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Modelling and optimization of a Biomass-to-Liquid process using VMGSim

Riccardo Costanzi

Chemical Engineering
Submission date: Januar 2016
Supervisor: Magne Hillestad, IKP

Norwegian University of Science and Technology
Department of Chemical Engineering

Contents

1 Introduction 3
1.1 Biomass and its products 4
1.1.1 Products of Biomass 5
1.1.2 Biomass conversion 6

2 Gasification 8
2.1 Modelling of pretreatment of the biomass 8
2.2 Gasification Process 11
2.2.1 Reactor 13
2.3 Modeling of Gasifier 15

3 Concentration and purification of Syngas 19
3.1 Concentration: Water-gas-shift Reactor 19
3.1.1 Modeling Water-Gas-Shift Reactor 21
3.2 Modeling purification of Syngas 28

4 Fischer-Tropsch Reactor 31
4.1 Fischer-Tropsch Process 31
4.1.1 Chemical concepts 31
4.2 Modeling the Fischer-Tropsch Product Distribution and Model Implementation 38
4.3 Modeling FT Reactor 43
4.3.1 Optimization 51
4.3.2 Rigorous Approach 56

5 Conclusion 60

Chapter 1

Introduction

In the last 10 years the global energy request has increased by approximately 26% and is predicted to grow by 47% by 2035. nowadays this request is primarily supplied by fossil resources i.e. natural gas, oil and coal. While considerable reserves of coal are available, it is partly responsible for CO_2 gas emissions and it has to be transfered from where it is abundant to where required for power production. It is supposed that utilization of coal will rise by an average of 1.5% per year from 2015 to 2035. Natural gas is plentiful and its providing has recently grown owing to technology allowing access to gas in shale beds. Coal bed methane is an another fount of natural gas. All these elements mantain the global market well provided and the use is supposed to rise by 1.6% from 2015 to 2035. Since the utilization is quickly catching up with the production and accessibility, the share of “liquid fuel” in world energy demand is projected to decrease by 2035. Against these valutations the use of liquid fuels in transportation sector will rise. The transportation sector depends almost exclusively on the hydrocarbon fuels as energy fount due to its high volumetric energy density. In order to protract peak oil, increased request in transportation sector must be supplied by alternative sources. Except fossil crude oil, hydrocarbon fuels can be generated from photo, bio-chemical and thermochemical way. These alternative ways use methane, coal, sun and biomass (alternative resource) as feedstock. Liquid fuels can be generated from natural gas by first producing syngas and then transforming the syngas to liquid fuels. Natural gas is a plentiful fossil fuel and thus provides to greenhouse gas (GHG) emissions. There is an incentive to produce renewable fuels from biomass. Liquid fuels can be produce from biomass by first transforming it to syngas via gasification. Biomass is a valuable renewable feedstock, its global request is predicted to rise over the next 20 years due to bring down the dependence on fossil liquid fuel. during the industrial revolution after the introduction of coal, The search for renewable sustainable energy resources has given biomass a importance it had lost. The share of biomass in meeting current world's primary energy mix is at a small level of 10%, but given the increasing preoccupation about global warming and sustainability, this share is inclined to grow. The most prevalent use of biomass for energy is direct combustion, followed by pyrolysis,gasification and carbonization. This thesis deals with gasification process. [1] Gasification is a chemical process that transform carbonaceous materials like biomass into functional convenient gaseous fuels or chemical feedstock. Pyrolysis, partial oxidation,and hydrogenation are connected processes. Combustion also transforms carbonaceous materials into product gases but with some important distinctions. For example, the outlet gas from combustion does not have any convenient heating value, but the outlet gas from gasification does. Gasification wraps energy into chemical bonds in the product while combustion liberates it. The process occurs in reducing (oxygen-deficient) environment releasing heat, while combustion occurs in a oxidizing environment releasing heat. The object of gasification or pyrolysis is not just energy conversion but another important application is the production of chemical feedstock.

1.1 Biomass and its products

Biomass is made of alive species like animals and plants; anything that is now alive or was alive a short time ago produces biomass. It is formed as soon as a seed germinates or an organism is born. Unlike fossil fuels, biomass doesn't request millions of years to evolve and it can be reproduced, and for that reason, it is considered renewable. Every year, a huge quantity of biomass is produced through photosynthesis by absorbing CO_2 from the atmosphere. When it burns, it liberates the carbon dioxide that the plants had assimilated from atmosphere only recently (a few years to a few hours). Thus, the combustion of biomass doesn't give a contribution to the world's carbon dioxide levels. This liberation also occurs for fossil fuels. So,by comparison,there is no addition to the CO_2 level by the burning of biomass and one can consider biomass a "carbon-neutral'. Only 5% of the huge quantity of biomass in the world can be potentially use to produce energy. Even this amount is big enough to furnish about 26% of world's energy waste which is equivalent to 6 billion tons of oil. The principal types of accumulated biomass are sugar (cereal),cellulosic (non cereal), and starch.

1.1.1 Products of Biomass

There are three types of mainly fuels that could be generated from biomass and are as follows:

- Liquid fuels (ethanol, biodiesel, methanol, vegetable oil, and pyrolysis oil)
- Gaseous fuels (biogas (CH_4, CO_2), producer gas (CO, H_2, CH_4, CO_2), syngas, substitute natural gas
- Solid fuels (charcoal, torrefied biomass, biocoke, biochar)

These biomass products find application in following four main types of industries:

1. Chemical industries for production of methanol, fertilizer, synthetic fiber and other chemicals.
2. Energy industries for generation of heat and electricity.
3. Transportation industries for production of gasoline and diesel.
4. Environmental industries for capture of CO_2 and other pollutants.

The application of ethanol and biodiesel as trasport fuels lessens the emission of CO2 per unit of energy production. It also reduces our reliance on fossil fuels.

Thus, the energy produced from biomass is not only renewable but also purify from the point of view of greenhouse gas (GHG) emission, and so it can become a crucial point in the global energy scene.

1.1.2 Biomass conversion

Bulkiness, low energy density, and awkward form of biomass are the main obstacles to a rapid conversion from fossil to biomass fuels. Unlike gas or liquid, biomass cannot be manipulated, accumulated, or transported easily. This gives an important reason for the transformation of solid biomass into liquid and gaseous fuels, which have a greater energy density and can be manipulated and stored with relative ease. This transition can be reached through one of two important ways (Figure 1.1): biochemical conversion (fermentation) and thermochemical conversion (pyrolysis, gasification). Thedisadvantage of bulkiness and other flaws of solid biomass are exceeded some extent through the production of more useful puree solid fuel through carbonization and torrefaction. Biochemical conversion is maybe the oldest process of biomass gasification. For local energy demand, India and China produced methane gas by anaerobic microbial digestion of animal wastes. nowadays the large amount of ethanol used for automotive fuels is produced from corn using fermentation. Thermochemical conversion of biomass into gases has developed much later. Large-scale consumption of small biomass gasifiers started during the Second World War, when more than a million units were operating. [2] .

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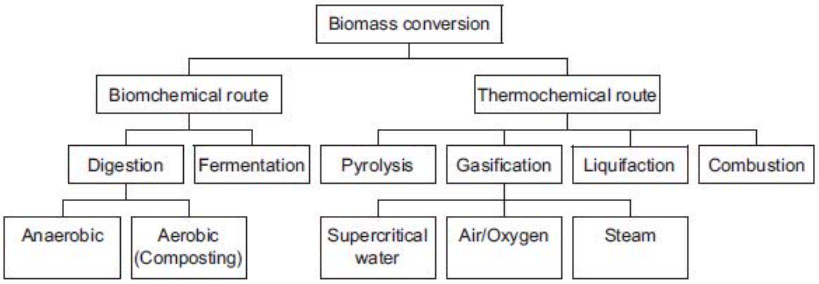


Figure 1.1: Different options for conversion of biomass

In this thesis the process from biomass to liquid (BtL) is examined. In the BtL process, biomass, such as woodchips and straw stalk, is firstly converted into biomass-derived syngas (bio-syngas) by gasification. Then, a cleaning process is applied to remove impurities from the bio-syngas to produce clean bio-syngas which meets the Fischer–Tropsch synthesis requirements. Cleaned bio-syngas is then conducted into a Fischer–Tropsch catalytic reactor to produce green gasoline, diesel and other clean biofuels.

This review will analyze the four main steps of BtL process:

1. Gasification of Biomass
2. Water Gas Shift Reactor
3. Fisher Tropsch Reactor

The main object is to explain the four main steps of the process, that can be processed with a new simulator called VMGSim.

The aim is to find the optimize variables to maximize the production.

Chapter 2

Gasification

2.1 Modelling of pretreatment of the biomass

First of all, the kind of biomass used is described.

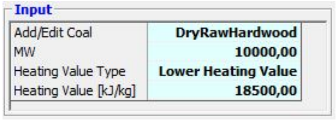
Like in most other simulators, the thermodynamic model must be determined first of all in the VMGSim; without this, it is impossible to calculate any equilibrium. After adding the needed components for the reaction, the property package has to opened and one of the models divided into chemical system categories is selected. The termodynamic model that represents in better way the first part of the project is Gasification_2010, in fact the first main operation for BtL is the gasification.

The second step is to characterize the biomass: the simulator offers the possibility to create an hypothetical compound from existing components.

Dry raw hardwood is created using three main inputs:

- Molecular weight: in this case it is considered, like default, 10000.
- Lower Heating Value: for wood the value is 18,5 MJ/Kg
- Chemical formula and composition

The elementary wood's composition has been added and it is 48.2% carbon, 45.5% oxygen and 6.3% hydrogen. The composition can change a little bit but approximately this is correct for all kinds of wood. The hypotetical compound has been created and now the first stream can be inserted in the flowsheet: Biomass.



Input

Add/Edit Coal	**DryRawHardwood**
MW	**10000,00**
Heating Value Type	**Lower Heating Value**
Heating Value [kJ/kg]	**18500,00**

Figure 2.1: characteristic biomass

This stream is characterized by 50% mass fraction of DryRawHardwood and 50% mass fraction for water. In this stream there aresome sulfides that will be subsequently absorbed by a chemical agent.

In the real process there are a lots of steps before the first main unit operation of Gasification. In fact the biomass chips have to be subjected to a process of torrefaction, then the chips are crushed inside the grinder and finally adding water is indispensable to create a slurry mixture, that can be putted into the gasifier.

Torrefaction is a thermochemical process in an inert or limited oxygen environment where biomass is slowly heated into a specified temperature range and retained there for a stipulated time such that it results in near complete degradation of its hemicellulose content while maximizing mass and energy yield of solid product. A typical temperature range for this process is between 200°C and 300°C. Though other ranges have been suggested, none exceeds the maximum temperature of 300°C. Torrefaction above this temperature would result in extensive devolatilization and carbonization of the polymers. Both processes are undesirable for torrefaction. Also, the loss of lignin in biomass is very high above 300°C. This loss could make it difficult to form pellets from torrefied products. Furthermore, fast thermal cracking of cellulose causing tar formation starts at temperature 300-320°C. These reasons fix the upper limit of torrefaction temperature as 300°C. [3]

A simple illustration of the torrefaction process is shown in Figure 2.2. It shows how the mass and energy content of biomass changes as it is converted into a torrefied product.

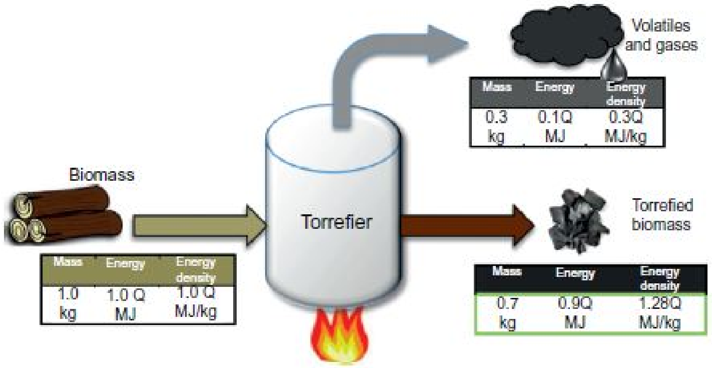


Figure 2.2: Mass and energy changes of a feed undergoing torrefaction

The heating medium here is represented by a flame but it also could be a hot substance, dry or wet. In wet torrefaction, the biomass is subjected to heating in hot compressed water. Dry torrefaction involves heating either by a hot inert gas or by indirect heating. The dry process is the accepted method for commercial torrefaction. The mass loss of the wood at this stage is about 20%.

Heating stages during the torrefaction are:

1. Predrying
2. Drying
3. Postdrying Heating
4. Torrefaction
5. Cooling

In the simulator it is not possible to study the torrefaction in detail. Nevertheless certain requirements need to be fulfilled, like charge at the temperature of 100°C that has evaporated losing water and a little bit of wood and it is pumpable until 20 bar, necessary for the gasifier.

Therefore a series of operations can be approximated using just one unit operation called Dryer. It has a physical function of separating the most of water from the rest of biomass. So the change from a solid biomass to a liquid and pumpable biomass is included and approximated in a single step.

After the pump, the stream has the following composition: 91% of Dry raw Hardwood and 9% of water.

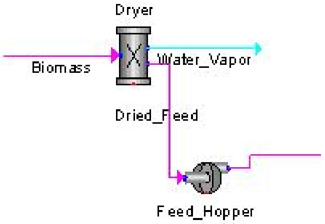


Figure 2.3: pretreatment biomass

2.2 Gasification Process

Gasification is convenient because it can transform solid or liquid feedstock into gaseous fuel or chemical feedstock that can be burned to produce energy or used for create output of value-added chemicals. Gasification and combustion are two closely connected thermochemical processes, but there is an important difference between them. Gasificationwraps energy into chemical bonds in the outlet gas; combustion breaks those bonds to liberate the energy. The gasification process adds hydrogen and strips carbon away from the hydrocarbon feedstock to produce gases with a higher hydrogen-to-carbon (H/C) ratio. In contrast combustion oxidizes the hydrogen and carbon into water and carbon dioxide. A typical biomass gasification process may contain the following steps: Drying Thermal decomposition or pyrolysis, partial combustion of some gases, vapors, and char Gasification of decomposed products. Gasification needs a gasifying medium like steam, air, or oxygen to reorganize the molecular structure of the feedstock in order to transform the solid feedstock into gases or liquids; it can also add hydrogen to the product. The use of a medium is essential for the gasification process, which is not the same for pyrolysis or torrefaction. Gasifying medium (also called "agent") reacts with solid carbon and heavier hydrocarbons to transform them into low-molecular-weight gases like CO and H_2. The main gasifying agents used for gasification are:

- Oxygen
- Steam
- Air

For this process, oxygen has been used. Oxygen is a popular gasifying agent although it mostly serves for the combustion or the partial gasification in a gasifier. It may be provided to a gasifier both in pure form or via air. The heating value and the composition of the gas created in a gasifier are strong characteristics of the nature and amount of the gasifying agent used. The conversion path proceed to the oxygen node. Its products include CO for low amount of oxygen and CO_2 for high amount of oxygen. When the amount of oxygen overcomes a certain (stoichiometric) level, the processchanges from gasification to combustion, and the product is “flue gas” instead of “fuel gas.” The flue gas or the combustion product doesn’t include remaing residual heating value.[4] The following is a delineation of some of those reactions with carbon, carbon dioxide, hydrogen, steam, and methane.

$$C + H_2O \longleftrightarrow CO + H_2 \quad \triangle H = 131 KJ/mol \ (1)$$

$$CH_4 + H_2O \longleftrightarrow CO + 3H_2 \quad \triangle H = 206 KJ/mol \ (2)$$

$$C + O_2 \longleftrightarrow CO_2 \quad \triangle H = -394 KJ/mol \ (3)$$

$$CO + H_2O \longleftrightarrow CO_2 + H_2 \quad \triangle H = -41 KJ/mol \ (4)$$

$$C + CO_2 \longleftrightarrow 2CO \quad \triangle H = 172 KJ/mol \ (5)$$

The total reaction are generally endothermic but there are some exothermic reactions because of the presence of partial combustion and reactions like water-gas-shift reaction. The rate of the consumption of char (comprising mainly of carbon) is influenced primarily by its reactivity and the reaction potential of the gasifying medium, in this case oxygen. In fact, amongst gasification medium, oxygen is most active, followed by steam and carbon dioxide.

- The reaction (1) is known as Water-gas-shift reaction and it is perhaps the most important gasification reaction. The big amount of hydrogen has a strong inhibiting effect on the gasificartion; in fact the best solution is to continuous removal of hydrogen from the reaction site. For example, 30% hydrogen in the gasification atmosphere can reduce the gasification rate by a factor as high as 15.

- The reaction (4) is called Shift reaction. The first feature is that it is a gas-phase reaction and it is less exothermic than the combustion. Unlike the above reactions, shift reaction takes place between an intermediate product of the gasification reaction and steam. At the expense of CO, this reaction increases the H_2 amount of the gasification product. The heat of enthalpy is $-41\frac{KJ}{mol}$, so, even if the yield decreases with the temperature, the equilibrium is not much influenced by the temperature. Anyway, the changing of the pressure has no importance on the process. Above 1000 °C, the shift reaction rapidly reaches equilibrium also without the usage of catalyst, but at a lower temperature, it needs heterogeneous catalysts. As every exothermic reaction, the difficulty is to find the compromise between the thermodynamic and the kinetic. With increasing temperature, the yield decreases, but the reaction rate increases. The optimum yield is obtained at about 225 °C.

- The reaction (5) is the gasification of char in carbon dioxide and it is popularly known as the Boudouard reaction. The rate of the char gasification reaction inCO_2 is insignificant below 1000 K.

2.2.1 Reactor

The succession of gasification reactions is based on some extent on the type of gas solid contacting reactors used. There are different kinds of reactor: Moving bed, Fluidized bed, Entrained flow reactor. In this thesis a Fluidized bed reactor has been considered. The fluidized-bed gasifier includes nonfuel granular solids (bed solids) that work as a heat carrier and mixer. In a bubbling fluidized bed, the fuel fed from either the top or the sides blends quite fast over the entire body of the fluid bed. The gasifying agent (air, oxygen, steam, or their mixture) also is used as the fluidizing gas and so it is fed through the bottom of the reactor. Although the bed solids are well amalgameted, the fluidizing gas keeps usually the plug-flow mode, getting in from the bottom and leaving from the top. In the moment it enters the bottom of the bed, the oxygen reacts quickly in exothermic reactions with char mixed with bed materials. The bed materials directly dissolve the heat produced by these reactions to the whole fluidized bed. The amount of heat produced close to the bottom grid is based on the oxygen amount of the fluidizing gas and the amount of char that comes in contact with it. The temperature of this region is based on how strongly the bed solids dissolve the heat from the combustion zone. The following gasification reactions occur further up as the gas increases. The bubbles of the fluidized bed can be used as the main channel to the top. They contain relatively no solids. While they support in mixing, the bubbles can also consent gas to bypass the solids without taking part in the gasification reactions. The pyrolysis products coming in contact with the hot solids collapsed into noncondensable gases. If they escape the bed and go up to the cooler freeboard, tar and char are formed. A bubbling fluidized bed cannot obtain the entire char conversion because of the back-mixing of solids. The high level of solid mixing supports a bubbling fluidized-bed gasifier to obtain the temperature uniformity, but due to the intimate mixing of completely gasified and partially gasified fuel particles, any solids leaving the bed carry some partially gasified char. Char particles dragged from a bubbling bed can also contribute to the waste in a gasifier. The other important question with fluidized-bed gasifiers is the slow diffusion of oxygen from the bubbles to the emulsion phase. This favors the combustion reaction in the bubble phase, which reduces gasification efficiency. In a circulating fluidized bed (CFB), solids flow around a loop that is characterized by severe mixing and longer solid residence time within its solid circulation loop. The absence of any bubbles avoids the gas-bypassing problem of bubbling fluidized beds. Fluidized-bed gasifiers typically operate in the temperature range of 800-1000°C to avoid ash agglomeration. This is satisfactory for reactive fuels such as biomass, municipal solid waste (MSW), and lignite. Since fluidized-bed gasifiers operate at relatively low temperatures, most high-ash fuels, depending on ash chemistry, can be gasified without the problem of ash sintering and agglomeration.[5]

This figure describes the model gasifier and its temperature trend.

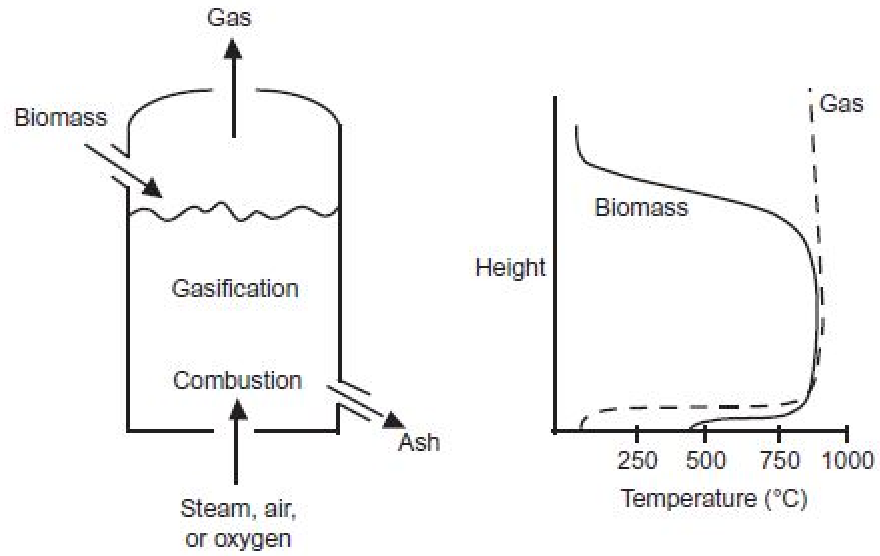


Figure 2.4: Trend of temperature inside the gasifier

2.3 Modeling of Gasifier

As indicated in Figure 2.5, there are two streams entering into the gasifier. The first stream is pretreated biomass, this has the following composition: 91% Dry Raw Hardwood and 9% water, so the most of water is evaporated into the dryer. The second stream is composed by pure oxygen that represents the gasifying medium.

The product of gassification is contained in the stream called Raw gas out, but it can include solid particles coming out from the bottom of gasifier.

The simulator allows to specify the function properties of the gasifier; for this reason a controller has been used to follow our needs.

The controller is composed by three main variables:

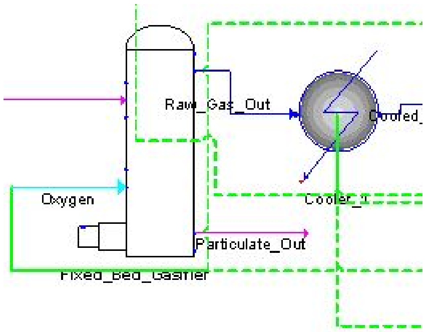


Figure 2.5: Gasifier simulated

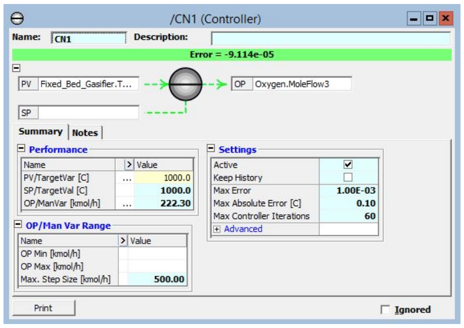
- PV: The connected PV (process variable). This is the variable that the controller monitors while manipulating the output variable (OP) until it matches the set point (SP).
- SP: The connected SP variable. This connection is optional, and would be used if it was desired to connect to another port in the simulation to obtain a set point.
- OP: The connected OP variable. This will be the variable that the controller manipulates in order to have the process variable (PV) match the set point (SP).

Temperature of the process and the H_2/CO ratio depends on the flowrate of gasifying. So we connect the controller to the oxygen stream, fixing the top temperature. The temperature of 1000°C has been fixed because that's the optimal temperature for gasification and for the correct ratios of products that the simulator calculates.

This optimal specification is reached after the following discussions: the gasifier works at high temperature and it is run at 800°C, 900°C, 1000°C, 1100°C and 1200°C.

It is possible to realize the different composition that the outlet stream has, changing the operation's temperature.

The concentration of the syngas and the carbon dioxide change in these cases, due to the influence of the temperature in the reactions of gasification.



Name: CN1
Description:
Error = -9.114e-05
PV Fixed_Bed_Gasifier.T...
OP Oxygen.MoleFlow3
SP

Performance

Name	>	Value
PV/TargetVar [C]	...	1000.0
SP/TargetVal [C]		1000.0
OP/ManVar [kmol/h]	...	222.30

OP/Man Var Range

Name	>	Value
OP Min [kmol/h]		
OP Max [kmol/h]		
Max. Step Size [kmol/h]		500.00

Settings

Active	☑
Keep History	☐
Max Error	1.00E-03
Max Absolute Error [C]	0.10
Max Controller Iterations	60
⊞ Advanced	

☐ Ignored

Figure 2.6: Controller

components	800°C	900°C	1000°C	1100°C
H_2O	200.23 kmol/h	150.7 kmol/h	183 kmol/h	211 kmol/h
H_2	310.86 kmol/h	437 kmol/h	481 kmol/h	467 kmol/h
CO	252.47 kmol/h	553 kmol/h	604 kmol/h	615 kmol/h
CO_2	178.95 kmol/h	152 kmol/h	141 kmol/h	136 kmol/h
CH_4	85 kmol/h	46 kmol/h	8 kmol/h	1.33 kmol/h

Table 2.1: Stream outlet of gasification

The flowrate of oxygen is the variable that has most influence on temperature profile. An increase in the flowrate promotes the combustion, which leads to an increasing temperature. However it is necessary not to have excess oxygen because the combustion needs to be stopped in the partial oxydation; having a total oxydation prevents CO_2 from forming and for subsequent treatment to absorb the gas, moreover CO is needed for the next step of water gas shift reaction.

The purpose is to increase the concentration of syngas, avoiding the total combustion and the huge presence of CO_2. For this reason, the top temperature of 1000°C is chosen. In fact, as seen in the Table 2.1, this temperature represents a compromise between high composition of hydrogen and carbon monoxide, and as little as possibile carbon dioxide concentration.

The oxygen molar flowrate to have the determined temperature is 222.31 kmol/h.

As can be seen in the Figure 2.7, the most important feature is the reaction model that we consider as the Gibbs reaction, in which the kinetics is not described because every reaction is at equilibrium. In the simulator the process can work at high temperature using Plasma Duty or just due to the presence of combustion, it is chosen just the heat released by oxydation. The other two settings, that are set for the gasifier, is the number of reactor and the Predicted Particulate C.

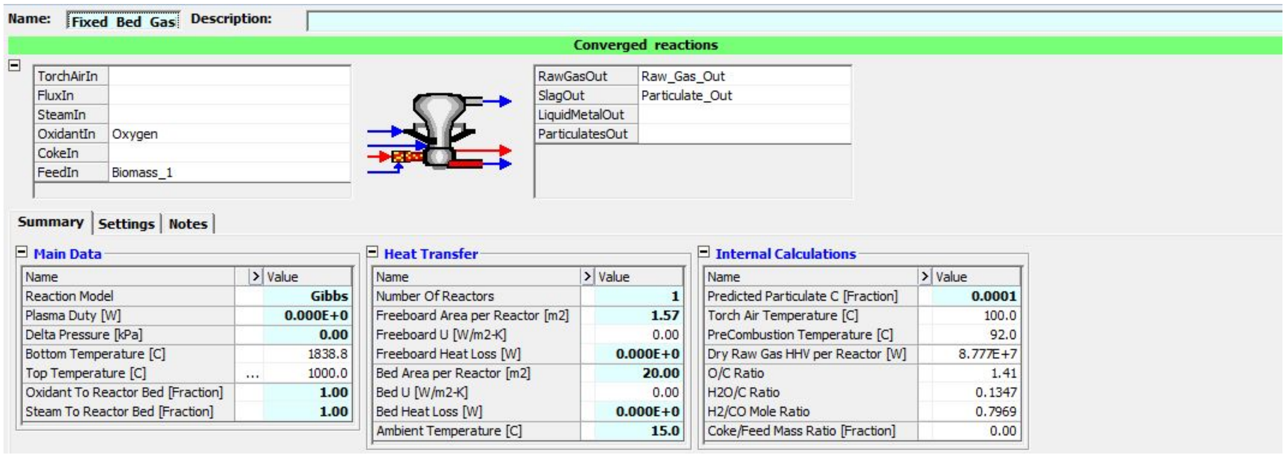
First the simplest case of only one reactor is considered; for the predicted particulated C (fraction) only a very small part it can be found like a particulate.

With the input given by user, the most important output are:

- Bottom and Top Temperature

- O/C ratio
- H_2O/C ratio
- H_2/CO mole ratio

In the figure below, it can be seen every output found, according our assumptions.



Name: Fixed Bed Gas **Description:**

Converged reactions

TorchAirIn	
FluxIn	
SteamIn	
OxidantIn	Oxygen
CokeIn	
FeedIn	Biomass_1

RawGasOut	Raw_Gas_Out
SlagOut	Particulate_Out
LiquidMetalOut	
ParticulatesOut	

Main Data

Name	>	Value
Reaction Model		**Gibbs**
Plasma Duty [W]		**0.000E+0**
Delta Pressure [kPa]		**0.00**
Bottom Temperature [C]		1838.8
Top Temperature [C]	...	1000.0
Oxidant To Reactor Bed [Fraction]		**1.00**
Steam To Reactor Bed [Fraction]		**1.00**

Heat Transfer

Name	>	Value
Number Of Reactors		**1**
Freeboard Area per Reactor [m2]		**1.57**
Freeboard U [W/m2-K]		0.00
Freeboard Heat Loss [W]		**0.000E+0**
Bed Area per Reactor [m2]		**20.00**
Bed U [W/m2-K]		0.00
Bed Heat Loss [W]		**0.000E+0**
Ambient Temperature [C]		**15.0**

Internal Calculations

Name	>	Value
Predicted Particulate C [Fraction]		**0.0001**
Torch Air Temperature [C]		100.0
PreCombustion Temperature [C]		92.0
Dry Raw Gas HHV per Reactor [W]		8.777E+7
O/C Ratio		1.41
H2O/C Ratio		0.1347
H2/CO Mole Ratio		0.7969
Coke/Feed Mass Ratio [Fraction]		0.00

Figure 2.7: Specifications of gasifier

Chapter 3

Concentration and purification of Syngas

3.1 Concentration: Water-gas-shift Reactor

The water-gas shift is a reversible, exothermic chemical reaction, usually assisted by a catalyst. It is the reaction of steam with carbon monoxide to produce carbon dioxide and hydrogen gas:

$$CO + H_2O \longleftrightarrow CO_2 + H_2 \quad \triangle H = -40.6\, KJ/mol$$

Many theoretical and mechanistic investigations has been done about the catalysis of this reaction, and the reaction represents one of the most used industrial processes. In fact it can be used in ammonia and hydrogen production. Hydrogen is mainly produced today by steam reforming of hydrocarbons and partial oxidation of hydrocarbons. However, the result of these processes give mixtures of hydrogen and carbon monoxide not suitable for many industrial applications. For instance, in ammonia production the amount of carbon monoxide must be very low, since CO can deactivate the ammonia synthesis catalyst. Hence the water gas shift reaction is used as a step in the overall process to minimize the CO levels and produce additional hydrogen.

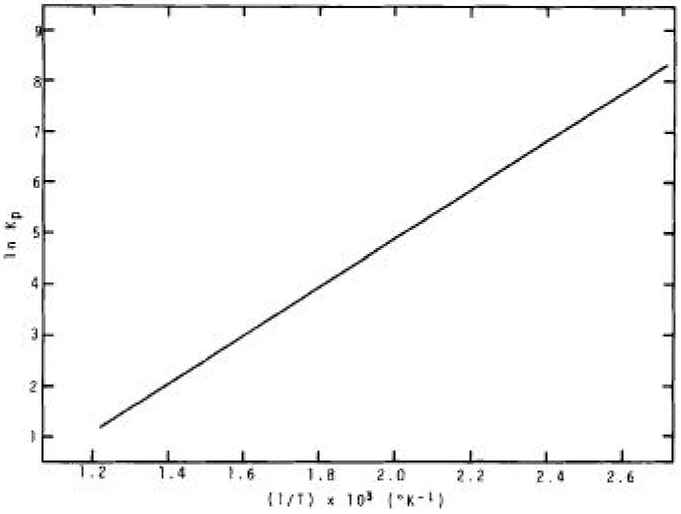


Figure 3.1: Equilibrium constant as a function of temperature

Some thermodynamic considerations can be made: the equilibrium constant Kp increases with decreasing temperature as the Figure 3.1 shows.

The following expression provides a right way to describe this trend in the range of operating temperature.

$$Kp = exp\left[\left(\frac{4577.8}{T}\right) - 4.88\right]$$

From the point of view of increased hydrogen production and reduced carbon monoxide content, it is desirable to conduct the reaction at low temperatures; from the point of view of steam economy, a lower reaction temperature is desirable. However, in order to achieve the necessary reaction rates, higher temperatures are often required. It can be seen that an ideal condition for the water-gas shift reaction would be the use of a catalyst active enough to operate at low temperatures where equilibrium is very favorable. Reaction pressure does not have any effect on the equilibrium of the shift reaction, since the number of moles of material in the shift reaction does not change during the course of the reaction.

Generally in the industrial processes two kinds of catalysts are used: iron based catalysts and copper based catalysts.

The iron based are the most popular catalysts used in industrial operation, because of operating in the range of temperature 320-450°C, they are called high-temperature-shift catalysts. The advantage is that iron oxide can tolerate small presence of solphur and are fairly rugged overall, the disadvantage is the low rate of reaction at high temperature.

The copper based are called low temperature shift catalysts and are therefore attractive since equilibrium is more favorable at lower temperatures. In addition to higher activity, another advantage claimed for the low-temperature shift catalysts is more selectivity and fewer side reactions at elevated pressures than high temperature shift catalysts. Copper-based low-temperature shift catalysts are completely sulfur intolerant, however, being irreversibly poisoned by even small quantities of sulfur compounds.

Another catalyst of remarkable interest (during last years) is sulfided cobalt oxide-molybdenum oxide on alumina, that, with its other variations, has been characterized in various papers and patents. This kind of catalyst is absolutely inert towards sulfur (doesn't suffer poisoning by sulfur) and some its variations are proved to be very active at both high and low temperatures. Industrial shift reactors are tipically adiabatic so the temperature will increase along catalytic bed, as the reaction is a little bit exothermic; if high purity is required, two stage reactor is generally used, while if purity isn't so important, single stage is considered better. Two-stage systems usually work with a high-temperature iron-based catalyst in the first stage, then the gases are cooled and steam is added. Furthermore, the shift of the residual CO over a copper-based low temperature shift catalyst is carried out. Thanks to acid gas and sulfur removal, the second-stage catalyst is free from poisons, so its life is much longer under these controlled conditions.[6]

3.1.1 Modeling Water-Gas-Shift Reactor

The stream leaving the gasifier is composed mostly by hydrogen and carbon monoxide, but there is also the presence of carbon dioxide, as you can see in the Table 3.1.

Compounds	Molar fraction	Molar flowrate
Water	0.12	150.7
Hydrogen	0.32	437.03
Carbon monoxide	0.41	553.23
Carbon dioxide	0.11	152.02
Methane	0.04	46.65

Table 3.1: Stream inlet WGS reactor

The task of Water-Gas-Shift reactor is to have a stream with a composition as close as possible to the optimal inlet stream the Fisher-Tropsch reactor.

It's useful to explain the composition of stream entering the FT reactor: the most of important property is $\frac{H_2}{CO}\approx 2$; in this case it is fixed the value 1.9. The reason is to avoid that $\frac{H_2}{CO}$ increases during the reactor and to avoid that C1-C3 product privileges on product with high content of carbon. In the final product it's better to have as less as possible the light carbon because of low energy content.

The reactor in VMG Simulator is an equilibrium reactor in which it is chosen an adiabatic type without pressure drop inside the equipment. In the section "reaction" the stoichiometich coefficients of water-gas-shift reaction are added. About the reaction constant, there is the possibility to choose between Gibb Free Energy, K-T Table or K specified; in this case the Gibb Free Energy and so the following regression equation $K = exp\left(\frac{\triangle G}{RT}\right)$ are considered.

The focus is on the operating conditions of Water Gas Shift reactor; concerning the pressure, there is no change of number of moles so it makes no sense to change the pressure from gasifier that was 20 bar. In terms of temperature, the situation is more complicated beacuse it depends on which type of stream is added before the reactor.

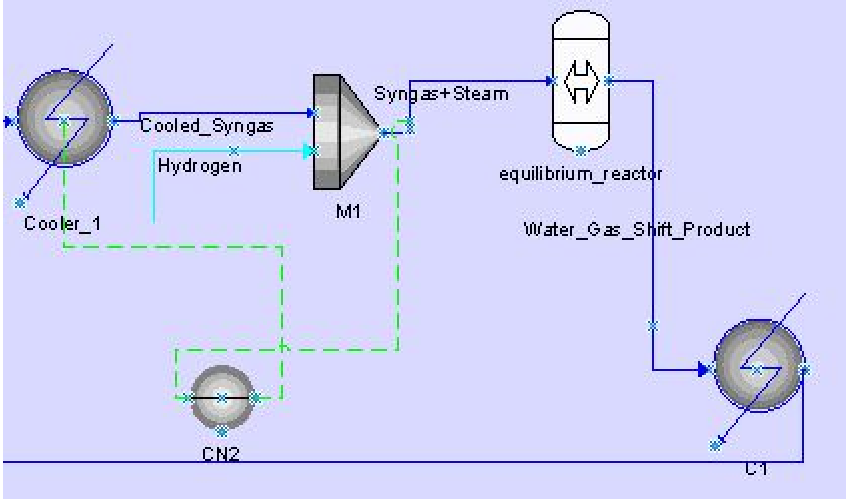


Figure 3.2: WGS reactor

As seen from the Figure 3.2, before the equilibrium reactor, there is a mixer in which can be added hydrogen or water. In the following the difference between both possibilities is explained. The WGSR is an exothermic reaction in nature, from thermodynamics it is known that an increase in reaction temperature will impede the forward reaction for H2 production in the WGSR.

- *using steam*

It is considered the reaction from CO, H_2O, and added steam to H_2 and CO_2, the reaction moves to the product increasing the $\frac{H_2}{CO}$. Anyway there is one important consequence: the rise of carbon dioxide. It is a disadvantage for both gas emissions and for the reduction of carbon efficiency of the whole plant. The carbon efficiency describes how much carbon we can find among the products. Increasing the carbon dioxide flowrate, a bigger portion of carbon leaves the plant like gas and not like hydrocarbons, so the intention is to minimize the production of CO_2 .

For this reason the analysis of the influence of the temperature and of steam flowrate entering in the mixer, before the reactor, will do.

About the flowrate, increasing the flowrate of the steam, the $\frac{H_2}{CO}$ increases. There is the focus on this rise because the stream has to have the ratio around

2 before the FT reactor. However it is disdvantageous to use an excessive steam flowrate, in fact this implies a bigger production of CO_2.

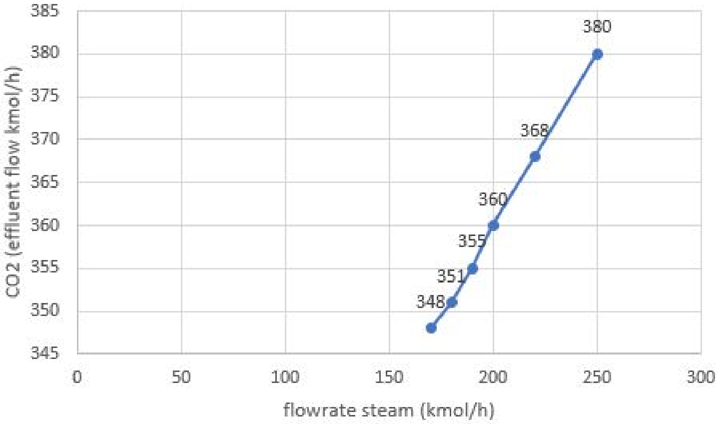


Figure 3.3: Trend steam flowrate-CO2 production

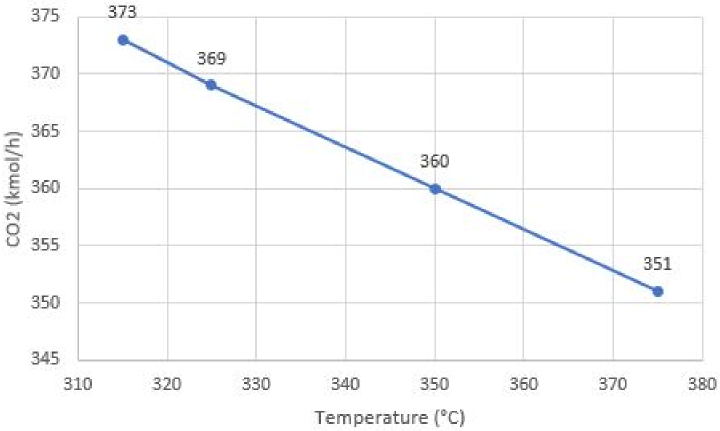
As shown in the Figure 3.3, the increasing of the steam flowrate corresponds to a decrease of the efficiency because it happens a loss of the carbon that it will go away as CO_2.

About the temperature, the reaction temperature on the design of the WGSR. Varies according with the type of catalyst used. For HTC, increasing reaction temperature, the concentration of CO declines with respect to the temperature, thus the conversion of WGSR increases, but between 400°C and 500°C the change in this propriety is small, so temperatures between 350°C and 400°C the major reaction occur.

So it is fixed a range 315-380°C, it is analyzed the trend of product with the increasing temperature. The water-gas-shift is an exothermic reaction and so we expect the decrease in products with temperature, anyway it works to minimize the gas emission but, at same time, trying to not reduce the $\frac{H_2}{CO}$ below 1.9.

The Figure 3.4 shows, in the best way, this concept.

Temperature WGSR (°C)	CO_2 effluent flow (kmol/h)	$\frac{H_2}{CO}$ inlet FTR
315	373	2,01
325	369	2
350	360	1.95
375	351	1.68



(a) Trend Temperature-CO2

Figure 3.4: Influence of temperature

After these considerations, a compromise is chosen to have high productivity and low CO_2 outgoing:

1. Flowrate steam = 240 kmol/h
2. Temperature of reactor = 350°C

- *using Hydrogen*

The approach to the problem, in this case, is totally opposite to the reactor with the introduction of steam. Now the main task of Water-Gas-Shift reactor is not to reach a specific $\frac{H_2}{CO}$ but to have as less possible CO_2 leaving the plant. To meet these needs, it has to work with the highest temperature possible, profiting by the high temperature from the gasification.

The reaction is not working with the conditions thermodynamically favored because our intent is to consume carbon dioxide, without lowering excessively the hydrogen to carbon monoxide ratio.

The composition of the outlet of the gasifier is summarised in the following table:

Compound	Flowrate (kmol/h)
Hydrogen	437
Carbon monoxide	553.23
Carbon dioxide	152.02
Water	150
Methane	46.05

Table 3.2: Outlet the gasifier

Our purpose will be to reduce as much as possible the content of CO_2, working with the highest temperature to move to left the reaction.

So there is the possibility to omit a cooler, described for the case without hydrogen, and take an advantage of this energetic content.

A controller is used for changing the hydrogen molar inlet flowrate to have $\frac{H_2}{CO} = 1.9$ outlet of the reactor. It ensures that the inlet WGSR stream has a temperature of 1000°C. In fact this temperature is used to take advantage of the high temperature outlet of the gasifier.

The water gas shift reactor takes place with different types of catalyst. It depends on low temperature or high temperature operating. For each case it needs a catalyst to work. It doesn't happen for this plant, using a temperature of 1000°C. The reaction takes place anyway, using or not the catalyst, because it is a thermodynamic equilibrium.

Actually, there are two different plants: the first is to add a part of the total hydrogen before the WGSR and the rest in the section before the FT reactor.

The final goal is to have a determined ratio in the stream inlet of the reactor. The second one is to add enough flowrate of hydrogen only before the water gas shift reactor to have $\frac{H_2}{CO} = 1.9$ outlet.

It is preferable to choose the last for a simple reason: as said before, the reaction takes place anyway, and so adding all hydrogen in the first section means to move to left the water gas shift reactor. The main consequence is the reduction of the amount of carbon dioxide and the increasing of carbon efficiency.

Compounds	Flowrate
Hydrogen	1261.06
Carbon monoxide	662
Carbon dioxide	82.62
Water	242.06
Methane	8

Table 3.3: Outlet the WGSR

The calculated hydrogen flowrate is 838 kmol/h.

The product stream from the Water-Gas-Shift reactor is the following:

As you can see from the Table 3.3, there is, even if small, the conversion of CO_2 in CO and the ratio is perfectly as it is fixed.

About the hydrogen flowrate, it is put two different make up streams in the flowsheet: one of them before the WGS reator and the other one before the second stage of FT reactor (it depends on how many reactor are used). The second stream is controlled and manipulated by the controller (mentioned above), in which the specific is $\frac{H_2}{CO} = 1.9$. Therefore it is not possible to manipulate the second stream, but just the stream useful for the water-gas-shift reactor.

In conclusion:

1. Hydrogen flowrate (before WGSR) =838 kmol/h
2. Hydrogen flowrate (before second FT reactor) = 100 kmol/h

Two possible designs of a plant have just described ; the first one offers economic advantages but lower carbon efficiency, the second one is more expensive but it increases exponentially the production.

The project includes not only material streams but also energy streams. The biomass is the energy source of the system. The energy balance shows how we find in the products the most of energy conferred by biomass and inlet streams. The difference, between the plant runed with steam or with hydrogen, is also indicated by the energy input: using hydrogen, there is a greater energy input than using steam and so the final products have a bigger energetic charge.

The work is finalized to maximize the production and so it is chosen to run the plant with hydrogen, for the reasons given above.

3.2 Modeling purification of Syngas

The stream, that comes from the separator, is composed by Syngas but also carbon dioxide and a very small part of sulphur.

There is the necessity to remove these gases out the plant, cleaning the main stream. We know that the typical used process is the absorption with amines.

Monoethanolamine (MEA), diethanolamine (DEA), and methyldiethanolamine (MDEA) are the chemical solvents that have proved to be of principal commercial interest for gas purification. Triethanolamine has been asided largely from the commercial usage because of its low capacity (resulting from higher equivalent weight), its low reactivity (as a tertiary amine), and its relatively poor stability. Amines with two hydrogen atoms directly attached to a nitrogen atom exist and they are called primary amines and are the most alkaline, such as monoethanolamine (MEA) and 2-(2-aminoethoxy) ethanol (DGA). Then it is possible called secondary: amines diethanolamine (DEA) and Diisopropanolamine (DIPA). They have one hydrogen atom directly attached to the nitrogen atom. Triethanolamine (TEA) and Methyldiethanolamine (MDEA) are called tertiary amines and represent completely substituted ammonia molecules with no hydrogen atoms attached to the nitrogen.

It is used an absorber with seven total stages in which the main gas stream enters from the bottom and the lean solution (liquid) from the top of the column. In this case the solution is composed by water and Diethanoamine (DEA).

For many years the streams that contain amount of CO_2 and H_2S are treated by aqueous solutions of diethanolamine (DEA). This amine shows the low vapor pressure and for this reason it is suitable for low-pressure operations where the vaporization losses are quite negligible. One disadvantage of diethanolamine solutions is that the cleaning of contaminated solutions may require vacuum distillation and then, absorbing carbon dioxide some problems of corrosion could

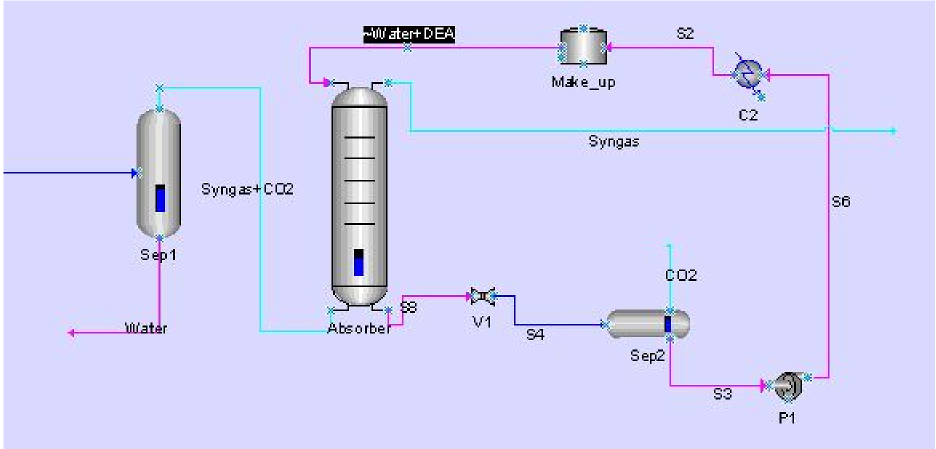


Figure 3.5: Amine absorber

exist.[7]

Generally, monoethanolamine and diethanolamine should be used in concentration from 20 wt% to 30 wt%. Expecially for treatment of refinery gases typically range in concentration is 20 to 25 wt%. Increasing the concentration there is a reduction of the required solution circulation rate and thereforethe plant cost. However, the effects are not as positive, as might expected. The principal reason for this is that the acid-gas vapor pressure is higher over more concentrated solutions at equivalent acid-gas/amine mole ratios. In addition, when an attempt is made to absorb the same quantity of acid gas in a smaller volume of solution, the heat of reaction results in a greater increase in temperature and a consequently increased acid-gas vapor pressure over the solution.

As you can see from the Figure 3.6, gas to be purified is passed upward through the absorber, counter-current to a stream of the solution. The rich solution from the bottom of the absorber is sent to a flash drum in which the most of gases is separated from the rest of lean solution and then it flows at some point near the top.

In the following the processes in this loop are explained;

The stream containing the carbon monoxide is fed on the bottom of the column, the lean solution on the top. In the absorber the pressure drop is 0.1 bar and the raise of the temperature is $\triangle T = 40$°C. In fact on the bottom, the solution, rich of the gases, is obtained at the temperature of 70°C. Our intention is to recover the solution and so it is possible to recirculate, introducing it on the top of the column.

The rich solution then flows to the low pressure flash unit, which operates close to atmospheric pressure, using a valve, as can be seen in the Figure 3.5. The low pressure flash tank needs to improve the efficiency of CO_2 removal in this vessel. A significant portion of the CO_2 contained in the rich solution is stripped in the low pressure flash unit. Completely regenerated solution from this “ physical stripping “ is fed to the pump that it increases the pressure until 20 bar and, after that, we need unit operation to cool down the temperature until 30°C. In fact the absorption is a exothermic process, favored by high pressure and low temperature. The last unit is the make up, because there is the possibility to lose a small amount of solution and, using a controller, we make sure to have a fixed stream inlet the column. The solution enters to the top absorption stage, completing the cycle.

Chapter 4

Fischer-Tropsch Reactor

4.1 Fischer-Tropsch Process

4.1.1 Chemical concepts

The main conversion processes of lignocellulosic feedstock into transportation fuels, a topic that is being more and more investigated, are fast pyrolysis and Fischer-Tropsch synthesis. The two processes have been proven to be faisable procedures in transforming biomass into liquid fuels.

The Fischer-Tropsch synthesis is a process of surface-catalyzed polymerization that produces hydrocarbons with a wide range of chain length and functionality by means of CHx monomers composed by hydrogenation of adsorbed CO. The addition of surface methylene species to adsorbed alkyl groups results in chain growth. The alkyl groups can undergo β-hydrogen abstraction to compose linear α-oleins or hydrogen addition to compose n-paraffins on Co catalysts. In presence of typical Fischer-Tropsch synthesis conditions, β-hydrogen abstraction is a reversible chain termination step while the readsorption of $\alpha-$olefins causes the reinitiation of alkyl surface chains and the generation/development of larger hydrocarbons.

Studies are currently being focused on producing syngas from gasification of lignocellulosic feedstock. FT synthesis can take place either at low temperatures (200°C-240°C, LTFT) using an iron or cobalt catalyst, or at high temperatures

(300-350°C, HTFT) using iron catalyst. Most commonly, slurry and fixed bed reactors are employed in LTFT, and fluized bed reactors in HTFT. The complex thermochemistry occurring in an FT reactor can be generalized as follows:

- Methanation Reaction

$$CO + 3H_2 \longrightarrow CH_4 + H_2O$$

- Fischer-Tropsch (FT) Reaction

$$nCO + 2nH_2 \longrightarrow (-CH_2-)_n + nH_2O$$

- Water gas shift (WGS)

$$CO + H_2O \longleftrightarrow CO_2 + H_2$$

Studies are currently being focused on producing syngas from gasification of lignocellulosic feedstock. FT synthesis can take place either at low temperatures (200°C-240°C, LTFT) using an iron or cobalt catalyst, or at high temperatures (300-350°C, HTFT) using iron catalyst. Most commonly, slurry and fixed bed reactors are employed in LTFT, and fluized bed reactors in HTFT. The complex thermochemistry occurring in an FT reactor can be generalized as follows:

The usage ratio may be profoundly affected by the water gas shift reaction. Being the extent of the WGS reaction negligible for the best cobalt catalyst, it can then be treated as a one way reaction producing a small quantity of carbon dioxide. In this case, carbon dioxide is commonly treated as a carbon containing product. When using iron catalysts at the upper end of the operating temperature range, the water gas shift reaction approaching equilibrium occurs. In such a situation, the mostused reactant is carbondioxide. The direction of the WGS reaction is determined by the composition of the dominating gas.

While when using cobalt catalysts, the usage ratio depends primarily on FT reaction and is significantly influenced by methanation reaction. The usage ratio depends on the extent of methane formation, the olefin content in the longer chain hydrocarbons and the slight water gas shift activity. Its range is typically 2.06 - 2.16.

At the other extreme, when the WGS reaction is in equilibrium, the combined usage ratio of hydrogen and carbon monoxide for the Fischer-Tropsch and water gas shift reactions together, is a moving target that depends on the feed gas composition.

Reaction conditions and catalyst composition strongly influence C_{2+} hydrocarbon selectivity. For example, when $\frac{H_2}{CO}$ ratio increases, C_{2+} hydrocarbon production decreases while methane production increases, increasing reaction temperature, and decreasing pressure

From the thermodynamic point of view, formation of methane and hydrocarbons is energetically favorable. To produce ethane and propane $\triangle G^o$ values at 227°C are -122 and -156 KJ/mol, respectively, while at 200°C $\triangle H^o$ values to create of methane, ethane, and propane are -209, -176, and -121 kJ/mol, respectively. Furthermore, equilibrium calculations show that the production of methan is highly favored over formation of hydrocarbons of heavier molecular weight. Therefore, FTS catalysts must be conceived with high selectivity for hydrocarbons other than methane; while Co, Fe, and Ru catalysts can be easily designed to meet this requirement, Ni catalyst is not useful since it produces too much methane.

One of the major cost factors is the production of purified synthesis gas (syngas), suitable as a feed gas to the FT reactor. Depending on the complexity of the overall downstream plant, syngas can represent up to about 70% of both the capital and operating cost, whether the raw material is coal or methane.

Hence, two things are of extreme importance: that the conversion of the syngas to hydrocarbon products from syngas in the FT reactors is as efficient and as complete as possible, and that the highest quantity possible of the reactans (CO, H_2, and CO_2) is consumed to produce useful products. The FT reaction selectivity should be supervised in order to minimize the production of unwanted products (e.g. methane).

To achieve the above-mentioned objectives, the syngas composition and the usage ratio of the FT reactions should match. The usage ratio will be determined by the overall product selectivity, which in turn is determined by several other factors. The effect of selectivity on the H_2 to CO usage ratio is illustrated in the following table.

FT product	Reactions	$\frac{H_2}{CO}$
CH_4	$CO + 3H_2 \longrightarrow CH_4 + H_2O$	3
C_2H_6	$2CO + 5H_2 \longrightarrow C_2H_6 + 2H_2O$	2.5
Alkanes	$nCO + (2n+1)H_2 \longrightarrow C_nH_{(2n+2)} + nH_2O$	(2n+1)/n
Alkenes	$nCO + 2nH_2 \longrightarrow C_nH_{2n} + nH_2O$	2
Alcohols	$nCO + 2nH_2 \longrightarrow C_nH_{(2n+1)}OH + (n-1)H_2O$	2

Table 4.1: Usage ratio of FT reactions

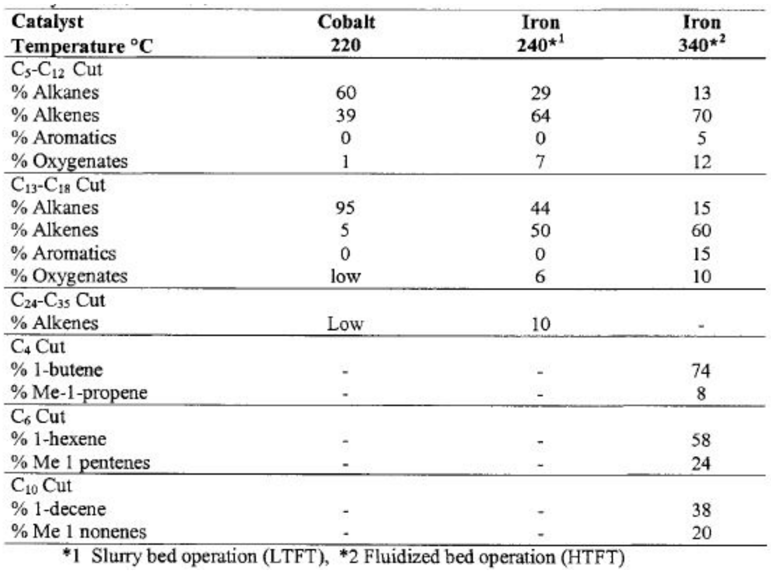
For all alkenes and alcohols the usage ratio is 2, independently of chain length. While in the case of alkanes, the more the chain length increases, the more the usage ratio decreases. The extent of the water gas shift reaction that takes place over the FT catalyst used is also important. For a cobalt catalyst (presenting little or no WGS activity) the overall H_2 to CO usage ratio under typical FT synthesis conditions is 2.05-2.15. The usage ratio of precipitated iron based catalyst operating in a fixed bed reactor at about 225°C is approximately 1.65.

For cobalt catalysts (presenting little or no WGS activity), increasing FT conversion levels do not influence the hydrogen to carbon monoxide usage ratio. On the contrary, iron catalysts are active for the WGS reaction, and when using them at the lower temperatures, the overall usage ratio decreases as the conversion increases. When using iron catalysts at the higher temperatures, however, the presence of excess hydrogen in the FT reactor would be extremely useful to minimize carbon deposition in the catalyst. If, as it is normally practiced, there is an excess of hydrogen in the FT reactor, it is theoretically impossible to attain a high % $(CO + H_2)$ conversion.

A wide range of hydrocarbon and oxygenated products results from The FT synthesis. Mechanistic and kinetic factors appear to control the formation of the various products and the product spectra differ significantly from what would be expected from thermodynamic point of view. It is calculated that if a gas with $\frac{H_2}{CO}$=1 were to go to complete equilibrium at 0.1 MPa and at a typical FT temperature then the main products would be methane, carbon dioxide and graphite and the amounts of higher hydrocarbons wuold be negligible. Similar calculations were then presented for 600 K, 1.6 MPa and a gas with $\frac{H_2}{CO}$=2, and it is possible to recognize the different kind of products. It is clear that, under normal operating conditions, the FT reactions are nowhere near thermodynamic equilibrium, the observed C_2 and higher products are produced in huge quantities relative in comparison with thermodynamic expectation.

About the alkanes, they should theoretically be completely hydrogenated to alkanes, they are the most produced hydrocarbons. This shows that alkenes must be primary FT products and that, if it occurs, their subsequent hydrogenation over iron catalyst in the gas atmosphere prevailing in the FT reactors must be slow. Even with cobalt catalysts (much more active for hydrogenation reactions than iron), the alkenes exceed the alkanes for the lower molecular mass hydrocarbons. Thermodynamically, ethene hydrogenation should be more complete than propene hydrogenation.

In the following figure, you can see the typical products, changing type of catalyst and temperature.



Catalyst **Temperature °C**	**Cobalt** **220**	**Iron** **240^{*1}**	**Iron** **340^{*2}**
C_5-C_{12} Cut			
% Alkanes	60	29	13
% Alkenes	39	64	70
% Aromatics	0	0	5
% Oxygenates	1	7	12
C_{13}-C_{18} Cut			
% Alkanes	95	44	15
% Alkenes	5	50	60
% Aromatics	0	0	15
% Oxygenates	low	6	10
C_{24}-C_{35} Cut			
% Alkenes	Low	10	-
C_4 Cut			
% 1-butene	-	-	74
% Me-1-propene	-	-	8
C_6 Cut			
% 1-hexene	-	-	58
% Me 1 pentenes	-	-	24
C_{10} Cut			
% 1-decene	-	-	38
% Me 1 nonenes	-	-	20

*1 Slurry bed operation (LTFT), *2 Fluidized bed operation (HTFT)

Figure 4.1: FT hydrocarbon isomers

FT reaction always produces a wide range of hydrocarbon and oxygenated hydrocarbon products, irrespective of the operating conditions. Methane, is an unwanted product that is always present and whose selectivity can change from as low as about 1% up to 100%. At the other end of product spectrum, the selectivity of long chain linear waxes can vary from zero to 70%. The alteration of the operating temperature, the type of catalyst, the amount or type of promoter present, the feed gas composition, the operating pressure, or type of reactor used can change the spread in carbon number products . Whatever the process conditions, clearly all the products formed are always interrelated. [8]

Figure 4.2 illustrates the link between the lower molecular mass hydrocarbons produced with a fused iron catalyst operating at about 330°C.

Figure 4.3 illustrates the relationship between the higher molecular mass hydrocarbons produced over a precipitated iron catalyst operating at about 225°C. (Remember that “Hard wax” is the hydrocarbon fraction boiling above 500°C).

Figure 4.4 shows how the selectivity of some different C_2 compounds varies with the methane selectivity.

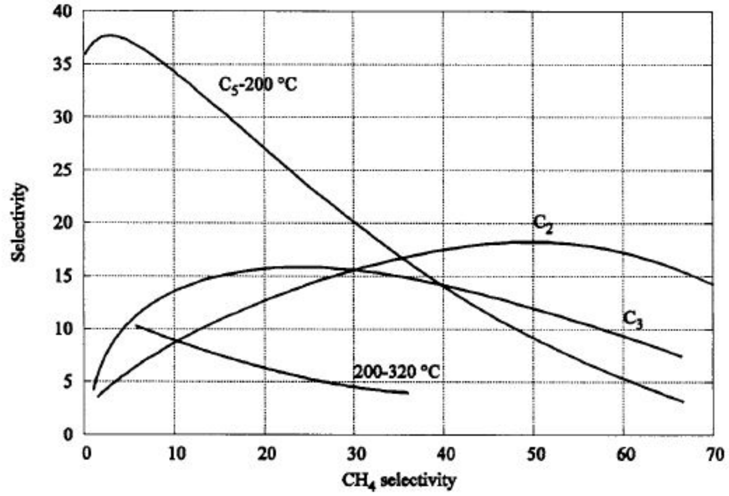


Figure 4.2: Hydrocarbons product selectivities relative to the methane selectivity

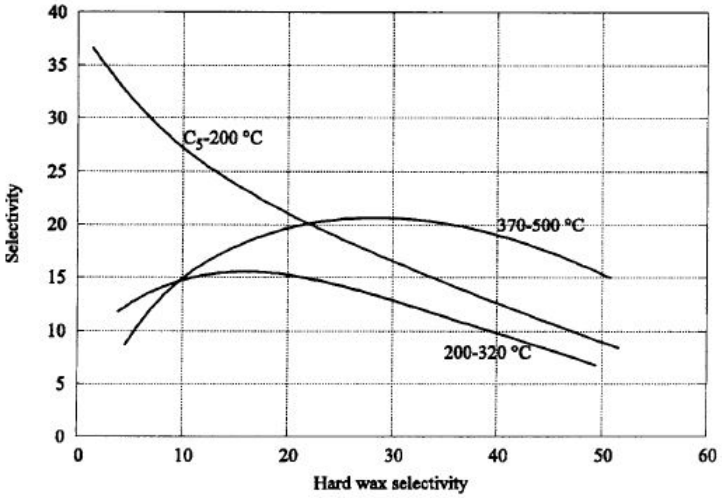


Figure 4.3: Selectivity for product distillation cuts relative to the hard wax selectivity

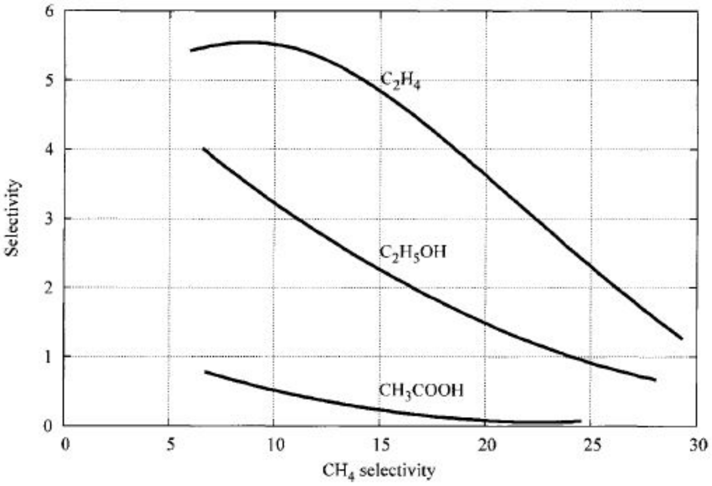


Figure 4.4: C_2 product selectivities relative to the methane selectivity

4.2 Modeling the Fischer-Tropsch Product Distribution and Model Implementation

The selectivities of hydrocarbon product are determined by chain propagation rate relative to chain termination rate. In FTS the distribution of the products is given by in part by a chain polymerization kinetics model ascribed to Anderson, Schulz, and Flory, henceforth referred to as Anderson-Schulz-Flory (ASF) model.

The Anderson-Schulz-Flory distribution, with propagation probability α (growth factor) as the only parameter, is the "ideal" ASF distribution. There are some assumtions: no chain limitation with the ASF distribution and having no chain limitation; but it may seems to be conceptually problematic. The probability of producing chain lenghts larger than N carbons from a distribution is: $p(i > N) = \alpha^N$. By the combination of two or more ideal ASF distributions and addition of single reactions, it is possible to represent most observed product distributions.

The ASF product distribution is mathematically defined by the equations:

$$\frac{w_n}{n} = \alpha^{n-1}(1-\alpha)^2 \quad \alpha = \frac{m_{n+1}}{m_n} = \frac{r_p}{r_p + r_t}$$

where n is the number of carbon atoms in the product, w_n and m_n are the weight and mole fractions of product containing n carbon atoms, r_p is the rate of chain propagation, and r_t is the rate of chain termination

It is observed that the growth factors are different between paraffins and olefins, instead oxygenates are often neglected because only very small amounts are formed.

In conclusion the followig expressions describe the production of paraffins and olefins with two different reactions, first one for n-paraffins and the second for distribution of 1-olefins. It is easy to understand that we use two different growth factors, $\alpha_1$and α_2.

$$CO + U_1H_2 \longrightarrow \sum_{i=1}^{\infty} \nu_{i,1}C_iH_{2i+2} + H_2O \qquad (1)$$

$$CO + U_2H_2 \longrightarrow \nu_{1,2}CH_4 + \sum_{i=2}^{\infty} \nu_{1,2}C_iH_{2i} + H_2O \qquad (2)$$

Notice that the second reaction also included CH_4. Even if it is not an olefin, there is a good reason for including also in the second reaction. So the total production of methane from these two reactions is therefore $R_{CH_4} = \nu_{1,1}r_1 + \nu_{1,2}r_2$ while the paraffins are $R_{C_iH_{2i+2}} = \nu_{i,1}r_1$ and olefins are $R_{C_iH_{2i}} = \nu_{i,2}r_2$.[9]

- *Stoichiometry*

The stoichiometric coefficients will follow the ASF distribution and must be given as:

$$\nu_{i,1} = (1 - \alpha_1)^2 \alpha_1^{i-1}$$

$$\nu_{i,2} = (1 - \alpha_2)^2 \alpha_2^{i-1}$$

Using the stoichiometric coefficient, the sum for reaction 1 is $1 - \alpha_1$ and, of course, this is the number of molecules of hydrocarbon for each consumed molecule of CO. The same consideration is for the second reaction but using α_2.

In the equation (1), the symbol U_1 is used but the exactly stoichiometric coefficient can be calculated:

$$U_1 = \sum_{i=1}^{\infty} (i+1)\nu_{i,1} + 1 = 3 - \alpha_1$$

$$U_2 = 2\nu_{1,2} + \sum_{i=2}^{\infty} i\nu_{i,2} + 1 = (1-\alpha_2)^2 + 2$$

- *lumping of components*

It can be useful, especially for the simulations, to introduce the concepts of lumping of components. The advantage is the ability to describe an infinite number of component in a model. The interest is in calculating the molar fractions, the stoichiometric coefficient and the average carbon number of a lump. It is indispensable to provide a detailed description of the lump.

The finite sum of molar fraction up to N carbon atoms is:

$$S_{[1,N]} = (1-\alpha) \sum_{i=1}^{N} \alpha^{i-1} = 1 - \alpha^N$$

If, instead, the sum is from N to M carbon atoms:

$$S_{[N,M]} = (1-\alpha) \sum_{i=N}^{M} \alpha^{i-1} = S_{[1,M]} - S_{[1,N-1]} = \alpha^{N-1} - \alpha^M$$

About the number average carbon number of a lump of components, it is very important to create an hypothetical compounds with a specific number of carbons. If the lump is composed by closed interval from N to M, the equation is:

$$\bar{n}_{n,[N,M]} = \frac{\sum_{i=N}^{M} i\alpha^{i-1}}{\sum_{i=N}^{M} \alpha^{i-1}} = \frac{N\alpha^{N-1} - (N-1)\alpha^N - (M+1)\,\alpha^M + M\alpha^{M+1}}{(1-\alpha)\left(\alpha^{N-1} - \alpha^M\right)}$$

The number average of the lump $[N, \infty]$ is reduced to:

$$\bar{n}_{n,[N,\infty]} = N + \frac{\alpha}{1-\alpha}$$

- *kinetic model*

The model should be able to predict reaction rates as function of temperature and composition and preferably also the product selectivity.

Most of the rate expressions originate from Langmuir-Hinshelwood (LH) or Eley-Rideal (ER).

Instead, in this case a more complex kinetic model, based on the study done by Todic et al., is used. The model is based on the CO-insertion mechanism. Both paraffins and olefins are included; the ratio between the paraffin and olefin growth factors is a constant.

The model describes the rate for each component and introduces different α for each polymerization step. In general the growth factors depends on the vacant site fraction, [S], which again is a function of changing growth factors, making the model implicit. Because of the changing growth factor, the model does not follow the ASF distribution and the formalism shown here can't be applied. On the other hand, the model can be simplified without much loss of accuracy. The main simplification, done in the FT reactor, is for all polymerization steps growth factors are assumed to be constant; α_1 for paraffins and α_2 for olefins, equal to the upper limit predicted by the original model. This makes the growth factors independent on the fraction of vacant sites [S] and the model becomes explicit.

$$\alpha_1 = \frac{1}{1 + \frac{k_7\sqrt{K_2 p_{H2}}}{k_3 K_1 p_{CO}}}$$

$$\alpha_2 = \alpha_1 e^{-0.27}$$

$$\alpha_M = \frac{1}{1 + \frac{k_{7,M}\sqrt{K_2 p_{H_2}}}{k_3 K_1 p_{CO}}}$$

After describing of the alpha value, this is the following semplification about the fraction of vacant sites, overall rates of reactions (1) and (2), respectively.

$$r_1 = k_7\sqrt{K_2 p_{H_2}}\,[S]^2\,\frac{\alpha_M}{(1-\alpha_1)^2}$$

$$r_2 = k_8\,[S]\,\frac{\alpha_M}{(1-\alpha_2)^2}$$

$$[S]^{-1} = 1 + K_1 p_{CO} + \sqrt{K_2 p_{H_2}} + \left(\frac{p_{H_2O}}{K_2^2 K_4 K_5 K_6 p_{H_2}^2} + \sqrt{K_2 p_{H_2}}\right)\frac{\alpha_M}{(1-\alpha_1)}$$

The rate expressions are given in [kmol/(kg h)] and the partial pressures are given in [MPa].

If the problem is analyzed more accurately, it could be said that the selectivity of methane is higher than predicted by ASF distribution, while ethylene is lower. To have the real distribution, another reaction can be introduced, such as the hydrogenolytic cleavage of ethylene; r_4 is the rate of the following reaction:

$$C_2H_4 + 2H_2 \longrightarrow 2CH_4$$

The rate r_4 will be the difference between the prediction according to the ideal ASF distribution of olefin production and the observed ethylene production.

$$r_4 = (1-\alpha_2)^2\alpha_2 r_2 - r_{C_2H_4}$$

About methane, the production is higher than the one predicted from r_1 and from the ethylene cleavage. So a reaction of methanation can be introduced. r_3

is the rate of the following reaction:

$$CO + 3H_2 \longrightarrow CH_4 + H_2O$$

The reaction rate will be the difference between the observed rate r_{CH_4} and the prediction according to the ideal ASF.

$$r_3 = r_{CH_4} - (1-\alpha_1)^2 r_1 - (1-\alpha_2)^2 r_2 - 2r_4$$

So, according with this reasoning, we can insert the Todic model and the reaction rate will be the following:

$$r_3 = k_{7,M}\sqrt{K_2 p_{H_2}}\,[S]^2\,\alpha_M - (1-\alpha_1)^2 r_1 - (1-\alpha_2)^2 r_2 - 2r_4$$

$$r_4 = (1-\alpha_2)^2\,\alpha_2 r_2 - k_{8,E}\,[S]\,\alpha_M \alpha_2$$

4.3 Modeling FT Reactor

The simulation can be divided into two parts: base case using vapour (before the Water-Gas-Shift Reactor) and advanced case using hydrogen (before the WGSR).

In this part, the effects, that some specifications lead on the products, are analyzed. The purpose of these considerations is to optimize the process and maximize the production of nC_{5+}.

At the beginning, the optimization on the base case will be done and their results will be compared with the advanced case to find the best possible flow sheet. The choice won't be the most economical choice but the most productive one.

First of all, the stream, entering in the FT reactor, should be fixed in temperature and composition.

About temperature, it works with the typical temperature used for LTFT process. Above it has been explained the types of reactor and for LTFT the range of temperature is 200°C-230°C. So a heater is used to bring the temperature up to 210°C.

As shown in the previous section, two types of catalystscan be used: iron type and cobalt type. In the simulation the Todic's expression is followed about the kinetics and Todic used a particular catalyst: $25\% Co/0.48\% Re/Al_2O_3$.

Instead, about composition, we have to divided our simulation into two sections: a plant with hydrogen and a plant without hydrogen.

- *with hydrogen*

The right composition is given by make-up stream of hydrogen, before the Water-Gas-Shift reactor.

The specification is $\frac{H_2}{CO} = 1.9$. This value has been fixed because the main FT reaction works with the ratio equal to 2 or little bit more. So working with lower ratio, the reaction moves towards hydrocarbons with higher molecular weight, getting closer to higher material and energy efficiency. In contrast , working with $\frac{H_2}{CO} = 2.1$, it produces a lot of C_1, C_2, C_3, C_4, which is useless for the main production.

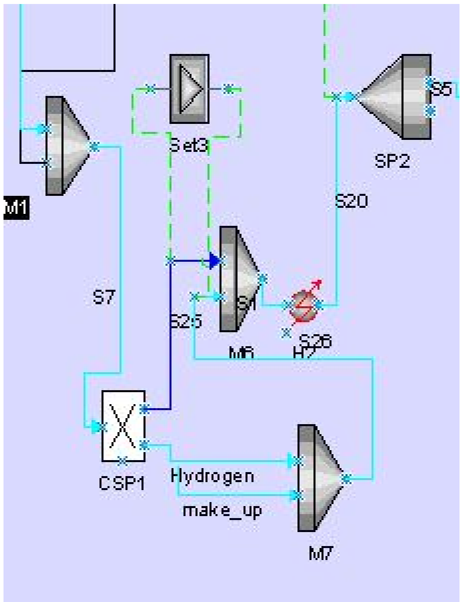


Figure 4.5: Controller of composition

Now all the unit operations are analyzed. On the left side of this Figure, the unit M1 can be seen. This unit mixes the stream from the main plant with the one from the recycler. On the lower left of the figure the unit CSP1 is shown, which is a component splitter. This unit is useful for dividing hydrogen from the rest of the stream.

In this way, the hydrogen stream S26 is created. It is directed into the controller.

We remember that this type of plant is more energy-intensive. As seen from the Figure 4.6, a unit calculator called Set3 is necessary. It manipulates the make up hydrogen stream in order fix the ratio of $\frac{H_2}{CO}$ to 1.9. Actually, the only stream, that has to be manipulated, is that of make up; in fact in this Set, the molar flowrate of CO is fixed and multiplied for the hydrogen to carbon monoxide ratio.

Input

Connection	Value
/SFS1.SFS1_1.S25.MoleFlow_CARBON_MONOXIDE	689.26

Multiplier

Value
1.90

Offset

Value
0.00

Output

Connection	Value
/SFS1.SFS1_1.S26.Mole Flow	1309.59

Figure 4.6: Set controller

In the following, a detailed explanation of the processes in the FT reactor is given.

In the VMGSim, the ideal Fischer-Tropsch reactor models the hydrogenation of carbon monoxide over a catalyst bed. The products of this unit operation are vapor, liquid, and wax outlet material streams. Enthalpy of formation is accounted for all products generated and enthalpy of fusion is calculated for any wax drop out. Carbon monoxide conversion, carbon dioxide selectivity, and paraffin/olefin/alcohol product distribution kinetics can be entered as signal values by the user to customize this operation. Alternatively, these values can be automatically estimated through methodologies from literature for both iron and cobalt based catalysts.

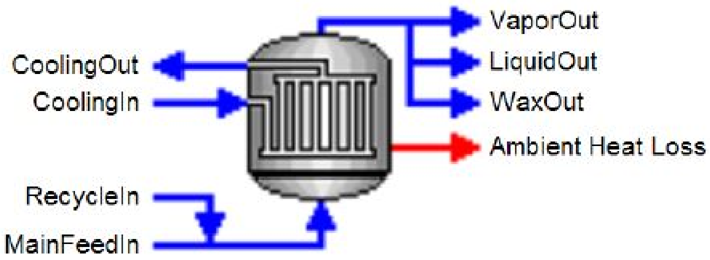


Figure 4.7: Model FTR

If the kinetic of the reactor is checked , it could be realized that it is too restrictive using this pre-set model. The kinetic and CO selectivity, used in the simulator, is the following:

$$-r = aP_{CO}^{-0.2}P_{H_2}^{0.7}$$

$$conversion\,CO = Ae^{-\frac{E}{RT}}P_{CO}^{-0.2}P_{H_2}(catalystactivity)$$

For this reasons, it would be better to build it yourself, using PF reactor where we have to set everything.

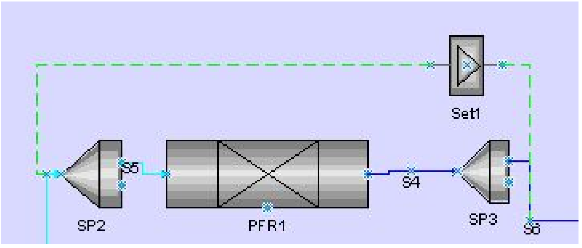


Figure 4.8: Single tube

In the Plug Flow (PFR) or tubular flow reactor the feed enters at one end of a cylindrical tube and the product exits at the other end. The PFR model used in VMGSim assumes that there is no mixing in the axial direction and a complete mixing in the radial direction. This unit operation works like a single tube. So the total mass flowrate is divided in so many tubes as it is necessary to have 0.5 m/s the space velocity inside the single tube. As you can see from the Figure 4.8, two splitters are inserted, rispectively before and after the FT reactor.

The stoichiometric coefficients has to be set, introducing different reaction. In the following part, an approximation will be done, about alpha value, already explained in the modeling FT section. This value depends on the temperature and the ratio $\frac{H_2}{CO}$. This ratio can change inside the reactor, especially for a high raise of temperature. At the moment of the first valutation, α_1 and α_2 are fixed and the reaction and his stoichiometric coefficients, inserted, is shown in the next table.

component	ν	$\bar{n}_n$
C_1	$(1-\alpha_1)^2$	1
C_2	$(1-\alpha_1)^2\alpha_1$	2
nC_3	$(1-\alpha_1)^2\alpha_1^2$	3
nC_{21+}	$(1-\alpha_1)\alpha_1^{20}$	$20+\frac{\alpha_1}{1-\alpha_1}$

component	ν	$\bar{n}_n$
C_2	$(1-\alpha_2)^2\alpha_2$	2
$1-C_3$	$(1-\alpha_2)^2\alpha_2$	3
$1-C_{10-20}$	$(1-\alpha_2)(\alpha_2^9-\alpha_2^{20})$	$\frac{10\alpha_2^9-9\alpha_2^{10}-21\alpha_2^{20}+20\alpha_2^{21}}{(1-\alpha_2)\left(\alpha_2^9-\alpha_2^{20}\right)}$
$1-C_{21+}$	$(1-\alpha_2)\alpha_2^{20}$	$20+\frac{\alpha_2}{1-\alpha_2}$

Table 4.2: component lumping with the stoichiometric coefficients and number average carbon number (first table for n-paraffins, second table for 1-olefins)

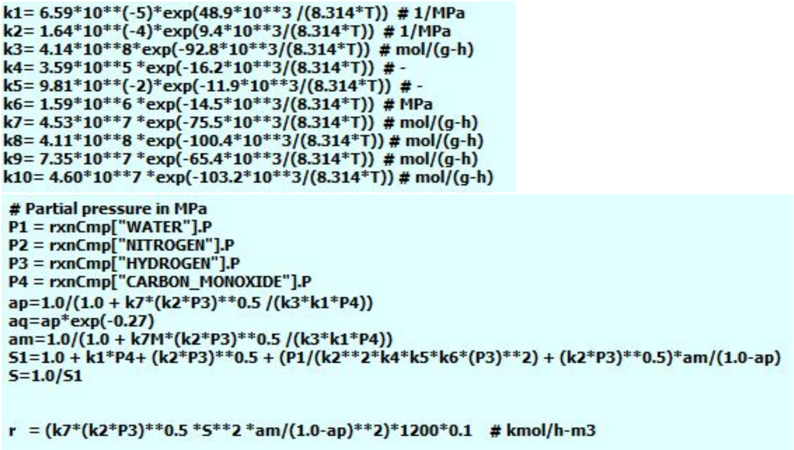
As you can see, there are also the lumps; they are compounds that describe a range of hydrocarbons . They are created as hypotetical compounds from already existing components, with the same molecular weight and number average carbon that is calculated in the section before. The stoichiometric coefficients should be balanced and we could modify the error tolerated from the settings of reactor.

The second step is to integrate the kinetics. Using the advanced kinetic, it is edited the different expressions, for every reaction that exists in the reactor. Every constant is specified and its dependencies and, due to the gas phase reaction, every partial pressure.

Instead, the traditional kinetic could be used adding E_a and A, respectively energy of activation and pre exponantial factor, but it is not allowed to use more complex kinetics, even if it is easier to manage. In the advanced section, every type of kinetics can be written. The VMGSim works with python language, so every variable introduced has to be write in the consistency way.

The Figure 4.9 is a example of kinetic for the reaction that produces n-paraffins.

Every constant as k, the growth probability factor as ap, aq and am, finally the partial pressure as P are defined.



```
k1= 6.59*10**(-5)*exp(48.9*10**3 /(8.314*T))  # 1/MPa
k2= 1.64*10**(-4)*exp(9.4*10**3/(8.314*T))  # 1/MPa
k3= 4.14*10**8*exp(-92.8*10**3/(8.314*T))  # mol/(g-h)
k4= 3.59*10**5 *exp(-16.2*10**3/(8.314*T))  # -
k5= 9.81*10**(-2)*exp(-11.9*10**3/(8.314*T))  # -
k6= 1.59*10**6 *exp(-14.5*10**3/(8.314*T))  # MPa
k7= 4.53*10**7 *exp(-75.5*10**3/(8.314*T))  # mol/(g-h)
k8= 4.11*10**8 *exp(-100.4*10**3/(8.314*T)) # mol/(g-h)
k9= 7.35*10**7 *exp(-65.4*10**3/(8.314*T))  # mol/(g-h)
k10= 4.60*10**7 *exp(-103.2*10**3/(8.314*T)) # mol/(g-h)

# Partial pressure in MPa
P1 = rxnCmp["WATER"].P
P2 = rxnCmp["NITROGEN"].P
P3 = rxnCmp["HYDROGEN"].P
P4 = rxnCmp["CARBON_MONOXIDE"].P
ap=1.0/(1.0 + k7*(k2*P3)**0.5 /(k3*k1*P4))
aq=ap*exp(-0.27)
am=1.0/(1.0 + k7M*(k2*P3)**0.5 /(k3*k1*P4))
S1=1.0 + k1*P4+ (k2*P3)**0.5 + (P1/(k2**2*k4*k5*k6*(P3)**2) + (k2*P3)**0.5)*am/(1.0-ap)
S=1.0/S1


r  = (k7*(k2*P3)**0.5 *S**2 *am/(1.0-ap)**2)*1200*0.1   # kmol/h-m3
```

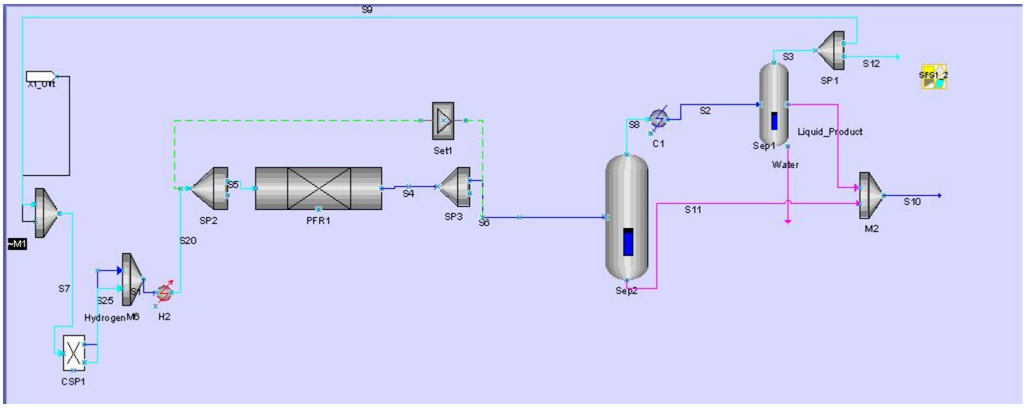
Figure 4.9: kinetic expression

A microscopic analysis are done on the reactor, but the FT section is not only consists of the reactor; it is composed by some different unit operations are explained in the following:

This part includes the separator immediately after the PF reactor. In fact there are two outlet streams from the real reactor, not just one as you can see from the Figure 4.10; so a separator has to add to model perfectly the real case.

The liquid stream, from the separator, is formed mainly by high hydrocarbon, instead the gas stream will be cooled down and split through three phases separator. This unit includes water, hydrocarbons and vapour composed by methane, that represents inert for the process, hydrogen, CO unconverted and other light hydrocarbons. This vapour stream will be recycled to increase the productivity.

The following picture shows that the product is in the stream S10.



.

Figure 4.10: FT section

First of all, it is necessary to describe the reactor and its properties.

There is a need to fix some specifications, without these, the reactor would not converge.

The reactor is working with catalyzed reaction so the most suitable correlation to calculate the pressure drop has to be chosen: Ergun expression; inside the reactor, the pressure drop, are of around 1.33 bar. This value depends also on reaction phase, that in our case is vapour.

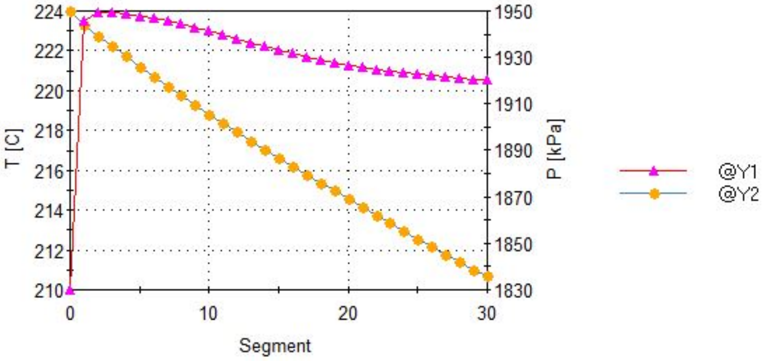


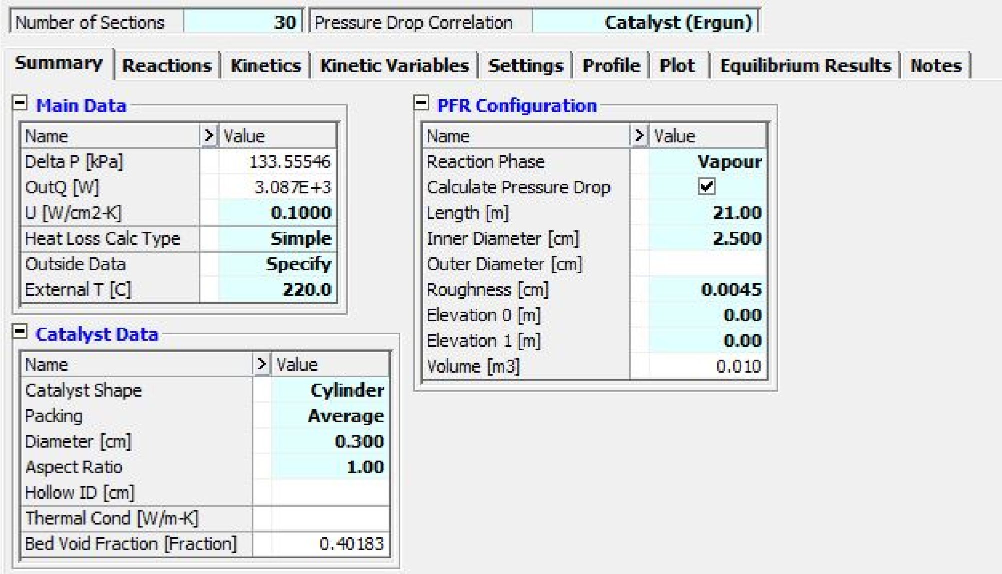
Figure 4.11: Tren temperature and pressure inside the reactor

The second specification is about the overall heat transfer coefficient, it depends on what type of utility we are using. The Fischer-Tropsch reaction is an exothermic reaction and the temperature rises to not have a stable control of it and the following embrittlement of tubes walls that are made of steel carbon. So, by using the boiler feed water, the temperature decreases and temperature control becomes stable. As you can see from th Figure 4.11, the trend shows a maximum where the rate reaction is very high. The following decrease is due to the presence of water at 220°C. The simulator shows how much heat is removed by the cold utility, and the main influence is given by the overall heat tranfer coefficient (U); which for water, it is 1000 $\frac{W}{m^2K}$.

Then, it's absolutely needful to insert some properties about the catalyst: catalyst shape, packing, diameter of catalyst and aspect ratio that, if a catalyst shapedifferent forma sphere is chosen the aspect ratio of the catalyst must be provided here. This value is taken as the Length/Diameter ratio.

The last values are the length of the tubes and the inner diameter. The inner diameter is strongly connected to the number of tubes, because the space velocity, the velocity inside the tube section, is set to 0.5 m/s.

The next Figure shows the input fields for these variables.



Number of Sections	30
Pressure Drop Correlation	Catalyst (Ergun)

Main Data

Name	Value
Delta P [kPa]	133.55546
OutQ [W]	3.087E+3
U [W/cm2-K]	0.1000
Heat Loss Calc Type	Simple
Outside Data	Specify
External T [C]	220.0

Catalyst Data

Name	Value
Catalyst Shape	Cylinder
Packing	Average
Diameter [cm]	0.300
Aspect Ratio	1.00
Hollow ID [cm]	
Thermal Cond [W/m-K]	
Bed Void Fraction [Fraction]	0.40183

PFR Configuration

Name	Value
Reaction Phase	Vapour
Calculate Pressure Drop	☑
Length [m]	21.00
Inner Diameter [cm]	2.500
Outer Diameter [cm]	
Roughness [cm]	0.0045
Elevation 0 [m]	0.00
Elevation 1 [m]	0.00
Volume [m3]	0.010

Figure 4.12: Properties FT reactor

- *without hydrogen*

In this case, the right composition is given by the steam introduced in the plant.

The inlet composition is given in Table 4.4. As you can see it is composed by less CO and H_2.

Compounds	Flowrate (kmol/h)
Hydrogen	664.22
Carbon monoxide	320.14
Methane	46.24
Water	0.66

Table 4.3: Inlet FT composition

However this case is not taken in consideration because the liquid production is too low and we are forced to work with one step because of the drop of hydrogen to carbon monoxide ratio. That's the main reason why it has been decided to use the previous plant. Using the same perfectly conditions of the optimized case (described above), the $\frac{H_2}{CO}$ is too low, equal to 1.16. So without introducing of hydrogen, it is impossibile to consider two FT reactor. The total nC_{5+} production is 2132.75 kg/h. The difference is considerable and so we prefer also do the optimization with the hydrogen case.

4.3.1 Optimization

In this section, our aim is to optimize the FT reactor and the connected unit operations . The goal will be to maxime the liquid production, without an interest of minimizing the costs. You could realize this purpose because we are using hydrogen despite the cost due by air separation.

In Figure 4.13 there are all specifications which it allows to manipulate to increase the productivity (kg/h) and these are: the cooling water temperature in the FT reactor, the length of the tube, the temperature used to separate the vapour, the recycle ratio (RR) and the possibility of useing two stages.

- *Cooling water temperature*

The productivity is stronghly linked to cooling water temperature. In fact the total rate reaction depends on how much heat the cold utility removes. The maximum of the curve, that describes the trend of the tempurature inside the

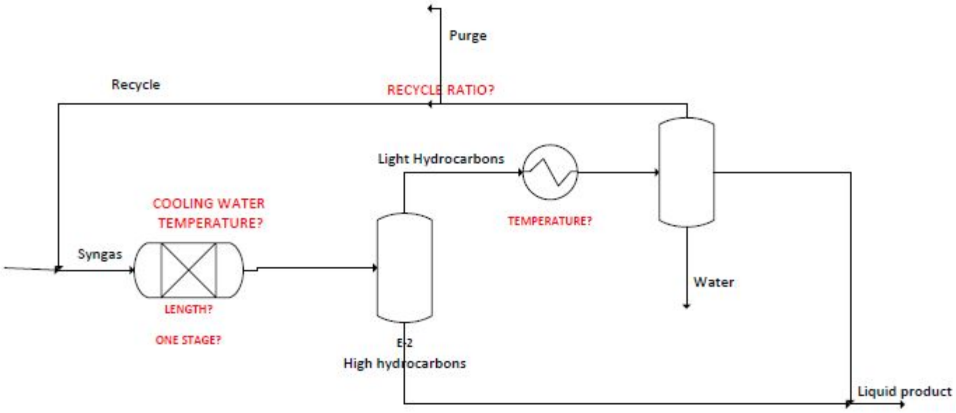


Figure 4.13: Variables to manipulate

reactor, moves to the right if less cold water is used. Additionally all rate reactions seem to be higher, and also the reacting species increases.

Of course, it is not possible to work with too high cooling water temperatures, because a unstable hot spots, inside the reactor, have to avoid. This water is boiler feed water that it is opposed to the exothermic reactions but, in the same time, it uses this heat to pass from liquid to medium pressure vapour at 20 bar. So the range of this cooling water is 210-220°C.

Actually, another real limit exists: the $\frac{H_2}{CO}$ outlet to the FT reactor. The stream, inlet of the unit operation, is a substoichiometric feed, so there is a decrease of this ratio. An excessive reduction represents a limit because it requires a substantial usage of hydrogen from make up, to have $\frac{H_2}{CO} = 1.9$.

In the next Figure, you can see the trend of these variables.

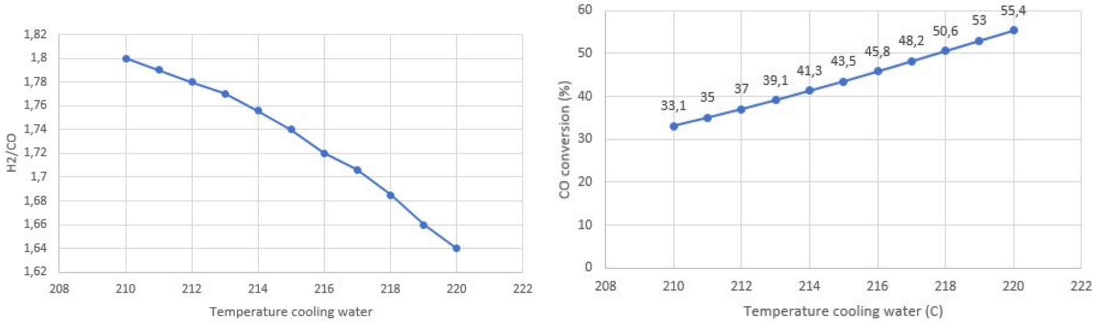


Figure 4.14: Trend changing cooling water temperature

By lowering the cooling water temperature, from 220°C to 210°C, the CO conversion drops from 55.4% to 33.1%. So it's convenient to work with higher temperature. Even if there is a drop of hydrogen to carbon monoxide ratio, it doesn't decrease until minimum ratio and so it is used the highest conversion that it is given by cooling water temperature of 220°C.

- *Length of tube*

As explained in the previous section, we have to set a CO conversion limit, for the reasons already given. The limit is 70% and so the length of the tube is changed until the CO conversion reaches a level of 65% , to work safe and because these simulations are without recycle so open-loop, so we expect a raise of the conversion when we will close the loop.

Length (m)	CO conversion (%)	$\frac{H_2}{CO}$	nC_{5+} (kg/h)
15	55.4	1.64	3628.34
16	57.9	1.6	3788
17	60.1	1.58	4931.7
18	62.2	1.55	4060
19	64	1.53	4175
20	65	1.5	4276

Table 4.4: Effects of length of tube

As you can see from the Figure 4.15, most of the reaction happens in the first segments of the reactor. Nevertheless the reaction continues until the temperature is equal of the one of the cold utility. So the volume of the reactor can be increased by changing the length of tube as far as possible. If the profile temperature remains constant at 220°C, there is no or just a little reaction. So the changing of the length wouldn't have a benefit.

- *Temperature of separator*

Now there is a discussion about the manipulation of the outlet temperature before the three-phases separator .

This is the least important specification. A variation of temperature doesn't have a big impact if it takes place below 70°C. The plant is simulated within a temperature range from 35°C (minimum temperature using industrial water as cold utility) to 60°C.

Temperature cooler (°C)	nC_{5+} (kg/h)
35	4276
40	4270.31
45	4260.15
50	4220.92
60	4170.24

Table 4.5: Effect of the separator's temperature

To have a bigger production, we choose T=35°C.

- *Stages*

In this section, the discussion is about whether on or two stagesare favourable. The configuration described, is an examplefor one stage, with the length of 20 m. The CO conversion is fixed to 65%. The total volume is around 38 m^3. The second possibility is to work with two reactors, that together have the same volume as the previous reactor. Our intention is to understand which configuration represents the highest production. From the simulation it is known that two reactors with the same volume are the optimum configuration. This is shown in the following table.

Stages	volume 1° reactor (m^3)	volume 2° reactor (m^3)	total volume (m^3)
1	37.8	/	37.8
2	26.44	11.36	37.8
2	37.8	13.17	51

Stages	1° CO conversion (%)	2° CO conversion (%)	total conversion (%)
1	65	/	65
2	53.6	51.6	77.6
2	65	65	88

Table 4.6: Effects of stages

After understanding that, because our purpose is to increase more and more the conversion, we force the reactor to work with the limit conversion (65%) and so each reactor works very close to the limit condition. It is obvious that the total conversion increases and reachs 88%.

- *Recycle ratio (RR)*

The recycle ratio is defined as the ratio between the recycled stream and the main stream (entering to the mixer). The recycled stream is composed by methane (a huge part of), unreacted hydrogen and carbon monoxide and small part of C_1,C_2, C_3, C_4. If we consider also this stream, the conversion increases as well as the production. So there is an economical benefit because of the re-use of unreacted stream.

The plant is simulated using different RR which shows two different effects: using a higher RR, there are more reagents and the possibility to convert becomes bigger. At the same time, there is a raise of methane that it is considered aa a disadvantage. In fact the presence of methane, that represents a product for the FT reaction, moves to left the reaction. The combination of these two effects means the presence of the maximum in the graphic RR-nC_{5+}.

To maximize nC_{5+}, we will choose RR=0.13 in which the liquid production is 6100 kg/h. The CO conversion in the first reactor is 66%, in the second reactor it is 68%, instead the total CO conversion is 88.8%.

In the last step, remembering that the limit conversion is 70%,each reactor is

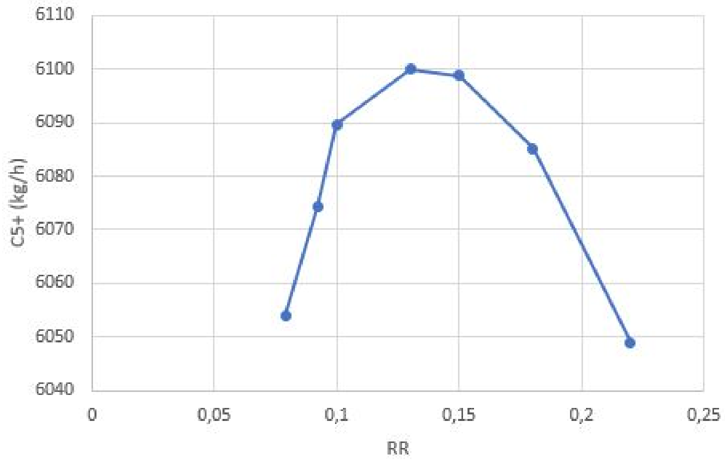


Figure 4.15: Effects of RR on the production

forced to work in this condition. The lenght of the tubes of the first reactor is 23m, for the second one it is 21m.

The optimized plant will be with total CO conversion equal to 90% and its final productivity is 6200 kg/h.

4.3.2 Rigorous Approach

In the previous section, the values for alpha could be calculated because they are considered as constants in the reactors. Actually these values change, if the temperature and the hydrogen to carbon monoxide ratio is changed.

For this reason, the reaction is splitted up into many small reactions. So it is possible to analyze the reaction in detail.

First of all, it seems to be better to divided into a lot of number of reactions, so we can analyze every reaction.

We used to work with a fixed stoichiometric coefficients, but in this case this is no longer possible, because the coefficients depend on the value of alpha that depends on the temperature and $\frac{H_2}{CO}$. This ratio decreases along the reactor and the temperature shows a maximum, so there is a change of temperature.

It could be possible to bypass the problem of stoichiometric coefficients in the following expressions for the paraffins:

$$i\nu_i CO + ((i+1) + i\nu_i)H_2 \longrightarrow \nu_i C_i H_{2i+2} + i\nu_i H_2O$$

in which $r = r_{FT} \cdot i\nu_i$; we divide for $i\nu_i$:

$$CO + \left(2 + \frac{1}{i}\right) H_2 \longrightarrow \frac{1}{i} C_i H_{2i+2} + H_2O$$

$$i\nu_i \cdot r_{FT} = k_7 \sqrt{k_2 P_{H_2}} S^2 \frac{\alpha_M}{(1-\alpha_1)^2} \cdot i\nu_i$$

$$\nu_i = (1-\alpha_1)^2 \, \alpha^{i-1}$$

$$i\nu_i \cdot r_{FT} = k_7 \sqrt{k_2 P_{H_2}} S^2 \alpha_M \cdot i\alpha_1^{i-1}$$

For olefins, the reaction will be:

$$i\nu_i CO + 2i\nu_i H_2 \longrightarrow \nu_i C_i H_{2i} + i\nu_i H_2O$$

$$CO + 2H_2 \longrightarrow \frac{1}{i} C_i H_{2i} + H_2O$$

$$i\nu_i \cdot r_{FT} = k_8 S \frac{\alpha_M}{(1-\alpha_2)^2} \cdot i\nu_i$$

$$\nu_i = (1-\alpha_2)^2 \, \alpha_2^{i-1}$$

The difficulty is the characterisation of the lump. It depends on the growth probability factor and we know that this value is not fixed, but it depends on temperature, $\frac{H_2}{CO}$ and molecular weight. So it is possible to calculate the stoichiometric coefficients or to describe in the simulator for a specific lump.

A way of overcoming this problem is by representing the lump of varying α with two lumps of constant α; one with low, α_L, and one with hight, α_H. The original and the modified reactions will then become as shown below.

$$CO + U_1H_2 \longrightarrow ... + \nu_l(\alpha)C_l + ...$$

$$CO + U_1H_2 \longrightarrow ... + \phi\nu_l(\alpha_L)C_{l,L} + (1-\phi)\nu_l(\alpha_H)C_{l,H} + ...$$

A different range is chosen for α_1 and α_2. Of course, for paraffins the bounds could be [0.7,0.97], and for olefins, the bounds could be [0.7,0.8]. As the growth factor α is changing, this will be reflected in a changing distribution between the two constant lumps, ϕ. The conservation of mass requires that the stoichiometric coefficient multiplied with the molecular mass of the lump remains the same.[10]

$$\nu_l(\alpha)\bar{M}_{n,L}(\alpha) = \phi\nu_l(\alpha_L)\bar{M}_{n,L}(\alpha_L) + (1-\phi)\nu_l(\alpha_H)\bar{M}_{n,H}(\alpha_H)$$

So the reaction will be:

$$CO + H_2 \longrightarrow \nu_l\left(\alpha_L\right)C_{l,L}$$

$$CO + \left(2 + \frac{1}{\bar{n}_L}\right)H_2 \longrightarrow \frac{1}{\bar{n}_L}C_{l,L} + H_2O$$

$$r_{FT}\cdot\bar{n}_L\left(1-\alpha_L\right)\alpha_L^{N-1} = k_7\sqrt{k_2P_{H_2}}S^2\frac{\alpha_M}{\left(1-\alpha_1\right)^2}\bar{n}_L\left(1-\alpha_L\right)\alpha_L^{N-1}\phi$$

where $\bar{n}_L$ and ϕ are:

$$\bar{n}_L = N + \frac{\alpha_L}{1-\alpha_L}$$

$$\phi = \frac{\nu_l\left(\alpha\right)\bar{M}_n - \nu_l\left(\alpha_H\right)\bar{M}_n\left(\alpha_H\right)}{\nu_l\left(\alpha_L\right)\bar{M}_n\left(\alpha_L\right) - \nu_L\left(\alpha_H\right)\bar{M}_n\left(\alpha_H\right)}$$

The liquid production is calculated in this case, with the optimized conditions. The productivity is lower and the reason comes from the variable alpha value. Even if the $\frac{H_2}{CO}$ is decreasing, the alpha value doesn't increase; probably it depends on $P_{H_2}^{-0.5}$ that it increases more than the hydrogen to carbon monoxide decreases.

So nC_{5+}will be 5000 kg/h.

Chapter 5

Conclusion

This project wants to give a “green” way to produce fuel. The aim is to optimize the plant, increasing the CO conversion and the carbon efficiency.

Certainly, gas to liquid process will have higher efficiency, but at same time the burning of traditional fossil fuels can also emit greenhouse gas, such as carbon dioxide, into the atmosphere and cause some other severe environmental issue.

This plant is produced in Norway, of course, the most of common type of biomass, in this country, has been chosen: Raw Wood.

Literature considers wood as one of the best kind of biomass, because of the high carbon efficiency and it is one of the richest in carbon, 48.2 wt%.

Pretreatment of the biomass should be properly performed to create suitable gasification feed with low cost and efficient logic chain. In the gasification process, some parameters have to be optimized, such as gasification temperature and gasifying agent; they are connected between them and so it should be optimized to convert biomass into hydrogen sufficient raw bio-syngas. With the cleaning process, the organic and inorganic impurities, such as sulfur and carbon dioxide, will need to be removed to meet requirements in the following catalytic conversion. The most of the attention is paid to optimize the FT reactor: cooling water temperature, lenght of reactor, number of stages, amount of the recycle. The catalyst is the heart of Fischer-Tropsch synthesis and in this case, using a determined kinetic (Todic model), the respective type of catalyst has been used (Cobalt based).

Two cases are done: alpha value fixed and alpha variable. It's possible to understand the difference from the following mass balance.

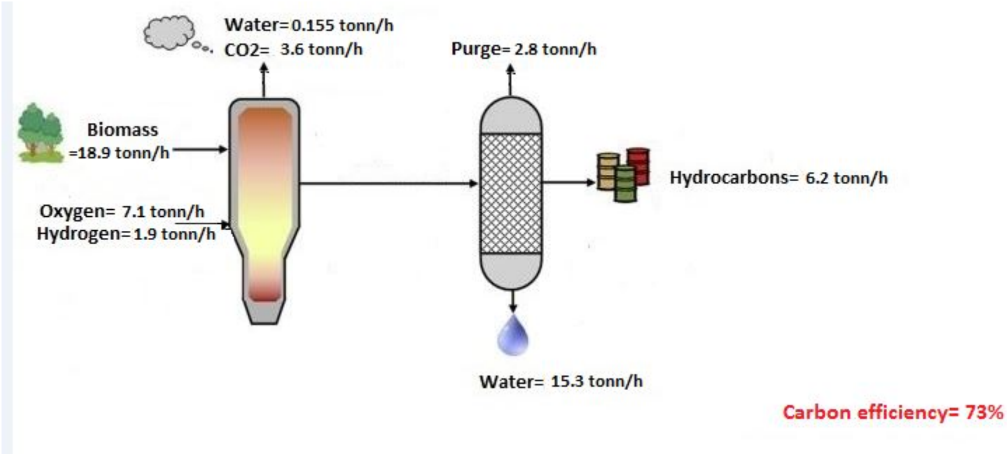


Figure 5.1: Mass balance (approximate case)

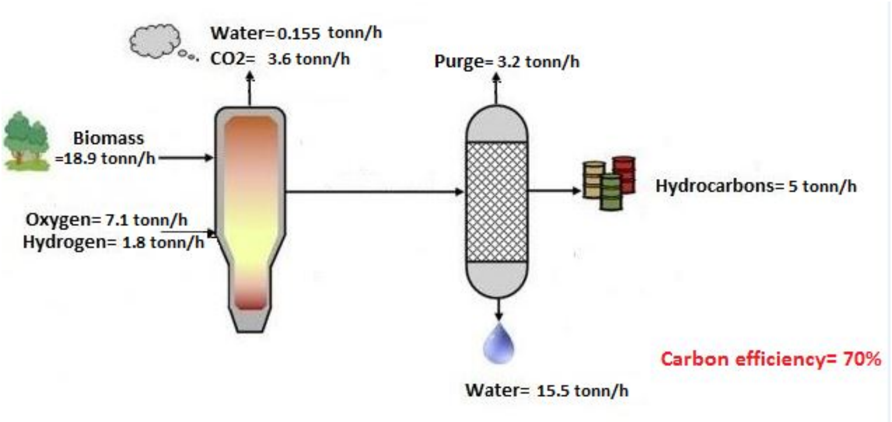


Figure 5.2: Mass balance (rigorous approach)

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