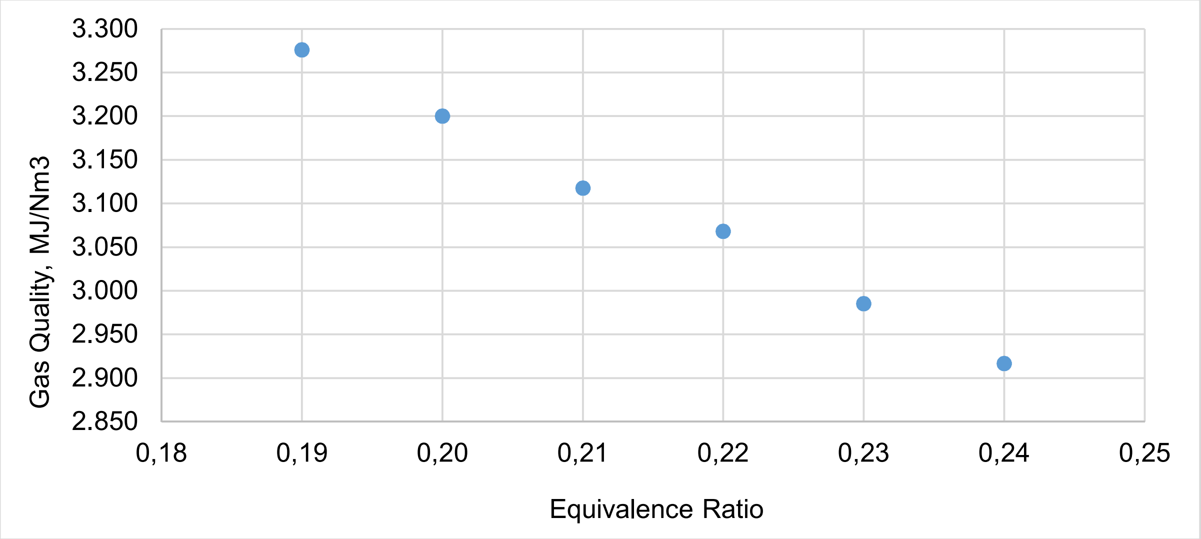

Figure 6. Effect of ER on quality of product gas **– base case**

Figure 6 shows how the quality of the gas (considering the energy generated if combusted, without considering the current state of the gas) is significantly compromised as the ER is increased. This is largely due to the high levels of Nitrogen being added to the system but also due to the increased levels of carbon dioxide.

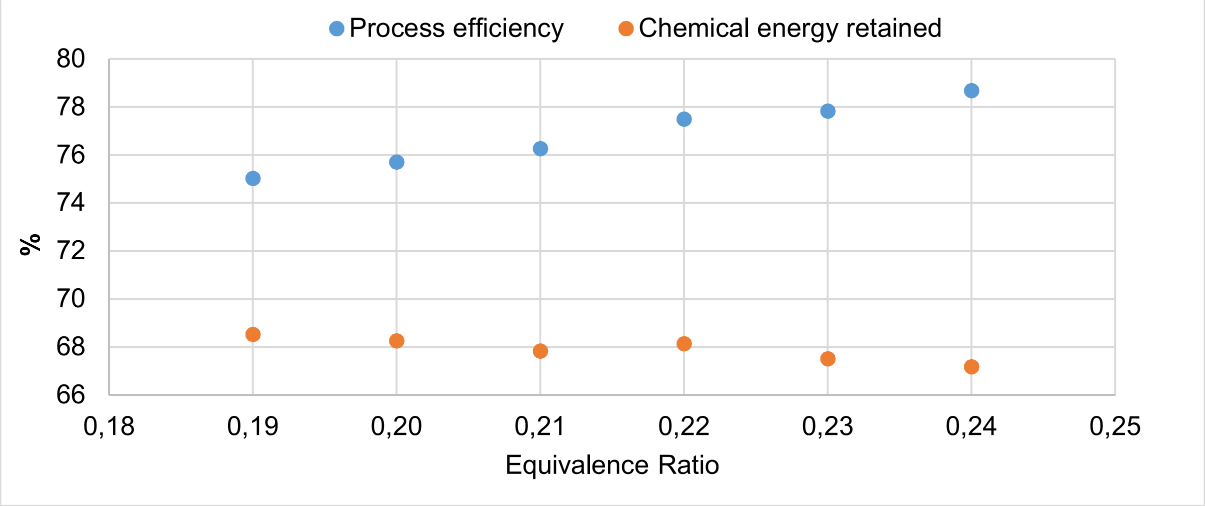

Figure 7. Effect of ER on gasification process efficiency and retention of chemical energy – base case

Figure 7 shows how the efficiency of the gasifier varies. Process efficiency generally improves with equivalence ratio since more char is converted in the gasifier at higher ER. The chemical energy in the product gas (per hour) decreases as equivalence ratio is increased. This is because, despite increased char conversion, volatiles with a higher heating value are combusted.

It should be noted that a higher ER increases efficiency - however, ERs above 0.24 would result in higher gasifier temperature since air preheating is at its lowest level.

2.1.4.3 Summary

Efficiency of the gasifier increases with both temperature and equivalence ratio, however increased equivalence ratio significantly degrades the product gas which increases downstream processing costs. An equivalence ratio which allows for the highest safe operation of the gasifier (without agglomeration) , with maximum levels of heat recovery should be investigated for the demonstration activities. The simulation showed an ER of approximately 0.22 with high levels of heat recovery would lead to a gasifier temperature of around 750 ºC. This seems a reasonable compromise between process efficiency and retaining of high energy gases which are more useful downstream.

Table 9. Optimised gasifier outputs (ER=0.22)

Parameter	Value
Height of bottom zone, m	1.51
Height of freeboard, m	12.49
TDH from correlation, m	7.57
TDH based on solids volume profile, m	3.87
Solids holdup, kg	51877
Number of particles in bed	6.16E+11
Bed surface area, m^2	132,424
Distributor pressure drop, bar	0.13
Bottom zone pressure drop, bar	0.15
Freeboard pressure drop, bar	0.03
Fluidized bed pressure drop, bar	0.18
Overall pressure drop, bar	0.31
Heat duty, kJ/h	-11,809
Minimum fluidization velocity, m/s	0.08
Bed temperature, ºC	750

According to the work developed in D.3.1 (laboratory test) and D.5.2 (demonstration activities), Table 10 summarises and compares the syngas composition obtained for each case, including the current simulation of the base case.

Table 10. Syngas composition (demo activities and simulations)

	Vol (%)			
Biomass	**CO**	**CO_2**	**CH_4**	**H_2**
Pruning	9-16.	16-19	1-3.	4-5
Two-phase	12-17	14-18	2-3	5-6
Three-phase	12-18	14-16	2-3	5-6
Wood	20-22	14-17	1-2	6-8
Simulation (Three-phase) – Base case	17.24	11.64	1.2	27.65
Olive pellets (screening tests)	18.8	14.84	2.06	23.5
Olive pellets (demonstration activities)- Vol % Dry	16	17	9	11

Outlet effluent from simulated gasifier shows similar results for CO,CO_2,CH_4 in comparison with the activities developed during WP3 and WP5. However, hydrogen composition (volume %) is quite different from these results, except in the gasification of olive pellets during the screening test, where the results are more accurate. The results are similar to shown in the model validation based on literature (% v/v). According to D.3.1, the average gas composition as outlet effluent of the downdraft gasifier is: CO (5-10 %), H_2 (5-10 %), CO_2 (15-20 %), CH_4 (0-4 %) and N_2 (60-70 %), without taking into account the different tar, ash, sulphur compounds, etc. The conditions used during the WP3 activities were: ER between 0.1-0.5. Results showed at ER=0.1, the temperature was 600 ºC and a lot of tars where reported; ER=0.5 at 800 ºC decreases the amount of tars but sintering where observed. The ER optimum was suggested at ER=0.20 and 700 ºC, but in this case the biomass conversion was reported too low and the ER should be increased up to 0.25 even 0.30. Gasification was developed in demonstration activities (WP5) at 600 ºC up to 800 ºC, in order to avoid the mentioned problems.

According to the results shown in this Task, the results are (% wt): CO (22 %), CO_2 (24 %), CH_4 (0.09 %), H_2 (3 %) and N_2 (44 %) which enabled the production of a syngas with a ratio H_2:CO 1.6:1. Differences can be also explained due to the thermodynamic model accurate. The simulation shows higher concentrations of the syngas components and lower nitrogen concentration due to the low ER used, lower N and higher O biomass content.

The model developed through the Aspen Plus simulations is quite similar to the experimental results, as the current summary collects and can be checked out in D.3.1 and D.5.2. The best results are obtained for ER=0.22, ER<0.20 show not feasible results at this scale during the simulations running. Minor variances between the syngas composition might be due to the thermodynamic model and its prediction in the compound mixture throughout the equipment and taking into account the simulated conditions (P,T...).

2.2 Purification

2.2.1 Purification Overview

In the FFW process there is a requirement for a relatively pure syngas (synthesis gas) due to the effect that impurities can have on the downstream catalysts. In the FFW demonstration process, produced gas purification is achieved using a Molten Salt Reactor (MSR) as well as additional particulate removal – achievable for small amounts using a guard bed. The equipment set up is shown in the figure below:

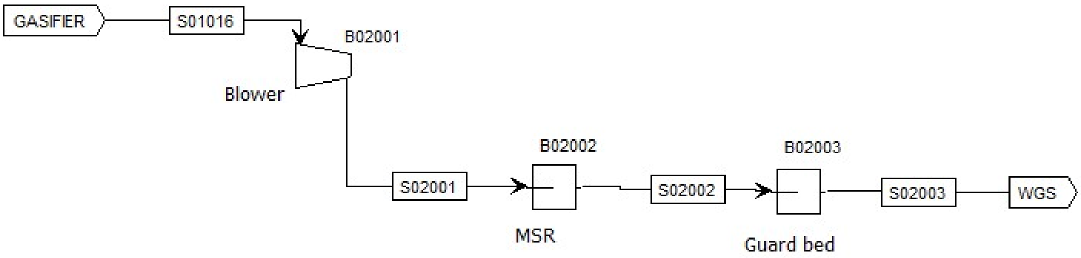

Figure 8. Gas purification Set-up scheme as per demonstration activities

As outlined in the report by EIFER in D3.3, the MSR works because the molten carbonates are absorbent for desulphurisation and dehalogenation and act as a catalyst for tar cracking. The reactor itself is formed from a reactor with optional external heating which means that should the temperature of the gas entering the reactor not be sufficient, the reactor will still function.

The guard bed is another fairly simple piece of equipment in terms of modelling in that it is formed from a tube filled with transition metals which react with and remove from the process streams any impurities which remain in the gas after the gas has passed through the MSR. Prior to the MSR, a blower is used to increase the pressure slightly to maintain a pressure difference.

Other potential applicable technologies for gas purification are:

- Thermal cracking. Tars are decomposed at temperatures exceeding 1,000-1,200 ºC. In this case, it is not necessary the use of catalyst and it is possible to perform with steam or oxygen. However, the use of quite expensive materials and the soot deposition are highlighted disadvantages for the use of this technology in gas cleaning.
- Catalytic cracking. This technology is not proved as viable yet. The use of catalyst forestalls the main problems associated to thermal cracking, as described above. Yet, it is still necessary to study how to optimise some important parameters, like the catalyst loading and the elevated costs(17).
- Scrubbing. This technology is a low temperature way to remove the tar present in the gas effluent. Below 400 ºC, it is possible to apply this technique by means of a selective oil or water. The best efficiencies are reported for oil, mainly canola , RME (according to D3.3) or soybean oil. Usually, the tar with the absorbent is come back to the gasifier and is burnt up after a regeneration stage (18).

For the industrial scale base case simulation, an oil scrubber is considered for removal of tars from the product gas (instead of the MSR) since the MSR is not yet proven at a commercially viable scale.

2.2.2 Purification Modelling / Design

- MSR simulation

Modelling of the purification steps is relatively simple. Prior to the MSR, a blower moderately increase the pressure. An isentropic compressor (COMPR) with an efficiency of 80% is used for this purpose (efficiency of blowers generally varies between 70 and 85 % (19). In the MSR, any chorine and sulphur compounds are removed. Tar compounds are destroyed to form hydrogen and carbon monoxide. The effects of both these processes on the model are small since sulphur, chorine and tar compounds are not currently modelled within the gasifier because they make up such a small amount of the product gas composition and increase in H_2 and CO is not significant compared to the error expected in the gasifier. A small heat loss can be modelled using a heater (HEAT) if required since the energy input into the reactor effects the process efficiency. The actual energy requirements for the FFW demonstration activities should be known after the first demonstration activities.

This simulation was considered at the beginning of the project. However, it has been removed and tar scrubber was the selected modelled option.

- Oil scrubber

Due to the lack of commercial scale for MSR system, the syngas product is cleaned by means of a tar scrubber in the process at industrial scale developed for the FFW project. In actual gasification plants, the removed tar is then recycled to a gasifier combustor where it is burnt up. However, in this simulation the tar together with the regeneration compound (air) is not treated or recycled.

Several authors have studied the effect of the use of oils as absorbents for this kind of tar purification. The use of oil has shown improvements in comparison with other scrubber systems, like water. It is possible to reach 60 % higher values of removed tar levels than using water as absorbent.

According to the study carried out by Phuphuakrat et al, the best kind of oil for this cleaning system is vegetable oil due to the enhanced properties in comparison with other oils, such as the low evaporation point . However, the performance order is : diesel>vegetable oil>biodiesel>engine oil. Water is not considered a good sorbent for tar removal, it is just able to remove hydrophilic tar. In water scrubber the purification is based on condensation and the main problem with a water scrubber is linked with the heavy fraction of the tars, which is not soluble in water (<2 $mg_{naphthalene}/100g_{water}$). Therefore, they will produce solid material in the scrubber immediately. (20) (21)

Literature describes the recent research in using cooking-oil for tar removal purposes. However, the use of vegetable oils have shown better results than the recycled cooking oil so far, likely due to the presence of some impurities as nitrogen and sulphur based. Amongst all the potential types of oils that can be suitable for this purpose, the most used are soybean, RME and canola oil. The oil selected for FFW process scale-up is soybean oil, which has been modelled in HYSYS taking into account its heterogeneous composition made up of oleic acid, linolenic acid, linoleic acid, stearic acid and palmitic acid. Other oils have been considered, such as olive oil and MRE from olive industry (linked with FFW project). RME is better in terms of viscosity (lower pressure drop along the column), but because it is a first generation biodiesel, it is expected, that the availability of the fuel will diminish in the future and therefore vegetable oils are preferred. Soybean oil has been chosen for the simulation due to competitive price and better environmental reputation than cheaper palm oil (22).

Tar removal process is placed after the cyclones that remove the char from gasification. The gas is then cooled up to 400 ºC and it is introduced into the oil scrubber equipment which works at 100 ºC. The oil scrubber is modelled as an absorption column in HYSYS flowsheet. This column has been modelled separately from the main flowsheet according to the literature information. In the main flowsheet, this section is represented using a component splitter, although there is not presence of tar since tar was not modelled in the gasification scale-up.

Scrubbers for tar removal (based on water or oil) are able to remove completely the BTX tar fraction and the sulphide compounds along with ammonia and chlorine when the scrubber is working at relatively low temperatures (100-200 ºC). (23)

The most promising oil scrubber system is commercially known as OLGA, which recycles the tar after separating from the oil through a stripping operation. This stripping stage is carried out using air as stripping agent (21).

The regeneration of the absorbent proposed in literature suggests the use of air or steam water for this stage. The agent selected has been based on the testing of these two compounds in the simulation and the recovery in the most favourable conditions (the least caudal, lower temperature and best recovery). A purge is used before the oil recycling since not all the tar components are completely removed from the oil absorbent. The Figure 9 and Figure 10 are the HYSYS flowsheets for this gas cleaning section. Figure 10 represents the B02004 block.

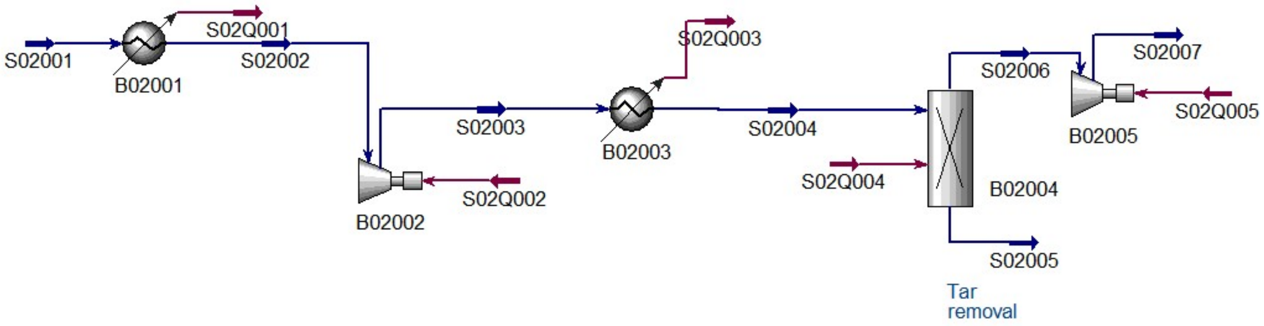

Figure 9. Post-gasification section - tar removal

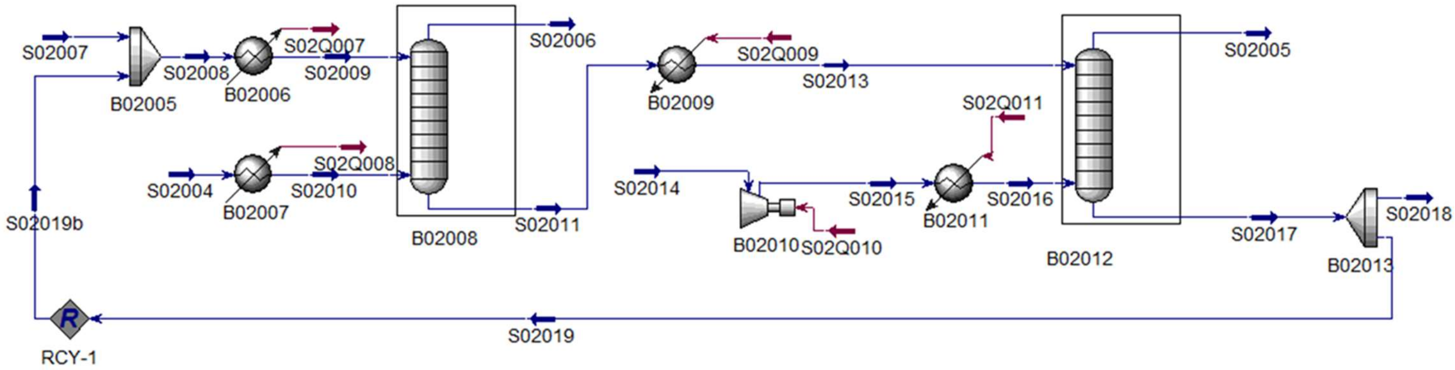

Figure 10. Tar cleaning section

The post-gasification gas (S02004), which has been chilled up to 400 ºC previously, is cooled again at 100 ºC and is introduced at the bottoms. The soybean oil make-up is blended with the recycled oil from the stripping and is chilled at 20 ºC before being introduced into the scrubber at the top of the column. The cleaned gas is leaving the scrubber at the top of the column (S02006) and will be sent to the first compression section. The absorbent will leave at the bottoms along with the tar and will be heated up at 140 ºC before being introduced into the top of the stripping column where it will be cleaned for reusing. On the other hand, an air stream (S02014) at atmospheric conditions is compressed and heated up to be introduced at the bottoms of the stripping as desorbing agent. The air along with the removed tar is leaving at the top (S02005) and the regenerated oil at the bottoms, where a part is purged (S02018) and the other is recycled (S02019).

2.2.3 Unit Specification and analysis

2.2.3.1 Inputs

According to references, as suggested by Li et at, the typical composition of a biomass gasifier product is represented in Table 11. (24)

Table 11. Typical composition of the outlet stream of a biomass gasifier (based on literature values)

Component	Typical composition, %	Base case composition, %
CO	24.5	24.7
H_2	18.4	2.9
CH_4	3.8	0.9
CO_2	12	29.9
C_nH_m[1]	0.5	-
N_2	40.4	44.5
O_2	0.04	-
H_2O	-	2

---

[1] Where the total tar composition is represented by C_nH_m

Taking into account the process scale-up and the literature composition, the composition has been normalised in order to simulate this section of the process according to the tar presence as shown in Table 12 with the gasification stream.

Table 12. Composition of the inlet gas to be cleaned in tar scrubber

Component	Mass composition, %
CO	23.8
H_2	2.89
CH_4	0.9
CO_2	28.8
C_nH_m	0.48
N_2	43
O_2	-
H_2O	0.19

Tar fraction composition is made up of different groups of organic compounds, where the most representative are: poly aromatic hydrocarbons (PAH), phenols, furans, naphtalenes and aromatic compounds. When gasification is carried out (high temperatures) the most characteristic tar fraction is PAH and naphtalenes, whilst for pyrolysis process (low temperatures),it is more common the presence of the phenolic fraction.

The PAH group is composed by different aromatic components (where the naphtalenes are not considered), like biphenyl, acenaphtylenem, fluorene, anthracene, phenantrene and pyrene, among others. For the modelling of the tar removal as part of this purification stage, tar is represented as PAH and the most representative compound is the anthracene. Naphthalene has been taken into account for this design as well as BTE fraction (50 % benzene, 30 % toluene and 20 % ethylbenzene). (25)

Either way, as reported by Aigner et al, the fractions obtained during gasification are represented in Table 13.

Table 13. Typical tar composition after gasification

Tar compound group	Composition, %
PAH	25
Phenol	4
Furans	3
Naphthalene	40
Aromatic compounds	28

The absorbent, soybean oil, has been modelled as a blend of different acids according to literature: (26)

Table 14. Soybean oil composition

Component	Composition, %
Palmitic acid (16:1)	9
Stearic acid (18:0)	4.4

Component	Composition, %
Oleic acid (18:1)	26.3
Linoleic acid (18:2)	51.6
Linolenic acid (18:3)	6.8

The following assumptions have been made for this section design:

- Sulphur based compounds, ammonia and chlorine are perfectly removed using the scrubber system.
- Tars are modelled as a mixing of PAH (anthracene), BTE and naphthalene.
- Soybean oil is represented in HYSYS as a blend of different acids.
- Bibliographic composition of tar have been assumed.
- Scrubber is modelled as an absorption tower

The inlet temperature of the gas that contains the tar has been fixed at 400 ºC as literature describes. However, at 400 ºC as inlet temperature, the absorption column does not show separation along the scrubber. The temperature has been decreased at the inlet up to 100 ºC, where the best separation has been obtained taking into account the minimisation of the oil required for the operation performance (27).

The regeneration stage was tested using both air and steam water. Steam water as stripping agent reported higher flow rates and poorer recoveries in the simulation in comparison with air. The air flow rate has been evaluated by means of a sensitivity analysis which has been represented in Figure 11. Higher flow rates up to 80,000 kg/h remove almost all the tar compounds from the oily agent. However, anthracene is difficult to remove (even using steam water). Oily absorbent has been recycled with a small amount of anthracene that has not shown any effect over the separation in the scrubber due to high boiling point of anthracene. Anthracene or other heavier (PAH) molecules could be recovered by crystallization, but this complicates the process and increases costs.

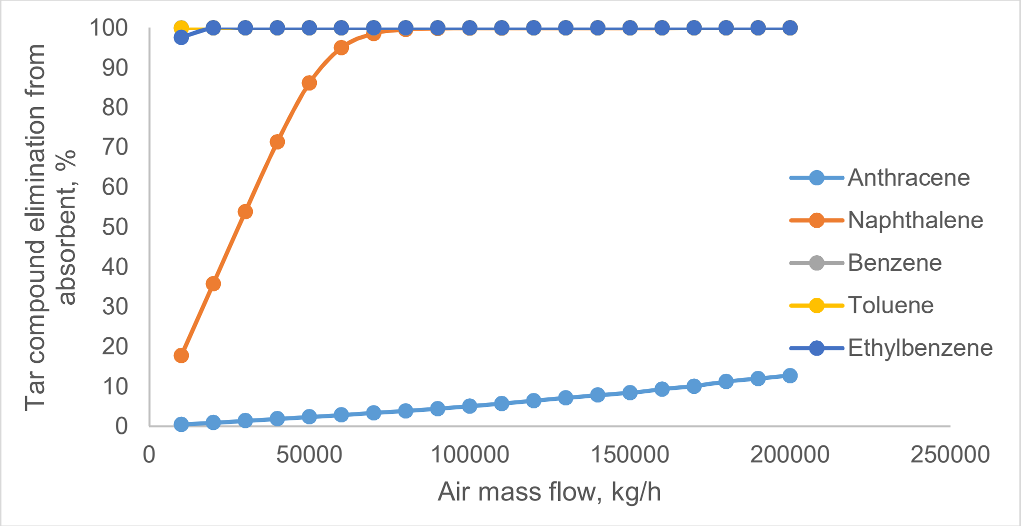

Figure 11. Sensitivity analysis to determine air flow rate in regeneration stage

Regeneration, needful stage for the reusing of the oil, is a stage favoured by high temperatures (in opposition to absorption which is usually favoured by lower temperatures). Air has been selected from literature sources (one of the agents used in OLGA technology). However, other agents might be further evaluated in future designs of the process, such as steam or nitrogen, which are more safer in terms of potential explosive mixtures with organic vapours. Feed air temperature also has been evaluated from 50 ºC up to 300 ºC as shown Figure 12 . Higher temperatures are not worth for the oil regeneration since the soybean oil has a boiling point around 230 ºC and oil is removed together with the air. Again, anthracene is the limiting compound and a low recovery is shown in the air outlet for all the air flow rates. Finally, the temperature of the feed of air has been established at 150 ºC in order to remove the rest of the components completely and a suitable fraction of anthracene than will be recycled to the scrubber column along with the absorbent make-up.

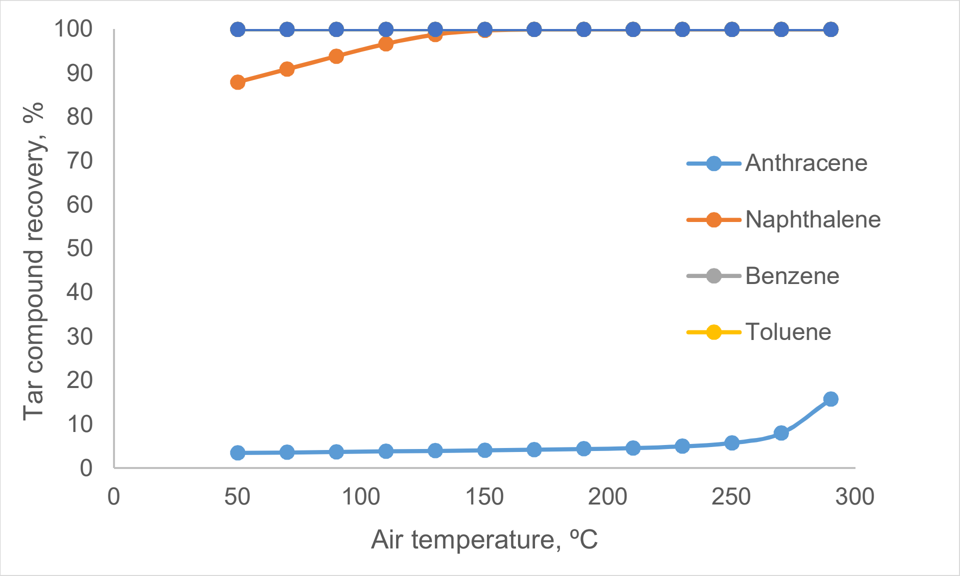

Figure 12. Sensitivity analysis of air temperature in regeneration stage

The purge has been set up as 5 % of the regenerated oil.

In the following tables (Table 15 and Table 16) are collected the inputs for the scrubber and the absorber cleaning.

Table 15. Oil scrubber inputs

Parameter	**Value**
Column type	Packing, rasching rings
Number of stages	10
Feed gas flow rate, kg/h (m^3/h)	21,132 (36.96)
Feed gas temperature, ºC	100
Oil flow rate, kg/h	32,500
Oil temperature, ºC	20
L/G	1.53

Table 16. Oil regeneration inputs

Parameter	**Value**
Column type	Packing, rasching rings

Parameter	Value
Number of stages	10
Feed oil flow rate, kg/h	32,617
Feed oil temperature, ºC	142.2
Air flow rate, kg/h (m^3/h)	80,000 (64,955)
Fed air temperature, ºC	290
L/G, kg/kg	0.41

2.2.3.2 Outputs

The first parameter to optimise in order to design this absorption system is the absorbent mass flow, in this case the soybean oil blend. A case study has been developed where the absorbent mass flow has varied between 1,000 kg/h and 51,000 kg/h (only considering pure soybean oil). The recovery of each representative tar compound has been studied. Results are showed in Figure 13.

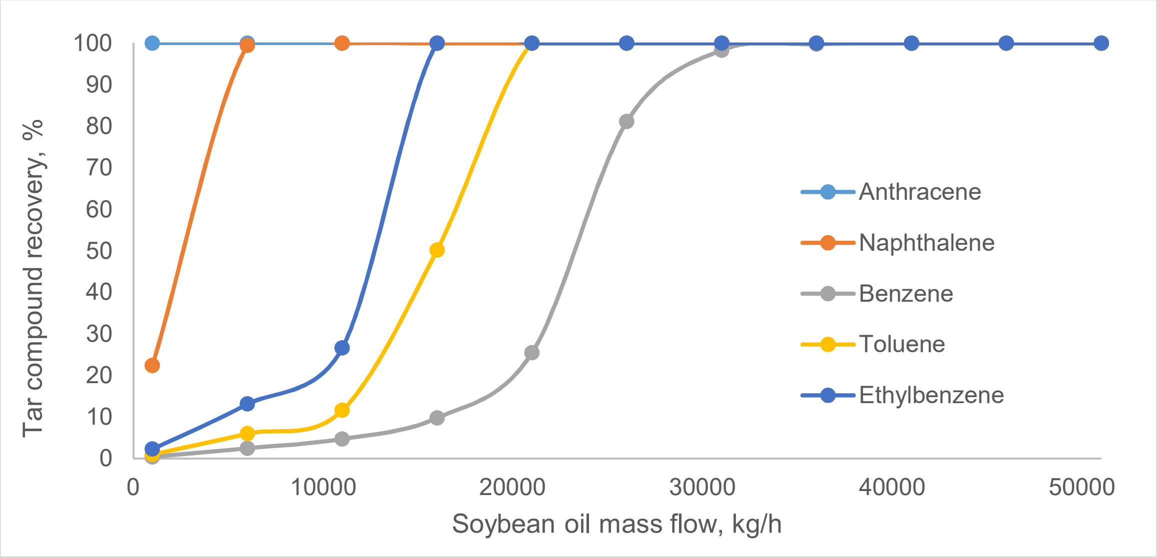

Figure 13. Tar compound recoveries according to the variation of absorbent mass flow

As shown , the anthracene is the compound most easily removable of the representative compounds included in this study. The rest of the compounds are ease of removing according to the increase in the soybean oil mass flow. The most difficult of removing component is the benzene, which needs the highest absorbent mass flow (around 30,000 kg/h) in order to have an almost complete removal from the stream (>99 % recovery in solvent stream). Finally, the solvent mass flow has been fixed at 33,000 kg/h.

The recovery of each compound after the design of the system (including the stripper system) has been represented in Figure 14.

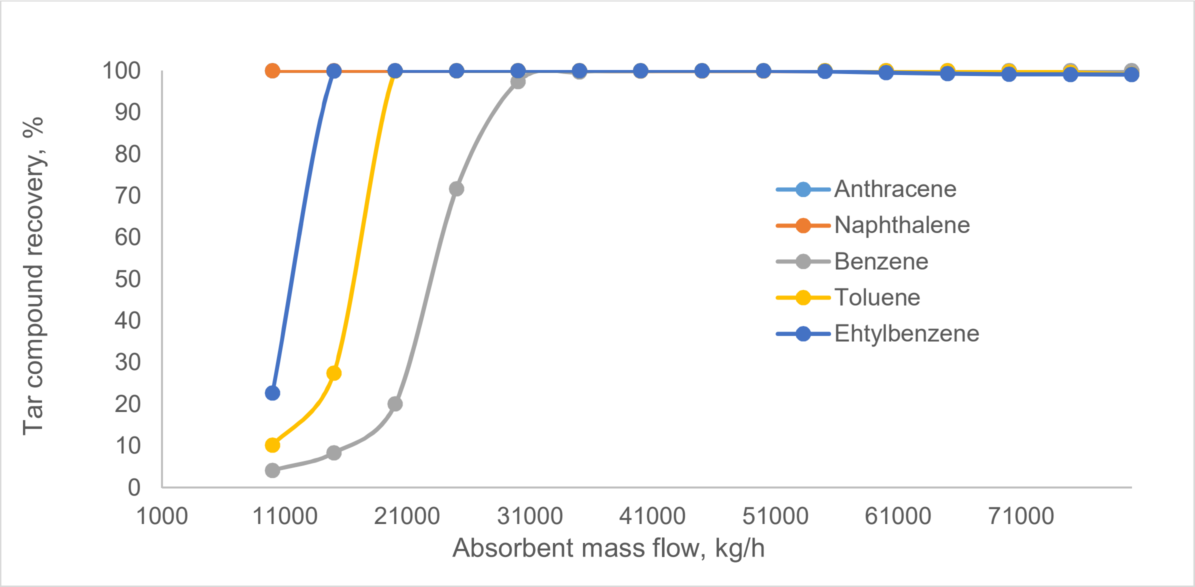

Figure 14. Tar recovery in oil scrubber taking into account the regenerated oil recycling

The recovery is slightly different due to the small change in the absorbent composition since the regenerated absorbent contains an important amount of anthracene. However, it is not important in separation terms. As observed, the tar (according to the assumed composition) is completely removed at higher mass flow rates to 33,000 kg/h. Anthracene and naphthalene are removed at flow rates above 1,000 kg/h.

The outputs are represented in the following tables:

Table 17. Achieved recoveries in oil scrubber

Compound	**Recovery in clean gas stream, %**	**Recovery in absorbent stream, %**
Linoleic Acid	0	100
Linolenic Acid	0	100
Oleic Acid	0	100
Stearic Acid	0	100
Palmitic Acid	0	100
CO_2	99.62	0.37
CO	99.97	0.03
Hydrogen	99.99	0.01
H_2O	91.94	8.05
Methane	99.89	0.10
Nitrogen	99.96	0.04
Anthracene	0	100
Naphthalene	0	100
Benzene	0.85	99.14
Toluene	0	100
E-Benzene	0	100

Table 18. Scrubber design

Parameter	Value
Column diameter, m	4.11
Pressure drop, bar	0.041
Height, m	11.65
Estimated pieces of rings	4 millons
Estimated mass of packing, tonnes	330

Table 19. Recoveries in oil regeneration[2]

Compound	Recovery in recovered oil stream, %	Recovery in air + tar stream, %
Linoleic Acid	99.51	0.49
Linolenic Acid	99.62	0.38
Oleic Acid	99.07	0.93
Stearic Acid	99.53	0.47
Palmitic Acid	97.91	2.08
CO_2	0	100
CO	0	100
Hydrogen	0	100
H_2O	0	100
Methane	0	100
Nitrogen	0.02	99.98
Anthracene	84.26	15.73
Naphthalene	0	100
Benzene	0	100
Toluene	0	100
E-Benzene	0	100

Table 20. Oil regeneration column design

Parameter	Value
Column diameter, m	3.2
Pressure drop, bar	0.011
Height, m	7.01
Estimated pieces of rings	400 millions
Estimated mass of packing, tonnes	265

The main energy requirements associated to this section are in terms of cooling and heating in order to reach the suitable conditions for the right performance of the columns. Air compression is also involved. Table 21 summarise the energy requirements in this section (further optimised through an energy integration).

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[2] H_2, H_2O,methane, nitrogen and CO_2 are negligible referred to mass flow.

Table 21. Energy requirements in the gas purification section

Equipment	Energy consumption, kJ/h
B02007 (cooler)	-1.61E+07
B02008 (cooler)	-9.30E+06
B02009 (heater)	6.34E+06
B02011 (heater)	1.52E+07
B02010 (compressor)	6.87E+06

The further energy integration (see D4.4) enables savings above 70 % of the energy required for cooling and heating showed above.

2.2.4 Validation with experimental results

As detailed in D3.3, tars were cleaned up through MSR during the experimental activities. The total conversion was reported as 80 %, obtaining a 63 % of the toluene conversion as reference compound at 800 ºC, were toluene is cracked to methane and hydrogen. As shown above, the use of a conventional scrubbing operation allows to remove 100 % of all the modelled tar components, including toluene (except benzene which is very close to 100 % removal), although they are not converted into any other components, just moved to a sorbent phase (scrubber). Nevertheless, in any case the conversion towards methane and hydrogen can be considered an major parameter, due to the low amount of tars in comparison to hydrogen and methane.

Both technologies cannot be directly compared, since they are totally different and the working procedure is different (one is conversion and the other is mass transfer). However, the achieved tar removal can be compared as shown. Other important point is the commercial scale. MSR is not commercially feasible yet, whilst scrubbing is a well-established technology at industrial scale. On the other hand, a potential increase in the energy requirement should be study for the technology selection.

2.3 Compression

2.3.1 Process Overview

For the CO_2 removal process, the inlet gas stream must be conditioned to the working pressure of the two following absorption column, 52 bar. The stream coming from the gasification is compressed (Figure 15), in a first step (B02002) from 1 bar to 5 bar and then to 25 bar (B02005). It is divided into two stream in the Splitter B03001, one stream, with 240 kmol/h, will be the feed for the WGS reactor and it will be compressed (B03004) to 52 bar (Figure 16) and the other, with 740.6 kmol/h, will be directly compressed (B04002) to the same pressure (Figure 17). Each stream will be send to the appropriate CO_2 removal absorption column.

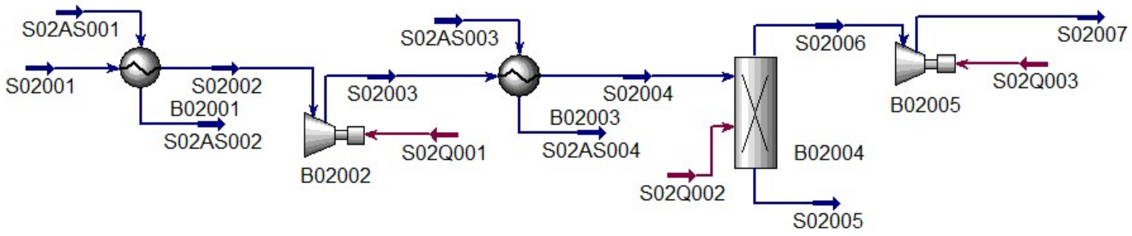

Figure 15 First compression step

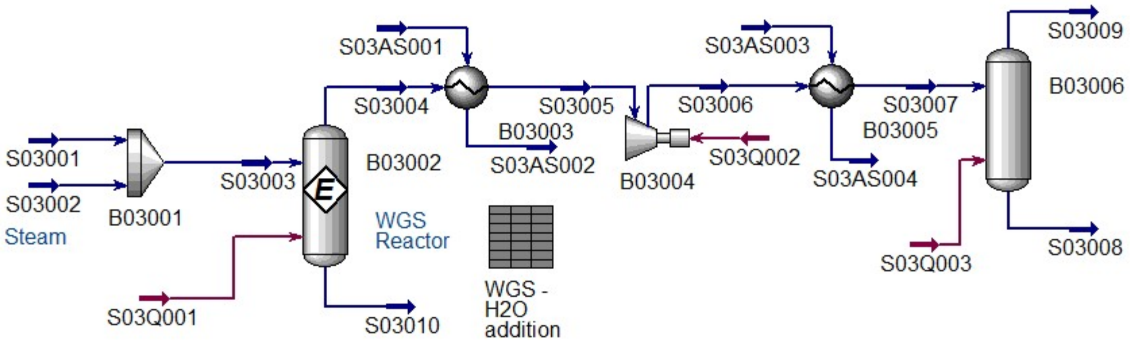

Figure 16 Second compression step – WGS path

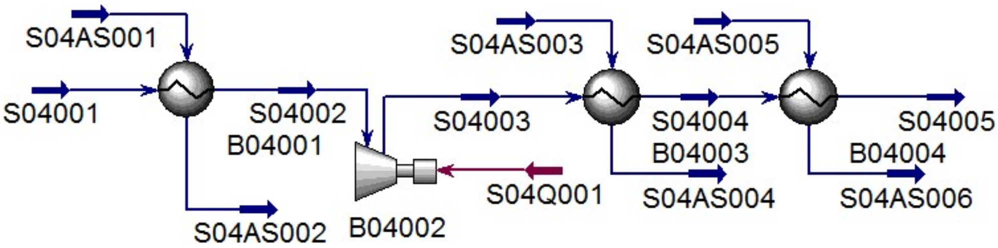

Figure 17 Third compression step

2.3.2 Process Modelling / Design

The multistage compressor is modelled using the Aspen HYSYS unit operation Compressor. Three stage is used with intermediate cooling. Currently, it is not assumed that the energy from cooling can be recovered, although it was considered at the beginning of the FFW process simulation. The outlet temperature is set according to the requirements of the absorption column solvent at 7 ºC.

2.3.3 Unit Specification and Analysis

2.3.3.1 Inputs

The inputs for the each compression step is shown in the Table 22. Apart from the inlet pressure, temperature and mass flow, it is fixed the outlet pressure (or pressure ratio/delta P) and compressor efficiency.

Table 22. Compression inputs

	First Step - 1		**First Step - 2**		**After WGS - Second Stage**		**Third Stage**	
Parameter	**In**	**Out**	**In**	**Out**	**In**	**Out**	**In**	**Out**
Pressure, bar	**1**	**5**	**5**	**25**	**25**	**52**	**25**	**52**
Delta P, bar	4		20		27		27	
Pressure Ratio	5		5		2,08		2,08	
Temperature, ºC	400	-	100	-	200	-	150	-
Mass flow, kg/h	21,130		21,130		9,165		15,600	
Adiabatic Efficiency, %	75		75		75		75	

2.3.3.2 Outputs

The inputs for the each compression step is shown in the Table 23, outlet temperature and required power.

Table 23. Compression outputs

	First Step		Second Step		After WGS Third Stage		Directly Third Stage	
Parameter	**In**	**Out**	**In**	**Out**	**In**	**Out**	**In**	**Out**
Temperature, ºC	-	827	-	362	-	323	-	270
Power, kW	4019		2272		526		788	

The total power needed for the compression is 7,605 kW in the base case.

2.4 Water Gas Shift (for Hydrogen production)

2.4.1 WGS Overview

Hydrogen is required for several stages along the FT process. The required amount varies according to several factors. The H_2 is required for the following processes:

- Changing the H_2-CO ratio before Fischer-Tropsch to 2.1:1
- Changing the H_2-CO ratio before methanation process to 3:1
- Hydrocracking of FT waxes.

Total required amount varies according to several factors including:

- Ratio of H_2-CO in the gasifier product gas – which varies according to design and operating conditions of the gasifier.
- Amount of conversion in the FT process (differing amounts of produced waxes and different amounts of gas for methanation

A hydrogen to carbon monoxide ratio of 3:1 is required for the methanation process. There are several ways of reaching this ratio:

1) Hydrogen can be produced and added to the stream – this option is not a good choice for an optimised process (which contains no nitrogen) since production of high purity hydrogen is relatively expensive.
2) If large amounts of methane are produced in the Fischer-Tropsch process, a reformer can be used to convert methane to hydrogen, in general according to the following reaction (28):

$$CH_4 + H2O \rightarrow 3H_2 + CO \qquad +206kJ/mol$$

With this method, assuming the above reaction is the main reaction, approximately three times as much hydrogen is produced compared to the carbon monoxide produced. Because the reaction is highly endothermic this will result in a requirement for energy or a significant fall in reactor temperature. Furthermore, since methane is a desired product of the methanation process and the price of the reformer is high, promoting conversion of methane may be unwise.

3) A reactor and catalyst which promotes conversion of carbon monoxide to hydrogen can be used. <u>This is more reliable and is considered in more detail for the optimised FFW process</u>. The following reaction should be dominant (28):

$CO + H_2O \rightarrow H_2 + CO_2$ -42kJ/mol

Although the WGS scale up has been developed using an Equilibrium Reactor, a molten salt reactor can be used to shift this reaction, as mentioned in others WPs. MSR is limited to high temperature WGS (400 °C - 450 °C). There is a risk of hydroxide formation if carbonate melt is used in WGS. Hydroxide formation induces loss of oxides layers in the reactor and increased corrosion.

Na_2CO_3 (l) + H_2O (g) <-> 2 NaOH (l) + CO2 (g)

4) Water gas shift reactors are often used in hydrocarbon processes to increase the hydrogen concentration for hydrocracking, ammonia or methanol production etc. This is often done through the use of a steam reformer or in the case outlined by Lima *et al* (29) a steam reformer and a water gas shift reactor.

There are 3 different commercially available WGS process and as a result information can be found from both literature and suppliers such a Linde (technology provider) or Haldor Topsoe (catalyst supplier). All three versions utilise the same reaction- see WGS reaction above- and some kind of catalyst – in a fixed bed reactor arrangement. As a result of the exothermic water gas shift reaction the process generates significant amounts of energy which often requires removal to avoid catalyst destruction. The three versions are:

- High temperature (HT) which occurs between 300 to 450 °C which can utilise CO down to approx. 2.5 % CO
- Medium temperature (MT) CO shift conversion or so-called isothermal shift conversion which occurs between 220 to 270 °C and can utilise down to approx. 0.5 % CO
- Low temperature (LT) CO shift conversion which occurs at about 180 to 250 °C and utilises CO down to approx. 0.2 % CO

Often a combination of reactors is used since the high temperature process is faster but the low temperature process (30). Pressure is up to 30 atm (31) and hence the last compression stage must be after the water gas shift reactor.

For every process a special catalyst is used in a fixed bed reactor to get maximum yield of H_2 product. The use of HT CO shift conversion is state-of-the-art in almost every hydrogen plant. The application of the low temperature CO shift conversion is normally installed downstream of the HT shift at already reduced CO content in the feed gas. The additional investment is considered for plants having a capacity above approx. 40,000 Nm^3/h H_2 product. The catalyst of the LT shift is very sensitive against sulphur, chlorine and liquid water and special attention is required during start up and plant upset conditions.

In former concepts, the LT shift was important because of the downstream methanation of CO following the CO_2 removal unit, to meet the product purity at minimum H_2 losses. After the implementation of the Pressure Swing Adsorption (PSA unit) for H_2 purification these process steps have become obsolete. However, PSA unit has not been implemented as H_2 purification technology and has been evaluated the use of a membrane for this purpose, as is explained and justified at the end of the case base.

The MT CO shift conversion as isothermal reaction can be approximated in several adiabatic reactors with intercoolers or better in an isothermal reactor with integrated steam generation for cooling of the process gas. The temperature of the shift reaction is controlled easily by setting the pressure of the generated steam.

In the low temperature shift reaction, the catalyst is a mixture of ZnO, CuO and Cr_2O3/Al_2O_3 at varying composition depending on the manufacturer. The typical composition of the catalyst are 68 – 73 % ZnO, 15 – 20% CuO, 9 – 14 % Cr_2O_3, 2 – 5 % Mn, Al and Mg oxides and 32-33% CuO, 34-53% ZnO, 15-33% Al_2O_3. Recent catalysts can also be operated at medium temperatures of around 300 ºC. The possibility of the WGS using noble metals and metals was studied and was found the activity of the metals in the order, Ni>Ru>Rh>Pt>Pd. Latest research works have started using mixed oxides of the above supports with the precious metals dispersed in them. Some of them are collected in the Table 24. (32)

Table 24. Medium Temperature Catalyst for WGS

Catalyst	**Operating Conditions**			**Reference**
	Temperature	**Pressure**	**CO/H_2O**	
Cu-ZnO- Al_2O_3 (EX-2 48)Sud	250 °C		1:2	Choi and Stenger (2003) (33)
Ru/ceria Rh/Ceria	300 °C			Wheeler et al. (2004) (34)
2% Pt/Al_2O_3	270 ºC	1 bar		Phatak et al. (2007) (35)
1%Pt/ CeO_2	240 ºC			Phatak et al. (2007)
1.4%Pt-8.3%CeO_2/Al_2O_3	260 ºC	1 atm		Phatak et al. (2007)
2%Pt- 1%Re/CeO_2-ZrO_2	210-260 ºC	1 atm		Phatak et al. (2007)
1.66%Pt/ Al_2O_3	285 ºC	1 atm		Phatak et al. (2007)
1% Pt/TiO_2				Thinon et al. (2009) (36)
5 at.% Ni-Ce (10%La)Ox	275 ºC		1.5	Li et al. (2000) (37)
8%CuO-CeO_2	240 ºC	1 atm		Koryabkina et al. (2003) (38)
5%Ni-Al_2O_3	300 ºC	1 atm	1:4	Wheeler et al (2004)

2.4.2 Process Modelling

For the demonstration process, since high purity (i.e. very low levels of CO_2) are not required, both high temperature and low temperature WGS reactor catalysts could be utilised if were required. However, high temperature WGS catalysts tend to be more robust and since the gas will leave the gasification stage of the process, a high temperature catalyst would be more desirable since less cooling would be required. Additionally, since the high temperature WGS reaction takes place at higher temperature the reaction is faster and a smaller reactor can be utilised.

The high temperature WGS reaction is widely assumed to reach equilibrium when a suitable catalyst is present. It was modelled as reaching equilibrium using an **adiabatic Equilibrium reactor** with the WGS reaction specified. A 'design specification' controlled the steam input so the H_2O:CO ratio was 5:1 when the gas entered the reactor.

After the WGS reactor, the stream is cooled and compressed (Third compression step – WGS path), then the temperature is adjusted to 150 ºC and it is introduced to a separator vessel which working conditions are 20 ºC and 52 bar and will remove the water. The process is shown in Figure 18.

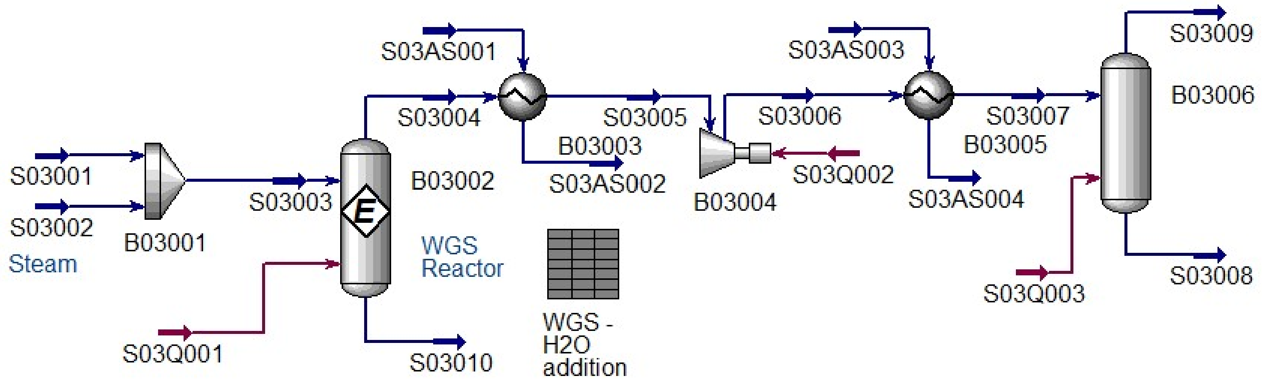

Figure 18. WGS Process scheme

2.4.3 Unit Specification and Analysis

2.4.3.1 Inputs

The inputs in the WGS reactor are shown in the Table 25. As already stated, H_2O:CO ratio is set in 5:1 (mole). Adiabatic reactor is configured through fixing heat flow as zero.

Table 25. WGS Reactor inputs

Parameter	**Inlet (S03003)**
Vapour	1
Temperature, ºC	299
Pressure, bar	25
Molar Flow, kmol/h	462
Mass Flow, kg/h	9,165
Mole fraction	
H_2O	0.4928
Hydrogen	0.1606
CO	0.0987
CO_2	0.0635
Nitrogen	0.1782
Methane	0.0062

The inputs in the vessel separator are shown in the Table 26. The vessel has to be cooled at 20 ºC in order to have <0.0001 (mass fraction) of water in the outlet stream.

Table 26 Vessel separator inlet stream

Parameter	**Inlet (S03007)**	**Outlet Vapor (S03008)**	**Outlet Liquid (S03009)**
Vapour fraction	0.67	-	-
Temperature, C	150	20	20
Pressure, bar	52	52	52
Molar Flow, kmol/h	462		
Mass Flow, kg/h	9,165		

Parameter	**Inlet (S03007)**	**Outlet Vapor (S03008)**	**Outlet Liquid (S03009)**
Mass fraction			
H_2O	0.3648		
Hydrogen	0.0255		
CO	0.0112		
CO_2	0.3421		
Nitrogen	0.2514		
Methane	0.0050		

2.4.3.2 Outputs

The outputs in the WGS Reactor, conditions, flows and mole fractions, are shown in the Table 27 and the reaction conversion obtained was **91.94 %.**

Table 27 WGS Reactor outputs

Parameter	**Outlet value (S03004)**
Vapour	1
Temperature, °C	397
Pressure, bar	25
Molar Flow, kmol/h	462
Mass Flow, kg/h	9,165
Mole fraction	
H_2O	0.4021
Hydrogen	0.2514
CO	0.0080
CO_2	0.1543
Nitrogen	0.1782
Methane	0.0062

The catalyst amount needed to reach equilibrium reaction was estimated by the GSHV found by Krause, *et al* (2004) for that purpose, 30,000 h^{-1}. (39)

Table 28. WGS Reactor sizing

Parameter	**Value**
STD Volumetric Flow, m^3/s	1.576
GHSV, h-1	30,000
Catalyst Volume, m^3	13.13
Catalyst Density, kg/m^3	3,850
Catalyst amount, kg	50,563
Bed Porosity	0.4
Catalyst Porosity	0.8

Parameter	Value
Reactor volume, m^3	41.04

The outputs in the vessel separator are shown in the Table 29. The vessel has to be cooled, therefore, a heat flow has to be extracted (negative). The outlet vapour and liquid are in chemical equilibrium.

Table 29 Vessel separator outputs

Parameter	**Outlet Liquid (S03008)**	**Outlet Vapour (S03009)**
Vapour	0	1
Heat Flow, kJ/h	-4,235,411	
Molar Flow, kmol/h	185.5	276.1
Mass Flow, kg/h	3,344	5,821
Mass fraction		
H_2O	0.9976	0.0006
Hydrogen	0	0.4202
CO	0	0.0177
CO_2	0.0024	0.5376
Nitrogen	0	0.3961
Methane	0	0.0078

2.5 CO_2 (and H_2O) Removal

2.5.1 Process Overview

A syngas with low moisture content and low CO_2 content is required to enable downstream fuel synthesis to work effectively. H_2O removal by itself can be undertaken by cooling the process stream and using condenser to remove H_2O. This process condenser can take standard heat exchanger configuration- probably of a shell an tube heat exchanger with necessary alterations (baffle spacing increased etc.). Generally speaking, different levels of cooling are undertaken at different stages thus meaning that some energy can be recovered. For instance a heat exchanger will usually remove the bulk of the energy, a partial condenser condenses vapours at a point high enough to provide a temperature difference sufficient to preheat a cold stream of process fluid. This again saves energy and eliminates the need for providing a separate preheater in some processes. A final condenser condenses the vapours to a final storage temperature of approximately 37.8 ºC. Final condensers usually use cooling water which means that the transferred heat is lost to the process (40). When coupled with a CO_2 removal process, the removed water can be used as make-up of water for certain CO_2 removal processes.

Many process exist for the removal of CO_2. Some have been commercialised with more success than others – amine processing being the most used commercially. Nearly all processes face barriers with the relatively high complexity and cost. Some of the available techniques are summarised in the table below which was adapted from work by Huertas *et al* (41):

Table 30 CO_2 removal techniques

Method	**Solvent/Materials Used**	**Advantages**	**Disadvantages**
Physical Solvent	Methanol (Rectisol) Dimethyl ethers (Selexol) DEPG	High Efficiency,	High Capital Cost, low separation efficiency, quite difficult operation due to low operation temperature and, thereupon, high energy consumption (Rectisol)
Water Washing	Pressurised water (PWS)	High Efficiency,	High Capital Cost, high operating costs, high water requirements
Pressure Swing Absorption	Various inc. Activated carbon	High efficiency, low energy use	High Capital Cost, extensive process control required
Chemical Solvent	• MEA • DEA • Washing fluid (Genosorb) • Sodium Hydroxide • TEA • MDEA • DGA	Very High efficiency, cheap operation,	High Capital Cost, high temperatures ore pressures often required
Membrane technology	Various membranes used	Simple construction, Simple operation, high reliability, small gas flows	Currently low membrane selectivity. Low purity unless several steps used. Limited to relatively small scale
Cryogenic Separation	-	Potential for CO_2 and separated gas in high purity.	High capital cost, High operating costs
Biological	Different micro-organisms	Removes CO_2 and H_2S	Not commercialised, effectiveness largely untested

In most of the physical or chemical processes, a solvent is used which absorbs CO_2 in a reactor/column. The mixture passes to a second reactor/column where a change in condition enables separation of the CO_2 and regeneration of the solvent ready for re-use.

In work by Williams *et al* (42)and Kreutz *et al* (43), on evaluation of biomass to fuels processes, all process scenarios used the Rectisol process. SASOL is also known to use Rectisol for their coal to liquid applications. However, due to the complexity of the process and requirement for refrigeration, economic operation on a smaller scale is challenging. DGA, MEA and MDEA have all been considered for syngas upgrading in coal to liquid applications and have considered more suitable. However, these solvents have not been considered at the last stages of the CO_2 removal study. A sodium hydroxide solvent would operate in a similar manner, however, very little experimental information is available and since sodium hydroxide is stronger than amines dissociation from CO_2 for regeneration is more difficult (44).

For FFW process scaling-up, two solvents have been studied: Rectisol (methanol) and Selexol (DEPG), which both are physical solvents, although in first stages chemical absorbents were considered in the development of this process (MEA). The operation manner of these solvents can be based on pressure or temperature change. There are some differences between these kind of solvents and chemical solvents, such as the increase in the energy for refrigeration (drawback) but a higher selectivity and recovery for CO_2. In this sense and aligned with FFW aims, Rectisol and Selexol solvents are suitable for FFW CO_2 removal purpose (45).

In Table 31 chemical absorption (MDEA solvent) against physical absorption (Rectisol and Selexol) is compared.

Table 31. Comparison among some CO_2 capture solvents

Parameter	MDEA	Rectisol	Selexol
Temperature, ºC	43	-40 to -60	-20 to 50
CO_2 selectivity	Medium-High	High	High
Advantages	CO_2 removal	Low H_2S removal limit	Effective for COS and CS_2 removal
Drawbacks	Limited removal selectivity	Higher capital investment/Higher power consumption is required	Higher capital investment

- Rectisol solvent

Rectisol solvent is widely used in the synthesis gas production for CO_2 capture. This solvent is based on methanol. Over the 75 % of the syngas produced worldwide is cleaned by means of Rectisol solvent.

This solvent has a lower freezing point than other solvents. Since it has to be supplied at low temperatures (-20 ºC) and 37 bar, the process uses to be less economically attractive than other solvent based processes, in spite of the easily access to the raw material and its relatively low cost.

Although the plant refrigeration requires a high power supply, Rectisol-based processes are characterised by a low solvent consumption (46).

Rectisol unit is similar to other acid gas removal process units. However, the main difference is the presence of an extra column in order to regenerate the chilled methanol. Rectisol is a good choice when a deeper H_2S removal is required and there are processes with a high sensitivity to sulphur or other contaminant presence. These reasons make Rectisol widely used in synthetic chemical processes.

Rectisol was developed by Lurgi during the 1950s and over the years, 50 units have been built and licensed worldwide. The main implantation has been done at ammonia, methanol and Fischer-Tropsch plants, among others (47).

- Selexol® Solvent

Selexol or DEPG ($CH_3O(C_2H_4O)nCH_3$ where n is between 2 and 9) it is a mixture of dimethyl ethers of polyethylene glycol that presents very similar characteristics to chemical absorbents. This physical solvent is widely used for acid gas cleaning, especially CO_2, H_2S and mercaptans (sulphur derived) along with heavy hydrocarbons. The use of this solvent for gas cleaning purposes requires no water wash for solvent recovery stage and its operation temperature takes place between -18 ºC and 175 ºC, what is translated into a more attractive solvent, in energy terms, than Rectisol because normally low temperature process heat is available in FT-process.

Selexol solvent based process is usually made up of a stripping, vacuum stripping or reboiler stripping stage. Depending on the requirements or the acid gas stream to be cleaned, it is necessary two stages, where the complete CO_2 removal is carried out at the second absorber. The regeneration of the solvent is performed through a stripping section followed by a second stage where the regeneration is done by means of air or nitrogen or a series of flash drums. The use of DEPG as solvent also contributes to the dehydration and other components removal in the gas treated.

Commercially, Selexol is supplied by Dow Chemical and UOP, although there are other companies that supplies DEPG based solvents similar to commercial Selexol (46).

Selexol applications have a wide use for natural gas, integrated gasification in combined cycle (IGCC) and petroleum refinery. Selexol has been chosen as the solvent for CO_2 removal for synthetic natural gas upgrading (refer to deliverable 4.4) for these reasons and due to the great separation of heavy hydrocarbons from methane (main product in natural gas according to normative).

Both commercial Rectisol and Selexol present similar direct and indirect emissions, there are differences due to the use of compressors for refrigerant recycle in Rectisol process though (47).

- Solvent selection

After an extensive analysis about the actual advantages and the drawbacks for each reported solvent, the FFW scale-up process is going to be carried out using Selexol® solvent.

The main reasons are listed below:

- Although the use of Rectisol implies lower solvent flows, the gas flow to be treated is not excessively high (in comparison with other industrial gas flow to treat for the same purpose). It will not make a big difference.
- Rectisol needs to be used at very low temperatures. DEPG can be used at higher temperatures, which implies cost savings in terms of operations to maintain the solvent cooling and compression.
- It is not considered the sulphur-based compounds for this stage.
- Selexol presents good separation for synthetic natural gas (methane) from other heavier hydrocarbons. This is a point presented in deliverable 4.4, where the same equipment is used to meet the requirements for SNG and the solvent regeneration is carried out in the same column as acid gas cleaning (no need for investment in other different column).

2.5.2 FFW process design /modelling

Figure 19, Figure 20 and Figure 21 represent the sections for CO_2 removal and regeneration solvent.

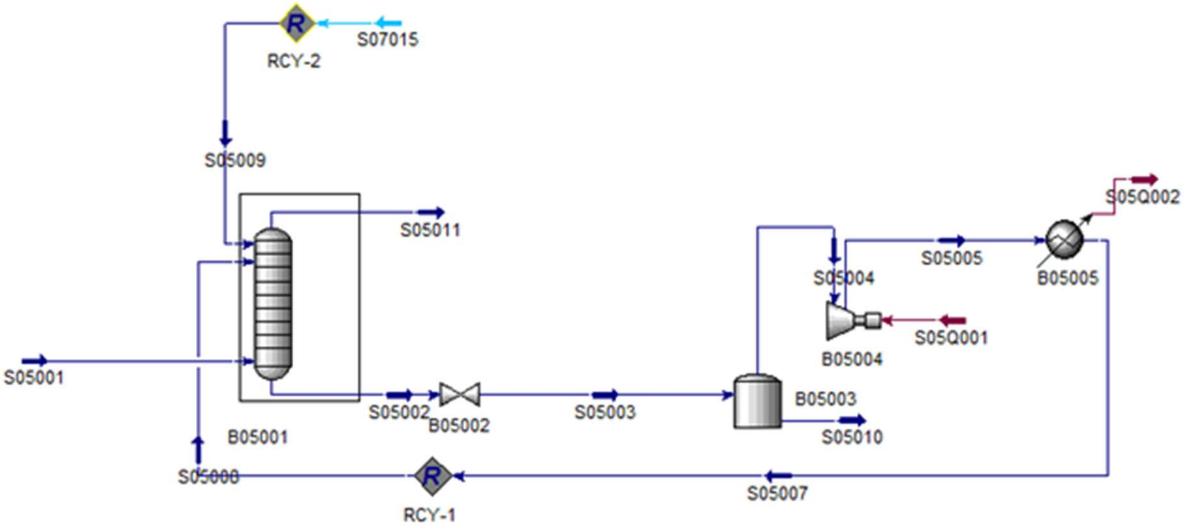

Figure 19. CO_2 removal section before Fischer-Tropsch (Section 5)

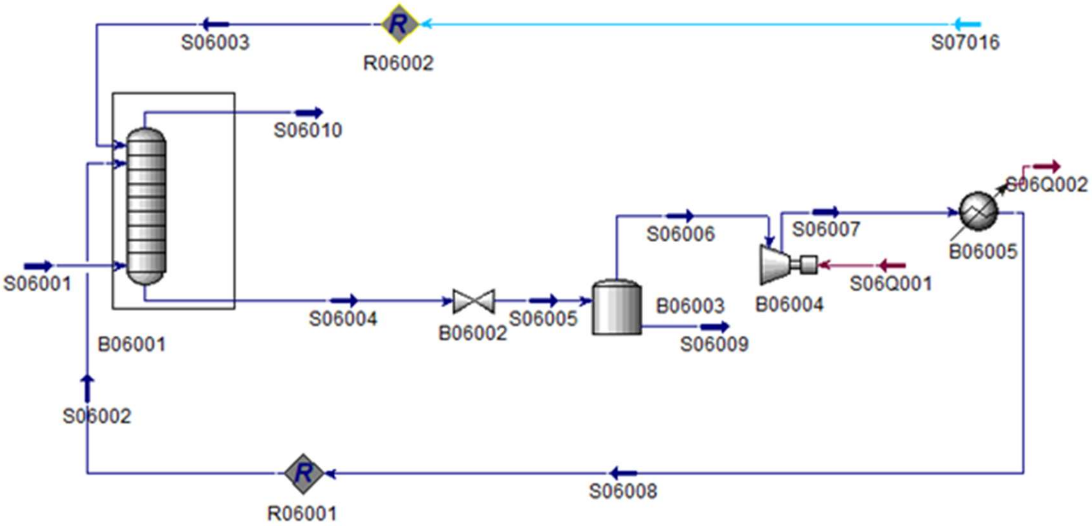

Figure 20. CO_2 removal after WGS (Section 6)

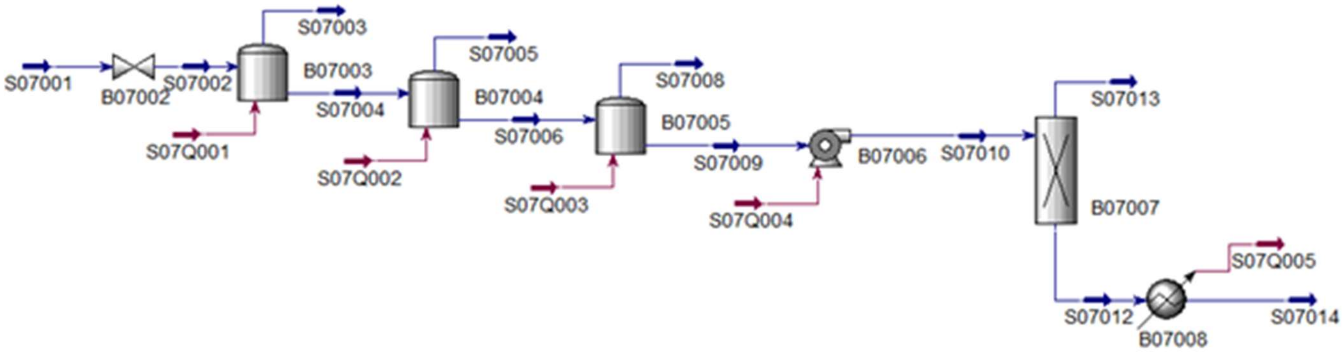

Figure 21. Regeneration stage for CO_2 removal- Section 7 (common for the entire process)

CO_2 removal has been designed for two purposes, due to the post-gasification stream is split into two streams: the first stream is conditioned to be the feed for Fischer-Tropsch process; the second stream is the feed along with steam water for water gas shift reaction, where will be obtained the hydrogen necessary to have the requirements for Fischer-Tropsch, methanation and hydrocracking.

Solvent regeneration is performed in the same section (section 7) for all CO_2 removal process developed along the process, which includes the methanation upgrading (deliverable 4.4)

Before absorption column, the feed gas is compressed in order to have the column at working pressure. Feed gas is introduced at the bottoms of the column, whilst the solvent is fed at the top of the column (although it does not coincide with the scheme shown by HYSYS). The clean gas leaves the column at the top and the solvent at the bottoms, where will be split by means of a tank into two streams: one recycle streams which returns to the column, and the stream that is regenerated in section 7.

The selected fluid package for the design of these sections has been Acid Gas (PC-SAFT state equation). This fluid package is incorporated into HYSYS software together with a component list that includes DEPG and typical components presented along this kind of operations.

Regeneration section is made up of a series of flash drums that remove CO_2 from the DEPG solvent through a pressure decrease in each stage of flash drums. DEPG is finally separated from water, it has been modelled through a component splitter block for this scale-up simulation.

The modelling of the absorption columns has been done according to the block “Absorber column sub-flowsheet”, which does not include any type of reflux.

Finally, each column has been sized by means of the *TPSAR tray sizing* Aspen HYSYS tool. This tool is able to size and characterise an absorption column introduced into HYSYS flowsheet from some basic info data such as the kind of tray that should be applied for the column. According to literature, such as Park et al, the most suitable column type for this kind of acid gas absorption is packaging, specifically IMTP packing (48).

2.5.3 Process Specs and Analysis

2.5.3.1 Inputs

According to the different CO_2 removal sections in the FFW project (except methane upgrading), the design inputs are listed below:

- CO_2 removal section before Fischer-Tropsch section.

The inputs of this section are presented according to Figure 19 scheme.

The composition of the column feed is shown in Table 32.

Table 32. CO_2 removal feed (before FT process) mass composition

Component	Mass fraction
DEPG	-
CO	0.25
CO_2	0.25
Hydrogen	0.03
H_2O	0.02
Nitrogen	0.45
Methane	0.01

Component	Mass fraction
Total mass flow, kg/h	15,959

For the same column, the design specifications appear in Table 33

.

Table 33. Absorption column design for CO_2 removal before FT

Specification	Input
Column	Absorption
Type	Packing, IMTP
Top pressure	51.7
Bottoms pressure	51.8
Feed gas temperature	20.09
Feed solvent temperature	7.22
Number of stages	10
Solvent mass flow, kg/h	207,691
Solvent stage	Top
Feed gas stage	Bottom

- CO_2 removal post-WGS inputs

This section is represented in Figure 20.

In Table 34 the inlet stream composition is represented.

Table 34. Post-WGS mass composition

Component	Mass fraction
DEPG	-
CO	0.017
CO_2	0.53
Hydrogen	0.042
H_2O	0.0006
Nitrogen	0.40
Methane	0.0078
Total mass flow. kg/h	5,817

A high amount of CO_2 and hydrogen is still remaining in this stream. They should be removed before being introduced into fuel production sections (FT and methanation). Nitrogen will be removed in the next section through a membrane (see section 2.6).

The design specifications for the absorption tower have been the same as the column shown previously. Those specifications are represented in Table 35, where it is appreciable a decrease in the solvent flow, mainly due to the smaller feed gas amount to be treated.

Table 35. Absorption column for CO_2 removal post-WGS

Specification	**Input**
Column	Absorption
Type	Packing, IMTP
Top pressure	51.7
Bottoms pressure	51.8
Feed gas temperature	20.09
Feed solvent temperature	7.22
Number of stages	10
Solvent mass flow, kg/h	129,807
Solvent stage	Top
Feed gas stage	Bottom

- Regeneration section

Before regeneration section, a mixer that blends all the used solvent streams (the coming streams detailed upper and methane upgrading solvent) is placed onto the flowsheet diagram. All streams will be treated together and split later into three solvent streams, one for each one section of the FFW project.

In the following tables (Table 36, Table 37, Table 38 and Table 39), the outlet mass composition for the solvent in each stage of the process and the final mixed stream composition are represented.

Table 36. Used solvent composition from section 5

Component (Stream S05010)	**Mass fraction**
DEPG	0.969
CO	0.0007
CO_2	0.027
Hydrogen	-
H_2O	0.0016
Nitrogen	0.0008
Methane	-
Mass flow, kg/h	211,037

Table 37. Used solvent composition from section 6

Component (Stream S06009)	**Mass fraction**
DEPG	0.964
CO	0.0001
CO_2	0.0343
Hydrogen	-
H_2O	-
Nitrogen	0.0009
Methane	0.0001
Mass flow, kg/h	132,611

Table 38. Used solvent composition from methane upgrading (Section 13)- See D4.4

Component (Stream S13006)	Mass fraction
DEPG	0.945
CO	-
CO_2	0.0502
Hydrogen	-
H_2O	0.0001
Nitrogen	0.0002
Methane	0.0041
Mass flow, kg/h	40,346

Table 39. Composition of total solvent (DEPG) to be regenerated

Component (Stream S07001)	Mass fraction
DEPG	0.9654
CO	0.0004
CO_2	0.0320
Hydrogen	-
H_2O	0.0009
Nitrogen	0.0008
Methane	0.0005
Mass flow, kg/h	383,995

The regeneration is carried out through a series of pressure based tanks as represented in Figure 21. The first tank pressure change is developed by means of a valve. The pressure for each tank is shown in Table 40.

Table 40. Pressure change for solvent regeneration

Equipment	Inlet pressure, bar	Outlet pressure, bar
Tank 1 (B07003)	30	13.79
Tank 2 (B07004)	13.79	6.89
Tank 3 (B07005)	6.89	1.72

Water separation has been modelled by a shortcut method, in this case by means of a component splitter block. Water presence is not abundant in this section (represents less than 0.1 % mass composition). Likely, water separation can be modelled through a flash vessel (pressure change based) or by means of a partial condensation, where the rest of the gases will be separated from the aqueous phase due to the temperature change.

2.5.3.2 Outputs

- CO_2 removal section before Fischer-Tropsch section.

The results for the cleaned syngas after CO_2 removal for previous FT section are showed in Table 41. The CO_2 concentration has been decreased in almost eleventh times.

Table 41. Cleaned gas to Fischer-Tropsch Section

Component (Stream S05011)	Mass fraction
DEPG	-
CO	0.2092
CO_2	0.046
Hydrogen	0.35
H_2O	-
Nitrogen	0.38
Methane	0.012
Mass flow, kg/h	12,679

The column design is shown in Table 42.

Table 42. Absorption column design for Section 5

Parameter	Value
Diameter, m	0.74
Height, m	5
Packing type	IMTP
HETP, m	0.5
Total pressure drop, bar	0.10

Sensitivity analysis have been developed since there is not a total CO_2 removal from the gas stream. The results are shown in Figure 22.

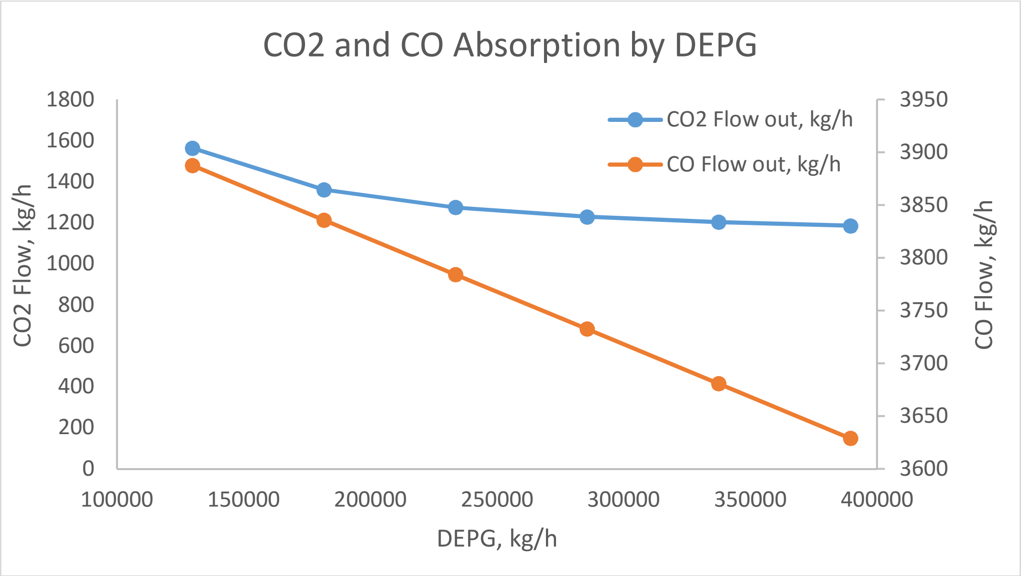

Figure 22. Sensitivity analysis for CO_2 removal before FT process

High DEPG flow rates decrease the CO_2 at the outlet effluent, although a total cleaning up of this component is not achievable and it implies CO losses, which is used for FT reaction.

- CO_2 removal post-WGS outputs

The composition of the outlet stream (outlet syngas) that will be introduced into methanation process mainly (after a nitrogen removal stage) is represented in Table 43.

Table 43. Cleaned gas after WGS Section

Component (Stream S06010)	Mass fraction
DEPG	-
CO	0.03
CO_2	0.16
Hydrogen	0.075
H_2O	-
Nitrogen	0.72
Methane	0.011
Mass flow, kg/h	3,014

In this case, CO_2 reduction is noted in 30 times regarding the inlet stream concentration.

The column design is represented in Table 44.

Table 44. Absorption column design for Section 6

Parameter	Value
Diameter, m	0.87
Height, m	9
Packing type	IMTP
HETP, m	0.9
Total pressure drop, bar	0.032

Another sensitivity analysis has been performed in this case. The results are shown in Figure 23.The graph shows a similar trend with Figure 22, where it is achieved a partial CO_2 elimination but not at all. Increases in the DEPG flow also implies CO loses. The main problem linked with this trend is due to the lately use of the hydrogen produced at WGS unit, which will be introduced into the hydrocracking operation (aside from the methanation unit). Hydrocracker requires high purity hydrogen in order to reduce cost, which should be further evaluated in this case.

In the case of the methanation unit, this results will imply the use of another CO_2 removal unit, using Selexol® as per this unit, in order to take advantage of the regeneration unit (see D4.4. for more info about the entire methanation process and upgrading). SNG needs to comply a requirements of purity according to the European Standards.

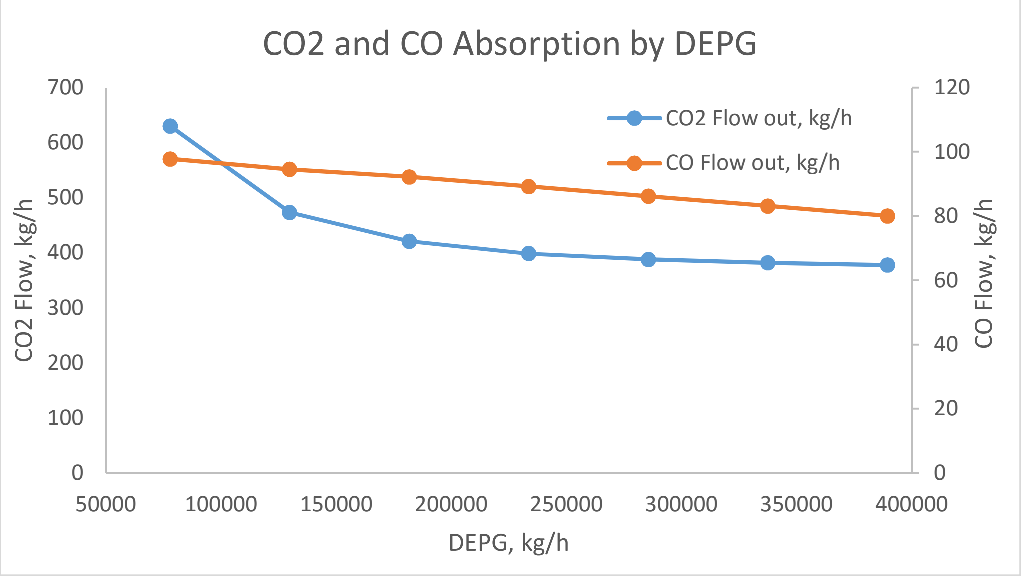

Figure 23. Sensitivity analysis for CO_2 removal after WGS

- Regeneration section

Regeneration section, represented as section 7 in the HYSYS flowsheet diagram, is a common stage for three different CO_2 removal sections (including methanation upgrading). The composition of the regenerated solvent at the end of this process is collected in Table 45.

Table 45. Regenerated DEPG composition

Component (Stream S07014)	**Mass fraction**
DEPG	0.9136
CO	-
CO_2	0.0861
Hydrogen	-
H_2O	0.0001
Nitrogen	-
Methane	0.0001
Mass flow, kg/h	376,213

CO_2 has not been completely removed from absorbent in this regeneration stage. Nevertheless, this composition is sufficient to ensure the CO_2 removal up to lower concentration for the coming downstream processes.

Apart from this regenerated absorbent stream, which will be split into three streams, there are several previous streams that likely will be treated as emissions. These streams come from the pressure vessel separation. The composition is shown in the following tables:

Table 46. Stream S07003 composition

Component	**Mass fraction**
DEPG	-
CO	0.1353
CO_2	0.4674
Hydrogen	0.0121
H_2O	-
Nitrogen	0.2917
Methane	0.0935
Mass flow, kg/h	639.6

Table 47. Stream S07005 composition

Component	**Mass fraction**
DEPG	-
CO	0.0770
CO_2	0.7022
Hydrogen	0.0031
H_2O	-
Nitrogen	0.1298
Methane	0.0878
Mass flow, kg/h	615

Table 48. Stream S07008 composition

Component	**Mass fraction**
DEPG	-
CO	0.0042
CO_2	0.9786
Hydrogen	0.0001
H_2O	-
Nitrogen	0.0049
Methane	0.0122
Mass flow, kg/h	6,195

The major component in these outlet streams is CO_2. Although there are other valuable compounds in energetic terms, like hydrogen and methane, the high amount of CO_2 makes difficult the valorisation of these streams. Methane should be destroyed catalytically in order to decrease methane emissions of the process.

The regeneration section is made up of pressure drums exclusively. These tanks are just based on pressure changes.

2.6 Nitrogen removal

Hydrogen must be separated from other compounds, mainly nitrogen, aiming to be used in the hydrocracking section and to reduce the nitrogen concentration in FT and methanation reactions. Several technologies has been studied. Although PSA cycles were considered at the beginning such as the best technology, finally membrane technology has been selected as the most suitable potential technology for nitrogen removal in alignment to the FFW purpose as is detailed below.

2.6.1 Process Overview

There are several technologies to remove nitrogen and purify hydrogen. These technologies can be based on physical or chemical principles. Depending on the origin of the hydrogen and the amount of it, the selected process could be different. In Table 49 are shown the different routes of hydrogen obtained from biomass.

Table 49. Hydrogen-containing gas mixtures of biogenic origin (49)

Source	Gas composition, vol %							Reference
	H_2	CH_4	C_2+	CO	CO_2	N_2	H_2S	
Biohydrogen	1-80.0	0-2	-	-	6.0-12	1.0-80	0-12	Geng et al Teplyakov et al (50)
Biohydrogen	57-60	-	-	-	39-43	1.0-5	-	Oh et at (51)
Biosyngas	25-42	1	-	25-42	10-35.0	2.0-5	1	Panzchava et al (52)
Biosyngas, model	33	-	-	17	-	50	-	Rafik et al (53)
Solid waste pyrolysis	31-32	25-31	-	20-27	7.0-13	-	-	Panzchava et al (52)
Catalytic pyrolysys of pine tree	49.7-52.8	3.8-5.3	1.1-1.6	33.7-34.5	8.6-8.7	-	-	Quinglan et al (54)
Pyrolysis of wet sewage sludge	36.7	14.7	7.1	21.8	13.6	6.3	-	Dominguez et al, 2006 (55)
Pyrolysis of coffe hulls	9.3-40.1	0-11.3	0-2.5	20.6-32.7	17.7-56.6	-	-	Dominguez et al, 2007 (56)
Gasification of Siberian elm	44.3	5.9-7.9	-	17.1	26.8-31.1	-	-	Demirbas, 2002 (57)

Technologies to purify hydrogen used in the industry are: membrane, adsorption, absorption, partial condensation and cryogenic distillation. Each one is explained below:

- **Adsorption:** Pressure Swing Adsorption (PSA) is a well-stabilised and demonstrated technology for hydrogen purification. Adsorption processes are the most important in the gas purification processes in the industry. This purification method is preferred when the concentration of the component to remove is quite important (a few percent) as rule of thumb (58). However, the normal composition and conditions used in the petrochemical industry to use PSA technology are shown in Table 50. In literature, information about PSA cycles to separate H_2/N_2 from off-gas effluents is relatively easy to find. However, nitrogen concentration of these streams are usually below 5 % (59).

Table 50. Common operation conditions in a petrochemical plant to obtain purified hydrogen using PSA (60)

Conditions	**Feed**	**Product**	**Tail gas**
Composition, mol %			
H_2	94.84	99.99	82.15
N_2	0.01	Balance	0.02
CO	0.29	0.03 ppm	1
CO_2	10 ppm	Balance	0
CH_4	4.86	-	16.93
C_2H_6	10 ppm	-	0
C_2H_4	10 ppm	-	0
Unit recovery, %		75	
Pressure, bar a	32.3	31.6	4.6
Pressure, mmHg	24.548	24.016	3.496
Temperature, ºC	35	40	25
Molar Weight, kg/kmol	2.78	2.02	4.65
Flow rate, m^3/s	10.1	7.575	30.735
Flow rate, kg/h	4,606.16	2,381.51	224.64
Flow rate, kmol/h	1,859.02	1,180.18	478.84

- **Absorption.** There are several absorption processes operating in the industry using solvents for purification of hydrogen. These processes can be physical or chemical (in the presence of chemical reactions). The process is based on two principal towers, a first column where the most soluble component or components is/are trapped by the solvent using high pressure or low temperature, and a second column where the components are separated from the solvent using high temperature (61).
- **Partial condensation.** This method is a gas-liquid separation based on volatility differences. Hydrogen is separated from the rest of the component in the mixture using water to condensate them at a lower temperature. Hydrogen is separated using this technology from components such as hydrocarbons, water (vapour), CO_2 and N_2 because the condensation is at higher temperatures than H_2. This method is mainly used in petroleum off-gases to recover hydrogen. The purity and recuperation reached for hydrogen depends on the feed composition and the conditions (pressure and temperature) and the purity is around 90-98 % and 95 % recovery. Partial condensation is used when the hydrogen content is low or when there are valuable components in the mixture (61).
- **Cryogenic distillation.** This operation is a conventional distillation, where the separation of the compounds is performed by the differences of temperatures from the bottoms toward the top, with the difference that temperatures are very low. The types of columns used for this distillation are the same that in conventional distillation: tray and, sometimes, packed columns. It is used for the separation of air, hydrogen and its isotopes and hydrogen from others compounds (such as hydrocarbons and other gases). The main reason to apply this technology is when is required a high purity for the application of the gases (62).
- **Membranes.** The principal issue to choose the technology is the consumption of energy. The main advantage in the use of membranes is the absence of energy for phase transitions. Over

the last decades, polymeric membranes for gas separation has become widely used in industrial separation of gases. This operation is based on the differences of the permeability rate of the compounds through the film. In this case, hydrogen is more permeable in polymers than other gases such as nitrogen, methane and CO, the selectivity of the polymer membranes to hydrogen is very high. The initial target of the membranes in the market was the separation of hydrogen from other gases. The first industrial-scale membrane to reach this target was Monsanto using a polysulfone hollow fiber called Prism® which archived 95 % purity for hydrogen (currently is owned by Air Products and Chemicals). Currently, this type of membrane is used for the recovery of hydrogen in ammonia purge gas, oxo-chemical synthesis and refinery off-gas purification. (63) (64) (65) (66) (67)

Considering the technological study shown above, the best options to purify hydrogen (at least up to 95 % purity required for hydrocracking process) are adsorption and membrane technologies. However, adsorption might not be a suitable technology in this specific case. Nitrogen concentration is high, near 40 % molar fraction, and usually adsorption is used to lower concentrations of nitrogen (below 5 %) and in the presence of other mayor components such as CO and CO_2.

Membrane technologies have been used to separate hydrogen/nitrogen moistures for 30 years and there are several companies operating with this technology. There are lots of advantages of using membranes to separate gases in industrial processes. These advantages are listed below (68):

- Do not involve phase changes/ chemical additives
- Operation and concept is simple
- Modular and easy to scale up
- Greater efficiency for raw materials use and potential for recycling of by-products
- Equipment size may be decreased

The main developers and producers of polymeric membrane systems to separate and purify gases are shown in Table 51.

Table 51. Producers and processes of polymeric membranes to separate gases at industrial scale (49)

Producer	**Process**	**Polymer**	**Type of module**[3]
Permea (Air Products)	Gas separation	Polysulfone	HF
Medal (Air liquide)	Air separation recovery of H_2	Polyimide, polyamide	HF
IMS (Praxair)	Air separation, recovery of H_2	Polyimide	HF
GENERON (MG)	Air separation, recovery of H_2	Tetrabromopolycarbonate	HF
Separex (UOP)	CO_2/CH_4 separation	Cellulose acetate	SW
Kvaemer	CO_2/CH_4 separation	Cellulose acetate	SW
Cynara (Natco)	CO_2/hydrocarbons separation	Cellulose acetate	HF
Aquilo	Air separation	Polyphenylenoxide	HF

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[3] HF= Hollow Fiber

SW= Spiral Wound Membrane Fiber

DT=Disk-Type Membrane Module

Producer	**Process**	**Polymer**	**Type of module**[3]
Parker-Hannifin	Air separation, recovery of H_2	Polyamide, polyphenylenoxide	HF
UBE	Vapor/gas separation, air separation	Polyimide	HF
GKSS licensses	Hydrocarbons recovery	Siloxane-containing copolymers	DT
MTR	C_6H_{10}/N_2 separation, hydrocarbons recovery	Polyalkylsiloxane	SW

Companies that recover hydrogen from other mixtures of gases using membranes are listed below:

- Air Products and Chemicals. It uses Prism® membranes from gas streams located in ammonia plants, refineries and petrochemical plants (69). Over 500 of these membranes are operating in the world. Gas molecules permeate through the hollow fiber membrane by pressure difference. These membranes can operate in series and parallel, it depends on the treated volume and are usually used in refinery for hydroprocessing treatments. It is possible to archive hydrogen purities up to 92-98 % and hydrogen recovery of 85-95 %. Even it is used for off-gas streams from cracker where the concentration of hydrogen is between 20-30 % and it is possible to upgrade up to 70-90 % purity or 95 % using two stages (70).
- Air Liquide. The technology used by this company is called Medal™ Membranes. Hydrogen is separated from nitrogen and other gases through a hollow fiber membrane (71).This technology is used in ammonia plants and refineries. First installation of this type of non-porous membrane was in 1987 and currently there are two types of polymeric membranes:
  - Polyaramide membrane: Its selectivity is very high (>400 for H_2/CH_4) and chemically is robust (useful for ammonia purge use).
  - Polyimide membrane: Its selectivity is moderate. However, it is the membrane used for an efficient recovery of H_2.

There are about 120 references worldwide in the use of these membranes with a capacity higher than 1,400 MMSFCD. All the commercial plants operating with Air Liquide membrane technology appear in Table 52 (72).

Table 52.Commercial uses of MEDAL membranes

Applications	**Number of plants**	**1st unit installed (year)**	**Feed rate (MMSCFD)**
Refining	70	1987	1.0-40
Ammonia	18	1990	7.0-35
Syngas	13	1992	2.0-63
Petrochemicals	11	1990	0.2-55
Others	8		

Typical data of refinery applications of these types of membrane separation is shown in Table 53.

Table 53.Refinery applications of membrane hydrogen purification system.

Process/Unit	**Feed H_2 % mole**	**H_2 Permeate Purity**	**Recovery**
Catalytic Reformer	70-80	90-97	75-95+
FCC off gas	15-20	80-90	70-80

Process/Unit	Feed H_2 % mole	H_2 Permeate Purity	Recovery
Hydroprocessing	60-80	85-95	80-95
PSA off Gas	50-60	80-90	65-85

- Praxair. Praxair technology is called Innovative Membrane Systems, Inc. (IMS) and the application of this technology is limited at low flow rates (474 m^3/h for nitrogen purification and 90 for dry air separation) (73).
- IGS Generon. This company has been focused on nitrogen membranes separation archiving over the past years an increase in the efficiency by 500 %. However, the company is not only focused on nitrogen separation, also supplies separation of other gases such as CO_2, H_2, syngas and biogas (74). The recovery of this technology is 90-99 % and the hydrogen purity from 90 to 99.9 %. If it is necessary a high purity hydrogen, it could be combined with PSA (Pressure Swing Adsorption) and it will archive a purity of 99.9 to 99.999+ %. The advantages using this technology are: feed pressures up to 138 bar, high recovery and purity and flow rates from 0.01 to 500 MMSCFD (75).

2.6.2 Design

The design of this membrane has been carried out mainly through an spreadsheet. The spreadsheet works out the separation values, which will be introduced into Aspen HYSYS. Aspen HYSYS Unitary operation used to simulate the performance of this equipment is the Component Splitter. Membrane design steps are explained below.

Considering information shown above, the membrane selected is a hollow fiber membrane (used by companies such as Air Products and Chemicals or Air Liquide). The general scheme of this membrane operating is shown below:

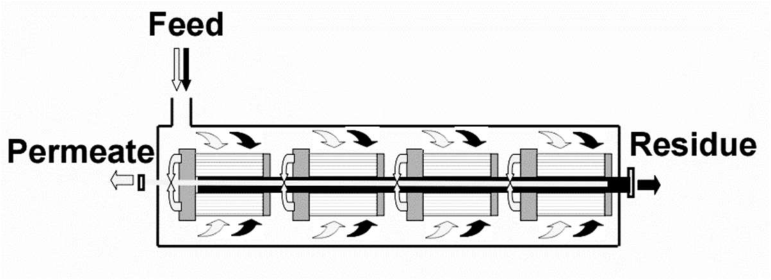

Figure 24 Membrane operating scheme

This system is considered as a cross flux membrane configuration. To design the membrane, an iterative equation system is solved (76):

$$\frac{dn}{n} = \frac{dx_A}{y_A - x_A} \quad [1]$$

$$y_A = \frac{\alpha\, x_A}{1+(\alpha-1)x_A} \quad [2]$$

$$\frac{dn}{n} = \left[\frac{1+(\alpha-1)x_A}{x_A(\alpha-1)/(1-x_A)}\right] dx_A \quad [3]$$

$$y_P = \frac{x_F - x_R(1-\theta)}{\theta} \quad [4]$$

$$y_p = \int_0^{np} \frac{y_A dn}{\theta n_F} \text{ [5.a]}$$

$$y_p = x_R^{\left(\frac{1}{1-\alpha}\right)} \left(\frac{1-\theta}{\theta}\right) \left| (1 - x_R)^{\left(\frac{\alpha}{\alpha-1}\right)} \left(\frac{x_F}{1-x_F}\right)^{\left(\frac{\alpha}{\alpha-1}\right)} - x_R^{\left(\frac{\alpha}{\alpha-1}\right)} \right| \text{ [5.b]}$$

$$A_M = \int_0^{np} \frac{y_A\, n_p}{P_{MA}(x_A p_F - y_A p_p)} \text{[6]}$$

Methane is considered for a preliminary design of the membrane in order to make simpler the process (methane quantity is very small) and it is designed as a binary system (hydrogen/nitrogen).

Membrane is solved from the following method:

$$\alpha_{A,B} = \alpha_{A,B}^* \left[\frac{x_A(\alpha_{A,B}-1)+1-r\,\alpha_{A,B}}{x_A(\alpha_{A,B}-1)+1-r}\right] \text{ [7]}$$

$$y_A = \frac{\alpha x_A}{1+(\alpha-1)x_A} \text{ [8]}$$

$$\frac{x_F - x_R(1-\theta)}{\theta} = x_R^{\left(\frac{1}{1-\alpha}\right)} \left(\frac{1-\theta}{\theta}\right) \left[(1 - x_R)^{\left(\frac{\alpha}{\alpha-1}\right)} \left(\frac{x_F}{1-x_F}\right)^{\left(\frac{\alpha}{\alpha-1}\right)} - x_R^{\left(\frac{\alpha}{\alpha-1}\right)}\right] \text{ [9]}$$

$$A_M = \sum \frac{y_A \Delta np}{P_{MA}(x_A p_F - y_A p_p)} \text{ [10]}$$

Where r is the pressure ratio, x_i the molar fraction at residue, y_i is the molar fraction at permeate, y_p is the local molar fraction, α_{ij} is the selectivity, α^* is the ideal selectivity and θ is the cut.

To get started the calculations, it is assumed the same molar fraction both at the residue and at the feed (from the feed value to 0). Using equation [7] is calculated α. Using α and x_R is possible to calculate y_p and the cut (θ). The area of the membrane will be the addition of each accumulated area calculated along all the possible values of x_F.

To calculate α* and r, data about the behaviour of the components in the membrane is necessary and it is solved by using the equations shown below:

$$\alpha^* = \frac{P_{MA}}{P_{MB}}$$

$$r = \frac{P_p}{P_F}$$

2.6.3 Process Specs and Analysis

2.6.3.1 Inputs

The information to solve the membrane is represented below:

Table 54. Membrane for nitrogen removal inputs

Parameter, unit	**Value**
Compound A	Hydrogen
Compound B	Nitrogen

Parameter, unit	**Value**
Feed molar fraction (A)	0.5282[4]
Feed molar fraction (B)	0.4718
P_F, bar	51 (72)
T_F, ºC	12.4
l_m, µm	0.05 (71)
P_p, bar	30 (72)
Flow rate, mol/s	57.5
P_{MA}, barrer	50 (77)
P_{MB}, barrer	0.6 (77)
P_{MA}, mol·m/m^2·s·bar	$1.67 \cdot 10^{-9}$
P_{MB}, mol·m/m^2·s·bar	$2.0088 \cdot 10^{-11}$
α*	83.33
r	0.5888
Selectivity H_2/N_2	>200 (MEDAL), 56-80 (Permea)

2.6.3.2 Outputs

The design outputs are represented in Table 55.

Table 55.Design of hollow-fiber membrane for separation of H_2/N_2

Parameter	**Value**
Molar fraction A (residue)	0.6863
A	1.709
Molar fraction local	0.529
Molar fraction A (permeate)	0.966
θ (cut)	0.998
Permeate flow rate, mol/s	80.656
Residue flow rate, mol/s	0.137
Area, m^2	4,400
H_2 recovery, %	99.8

In addition, the cost of this kind of equipment has been roughly estimated.

---

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

Membrane market and its competitiveness have been studied for 30 years. There are 3 main markets about H_2 recovery where this technology is a good option compared to established technologies such as cryogenic distillation or adsorption:

- Ammonia purge streams
- Hydrotreater off-gas
- Separation from hydrocarbons (enhanced oil recovery)

Over time, this technology has been developed for more additional processes.

In Table 56, the cost between membrane and PSA cycles in refinery is compared.

Table 56. Cost comparison between membrane and PSA use for off-gas treatment in refinery[5] (78)

Parameter	Membrane	PSA	PSA
Waste gas pressure, psig	-	60	5
H_2 recovery, MMSCFD	4.10	3.02	4.05
Capital cost, $M			
Equipment	530	1,050	875
Suggested installation	100	175	150
By manufacturer	-	-	-
Total cost	630	1,225	1,025
H_2 cost, $ Mscf	0.09	0.24	0.15
Operating cost, $M/yr	-	-	-
Steam for feed preheat	10	-	-
Compression to reactor pressure	140	46	130
Contribution to H_2 cost $/Mscf	0.11	0.05	0.09
Total H_2 cost, $/Msfc	0.20	0.29	0.24

The use of membranes is competitive in comparison with traditional implemented technologies, such as adsorption, in overall terms.

The estimated cost for fabrication of hollow fibers membranes can vary between 2-10 USD/m^2 and price of selling ranges between two and three times manufacture cost. In 2002, hollow fiber membrane selling price was 108 USD/m^2 (79). Equipment CE Index in 2002 was 395. Making the change using Equipment CE Index among 2002 and 2014, the current proximate price for this membrane (4,344 m^2 area) would be around 836,400 USD.

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[5] Note: Utility cost base don $0.5/kWh and $5/MMBtu.

H_2 cost based on 8,000 h/year operation for a five year span

2.7 Base case Summary

The tables below show the estimated energy and material inputs of the process. ER= 0.22, Gasifier Temperature = 750 ºC. The basis is 10,000 kg/hr but these figures can be manipulated to give a different basis according to the requirements of the LCA.

The validation of the main units (gasification and syngas purification though tar cleaning up) according to the experimental activities is detailed at the end of the correspondent section.

CO_2 removal unit does not achieve a total elimination of this component from the syngas stream (to FT process) and the hydrogen stream (after WGS and addressed to hydrocracking and methanation). Previous versions of this deliverable where chemical absorption was considered (amines) did not report a good separation of CO_2. Besides, high amount of absorbent implies removal of CO, which is the raw material for the following steps of the process. Several configurations can be made in order to improve this process in future research lines (not considered or evaluated at this point): CO_2 removal unit can be placed before WGS and evaluate the total removal of carbon dioxide, even considering the loses of monoxide if required. This configuration is able to eliminate the need for a CO_2 removal unit after methanation as part of methane upgrading.

On the other hand, at this point should be recommendable to study the costs associated to the hydrogen at hydrocracking section, since the hydrogen produced in WGS unit will be partially unpurified with the presence of CO_2.

In the following tables, Table 57 and Table 58, the summary of the different mass and energy balances is represented. Note that energy balance is after the energy integration performance, which is explained in detail within Deliverable 4.4. The energy requirements before energy integration are shown along the entire current deliverable and deliverable 4.4 for each section. Energy integration enables an important energy saving in the whole scale-up process. This is an important point when an industrial process is being performed.

Table 57. Energy inputs/outputs of chemical pre-treatment process-base case

Process	**Energy Input/Output**	**Energy added (kJ/h)**	**Per 1kg of biomass (kJ/h)**	**Service/Comments**
Gasification	Blower	377,805	37.8	
	Air heater	1,411,467	141.1	Fired Heater
	Heater	303,422	30.3	Fired Heater
	Heater	1,641,087	164.1	Fired Heater
	Reactor Heat	-2,857,699	-285.8	HP Steam Generation
	Cooler	-492,986	-49.3	HP Steam Generation
Purification	Cooler	-2,785,537	-278.6	MP Steam Generation
	Blower	14,467,578	1,446.8	
	Cooler	-14,256,866	-1,425.7	HP Steam Generation
	Tar removal coolers	-4,760,400	-476.0	Chilled water
	Tar removal heaters	941,880	94.2	HP Steam

Process	Energy Input/Output	Energy added (kJ/h)	Per 1kg of biomass (kJ/h)	Service/Comments
	Tar removal compression	6,872,661	687.3	
	Blower	8,180,152	818.0	
WGS	Cooler	-3,242,473	-324.2	MP Steam Generation
	Blower	1,894,425	189.4	
	Cooler	-6,028,273	-602.8	MP Steam Generation
	Cooler	-2,434,468	-243.4	LP Steam Generation
	Cooler	-4,235,411	-423.5	Chilled Water
Compression	Cooler	-5,056,671	-505.7	LP Steam Generation
	Blower	2,836,836	283.7	
	Cooler	-3,423,867	-342.4	LP Steam Generation
	Cooler	-3,291,509	-329.2	Chilled Water
CO_2 removal	Blower	3,198	0.3	
	Cooler	-2,278	-0.2	Chilled Water
	Blower	1,7972	1.8	
	Cooler	-11,356	-1.1	Chilled Water
	Pump	2,359,165	235.9	
	Heater	790,818	79.1	Refrigerant
Total (Net)	Net	**-10,781,329**	**-1,078.1**	kJ/h
	Net	**-107,813**	**-10.8**	Net MJ/hr energy added
	Compression	**37,009,791**	**3,701.0**	MJ/hr energy added

Table 58. Continuous material inputs of chemical pre-treatment process-base case

Section	Materials in/out	Amount in (kg/h)	Per 1kg of biomass (kg/h)	Comments	HHV, kJ/kg
Gasification	Biomass	10,000.0	1.000		19900
	Air	11,509.0	1.151		
	Bed material (Olivine)	0.0	0.000		
	Ash	-326.5	-0.033		
	Char	-910.8	-0.091		
	Olivine (not recoverable)	0.0	0.000		
	Gasification outlet	-20,616.2	-2.062		
Purification	Dirty Gas	20,616.2	2.062	0.5% Tar (anthracene,	

Section	Materials in/out	Amount in (kg/h)	Per 1kg of biomass (kg/h)	Comments	HHV, kJ/kg
				naphthalene, BTE)	
	Oil in	1,842.5	0.184	Soybean Oil (palmitic acid, stearic acid, linoleic acid, linolenic acid, oleic acid)	
	Oil Out	-1,842.5	-0.184		
	Air in	80,000.0	8.000		
	Air out + tar	-80,000.0	-8.000		
	Clean Gas	-20,616.2	-2.062		
WGS (H_2 Production)	WGS Feed from Gasification	5,172.2	0.517		
	Water (steam)	3,993.3	0.399		
	Water	-3,348.3	-0.335		
	Gas out from WGS	-3,013.9	-0.301		
CO_2 removal	Feed from Gasification	15,959.9	1.596		
	Feed from WGS	3,013.9	0.301		
	DEPG (Selexol) dirty from Methanation	40,346.7	4.035		
	DEPG (Selexol) clean to Methanation	-38,725.0	-3.873		
	Water	-333.3	-0.033		
	Off gas	-7,449.1	-0.745	CO2: 0.912, CO: 0.021, CH4: 0.025, N2: 0.040, H2: 0.001	1818
	CO-enriched	-12,679.9	-1.268	H2: 0.106; CO: 0.7053; CO2: 0.152; N2: 0.020	
N_2 removal	Membrane Feed	3,013.8	0.301	Membrane: Polyaramide	
	Off gas	-2,549.0	-0.255	CO2: 0.093, CO: 0.037, CH4: 0.014, N2: 0.856	1158
	Hydrogen-enriched	-464.9	-0.046	H2: 0.416; CO2: 0.370;	

Section	Materials in/out	Amount in (kg/h)	Per 1kg of biomass (kg/h)	Comments	HHV, kJ/kg
				N2:0.048; CO:0.155	
Total		2,591.9	0.259	It was not null because of the component lost and errors between simulations and Thermodynamic Packages	

Table 59 gathers the equipment list and the operation model used for modelling each one (in AspenPlus or Aspen HYSYS). This equipment list is before the energy integration carried out for the energy saving. However, this point just has influence over the heat exchangers and the new heat exchangers after the integration are available to be checked in deliverable 4.4.

Table 59. Equipment list throughout base case (pre-treatment section only)

Equipment	Section	Unit Operation Model
B01001	1 (Gasification)	Compressor
B01002	1 (Gasification)	Heater
B01003	1 (Gasification)	Heater
B01004	1 (Gasification)	Mixer
B51001	1 (Gasification)	RYield reactor (decomposition)
B51002	1 (Gasification)	Split fraction (dryer)
B51003	1 (Gasification)	RGibbs reactor (devolatilisation)
B51004	1 (Gasification)	Cooler
B51005	1 (Gasification)	Split fraction
B51008	1 (Gasification)	Mixer
B51007	1 (Gasification)	Mixer
B51010	1 (Gasification)	Mixer
B52008	1 (Gasification)	Mixer
B52009	1 (Gasification)	FLUIDBED (Fluidised bed-Gasifier)
B01006	1 (Gasification)	Cyclone
B01007	1 (Gasification)	Cooler
B01008	1 (Gasification)	Cyclone
B01002B	1 (Gasification)	Cooler

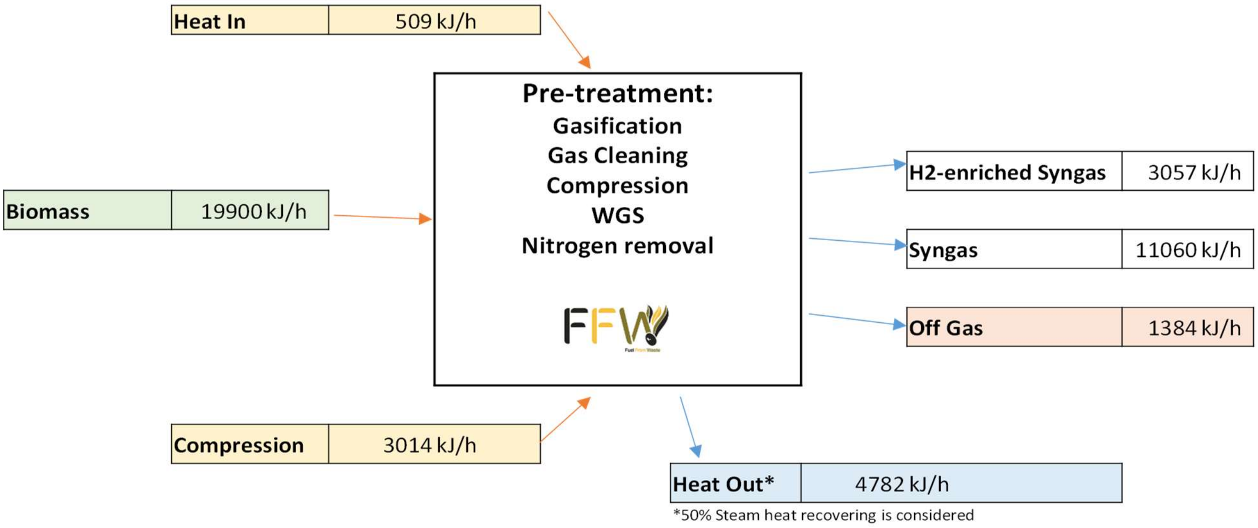
B01003B	1 (Gasification)	Cooler
B02001	2 (Post-Gasific.)	Heat Exchanger
B02002	2 (Post-Gasific.)	Compressor
B02003	2 (Post-Gasific.)	Heat Exchanger
B02005	2 (Post-Gasific.)	Mixer
B02006A	2 (Post-Gasific.)	Compressor
B02006B	2 (Post-Gasific.)	Cooler
B02007	2 (Post-Gasific.)	Cooler
B02008	2 (Post-Gasific.)	Absorption column (Tar scrubber)
B02009	2 (Post-Gasific.)	Heater
B02010	2 (Post-Gasific.)	Compressor
B02011	2 (Post-Gasific.)	Heater
B02012	2 (Post-Gasific.)	Absorption column (Stripper)
B02013	2 (Post-Gasific.)	Splitter
B03001	3 (WGS)	Mixer
B03002	3 (WGS)	Equilibrium reactor
B03003	3 (WGS)	Heat Exchanger
B03004	3 (WGS)	Compressor
B03005	3 (WGS)	Heat Exchanger
B03006	3 (WGS)	Separator (Flash Vessel)
B04001	4 (Compression)	Heat exchanger
B04002	4 (Compression)	Compressor
B04003	4 (Compression)	Heat Exchanger
B04005	4 (Compression)	Heat Exchanger
B05001	5 (CO_2 cleaning)	Absorber
B05002	5 (CO_2 cleaning)	Valve
B05003	5 (CO_2 cleaning)	Tank
B05004	5 (CO_2 cleaning)	Compressor
B05005	5 (CO_2 cleaning)	Heat Exchanger
B06001	6 (CO_2 cleaning)	Absorber
B06002	6 (CO_2 cleaning)	Valve
B06003	6 (CO_2 cleaning)	Tank
B06004	6 (CO_2 cleaning)	Compressor
B06005	6 (CO_2 cleaning)	Heat Exchanger

B07001	7 (Regeneration)	Mixer
B07002	7 (Regeneration)	Valve
B07003	7 (Regeneration)	Tank
B07004	7 (Regeneration)	Tank
B07005	7 (Regeneration)	Tank
B07006	7 (Regeneration)	Pump
B07007	7 (Regeneration)	Component Splitter
B07008	7 (Regeneration)	Heat Exchanger
B07009	7 (Regeneration)	Tee
B08001	8 (N_2 Membrane)	Component Splitter (Membrane)
B08002	8 (N_2 Membrane)	Tee

Figure 25 and Figure 26 summarised the mass and energy balances for the base case of the chemical pre-treatment. The energy efficiency of the entire chemical pre-treatment in the base case is 75 %.

Taking into account these results, it is highlighted that larger scale process would have higher efficiency due to lower heat losses (low A/V ratio) and larger integration potential.

Figure 25. Base case mass balance scheme (chemical pre-treatment)



$$\text{Process efficiency} = \frac{3057+11060+4782}{19900+509+3014} = 75\%$$

Figure 26. Base case energy balance scheme (chemical pre-treatment)

3 Case Study: Gasification with oxygen/ steam

The case study evaluates the potential application of gasifying using oxygen or steam or both rather than air. Air includes nitrogen and as per base case pre-treatment and process scale-up (D.4.4) show, it is a problem along the entire process that needs to be solved.

An air separation unit (ASU) is commonly used in order to obtain oxygen in this kind of processes.

3.1 Air Separation

An Air Separation Unit (ASU) has been designed as previous operation before gasification process in order to separate oxygen and nitrogen from air and modelling a further process without nitrogen.

The ASU has been modelled using Aspen Plus software and previous pre-treatment operations for air have not been considered for this design, such as filtration.

3.1.1 Process Overview

In order to minimize the compression stage costs and energy required, the installation of a cryogenic distillation unit is common in gasification plants (80). The efficiency and the costs of this installation would be optimised with a potential integration in a fossil based refinery.

Currently, cryogenic air separation is the most efficient and cost effective technology to produce industrial quantities of oxygen, as well as nitrogen and other valuable gases (e.g. argon). An ASU is made up of a conventional, multi-column cryogenic distillation that produces oxygen from compressed air. This oxygen has high recoveries and low impurities (81).

Gasifiers typically operate with 95 % purity oxygen, which is obtained through an air separation unit (ASU) that supplies the oxygen rather than purchasing it. It is an operation with two cryogenic oxygen-nitrogen separation column. Air precooling is accomplished by exchanging heat with exiting nitrogen in low pressure column and this section of the plan consumes a significant portion of power. This kind of air separation technology is used up to 2,725 tonnes/day of oxygen, in this case is necessary multiple trains of ASUs and the economies of scale could be reduced (82).

The different technologies for pure oxygen obtaining from air are summarised in Table 60.

Table 60. Comparison between technologies to purify oxygen from air

Process	Status	Economic range (Stdp)	Byproduct capability	Purity limit (vol. %)	Start-up time
Adsorption	semi-mature	<150	poor	95	minutes
Chemical	developing	undetermined	poor	99+	hours
Cryogenic	mature	>20	excellent	99+	hours
Membrane	semi-mature	<20	poor	~ 40	minutes
Ion Transporting Membrane (ITM)	developing	undetermined	poor	99+	hours

Cryogenic technology can also produce high-purity nitrogen as an useful by-product stream at relatively low incremental cost. In addition, liquid argon, liquid oxygen and liquid nitrogen can be added to the product slate for stored product backup or by-product sales at low incremental capital and power costs (81). It is the most mature technology for this purpose and has been successfully employed for many years to supply oxygen for the gasification of a wide range of hydrocarbon feedstocks to generate synthesis gas for the production of fuels, chemicals and other valuable products.

3.1.2 Design

AspenPlus software has been used for the design of the process.

Although it has not been designed in this preliminary conceptual design, there is a previous filtration step in order to remove particulate matter that could damage other downstream equipment and a stage of CO_2 and water steam removal in this plant (83).

The first designed step is the compression of air up to the high pressure section of the column (where the feed is placed). In this case, it is 5.5 bar. Depending on the process requirement, sometimes multistage compressors with intermediate cooling are necessary. Due to the compression, air has been heated. Column feed should be near 99 K and in order to decrease the required power in cooling, this stream is integrated with one of the products streams (in this case with N_2 product). This integration is considered in the energy integration developed in D4.4. The design developed along this section collects the requirements of energy and mass that are necessary to obtain the oxygen for gasification. Energetic optimisation is further developed.

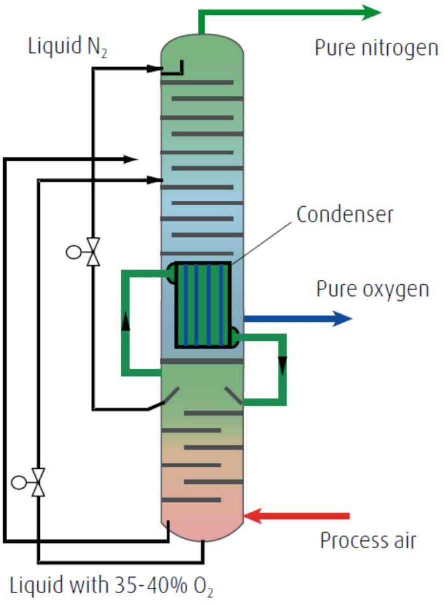


Figure 27. Single ASU column to separate air through high pressure and low pressure

Cryogenic distillation column is divided into two parts: one that operates at high pressure (about 5-6 bar) and other at low pressure (about 1.3-1.5 bar) (84). In high pressure column is obtained as residue product a stream with a composition between 36-40 % in oxygen (85) and distillate is rich in nitrogen. This distillate works as a reflux in low pressure column where high purity oxygen is obtained as a residue product (target of this design) and nitrogen as distillate (with a purity near 90 % in this case because is not the target of the design).

To design the column, RADFRAC equilibrium model has been the start point. Two columns have been optimized using different sensitivity analysis to achieve the maximum high oxygen purity. Column heat exchanger consumptions have been taken into account. After this first design and in order to make a more realistic design, the model has been changed to RADFRAD rate-based model and was checked that an increase in the number of stages is necessary to achieve the desired oxygen purity.

The information related to this kind of columns has been taken into consideration for the internal column. Until 1980, sieve trays were used for these processes. However, the use of structural packing in cryogenic distillation was introduced in this decade. Structural packing is better than trays due to the decrease of pressure drop, which means a reduction of energy costs and a more viable processes. The type of packing most used for this purpose is Mellapack (Sulzer manufacturer) (86). At the beginning, designs have been used Mellapack 125 X in both columns. However, Mellapack 250 X has been selected in low pressure column in the last design with rate-based model due to a high oxygen purity is reached with the same number of stages.

Although the design made using AspenPlus has been carried out using two different distillation columns (high and low pressure), the actual column is one equipment divided into two sections.

3.1.3 Process Specs and Analysis

Figure 28 represents the ASU modelled by Aspen Plus for FFW case study. This section has been considered as Section 0 (previous to the rest of the process and in order to keep the same section names of base case).

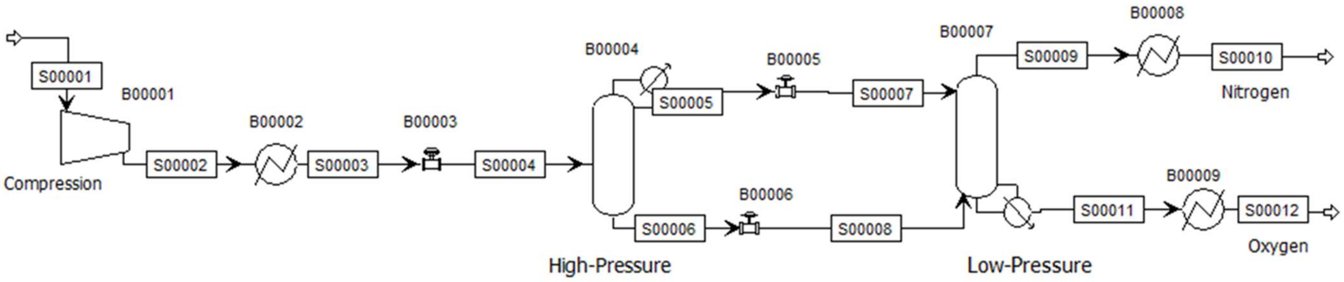


Figure 28. ASU flow diagram (Aspen Plus)-case study

3.1.3.1 Inputs and outputs

To design a cryogenic method for this purpose, the quantity of oxygen that is necessary obtain at the end of the process to feed the FT process is essential. In this case, it was roughly estimated at 70 tonnes/day (8/6 of the quantity of feed biomass: 250 tonnes/day) in order to have an initial mass flow. After a optimisation along the rest of the simulation, the necessary amount of air was recalculated as Table 61 shows.

The heat exchangers are optimised by an energy integration developed in deliverable 4.4. The design represented in this report is the preliminary engineering for this section and the main requirements.

The following tables show the mass balances and the ASU equipment designs. Distillation columns have been firstly modelled using equilibrium mode and have been optimised later through rate based.

Table 61. ASU Stream Summary – case study

			Component mass fraction				
Stream	**Phase**	**Mass flow, kg/h**	N_2	**O_2**	**AR**	**Temperature, ºC**	**Pressure, bar**
S00001	Vapor	19,572	0.76	0.23	0.01	25.00	1.01
S00002	Vapor	19,572	0.76	0.23	0.01	742.24	40
S00003	Vapor	19,572	0.76	0.23	0.01	-138.15	40
S00004	Mixed	19,572	0.76	0.23	0.01	-174.07	5.5
S00005	Liquid	8,318	0.97	0.02	0.01	-178.82	5.5
S00006	Liquid	11,253	0.60	0.38	0.02	-175.37	5.5
S00007	Mixed	8,318	0.97	0.02	0.01	-193.30	1.3
S00008	Mixed	11,253	0.60	0.38	0.02	-190.29	1.3
S00009	Vapor	16,337	0.91	0.08	0.01	-191.77	1.3
S00010	Vapor	16,337	0.91	0.08	0.01	50.00	1.3
S00011	Liquid	3,234	0.00	0.98	0.02	-180.66	1.32
S00012	Vapor	3,234	0.00	0.98	0.02	279.00	1.32

Table 62. ASU compressor design – case study

Parameter	**Value**
Compressor model	Isentropic compressor
Phase calculations	Vapour phase calculation
Net work required, kW	4175.38
Efficiency	0.72
Outlet pressure, bar	40

Table 63.ASU high pressure column design – case study

Parameter	**Value**
Packing	Mellapack 125 X, standard material
Number of stages	16
Diameter, m	0.7
Condenser / top stage temperature, ºC	-178.78
Condenser / top stage pressure, bar	5

Parameter	Value
Condenser / top stage heat duty, Gcal/h	-0.71
Reboiler pressure, bar	5.5
Reboiler temperature,ºC	-175.4
Calculated mass boilup ratio	1.51

Table 64. ASU high pressure column rate-based design – case study

Stage	Packed height meter	Fractional capacity	HETP meter	Pressure drop bar	Liquid velocity m/sec
2	0.2	0.64	1.27	0.00056	0.0084
3	0.5	0.64	1.28	0.00056	0.0083
4	1	0.64	1.28	0.00055	0.0082
5	1.5	0.63	1.28	0.00054	0.0081
6	2	0.63	1.29	0.00053	0.0080
7	2.5	0.63	1.29	0.00053	0.0079
8	3	0.62	1.30	0.00052	0.0078
9	3.5	0.62	1.30	0.00052	0.0078
10	4	0.61	1.31	0.00051	0.0077
11	4.5	0.61	1.31	0.00050	0.0076
12	5	0.61	1.32	0.00050	0.0075
13	5.5	0.60	1.32	0.00049	0.0075
14	6	0.60	1.33	0.00049	0.0074
15	6.5	0.60	1.33	0.00048	0.0073
16	7	0.60	1.33	0.00048	0.0073
17	7.5	0.63	1.23	0.00056	0.0099

Table 65. ASU low pressure column design – case study

Parameter	Value
Packing	Mellapack 250 X, standard material
Number of stages	21
Diameter	0.86 m
Condenser / top stage temperature, ºC	-192
Condenser / top stage pressure, bar	1.3
Reboiler pressure, bar	1.31
Reboiler temperature, ºC	-180
Reboiler heat duty, Gcal/hr	0.51
Calculated mass boilup ratio	4

Table 66. ASU low pressure column rate based column design – case study

Stage	Packed height meter	Fractional capacity	HETP meter	Pressure drop bar	Liquid velocity m/sec
1	0	0.63	0.57	0.00066	0.0033
2	0.6	0.63	0.49	0.00053	0.0070
3	1.2	0.62	0.49	0.00053	0.0069
4	1.8	0.61	0.49	0.00052	0.0067
5	2.4	0.60	0.49	0.00051	0.0065
6	3	0.59	0.49	0.00049	0.0063
7	3.6	0.57	0.50	0.00048	0.0060
8	4.2	0.56	0.51	0.00047	0.0058
9	4.8	0.54	0.52	0.00046	0.0056
10	5.4	0.54	0.52	0.00046	0.0055
11	6	0.53	0.53	0.00046	0.0054
12	6.6	0.53	0.53	0.00046	0.0054
13	7.2	0.53	0.54	0.00045	0.0054
14	7.8	0.53	0.54	0.00045	0.0054
15	8.4	0.53	0.54	0.00045	0.0054
16	9	0.53	0.54	0.00045	0.0054
17	9.6	0.53	0.55	0.00045	0.0054
18	10.2	0.53	0.55	0.00045	0.0053
19	10.8	0.53	0.55	0.00045	0.0053
20	11.4	0.53	0.55	0.00045	0.0053
21	12	0.53	0.55	0.00045	0.0053

3.2 Gasification

3.2.1 Design

The gasifier was redesigned according to a gasification process which utilises oxygen instead of air. The updated design reflects that no nitrogen is presence in the system. Total volume can be reduced because reactions can approach equilibrium in a smaller volume. Importantly, diameter of the gasifier is reduced so that a minimum superficial gas velocity of 0.5 can be maintained in the bed of the gasifier thus ensuring the bed remains fluidised.

Different scenarios are considered. These included:

- Varying oxygen addition whilst maintaining biomass flow rate and gasifier temperature whilst
- Steam addition – whilst maintaining biomass flow rate, gasifier temperature – but considering different equivalence ratios.

3.2.2 Process Specs and Analysis

3.2.2.1 Inputs

The table below includes the gasifier specs - all other inputs remain constant with the base case

Table 67. Demonstration Gasifier simulation inputs – case study

Gasifier Dimensions	
Bed pressure drop (mbar)	178
Total height (m)	8
Lowe tube length (m)	1.34
Conical Adapter length (m)	1.34
Upper tube length (m)	5.32
Lower tube diameter (m)	4.7
Upper tube diameter (m)	6.5

3.2.2.2 Outputs

Optimisation of the oxygen gasification case is limited because at low ER high levels of energy need to be added to the process – however low ER is of lower value. More importantly, at higher ER temperature of 750 ºC are difficult to maintain because no further energy can be removed from the oxygen.

The figure below shows how product composition varies with equivalence ratio. The trends are similar to the base case and follow the same explanation.

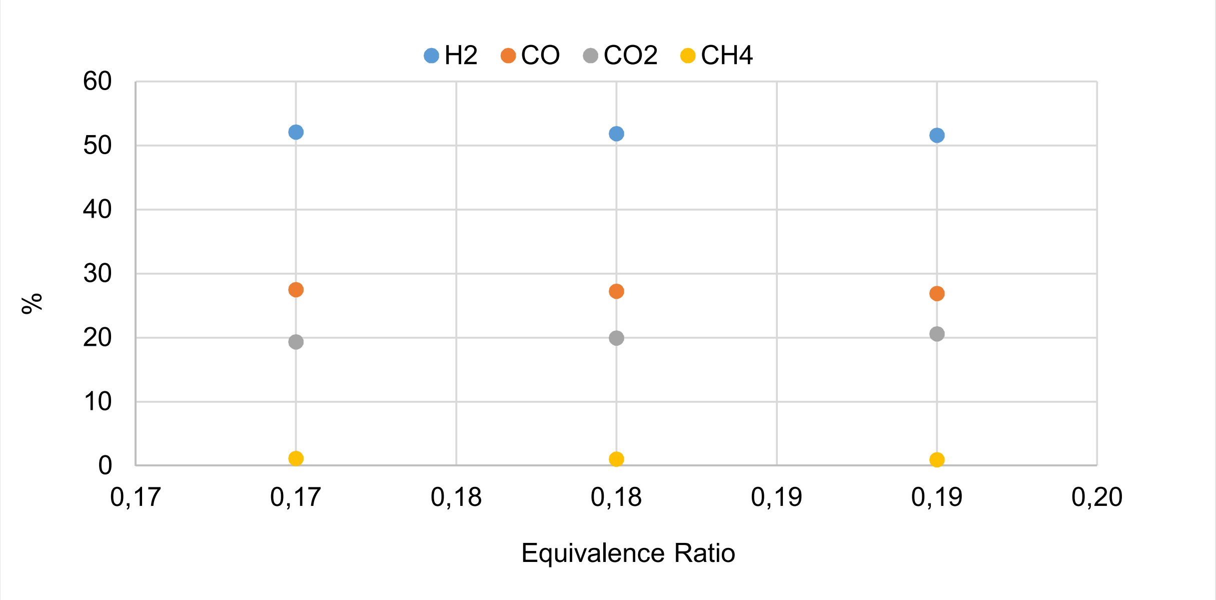


Figure 29. Effect of change in ER on product composition –case study

The figure below shows how gas quality decreases with equivalence ratio – but only a small amount- this is because oxidation reactions result in increased levels of CO_2 and relatively lower levels of H_2 and CO.

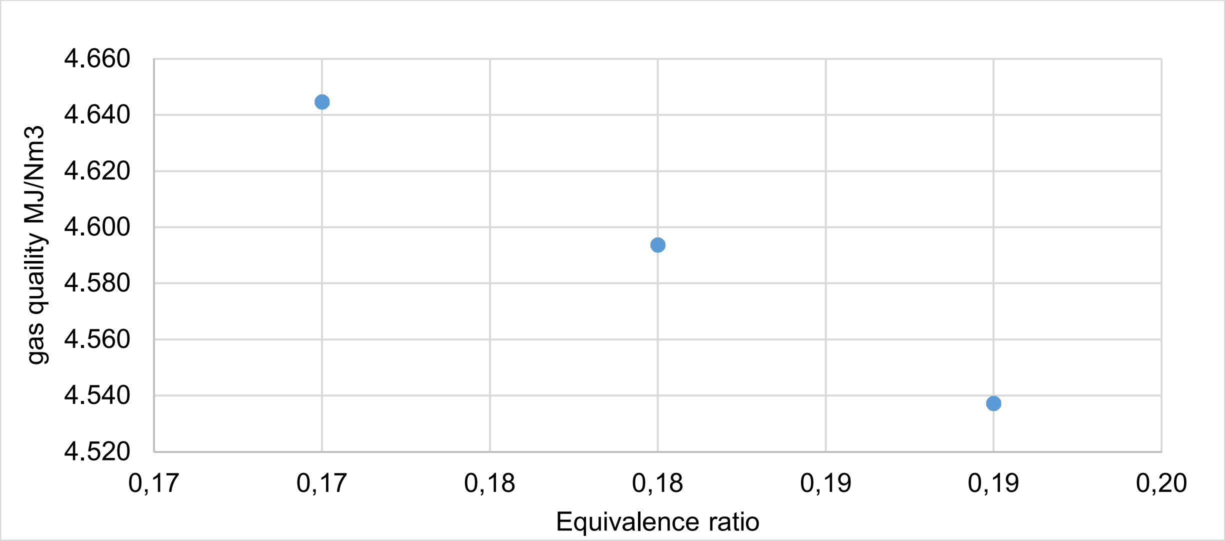


Figure 30. Effect of ER on quality of product gas – base case (wet basis)

This figure below shows how process efficiency increases with equivalence ratio – this is to be expected because at higher ER increased gasification of char occurs. The process efficiency is lower than in air gasification since the ER is limited.

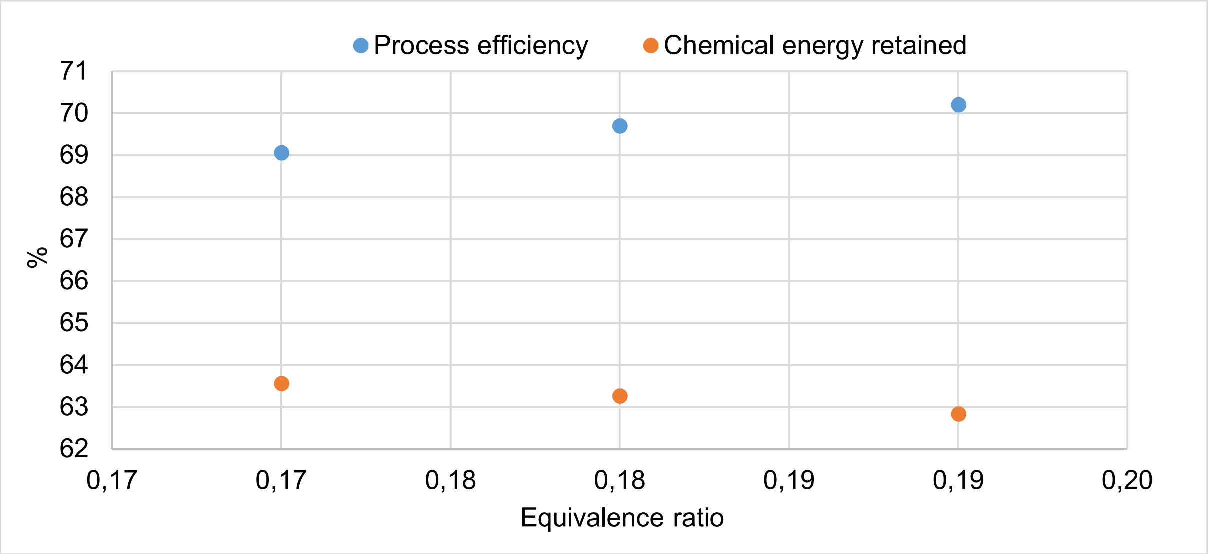


Figure 31. Effect of ER on gasification process efficiency and retention of chemical energy – oxygen

The simulations showed that **addition of steam was not a feasible option** since addition of only a small amount (steam: biomass 0.05) resulted in a H_2 to CO ratio higher than 2:1 making the gas unsuitable for Fischer Tropsch unless additional processing took place.

Despite lower process efficiency (poor char conversion), generally speaking gasification with oxygen is preferable to air because the quality of the produced gas is much higher and lack of nitrogen in the process means downstream processes are simpler and more efficient. The optimised ER is 0.19

Final outputs of the best case scenario are summarised in the table below:

Table 68. Optimised gasifier outputs (ER=0.19)- case study

Parameter	**Value**
Height of bottom zone, m	1.50
Height of freeboard, m	6.50
TDH from correlation, m	6.91
TDH based on solids volume profile, m	3.90
Solids holdup, kg	33,752
Number of particles in bed	1.12E+12
Bed surface area, m^2	76,102.14
Distributor pressure drop, bar	0.04
Bottom zone pressure drop, bar	0.15
Freeboard pressure drop, bar	0.03
Fluidized bed pressure drop, bar	0.18
Overall pressure drop, bar	0.21
Heat duty, kJ/h	-8,435,630
Minimum fluidization velocity, m/s	0.09
Bed temperature, ºC	750

Building and validation of a gasifier model according to literature where (when available) similar gasifier, fuel, bed material and oxidising agent have been utilised.

The validation in the deliverable has been performed with literature data and olive residues characterization data. Data provided by Fraunhofer and Soil Concept were utilised to provide input into the gasifier model.

As shown in base case, a validation is going to be developed considering the experimental results - according to the work developed in D.3.1 (laboratory test) and D.5.2 (demonstration activities)-, The table below summarises and compares the syngas composition obtained for each case, including the current simulation of the case study.

Table 69. Syngas composition (demo activities and simulations)

	Vol (%)			
Biomass	CO	CO_2	CH_4	H_2
Pruning	9-16	16-19	1-3.	4-5
Two-phase	12-17	14-18	2-3	5-6

	Vol (%)			
Biomass	CO	CO_2	CH_4	H_2
Three-phase	12-18	14-16	2-3	5-6
Wood	20-22	14-17	1-2	6-8
Simulation (Three-phase) – Base case	22	17	1	48
Olive pellets (screening tests)	18.8	14.84	2.06	23.5
Olive pellets (demonstration activities)- Vol % Dry	16	17	9	11

Outlet effluent from simulated gasifier shows similar results for CO,CO2,CH4 in comparison with the activities developed during WP3 and WP5. Hydrogen composition (volume %) is different from these results and enables the production of a syngas with a ratio H2:CO 2.1:1.

The best results are obtained for ER=0.19, which is lower than base case, ER<0.19 is non-feasible in the simulations with AspenPlus. The gas composition keeps similar to the base case, except for hydrogen, where is reported an increase in the presence of this gas.

3.3 Purification

Gas cleaning has been designed according to the study carried out in base case.

3.3.1 Process Overview

As per base case, an oil scrubber has been chosen for the tar cleaning from the syngas obtained during the gasification step. Although in demonstration stages a molten salt reactor has been used for this purpose, the limitations regarding to its commercial viability are the main reason to select another system for the simulations of the process scale-up.

3.3.2 Design

The flowsheet diagram for this section is the same than was presented in base case.

The process has been designed in the same manner using HYSYS software and the main difference is the composition of the feed syngas since nitrogen concentration is much lower than base case.

No further differences in the equipment design have been made.

3.3.3 Process Specs and Analysis

Since the main parameters have been optimised during base case design, both the scrubber and the oil regeneration system have been design according these results.

3.3.3.1 Inputs

The feed composition of the syngas, considering the potential appearance of tars, has been introduced in accordance with the bibliographic study developed in case base. Table 70 represents the feed composition for the case study.

Table 70. Syngas feed composition in tar removal section-case study

Compound	Value
CO_2	0.51
CO	0.39
Hydrogen	5.65E-02
H_2O	1.01E-02
Methane	1.04E-02
Nitrogen	1.08E-02
Anthracene	1.24E-03
Naphthalene	2.07E-03
Benzene	7.26E-04
Toluene	4.35E-04
E-Benzene	3.11E-04

At the beginning, the oil feed has been calculated according to the L/G relation obtained in case base (1.53 for scrubbing). However, the benzene removal using the oil flow rate calculated from this expression is not sufficient high as it could be (around 85 % recovery in absorbent + tar outlet stream). Thus, a sensitivity analysis has been carried out in order to determine the most suitable oil flow rate (absorbent).

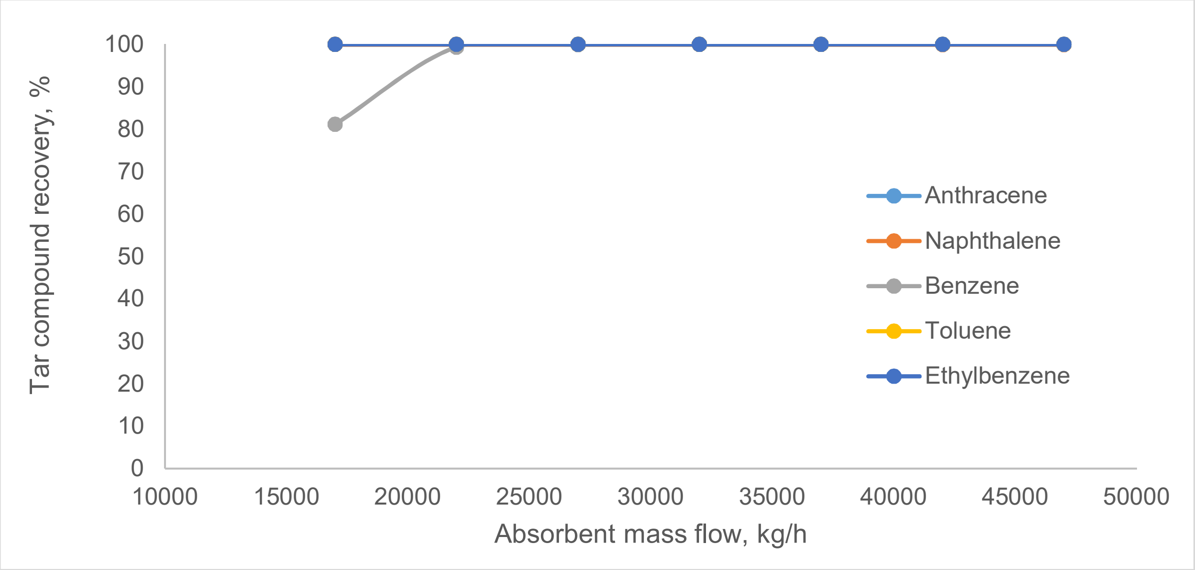


Figure 32. Sensitivity analysis of absorbent required - case study

Figure 32 shows the recovery for each compound (tar) according to the mass flow rate. The minimum flow rate studied is 17,000 kg/h (close the relation L/G=1.53 established in base case). The limiting compound is again the benzene, which shows lower recovery for the L/G=1.53 ratio. An increasing of the flow rate contributes to a better benzene recovery. A completed recovery in the oily absorbent is presented by the rest of the components.

After this first study, the inputs for the scrubber column are shown in Table 71.

Table 71. Oil scrubber inputs - case study

Parameter	Value
Column type	Packing, rasching rings
Number of stages	10
Feed gas flow rate, kg/h (m^3/h)	11,270 (52.59)
Feed gas temperature, ºC	100
Oil flow rate, kg/h	37,000
Oil temperature, ºC	20
L/G, kg/kg	3.28

The L/G relation has increased with regards to the base case scrubber. The main reason could be linked to the different syngas composition (e.g. reduction of nitrogen and different mass fractions of the rest of the components).

Regarding the regeneration stage, other sensitivity analysis has been performed with the aim of determining the most suitable air flow rate. The results are shown in Figure 33.

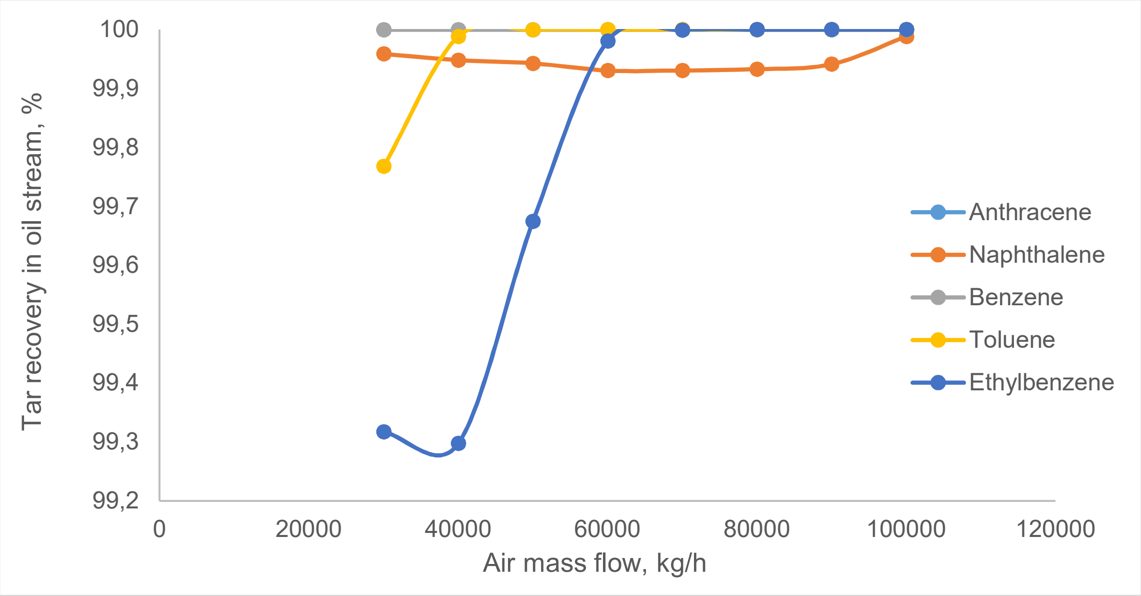


Figure 33. Sensitivity analysis of air required for regeneration - case study

The recovery is completed for feed air rates higher to 100,000 kg/h. The inputs are collected in Table 72. It is necessary to note that in this case simulations show ideal results. Benzene and toluene forms non-ideal mixtures and needs lower scrubbing temperatures in order to be separated totally. -10 °C is normally necessary.

Table 72. Oil regeneration inputs - case study

Parameter	Value
Column type	Packing, rasching rings
Number of stages	10
Feed oil flow rate, kg/h	47,144
Feed oil temperature, ºC	83.08

Parameter	Value
Air flow rate, kg/h (m^3/h)	100,000 (81,194)
Air temperature, ºC	290
L/G, kg/kg	0.47

3.3.3.2 Outputs

As shown in base case, the outputs are represented in the following tables:

Table 73. Achieved recoveries in oil scrubber - case study

Compound	Recovery in clean gas stream, %	Recovery in absorbent stream, %
Linoleic Acid	0	100
Linolenic Acid	0	100
Oleic Acid	0	100
Stearic Acid	0	100
Palmitic Acid	0	100
CO_2	98.92	1.08
CO	99.99	0.01
Hydrogen	99.99	0.01
H_2O	64.92	35.08
Methane	99.76	0.34
Nitrogen	99.92	0.08
Anthracene	0	100
Naphthalene	0	100
Benzene	0	100
Toluene	0	100
E-Benzene	0	100

Table 74. Scrubber design – case study

Parameter	Value
Column diameter, m	3.35
Pressure drop, bar	0.026
Height, m	8.13
Estimated pieces of rings	223 millions
Estimated mass of packing, tonnes	153

Table 75. Recoveries in oil regeneration[6]-case study

- Compound	Recovery in recovered oil stream, %	Recovery in air+tar stream, %
Linoleic Acid	100	0
Linolenic Acid	100	0
Oleic Acid	100	0
Stearic Acid	100	0
Palmitic Acid	100	0
CO_2	0	100
CO	0	100
Hydrogen	0	100
H_2O	0	100
Methane	0	100
Nitrogen	0.02	99,98
Anthracene	99.76	0.24
Naphthalene	15.28	84.72
Benzene	0	100
Toluene	0	100
E-Benzene	0	100

Table 76. Oil regeneration column design-case study

Parameter	Value
Column diameter, m	5.47
Pressure drop, bar	0.02
Height, m	7.62
Estimated pieces of rings	775 millions
Estimated mass of packing, tonnes	530

As reported in base case, not all the tar components are completely removed from the oily absorbent in the regeneration stage. However, this outlet composition is sufficient for the reuse of the absorbent in the scrubber and achieve the recovery shown above, which will ensure that further downstream catalyst will not be poisoned by tar deposition. It is remarkable the regeneration column dimensions. It has a tight high/diameter ratio, likely the diameter is too big. The packing selected for this column (rasching rings) might not be the most suitable for this purpose and it would be necessary to perform a study of the packing according to the column specifications and flow rate, even it could be suitable the potential use of tray rather than packing.

On the other hand, tars contain also heavier molecules than anthracene. These heavier molecules and particles will accumulate in the process, and they needs to be removed somehow e.g. by filtration.

The energy requirements are shown in Table 77.

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[6] H_2, H_2O,methane, nitrogen and CO_2 are negligible in mass flow.

Table 77. Energy requirements throughout the purification section- case study

Equipment	Energy consumption, kJ/h
B02007 (cooler)	-2.15E+07
B02008 (cooler)	-6.18E+06
B02009 (heater)	4.53E+06
B02011 (heater)	1.89E+07
B02010 (compressor)	8.49E+07

The energy consumption is higher for all the oil streams to be heated/chilled along with the air compression since the flow rates are higher than base case flow rates. The only exception is the post-gasification gas to clean, where the energy required for cooling is lower, due to the lower flow rate in comparison to base case rate and the absence (lower concentration) of nitrogen in the system.

3.3.4 Comparison with experimental MSR

The parameters reported in D.3.3 are collected in base case comparison. In this case study, a complete tar removal is achieved (for the modelled tar compounds and under the same assumptions).

3.4 Water Gas Shift

3.4.1 Process Modelling

WGS reactor has been performed through an equilibrium reactor in HYSYS.

The WGS reactors design follows the same stages than in base case and the same considerations have been taken into account for its design.

WGS high temperature is assumed to reach equilibrium if a suitable catalyst is loaded. The model used has been HYSYS equilibrium reactor. The relation H_2O/CO through an inlet steam water stream is controlled through a spreadsheet in HYSYS.

WGS product needs to be separated from the water. A flash drum has been included after a heat exchanger (cooler) for this purpose.

3.4.2 Unit Specification and analysis

WGS simulation in the case study is represented in Figure 34.

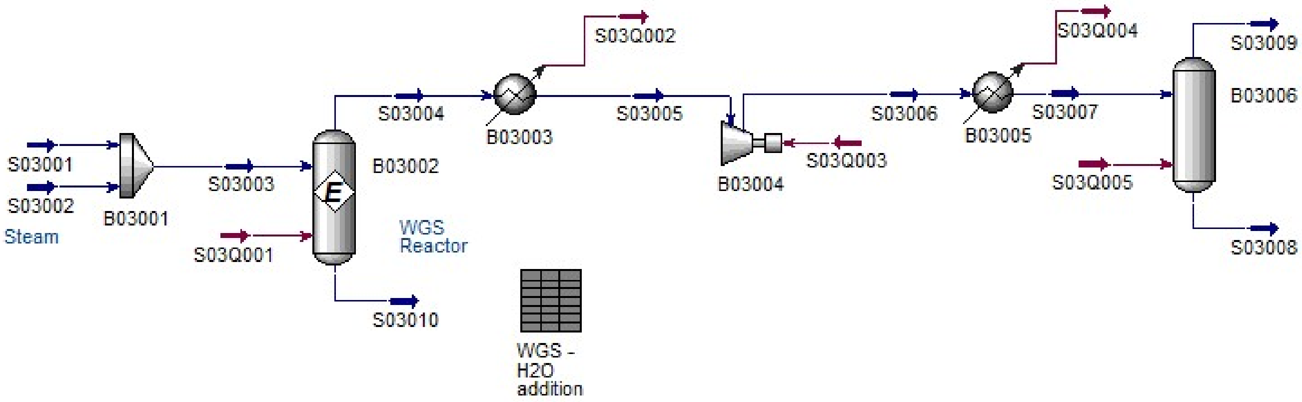


Figure 34. WGS section-case study

The syngas coming from gasification section (prior to being cleaned from carbon dioxide) is mixed with water (steam) before to be introduced into the WGS reactor (equilibrium reactor). The ratio H_2O/CO is 5:1 and it is achieved through a specification using a spreadsheet which controls the inlet steam water. No pressure drop is assumed along the design of all equipment in this section of FFW.

The inlet stream specifications in this system appear in Table 78.

Table 78. WGS Inlet Stream Specifications - case study

Stream specification	**Value**
Phase	Vapour
Temperature, ºC	289.2
Pressure, bar	25
Mass flow, kg/h	3051
Component Mass Fraction	
H_2O	0.56
Hydrogen	0.025
CO	0.17
CO_2	0.23
Nitrogen	0.005
Methane	0.005

As detailed in base case, there is a flash vessel in order to remove the maximum possible amount of water from this system. Before designing this vessel is necessary a change in the temperature and pressure of the system through heat exchangers and compressor. The main inputs for these equipment are shown in Table 79:

Table 79. WGS auxiliary equipment design-case study

Equipment	**Inlet Temperature**	**Outlet Temperature**	**Inlet Pressure**	**Outlet Pressure**	**Efficiency, %**
B03003 (Cooler)	395.4	200	25	25	100
B03005 (Cooler)	320.1	150	52	52	100

Equipment	**Inlet Temperature**	**Outlet Temperature**	**Inlet Pressure**	**Outlet Pressure**	**Efficiency, %**
B03004 (Compressor)	200	320.1 (HYSYS)	25	52	77.06
B03006 (Flash)	150	20.09	52	52	-

WGS product mass composition is represented in Table 80:

Table 80. WGS outlet composition-case study

Component	**Mass Fraction**
H_20	0.46
H_2	0.04
CO	0.018
CO_2	0.48
N_2	0.005
CH_4	0.005

Table 81. WGS Reactor sizing-case study

Parameter	**Value**
STD Volumetric Flow, m3/s	0.514
GHSV, h-1	30,000
Catalyst Volume, m3	4.28
Catalyst Density, kg/m3	3,850
Catalyst amount, kg	16,491
Bed Porosity	0.4
Catalyst Porosity	0.8
Reactor volume, m3	13.39

After flash separation (52 bar and 20.1 ºC), two streams are obtained: a water stream and a hydrogen product stream which will be a post-treatment. The composition results for these streams appears in Table 82.

Table 82. WGS product separation-case study

	Mass Fraction	
Component	**S03009 (Hydrogen)**	**S03008 (Water)**
H2O	0	1.00
Hydrogen	0.07	0
CO	0.03	0
CO2	0.88	0
Nitrogen	0.01	0

	Mass Fraction	
Component	**S03009 (Hydrogen)**	**S03008 (Water)**
Methane	0.01	0

Nitrogen and methane are present in a very small amount. However, CO_2 remains in high concentration for hydrogen stream, which means that should be treated. Absorption with DEPG as solvent is designed as CO_2 capture treatment for CO_2 removal before FT process.

Energy requirements for the equipment that is described along this section are represented in Table 83.

Table 83. Energy requirements for WGS section- case study

Stream	**Energy requirements, kJ/h**
S03Q001	0 (adiabatic)
S03Q002	-1,212,067
S03Q003	688,683
S03Q004	-3,520,004
S03Q005	1,570,027

3.5 Compression

3.5.1 Process Overview

Compression stages are the same as per base case. Flowsheets are represented in section 2.3.

3.5.2 Process Specs and Analysis

3.5.2.1 Inputs

Table 84 summarised the inputs for the different compression sections (with intermediate cooling) throughout the FFW process scale-up.

Table 84. Compression inputs- case study

	First Step		**Second Step**		**After WGS - Third Stage**		**Directly Third Stage**	
Parameter	**In**	**Out**	**In**	**Out**	**In**	**Out**	**In**	**Out**
Pressure, bar	**1**	**5**	**5**	**25**	**25**	**52**	**25**	**52**
Delta P, bar	4		20		27		27	
Pressure Ratio	5		5		2.08		2.08	
Temperature, °C	400	806.9	100	626.7	200	320.1	150	266.6
Mass flow, kg/h	11,268		11,268		3,051		9,850	
Adiabatic Efficiency, %	75		75		75		75	

3.5.2.2 Outputs

The outputs for the each compression step is shown in the Table 85, outlet temperature and power needed.

Table 85. Compression outputs- case study

	First Step		Second Step		After WGS Third Stage		Directly Third Stage	
Parameter	**In**	**Out**	**In**	**Out**	**In**	**Out**	**In**	**Out**
Temperature, ºC	-	806.7	-	626.7	-	320.8	-	266.6
Power, kW	2,548		1,442		191.3		580.7	

The total power needed for the compression is 4,762 kW. In comparison with base case, the compression required power is 2,843 kW consumed less than base case.

3.6 H_2O and CO_2 Removal

3.6.1 Process Overview

The process overview about the carbon dioxide and water removal has been detailed along the section 2.5. Selexol has been chosen previously as better absorbent than Rectisol, mainly due to the energy consumption since Rectisol (based on methanol) needs to keep the temperature at -20 ºC in order to achieve the desired absorption separation.

3.6.2 Design

The process design is the same shown in base case. The main difference is again the decrease in the presence of nitrogen, which will be present in the energy consumption mainly.

Water removal, as per base case, has been designed in HYSYS through a component splitter. This means that the water removal is considered completed (likely the most suitable operation would be a partial condensation although costs should be considered since it is an expensive operation in energetic consumption terms).

3.6.3 Process Specs and Analysis

3.6.3.1 Inputs

As presented in base case, the inputs of this section are presented according to Figure 19 scheme.

The composition of the column feed is shown in Table 86

Table 86. CO_2 removal feed (before FT process) - case study

Component	Mass fraction
DEPG	-
CO	0.38
CO_2	0.50

Component	Mass fraction
Hydrogen	0.05
H_2O	0.05
Nitrogen	0.01
Methane	0.01
Total mass flow. kg/h	9,859

The inlet mass flow is lower than base case. The carbon dioxide concentration is higher, around twice in comparison tp base case. The syngas (H_2/CO) concentration is lightly higher than base case syngas concentration for the same stream.

For the same column, the design specifications appear in Table 87.

Table 87. Absorption column for CO_2 removal before FT - case study

Specification	Input
Column	Absorption
Type	Packing, IMTP
Top pressure	51.7
Bottoms pressure	51.8
Feed gas temperature	20.09
Feed solvent temperature	7.22
Number of stages	10
Solvent mass flow, kg/h	208,401
Solvent stage	Top
Feed gas stage	Bottom

Solvent flow rate is similar to base case.

- CO_2 removal post-WGS inputs

This section is represented in Figure 20.

The inlet stream composition is represented in Table 88.

Table 88. Post-WGS mass composition – case study

Component	Mass fraction
DEPG	-
CO	0.032
CO_2	0.88
Hydrogen	0.068
H_2O	0.0007
Nitrogen	0.0089
Methane	0.0085
Total mass flow. kg/h	1,642

As the previous CO_2 removal section, mass flow rate to be cleaned is smaller than base case. CO_2 concentration is quite higher than base case due to the decrease in nitrogen concentration (concentration close to 90 % mass).

The design specifications for the absorption tower are represented in Table 89. The solvent amount required is again higher than base case.

Table 89. Absorption column for CO_2 removal post-WGS inputs – case study

Specification	Input
Column	Absorption
Type	Packing, IMTP
Top pressure	51.7
Bottoms pressure	51.8
Feed gas temperature	20.09
Feed solvent temperature	7.22
Number of stages	10
Solvent mass flow, kg/h	130,251
Solvent stage	Top
Feed gas stage	Bottom

- Regeneration section

In the following tables, the mass composition of outlet stream of the solvent in each stage of the process and the final mixed stream composition are represented.

Table 90. Used solvent composition from section 5- case study

Component (Stream S05010)	Mass fraction
DEPG	0.963
CO	0.0011
CO2	0.033
Hydrogen	-
H2O	0.0023
Nitrogen	-
Methane	0.0001
Mass flow, kg/h	213,287

Table 91. Used solvent composition from section 6-case study

Component (Stream S06009)	Mass fraction
DEPG	0.975
CO	0.0001
CO_2	0.0241
Hydrogen	0.0001

Component (Stream S06009)	**Mass fraction**
H_2O	-
Nitrogen	-
Methane	0.0001
Mass flow, kg/h	131,651

Table 92. Used solvent composition from methane upgrading (Section 13)- case study

Component (Stream S13006)	**Mass fraction**
DEPG	0.938
CO	-
CO_2	0.0572
Hydrogen	-
H_2O	0.0001
Nitrogen	0.0001
Methane	0.0041
Mass flow, kg/h	17,788

Table 93. Composition for total solvent to be regenerated- case study

Component (Stream S07001)	**Mass fraction**
DEPG	0.9667
CO	0.0007
CO_2	0.0309
Hydrogen	0.0001
H_2O	0.0014
Nitrogen	-
Methane	0.0003
Mass flow, kg/h	362,726

The pressure for each tank is shown in Table 94. The values are the same in case base.

Table 94. Pressure change for solvent regeneration- case study

Equipment	**Inlet pressure, bar**	**Outlet pressure, bar**
Tank 1 (B07003)	30	13.79
Tank 2 (B07004)	13.79	6.89
Tank 3 (B07005)	6.89	1.72

Water separation has followed the same steps as per base case. Its modelling has been symbolically represented by a component splitter and the composition of water in this section is quite low.

3.6.3.2 Outputs

- CO_2 removal section before Fischer-Tropsch section.

The results for the clean syngas after CO_2 removal for previous FT section are showed in Table 95. The CO_2 concentration remains similar to base case. However, the syngas concentration is higher, mainly since the nitrogen concentration is quite smaller.

Table 95. Cleaned gas to Fischer-Tropsch Section- case study

Component (Stream S05011)	**Mass fraction**
DEPG	-
CO	0.3029
CO_2	0.041
Hydrogen	0.6348
H_2O	-
Nitrogen	0.0085
Methane	0.0123
Mass flow, kg/h	4,973

The column design is shown in Table 96

Table 96. Absorption column design for Section 5- case study

Parameter	**Value**
Diameter, m	0.64
Height, m	5
Packing type	IMTP
HETP, m	0.5
Total pressure drop, bar	0.20

In Figure 35 the sensitivity analysis for the DEPG flow required for CO_2 removal before FT is represented. The trends are similar to base case.

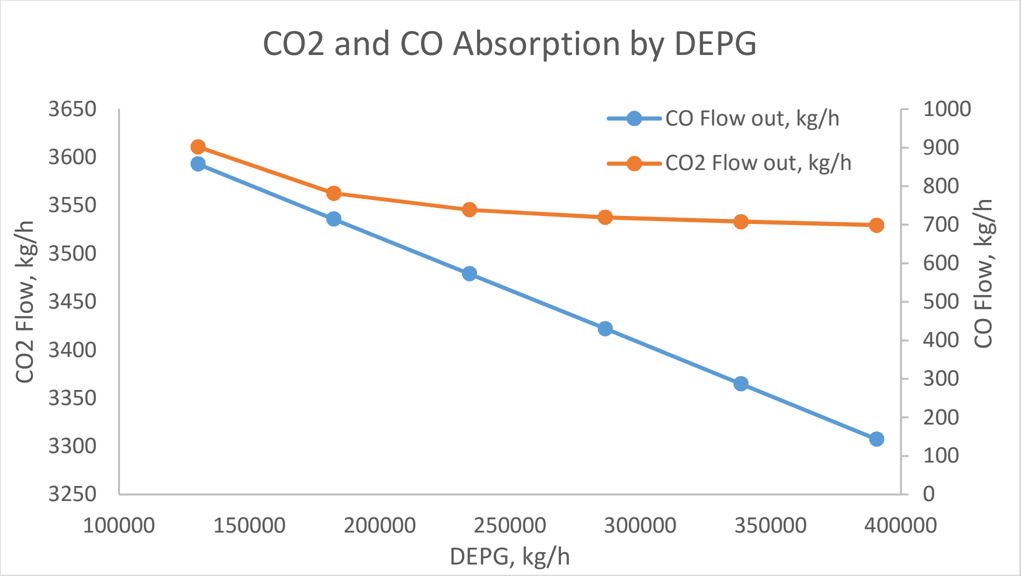


Figure 35. Sensitivity analysis for CO_2 removal before FT process- case study

- CO_2 removal post-WGS outputs

The composition of the outlet stream is represented in Table 97.

Table 97. Cleaned gas after WGS Section- case study

Component (Stream S06010)	**Mass fraction**
DEPG	-
CO	0.155
CO_2	0.369
Hydrogen	0.416
H_2O	-
Nitrogen	0.0484
Methane	0.0106
Mass flow, kg/h	243

Again, the outlet flow rate is much smaller than base case. The nitrogen presence in lower concentrations makes a remarkable difference regarding base case. Flow rates are smaller and the further energy required for compression will decrease.

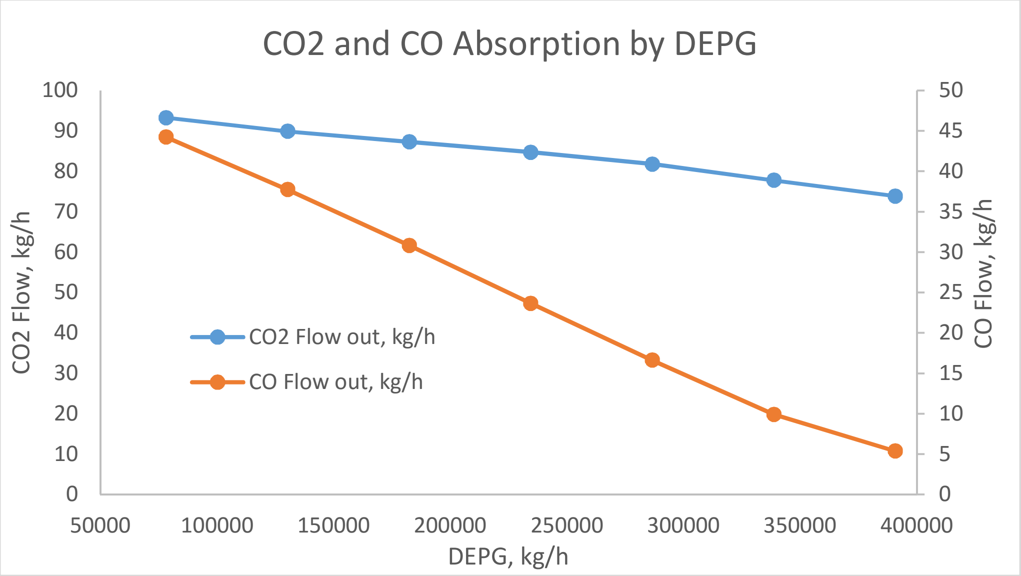


Figure 36. Sensitivity analysis for CO_2 removal after WGS process-case study

The column design is represented in Table 98.

Table 98. Absorption column design for Section 6- case study

Parameter	**Value**
Diameter, m	0.32
Height, m	9
Packing type	IMTP
HETP, m	0.9
Total pressure drop, bar	0.001

- Regeneration section

. The composition of the regenerated solvent at the end of this process is gathered in Table 99.

Table 99. Regenerated DEPG composition- case study

Component (Stream S07014)	**Mass fraction**
DEPG	0.9847
CO	-
CO_2	0.0139
Hydrogen	-
H_2O	0.0014
Nitrogen	-
Methane	-
Mass flow, kg/h	356,079

Although again the complete removal of carbon dioxide has not been possible, if these results are compared with base case, an increase in the DEPG purity has been achieved and a lower concentration of carbon dioxide is present in the system.

The composition of the off-gas streams (likely will be treated as emissions) from the pressure vessel separation is shown in the following tables:

Table 100. Stream S07003 composition- case study

Component	Mass fraction
DEPG	-
CO	0.3005
CO_2	0.5823
Hydrogen	0.0348
H_2O	-
Nitrogen	0.0121
Methane	0.0704
Mass flow, kg/h	387.9

Table 101. Stream S07005 composition- case study

Component	Mass fraction
DEPG	-
CO	0.1673
CO_2	0.7569
Hydrogen	0.0093
H_2O	-
Nitrogen	0.0054
Methane	0.0611
Mass flow, kg/h	448

Table 102. Stream S07008 composition- case study

Component	Mass fraction
DEPG	-
CO	0.0088
CO_2	0.9828
Hydrogen	0.0002
H_2O	0.0001
Nitrogen	0.0001
Methane	0.0080
Mass flow, kg/h	5,810

In comparison to base case, the total flow rate for the addition of all these off-gas streams is quite smaller. In addition, due to the lower nitrogen concentration, there is an increase in the concentration of syngas (hydrogen and carbon monoxide) that is being lost by these streams. A slightly increase in the carbon monoxide concentration is reported as a consequence of the nitrogen low concentration.

3.7 Case study /Optimisation Summary

As shown in base case, the mass and energy balances (including energy integration) for the case study are represented in Table 103 and Table 104.

Table 103. Energy balance summary in case study (after energy integration)

Process	Energy Input/Output	Energy added (kJ/h)	Per 1kg of biomass (kJ/h)	Service/Comments
ASU	Blower	15,031,379	1,503.1	
	Cooler	-10,860,000	-1,086.0	Water
Gasification	Blower	377,805	37.8	
	Air heater	1,411,467	141.1	Fired Heater
	Heater	303,422	30.3	Fired Heater
	Heater	1,641,087	164.1	Fired Heater
	Reactor Heat	-2,857,699	-285.8	HP Steam Generation
	Cooler	-492,986	-49.3	HP Steam Generation
Purification	Cooler	-3,308,283	-330.8	HP Steam Generation
	Blower	9,172,857	917.3	
	Cooler	-8,287,289	-828.7	HP Steam Generation
	Tar removal coolers	-11,622,000	-1,162.2	Chilled water
	Tar removal heaters	4,384,800	438.5	HP Steam
	Tar removal compression	8,590,826	859.1	
	Blower	5,191,230	519.1	
WGS	Cooler	-1,212,068	-121.2	MP Steam Generation
	Blower	688,683	68.9	
	Cooler	-2,686,506	-268.7	MP Steam Generation
	Cooler	-3,267,967	-326.8	LP Steam Generation
	Cooler	-1,570,028	-157.0	Chilled Water
Compressor	Cooler	-2,481,772	-248.2	LP Steam Generation
	Blower	2,090,373	209.0	

Process	Energy Input/Output	Energy added (kJ/h)	Per 1kg of biomass (kJ/h)	Service/Comments
	Cooler	-1,305,219	-130.5	LP Steam Generation
	Cooler	-1,492,416	-149.2	Chilled Water
CO_2 removal	Blower	2,605	0.3	
	Cooler	-2,116	-0.2	Chilled Water
	Blower	14,803	1.5	
	Cooler	-13,402	-1.3	Chilled Water
	Pump	2,236,458	223.6	
	reboiler	2,331,380	233.1	Refrigerant
Total (Net)	Net	**-2,161,953**	**-216.2**	Net kJ/h
	Net	**-21,620**	**-2.2**	Net MJ/h energy added
	Compression	**43,382,217**	**4,338.2**	kJ/h

Table 104. Mass balance summary in case study

Section	Materials in/out	Amount in (kg/h)	Per 1kg of biomass (kg/h)	Comments	HHV, kJ/kg
ASU	Air	19,572	1.957		
	Nitrogen	-16,340	-1.634	N2: 0.906; O2:0.083; Ar: 0.011	
	Oxygen	-3,232	-0.323	O2: 0.982	
Gasification	Biomass	10,000	1.000		19900
	Oxygen	3,232	0.323		
	Water Steam	1,500	0.150		
	Bed material	0	0.000	Make up TBD based on rate of loss	
	Ash	-326	-0.033		
	Char	-911	-0.091	For analysis deemed to have no energetic value	
	Olivine (not recoverable)	0	0.000		
	Gasification outlet	-11,268	-1.127		
	Other gases	-2,433	-0.243	Not considered in post-gasification	
Purification	Dirty Gas	11,268	1.127	0.5% Tar (anthracene,	

Section	Materials in/out	Amount in (kg/h)	Per 1kg of biomass (kg/h)	Comments	HHV, kJ/kg
				naphthalene, BTE)	
	Oil in	1,842.5	0.094	Soybean Oil (palmitic acid, stearic acid, linoleic acid, linolenc acid, oleic acid)	
	Oil Out	-1842.5	-0.094		
	Air in	100,000,0	5.109		
	Air out + Tar	-100,000,0	-5.109		
	Clean Gas	-11,268	-1.127		
WGS	WGS Feed from Gasification	1,409	0.141		
	Water (steam)	1,642	0.164		
	Water	-1,408	-0.141		
	Gas our from WGS	-1,643	-0.164		
CO_2 removal	Feed from Gasification	9,859	0.986		
	Feed from WGS	1,643	0.164		
	DEPG dirty from Methanation	17,786	1.779		
	DEPG clean to Methanation	-16,928	-1.693		
	Water	-495	-0.050		
	Off gas	-6,646	-0.665	CO2: 0.944, CO: 0.037, CH4: 0.015, N2: 0.001, H2: 0.003	1613
	CO-enriched	-4,973	-0.497	H2: 0.036; CO: 0.209; CO2: 0.046; N2: 0.383	
	Hydrogen-enriched	-243	-0.024		
Total		-203	-0.020	It was not nule because of the component lost and errors between simulations and Thermodynam	

Section	Materials in/out	Amount in (kg/h)	Per 1kg of biomass (kg/h)	Comments	HHV, kJ/kg
				ic Packages, therefore, Biomass flow was recalculated to make it zero, 250 kg/h is needed. Error is 2%.	

Table 105 shows the equipment list, which does not have the membrane for nitrogen removal and includes the ASU as main differences in regards with base case.

Table 105: Equipment list in case study (pre-treatment section only)

Equipment	Section	Unit Operation Model
B00001	0 (ASU)	Compressor
B00002	0 (ASU)	Cooler
B00003	0 (ASU)	Valve
B00004	0 (ASU)	Distillation column (High Pressure)
B00005	0 (ASU)	Valve
B00006	0 (ASU)	Valve
B00007	0 (ASU)	Distillation column (Low Pressure)
B00008	0 (ASU)	Heater
B00009	0 (ASU)	Heater
B01001	1 (Gasification)	Compressor
B01002	1 (Gasification)	Heater
B01003	1 (Gasification)	Heater
B01004	1 (Gasification)	Mixer
B51001	1 (Gasification)	RYield reactor (decomposition)
B51002	1 (Gasification)	Split fraction (dryer)
B51003	1 (Gasification)	RGibbs reactor (devolatilisation)
B51004	1 (Gasification)	Cooler
B51005	1 (Gasification)	Split fraction
B51008	1 (Gasification)	Mixer
B51007	1 (Gasification)	Mixer
B51010	1 (Gasification)	Mixer
B52008	1 (Gasification)	Mixer

Equipment	**Section**	**Unit Operation Model**
B52009	1 (Gasification)	FLUIDBED (Fluidised bed-Gasifier)
B01006	1 (Gasification)	Cyclone
B01007	1 (Gasification)	Cooler
B01008	1 (Gasification)	Cyclone
B01002B	1 (Gasification)	Cooler
B01003B	1 (Gasification)	Cooler
B02001	2 (Post-Gasific.)	Heat Exchanger
B02002	2 (Post-Gasific.)	Compressor
B02003	2 (Post-Gasific.)	Heat Exchanger
B02005	2 (Post-Gasific.)	Mixer
B02006A	2 (Post-Gasific.)	Compressor
B02006B	2 (Post-Gasific.)	Cooler
B02007	2 (Post-Gasific.)	Cooler
B02008	2 (Post-Gasific.)	Absorption column (Tar scrubber)
B02009	2 (Post-Gasific.)	Heater
B02010	2 (Post-Gasific.)	Compressor
B02011	2 (Post-Gasific.)	Heater
B02012	2 (Post-Gasific.)	Absorption column (Stripper)
B02013	2 (Post-Gasific.)	Splitter
B03001	3 (WGS)	Mixer
B03002	3 (WGS)	Equilibrium reactor
B03003	3 (WGS)	Heat Exchanger
B03004	3 (WGS)	Compressor
B03005	3 (WGS)	Heat Exchanger
B03006	3 (WGS)	Separator (Flash Vessel)
B04001	4 (Compression)	Heat exchanger
B04002	4 (Compression)	Compressor
B04003	4 (Compression)	Heat Exchanger
B04005	4 (Compression)	Heat Exchanger
B05001	5 (CO_2 cleaning)	Absorber
B05002	5 (CO_2 cleaning)	Valve
B05003	5 (CO_2 cleaning)	Tank
B05004	5 (CO_2 cleaning)	Compressor
B05005	5 (CO_2 cleaning)	Heat Exchanger

Equipment	Section	Unit Operation Model
B06001	6 (CO_2 cleaning)	Absorber
B06002	6 (CO_2 cleaning)	Valve
B06003	6 (CO_2 cleaning)	Tank
B06004	6 (CO_2 cleaning)	Compressor
B06005	6 (CO_2 cleaning)	Heat Exchanger
B07001	7 (Regeneration)	Mixer
B07002	7 (Regeneration)	Valve
B07003	7 (Regeneration)	Tank
B07004	7 (Regeneration)	Tank
B07005	7 (Regeneration)	Tank
B07006	7 (Regeneration)	Pump
B07007	7 (Regeneration)	Component Splitter
B07008	7 (Regeneration)	Heat Exchanger
B07009	7 (Regeneration)	Tee

Figure 37 and Figure 38, as shown in base case, summarised the M&E balances for the case study and show the energy efficiency of the chemical pre-treatment after gasifying with oxygen. The energy efficiency in this case is slightly higher (78 %).

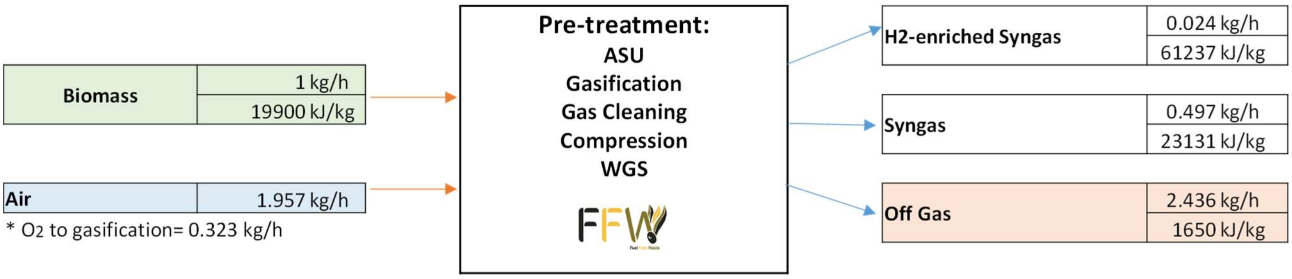
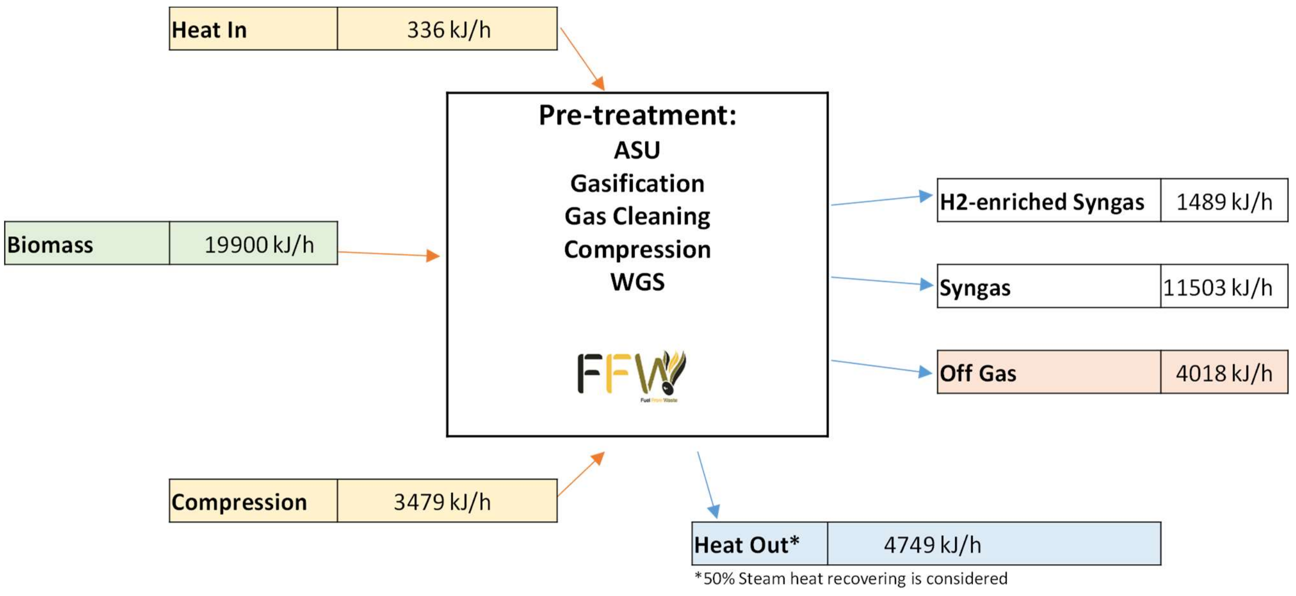


Figure 37. Case study mass balance scheme (pre-treatment)



$$\text{Process efficiency} = \frac{1489+11503+4018}{1990+336+3479} = 78\%$$

Figure 38. Case study energy balance (pre-treatment)

The mass basis remains in 10,000 kg/h for this case study. In comparison with the base case, some differences are found:

- Energy consumption in compression section has decreased since the decrease in the concentration of nitrogen becomes easier some operations, like the gas compression. This is translated into a reduction in the energy requirements in some operations.

- In spite of the reduction of energy requirements in critical operations such as compression, an increase in the services, especially cooling, are noted in comparison with case base. This is mainly due to the presence of an Air Separation Unit, which requires a high energy consumption for the cryogenic air distillation.

- The absence/reduction of nitrogen allows the equipment size reduction. This point means a reduction in the CAPEX. Nitrogen is not a desirable compound in this kind of plants, apart from the increase in the energy consumption in compressors and the increase of the equipment size, it is necessary to use additional operations that enables the nitrogen removal. Membranes were selected as a suitable technology in base case for nitrogen removal due to availability restrictions of FFW feedstock and small scale of the process. However, along case study is not necessary the use of any nitrogen removal technology.

- Some sections are not comparable in base case and in case study, such as the gas cleaning. Due to the different composition for both studies, it is not comparable the relations of solvent/gas in the two both cases and it is necessary to recalculate the variables for the section design.

- In overall terms, the case study is preferable in comparison to case base. The losses associated to the high energy requirements for the ASU section can be balanced through the nitrogen product selling. Through an adjustment of the distillation column, nitrogen can be obtained in high purity, as our interest product at this stage (oxygen). Therefore, nitrogen can be sold to other industries since this is a valuable by-product. If nitrogen selling is not a viable option, the oxygen purchasing or other separation alternatives can be evaluated instead of installing an ASU in economic terms.

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