



**Faculty of Engineering**

**Master in Hydrocarbon Processing Engineering**

**Design and Cost Estimation of a Fisher-Tropsch Gas to Liquid  
Plant Using Natural Gas from Cabo Delgado and Air Blown  
Reformers**

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Supervisors:

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Maputo, 6<sup>th</sup> December 2021

University Eduardo Mondlane  
Faculty of Engineering  
Department of Chemical Engineering

Master in Hydrocarbon Processing Engineering

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Dissertation submitted to the Faculty  
of Engineering of Eduardo Mondlane University  
as a requirement to obtain a Master's Degree in  
Hydrocarbon Processing Engineering

Maputo, 6<sup>th</sup> December 2021

### **Declaration of Document Originality**

I, Lina Domingos Sambo declare that this dissertation is a product of my own work, and research, all the sources of information used here where accordingly referenced. I also declare that this is the first time this dissertation is being submitted to an academic institution with the purpose of obtain a master qualification.

Lina Domingos Sambo

## **Dedication**

My parents Domingos Sambo and Ana Filipe Messenga for  
their unconditional love and support.

## **Acknowledgments**

My gratitude to the Lord Jesus Crist, who gave me strength to go through this journey and this path.

To my parents Domingos Sambo and Ana Filipe Messenga who are always there to support me and my brother Domigos Sambo Jr., Anivaldo Sambo and Cleilson Sambo for their love and support.

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## **Abstract**

Natural gas, has been seen as a bridge between the fossil fuels and renewables, due to fact that natural gas is cleaner than other fossil fuels. But natural gas as such offers few utilities when compared to crude oils, so in order to take a best advantage of natural gas, different technologies can be used to convert natural gas into synthetic crude oil what gives a higher variety of products as crude oil but without sulphur and aromatics. In countries with natural gas reserves, gas to liquid has proven to be an ally to reduce the dependence on importation of crude oil products. Gas to liquid plants, from small to large scale have different cost of manufacturing involved.

Different techniques can be applied to estimate the cost of manufacture, these techniques involve empirical equations for cost considering the size of equipment proposed by different books, and cost available on websites.

COCO simulator was used to simulate three gases to liquid plants using the Fischer Tropsch process, and natural gas from Cabo Delgado province. Natural gas was composed mainly by methane (96.86%), hydrocarbons from ethane to decane (3.08%), and traces of benzene and toluene (0.06%), was fed to three plants at different capacities (100%, 75%, 50%) all of them following the same procedure so, prior to syngas production it was necessary to pass through an hydrotreater in order to remove the aromatics, and the Autothermal Reactor (Fired Reactor) was used to burn the higher hydrocarbons with air converting them into CO<sub>2</sub> and H<sub>2</sub>O. For the final step converting methane into syngas gas by reacting methane with steam, what lead to a CO:H<sub>2</sub> ratio of 1to 3, and with a high amount of nitrogen. Carbon monoxide to hydrogen ratio was adjusted with the use of a reverse water gas shift reactor. Fisher Tropsch reactor was simulated to operate at 220°C and 23 bar, in a fixed bed reactor, with no recycle of the unconverted CO and H<sub>2</sub>.

The annual production obtained from the three plants simulated, in metric tons per year was 82,624.25 Plant1; 68,845.65 Plant2; 49,589.96 Plant3, of synthetic crude starting from C1 to C29 and the main by product was water, and the final cost of manufacturing was estimated to be 5,180,497,221.01USD/year Plant1; 4,124,974,247.09 USD/year Plant2 and 1,608,009,196.52 USD/year Plant3 with 10% of accuracy.

**Keywords:** Natural gas, gas to liquid, cost of manufacturing, COCO

## Resumo

O gás natural tem sido visto como uma ponte entre os combustíveis fósseis e os combustíveis renováveis, pelo facto de o gás natural ser mais limpo que os outros combustíveis fósseis. Porém o gás natural como tal não oferece uma variedade de utilidades quando comparado ao petróleo bruto, então de modo a tirar maior proveito do gás natural, diferentes tecnologias podem ser aplicadas para converter o gás natural em crude sintético o que oferece assim uma maior variedade de produtos como o petróleo bruto, mas sem o enxofre e os produtos aromáticos. Em países que contém reservas de gás natural, o processo de conversão de gás para líquidos tem se mostrado um grande aliado para reduzir a dependência na importação de produtos derivados de petróleo bruto. As plantas de conversão de gás para líquido de pequenas a grandes escalas apresentam diferentes custos de manufacturação.

Diferentes técnicas para estimação de custos de manufacturação podem ser usadas, essas técnicas envolvem equações empíricas para determinar o custo em função do tamanho do equipamento apresentados por diversos livros ou custos publicados em websites.

O simulador COCO foi usado para simular três plantas de conversão de gás para líquidos usando o processo de Fischer Tropsch, e gás natural da provincial de Cabo Delgado, a simulação foi feita usando apenas um reactor para o processo de Fischer Tropsch (reactor de leito fixo). O gás natural usado era composto maioritariamente por metano (96.86%), hidrocarbonetos de etano a decano (3.08%) e traços de benzeno e tolueno (0.06%) foi usada para alimentar três plantas com diferentes capacidades (100%, 75%,50%) todos seguindo os mesmos procedimentos.

A produção anual obtida das três plantas simuladas em toneladas métricas por ano foi de 82,624.25 planta1, 68,845.65 planta2 e 49,589.96 planta 3 de crude sintético começando de C1 à C29 e o maior subproduto foi a água, e o custo final de manufacturação foi estimado em 5,180,497,221.01 dólares/ano planta1, 4,124,974,247.09 dólares/ano planta 2 e 1,608,009,196.52 dólares por ano com 10% de exactidão.

**Palavras-Chave:** Gás natural, gás para líquidos, custo de manufacturação, COCO

## **Abbreviations**

ASF: Anderson-Schultz-Flory

ATR: Autothermal Reformer

CTL: Coal to Liquids

FTS: Fisher-Tropsch Synthesis

ft<sup>3</sup>: Cubic feet

GJ: Giga Joule

GTL: Gas to Liquid

HTFT: High Temperature Fisher Tropsch

hp: Horse power

J: Joule

Kg: kilogram

K: Kelvin

LPG: Liquefied Petroleum Gas

LNG: Liquefied Natural Gas

LTFT: Low Temperature Fischer Tropsch

m: Meters

m<sup>2</sup>: Square meters

Mbpd: Millions of barrels per day

MZN: Mozambican metical

P: Pressure

Pa: Pascal

RWGS: Reverse Water Gas Shift

T: Temperature



USD: United States Dollar

W: Watt

**Greek Letters**

Variant  $\alpha$ : alpha

Variant  $\beta$ : beta

Variant  $\gamma$ : gama

Variant  $\Delta$ : delta

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## 1. Introduction

Mozambique has been in the center of world's attention due to the huge gas reserves that have been discovered. The project of exploration of this natural gas will consist of liquefying the gas to produce liquefied natural gas (LNG) and transport to Asian market (CIP, 2015). To transform natural gas into liquid form, is necessary to shrink the gas more than 600 times by applying cryogenic temperatures to induce a physical transformation from the gaseous state to the liquid state that will then be transported in ships to its final destination (Wood *et al*, 2012).

But natural gas can be raw material to many other processes not only the production of LNG, the other possibility that has been gaining attention is the production of synthetic fuels through the gas to liquids (GTL) process using the Fischer-Tropsch reaction, where the final product is synthetic crude that can be distributed as crude oil and upgrade to obtain a range of synthetic fuels (Al- Shalchi, 2006). While LNG offers a physical transformation (the final product is still natural gas), GTL technology gives the possibility of chemically convert methane into long chain hydrocarbons that exists in liquid state at or closed to atmospheric conditions (Wood *et al*, 2012) and can be transported using the same crude oil distribution routes (Wakamura, 2005).

South Africa, Qatar and Malaysia are examples of countries that have been successful on the development of FTGTL technologies (Glebova, 2013), what has contributed significantly to reduce their dependence on crude oil products. In South Africa for example 30% of gasoline and diesel needs are coming from FT technology (World Coal Institute, 2006).

This dissertation is going to be about the design a FTGTL process using natural gas from Mozambique specifically from Cabo Delgado and air as opposed to oxygen in production of syngas, and the economic costs involved with the manufacture of synthetic fuel.

## **1.1. Motivation**

Although GTL and LNG are both forms of transforming natural gas into liquids, it is important to understand that from LNG the final product is still natural gas, which needs to be regasified for use. But regarding GTL the final product is a synthetic crude oil that can then be distilled into a high range of products, contributing to add value to natural gas as raw material.

Besides, GTL offers huge economic value to the countries and companies that control the gas reserves, contribute to the monetization of existing natural gas reserve and the creation of environmentally superior clean liquid fuels ranging from gasoline to middle distillates (Al- Salchi, 2006). In addition, the GTL technology, contributes to the production of almost zero Sulphur, high cetane, low aromatic diesel and naphtha which can be sold regionally and internationally (El Shami, 2004).

## **1.2. Objectives**

This dissertation was written with the following objectives:

### **General Objective**

Design and cost estimation of a Fisher-Tropsch Gas to Liquid Plant using natural gas from Cabo Delgado and air blown reformers.

### **Specific Objective:**

- Simulate a FTGTL plant using COCO software;
- Estimate the cost of manufacturing of synthetic crude oil; and
- Perform a comparison between FTS process and liquid fuel importation.



### **1.3. Contribution**

This project is driven by the need of adding value to the abundant resource, that is going to be commercialized as a raw material, by converting it into synthetic crude oil what can contribute to increase the range of products obtained from natural gas. This will also contribute to the reduction on the dependence on crude oil fuels importation, since the fuel that is commercialized in the country is imported.

### **1.4. Problem Statement**

In the year of 2020 Mozambique expended USD 639 million, to import liquid fuels in an amount of 1.3 million of metric tons, these liquid fuels include LPG (2%), Jet oil (5%), Diesel (70%), and Gasoline (23%) (MIREME, 2020).

Most of fuel coming to Mozambique is imported from Persian Gulf and Mediterranean Sea, from the liquid fuel imported only 35% stays in Mozambique and 65% goes to the countries that do not have access to the sea as Malawi, Zambia and Zimbabwe (CIP, 2016).

But on the other side, Mozambique has discovered to possess gas reserve of about 150 TCF that is going to be liquefied and exported to Asia (CIP, 2016), an option that is considered uneconomic by Al-Shalshi, 2006 because the transportation by pipeline or liquifying the gas and transport LNG tankers is expensive and leaves the field undeveloped.

The solution proposed here is to convert natural gas into synthetic crude oil to satisfy the market and reduce the dependence on liquid fuels importation because, GTL technology offers tremendous economic value to the countries that control the gas reserves, and gives the possibility to convert a significant percentage of gas into several hundred billion barrels of liquid petroleum, enough to supply the world for the next 25-30 years (Al-Shalshi, 2006).

Smaller and modular GTL plants (using fixed bed reactors for easily scale up or down by increasing the number of tubes) are suitable for use in remote location, in contrast to conventional GTL plants, they are designed for economical processing of smaller amount of gas ranging from 100 million cubic meters to 150 million cubic meters and is possible to produce 1,000-15,000 barrel/day (Brancaccio et al., 2017). Smaller scale

GTL operation also represents lower risks to producers, since plants are smaller the construction costs are reduced and since the plants are modular investment can be phased and the time construction is short, vary from 18-24 months (Brancaccio et al.,2017). So, the problems stated in this dissertation are:

- What are the costs involved in the production of synthetic crude oil?
- How the process is affected by the usage of air instead of oxygen?

### **1.5. Dissertation Structure**

The structure used in this dissertation is the same adopted by the Faculty of Engineering, Eduardo Mondlane University. The dissertation is composed by 6 chapters that contain the theoretical review, methodologies, results and conclusion. The dissertation breakdown is as follows:

#### **Chapter 1**

In the first chapter is made the introduction of the dissertation, the objectives, contribution and motivation are presented and also. The problem statement is also made here.

#### **Chapter 2**

The chapter 2 presents the literature review and all the theories related to the topic in discussion, steps involved in the Fischer Tropsch process, the equipment needed and chemical and mathematical equations.

#### **Chapter 3**

In the chapter 3 is presented the methodology used to develop the dissertation, the process steps description and flowsheet of the process.

## **Chapter 4**

The fourth chapter contains the cost estimation of all the products involved in the simulation. The costs calculated here involve raw material, equipment, energy demand and waste treatment.

## **Chapter 5**

The chapter 5 presents the results and discussion of all the costs obtained in the chapter 4, and comparing to cost obtained by other authors.

## **Chapter 6**

The chapter 6 contains all the conclusions from all the calculations and simulations done and recommendations for future works to be developed.

## **2. Literature Review**

Gas-to-liquid (GTL) consists a series of processes, mainly chemical reactions, to convert natural gas into synthetic fuels, that can be further processed (Al-Shalshi, 2006) into clean- burning diesel fuel, kerosene, gas base oil and naphtha (Brancaccio et al., 2017), being the Fischer-Tropsch reaction the heart of the process (Siemens, 2007).

The GTL technology enables the conversion of natural gas into clean naphtha, kerosene and light oils, what makes possible to ensure that the same routes of distribution of petroleum can be used to the distribution of synthetic fuels ( Wakamura, 2005), thus this technology also contribute to the preservation of the environment, with the production of odorless and colorless hydrocarbon with very low levels of impurities (Brancaccio et al., 2017) and diversification of local resources (Wakamura,2005).

Speight, 2008 refers that the advantages of GTL technology include:

- Allowing the owners of natural gas reserves a way to bring their gas to the market;
- Tighter air quality standards will create high demand for low sulphur diesel;
- Diesel fuel is ultra-low sulphur free and has higher cetane number than diesel from crude oil.

### **2.1. Theoretical framework**

#### **History review**

GTL and CTL (coal to liquids) technologies were developed in Germany during the 1920s, using a process that came to be known as Fischer- Tropsch (Wood, 2012), when Germany found it increasingly difficult to source conventional oil and refined product supplies for its war effort and thus incentivized to develop alternative options (Glebova, 2013).

The first production of synthetic liquid hydrocarbons has been made from syngas by Franz Fischer and Hans Tropsch. By 1944, using the Fischer- Tropsch technology Germany had developed this to an industrial scale with 25 plants producing 124 Mbpd of synthetic fuels from coal (Brancaccio et al., 2017).

The first GTL plant was developed by PetroSA in 1992, this plant was producing 36Mbpd and was located in Mossel Bay, South Africa. The plant uses methane –rich natural gas into high quality, low Sulphur synthetic fuels products including unleaded petrol, kerosene, diesel, propane, distillate, process oils and alcohols (Brancaccio et al., 2017).

In the table below is possible to have an overview of GTL process worldwide:

Table 1: GTL Plants worldwide edited from Pondini and Erbert ,2013

Company	Country	Capacity (barrels/day)	Raw Material	Status
Sasol	South Africa	150,000	Coal	Operational
	China	2x80,000	Coal	Abandoned
	Australia	30,000	Natural Gas	Study
	Qatar	34,000	Natural Gas	Operational
	Nigeria	34,000	Natural Gas	Operational
Shell	Malaysia	14,700		Operational
	Qatar	140,000		Operational
	Indonesia	75,000		Study
	Iran	70,000		Abandoned
	Egypt	75,000		Study
	Argentina	75,000		Study
	Australia	75,000		Study
BP	USA	300	Natural Gas	Operational
Mossgas	South Africa	22,500	Natural Gas	Operational

## 2.2. Fischer-Tropsch process description

### Definition

Fisher-Tropsch process is defined as a catalyzed chemical reaction, in which carbon monoxide and hydrogen are converted into long chain liquid hydrocarbons of various forms mainly using catalysts based on iron and cobalt (Speight, 2008).

Being the main purpose of this process to produce synthetic petroleum substitute to use as synthetic lubrication oil or as synthetic fuel (Speight, 2008).

So, the Fischer-Tropsch synthesis will convert hydrogen and carbon monoxide-synthesis gas which can be produced from a variety of carbon bearing feed stock (natural gas, coal, biomass)- into a boiling range of hydrocarbons (El Shamy, 2004).

And this can be considered an alternative route to obtain fuels and chemicals, rather than the actual dominant petroleum resources (Al-Shalchi, 2006). Due to absence of Sulphur in the final products, fuels from FT process can be used as blending stocks for transportation fuels derived from crude oil.

### 2.2.1. Process steps

The production of synthetic fuels from natural gas comprises 3 steps:

- **Synthesis gas production:** for this step carbon and hydrogen are divided from the methane molecule and reconfigured by steam reforming or partial oxygenation, the syngas produced consists primarily of carbon monoxide and hydrogen (wood *et al.*, 2012)
- **Fischer Tropsch Synthesis:** this is central part of the process, in the Fischer Tropsch reactors the syngas is processed creating a wide range of paraffinic hydrocarbons (Synthetic crude or syncrude) (wood *et al.*, 2012)
- **Product upgrade:** here is where the synthetic fuel is upgraded into different products, using conventional refinery cracking processes to produce diesel naphtha and lube oil for commercial markets (wood *et al.*, 2012)

These 3 steps are represented in the flowsheet that is shown in the figure 1:

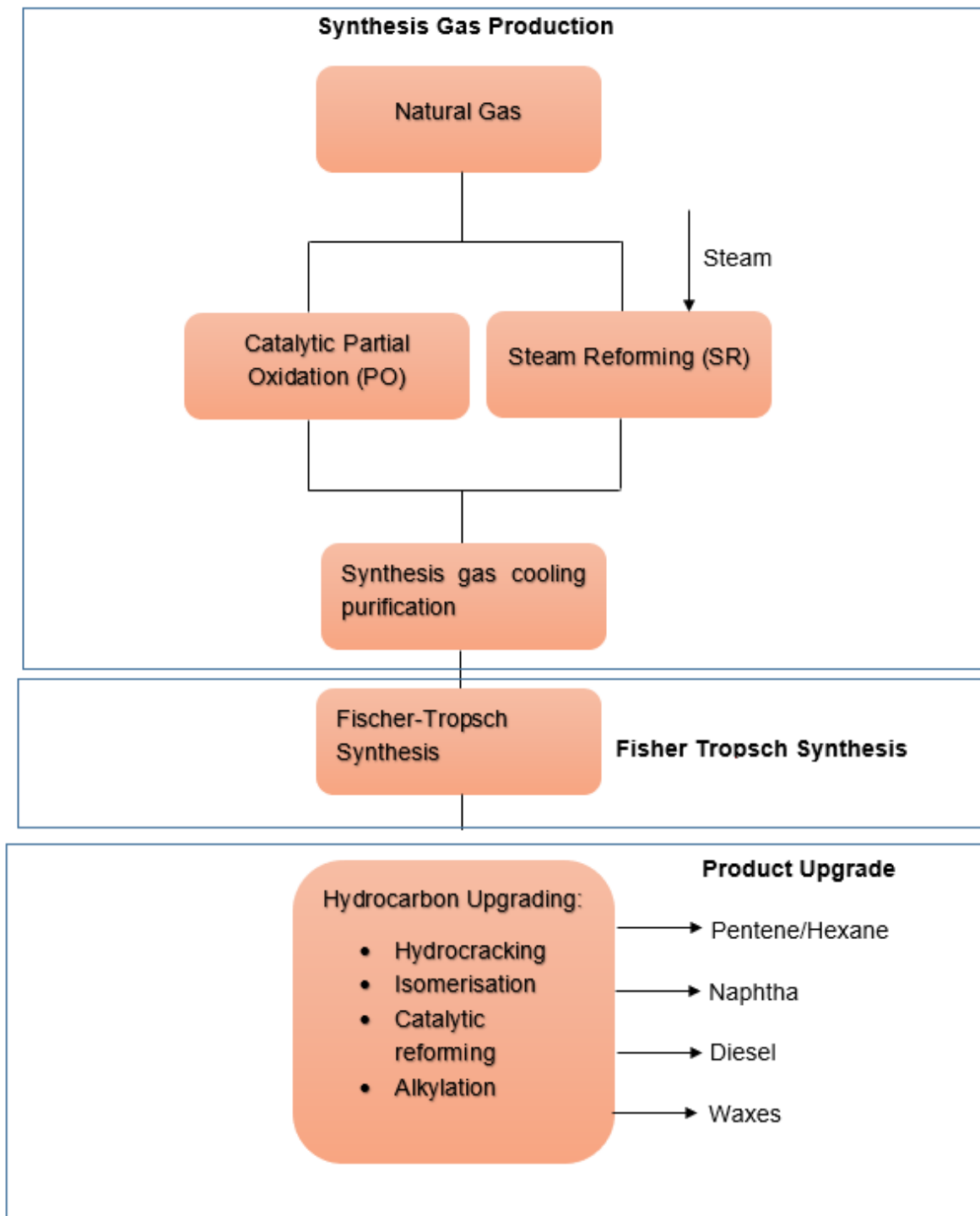


Figure 1: Fisher- Tropsch process flowsheet Edited from: [www.scribd.com/doc/GTL-technology](http://www.scribd.com/doc/GTL-technology)

The process of production of syngas starting from natural gas as raw material, begins with the cleaning of natural gas.

Natural gas is a gaseous fossil fuel consisting primarily of methane but including significant quantities of ethane, propane, butane, carbon dioxide, nitrogen, helium and hydrogen sulfide (Speight, 2008).

Natural gas is considered as an environmentally friendly clean fuel, offering important environmental benefits when compared to other fossil fuels. The superior environmental qualities over coal or crude oil are that emissions of sulphur dioxide are negligible or that the levels of nitrous oxide and carbon dioxide emissions are lower, this helps to reduce problems of acid rain, ozone layer, or greenhouse gases (Mokhatab, *et al.*, 2006).

The typical composition of natural gas is described by Mokhatab, *et al.*, 2006 as being the following:

Table 2: typical composition of natural gas edited from: Mokhatab, *et al.*, 2006

Name	Formula	Volume (%)
Methane	CH <sub>4</sub>	85
Ethane	C <sub>2</sub> H <sub>6</sub>	3-8
Propane	C <sub>3</sub> H <sub>8</sub>	1-2
Butane	C <sub>4</sub> H <sub>10</sub>	<1
Pentane	C <sub>5</sub> H <sub>10</sub>	<1
Carbon dioxide	CO <sub>2</sub>	1-2
Hydrogen sulfide	H <sub>2</sub> S	<1
Nitrogen	N <sub>2</sub>	1-5
Helium	He	<0.5



### **2.2.2. Production of syngas:**

The production of syngas is described in this sub-chapter

#### **Natural gas pre-reformer**

The carbon monoxide and hydrogen needed for the conversion in the FT process are obtained from methane molecule and reconfigured by steam reforming. (Brancaccio et al., 2017).

Oil and natural gas are the most important raw material for organic chemical industry, the methods employed to remove acidic components that include mainly H<sub>2</sub>S and CO<sub>2</sub> and other impurities from hydrocarbons include chemical reactions, absorption, adsorption and permeation (Kolmetz, 2013).

Pre-reforming constitutes an established technology with economic and operational benefits, on the overall syngas production, representing an important tool especially for the revamping of steam reforming plants (Trunfio & Arena 2014).

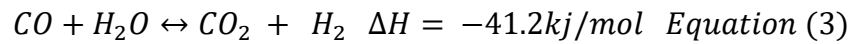
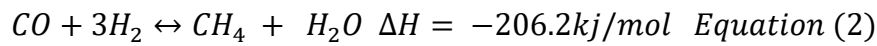
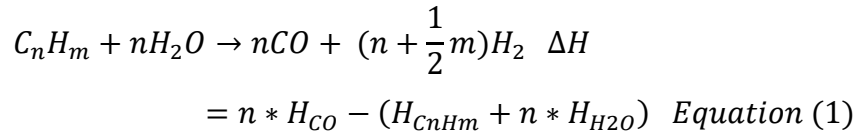
A pre-reforming unit consists of a tubular adiabatic reformer allowing higher hydrocarbons feed to be converted to CH<sub>4</sub>, CO<sub>2</sub> and CO at low temperatures typically between 450°C-550°C, pressure from 5 to 30 bar and steam to carbon ratio between 2-8 (Christensen, 1996) with the following advantages (Trunfio & Arena, 2014):

- An increased production capacity with smaller reformer furnace;
- A higher feedstock flexibility;
- Enhanced steam reformer tube and catalyst lifetime;
- Design of innovative process configuration for low energy cost consumption and investment cost

Industrial gas reforming catalysts are mainly based on nickel, and nickel catalysts are sensitive to sulphur, and halogen compounds present on natural gas that act as poison to the catalyst (De Klerk, 2011). The pre-reforming process helps to avoid the risk of carbon formation inside tubular reformer (Trunfio & Arena, 2014), by conversion of higher hydrocarbons in the feedstock.

Moreover, the pre-reforming process, ensure the elimination of any traces of unsaturated compounds and to convert all sulphur, (Trunfio & Arena, 2014) and halogens into hydrogen sulfide and hydrogen acid respectively.

On the second step the hydrogen sulfide and hydrogen acid are quantitatively removed (De Klerk, 2011) to enhance steam reformer catalyst lifetime.



The reaction in the steam reformer of higher hydrocarbons is irreversible, and all higher hydrocarbons are converted if provided sufficient catalyst activity exists. The steam reformer reaction (1) is followed by the establishment of the equilibrium of the exothermic methanation (2) and water gas shift reaction (3) (Christensen, 1996).

The kinetics of higher hydrocarbon steam reforming is described by Tottrup., 1982 as being the following:

$$r_i = \frac{8 * 10^5 * \exp\left(\frac{-67.8 \text{ kJ}}{RT}\right) * P_{C_nH_m}}{\left[1 + 25.2 * P_{C_nH_m} * \left(\frac{P_{H_2}}{P_{H_2O}}\right) + 0.077 * \left(\frac{P_{H_2O}}{P_{H_2}}\right)\right]^2} \left(\frac{\text{mol}}{\text{gh}}\right) \quad \text{Equation (4)}$$

The methanation kinetics is given by Ken & Jess, 2018

$$r_{CO} = \frac{K_{CO}(T)C_{CO}C_{H_2}}{(1 + k_1C_{CO} + k_2C_{CH_2O})^2} \quad \text{Equation (5)}$$

$$K_{CO}(T) = K_{0,CO} * \exp\left(\frac{-E_{a,CO}}{RT}\right) \quad \text{Equatio (6)}$$

$$E_{a,CO} = 90 \frac{\text{kJ}}{\text{mol}} \quad \text{Equation(7)}$$

$$K_{0,CO} = 3.61 * 10^7 \text{ m}^6 \text{ s}^{-1} \text{ kg}^{-1} \text{ mol}^{-1} \quad \text{Equation (8)}$$

$$k_1 = \frac{23m^3}{mol} \text{ Equation(9)}$$

$$k_1 = \frac{0.3m^3}{mol} \text{ Equation(10)}$$

The water gas shift kinetics is given by Luyben,2016

$$r_{wgs} = 2.610^{-7} \exp\left(\frac{-47,400}{RT}\right) P_{CO}P_{H_2O} \text{ Equation (11)}$$

### **Steam Reforming**

Steam reforming employs steam to convert methane on a nickel catalyst at a temperature of 820°C-1,000°C and pressure of 20-25 bar. This process produces a H<sub>2</sub>: CO ratio typically above 5:1, so higher than required to the Fischer-Tropsch synthesis (De Klerk, 2011).

The reaction is endothermic and heat is supplied externally by combustion of a fuel to drive the reforming reaction (De Klerk, 2011), natural gas must be desulphurized to prevent nickel catalyst deactivation (Al-Shalshi, 2006).

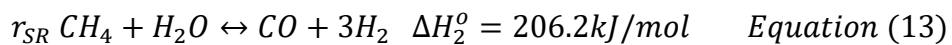
### **Autothermal reforming**

The combined Autothermal Reforming, involves reactions between a treated natural gas and steam at elevated temperature and pressure over a catalyst, normally nickel. The autothermal reforming is preferred because contributes to lower the total reaction temperature and a reduction in oxygen consumption. The ratio H<sub>2</sub>: CO is of 2:1 what is ideally needed for the next step that is the FT synthesis (Al- Shalchi, 2006).

The reaction ranges up to 1,000°C and 30 atm, the reaction products are H<sub>2</sub>, CO, CO<sub>2</sub> and methane together with undecomposed steam. These gases are then passed through a second reforming stage in a secondary reactor (Al-Shalchi,2006).

Since the outlet stream of the Autothermal reformer contains high percentage of carbon dioxide, a methane dry reformer is added to react the CO<sub>2</sub> and methane with the purpose of reducing greenhouse gas emission and increase syngas production (Wu and Tunpanututh, 2012)

The major reactions that take place in the autothermal reformer are described as being the following (Wu and Tunpanututh, 2012):



The autothermal reforming takes place in the autothermal reformer and this equipment as the following general design:

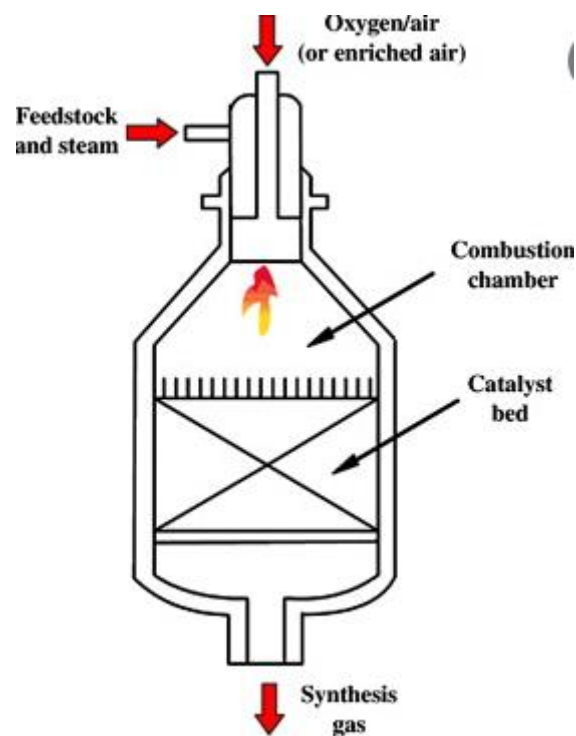


Figure 2: Autothermal Reformer from: [www.sciencedirect.com](http://www.sciencedirect.com)

## Reverse water gas shift

The RWGS reaction is the reversible hydrogenation of carbon dioxide to produce carbon monoxide and water, since carbon dioxide is an unreactive molecule so the reaction to convert it to the more reactive is energy intensive (Pastor-Perez *et al.*,2017). The Fischer- Tropsch process has been proposed as feasible solution for carbon dioxide conversion and intended to be carried out in conjunction with RWGS (Pastor-Perez *et al.*,2017).

Carbon dioxide has been recognized as an abundant and inexpensive source of carbon for chemical industries.

Reverse water gas shift reaction is one of the important reactions because result in carbon monoxide that can be utilized for the production of valuable compounds such as methanol and hydrocarbons (Ishito *et al.*,2015), so the conversion of carbon dioxide into carbon monoxide through RWGS is a suitable route that can contribute to the valorization of carbon dioxide (Pastor-Perez *et al.*,2017).



The kinetics for RWGS is given by Luyben,2014 as being the following

$$r_{RWGS} = 10^{-11} * \exp\left(\frac{-50,000}{R*T}\right) * P_{CO_2}P_{H_2} \text{ Equation (15)}$$

The kinetics of reactions of combustion (equation12) and steam reforming (equation13) are described by Arpornwichanop *et al*, 2010 and Wu and Tungpanututh, 2012 as being the following:

$$r_{comb.} = \frac{k_{1a}P_{CH_4}P_{O_2}^{0.5}}{(1 + K_{CH_4}^cP_{CH_4} + K_{O_2}^cP_{O_2})^2} \text{ Equation (16)}$$

$$r_{SR} = \frac{\frac{k_2}{P_{H_2}^{2.5}} * \left(P_{CH_4}P_{H_2O} - \frac{P_{H_2}^3P_{CO}}{K_{eq2}}\right)}{\left(1 + K_{CO}P_{CO} + K_{H_2}P_{H_2} + K_{CH_4}P_{CH_4} + K_{H_2O} \frac{P_{H_2O}}{P_{H_2}}\right)^2} \text{ Equation (17)}$$

Where:

$k_{1a}$ ,  $k_2$ : are the reaction constants:

$$k_i = k_{0i} \exp\left(\frac{-\Delta E_i}{RT}\right) \text{ Equation (18)}$$

$K_{CH_4}^C, K_{O_2}^C$  : are the adsorption constants for the combustion of methane:

$$K_i^C = K_{0i}^C \exp\left(\frac{\Delta H_i^C}{RT}\right) \text{ Equation (19)}$$

$K_{eq1}$ ,  $K_{eq2}$ : are the equilibrium constants:

$$K_{eqi} = K_{eq0} \exp\left(\frac{-\Delta H_i}{RT}\right) \text{ Equation (20)}$$

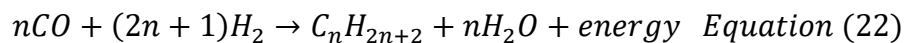
$K_{CH_4}$ ,  $K_{H_2}$ ,  $K_{CO}$ ,  $K_{H_2O}$ : are the adsorption constants of the species:

$$K_i = K_{0i} \exp\left(\frac{-\Delta H_i}{RT}\right) \text{ Equation (21)}$$

The values of the constants are found on the appendix A.

### 2.2.3. Fischer Tropsch synthesis

In the FT synthesis, carbon monoxide and hydrogen are polymerized into long chain hydrocarbons according to the reaction (Wood *et al*, 2012):



Fischer-Tropsch synthesis has been recognized as a polymerization reaction with the basic steps (Vander Laan ,1999):

- CO adsorption on the catalyst surface;
- Chain initiation by the CO dissociation followed by hydrogenation;
- Chain growth by insertion of additional CO molecules followed by hydrogenation;
- Chain termination;

- Product desorption from catalyst surface.
- Reabsorption and further reaction

The kinetics of these processes has been described by Jess and Kern 2009 as being the following:

$$-r_{m,H_2} = \frac{K_{mH_2LH} C_{CO,g} C_{H_2,g}}{(1 + K_{CO} C_{CO})^2} \text{ Equation (23)}$$

$$K_{m,H_2,LH} = 0.8 \exp\left(\frac{-37.400}{RT}\right) \left[\frac{m^6}{kgcat \text{ mol s}}\right] \text{ Equation (24)}$$

$$K_{CO} = 5 * 10^{-9} \exp\left(\frac{68.500}{RT}\right) \left[\frac{m^3}{mol}\right] \text{ Equation (25)}$$

$$r_n = \frac{i * \alpha^{(n-1)} r_{CO}}{\sum_i i \alpha^{i-1}} \text{ Equation (26)}$$

The process involves some carbon dioxide emission and water/steam production with the liquid hydrocarbon production.

Typically, FT reaction compete with methanation, so in order to promote the FT over the methanation the reaction is run at low temperature 220°C-250°C and a pressure of 2-3 MPa with carefully selected cobalt-based catalyst (Wood *et al*, 2012).

According to Pondini,2013, many authors divide the FT reaction operation condition in Low temperature (LTFT) and high temperature (HTFT)

**HTFT:** the high temperature FT because of process condition,320°C- 350°C (Abusrafa *et al.*,2020) temperature range and 2.5MPa of pressure, and iron catalyst involved only (Pondini and Erberts, 2013), the Syncrude produced includes a high percentage of short chain (<10 carbon atoms) with significant amount of propane and butane mixed with olefins, with the HTFT is possible to achieve a conversion of 85% (Wood *et al*,2012)

**LTFT:** the low temperature FT is based on cobalt or iron catalyst, depending on the needed final product (Pondini and Erbert, 2013) and the operational conditions are temperature range of 200°C-250°C and pressure of 2MPa, produce longer chain

hydrocarbons up to 100 atoms of carbon and is possible to achieve a once through conversion of 60% (Wood *et al*, 2012).

The table 3 shows the composition of synthetic crude oil (High temperature Fischer Tropsch and Low temperature Fischer Tropsch) and crude oil

Table 3: composition of sycrude oil and crude oil from Pondini and Erbert, 2013

Property	HTFT <sup>a</sup>	LTFT <sup>b</sup>	Crude oil
Paraffins	>10%	Major product	Major Product
Naphthalene	<1%	<1%	Major product
Olefins	Major products	>10%	None
Aromatics	5-10%	<1%	Major product
Oxygenates	5-15%	5-15%	<1% O(heavy)
Sulphur species	None	None	0.1-5% S
Nitrogen Species	None	None	<1% N
Water	Major by product	Major by product	0-2%

a Sasol advanced Synthol (Secunda); Synthol (Mossel bay)

b Shell middle distillate synthesis (Bintulu) Sasol slurry phase distillate process (Ras Laffan and SasolBurg) Arge Sasolburg

#### 2.2.4. Product Upgrade

Conventional refinery process can be used to upgrade the FT synthetic crude (Vander Laan, 1999), and although refining FT crude and crude oil, can be equally complex, FT-crude has more favorable characteristics than crude oil due the absence of sulphur and nitrogen compound, so, the overall FT crude refinery can be considered more environmentally friendly (Pondini, 2013).

Vander Laan, 1999 describe the fuels produced from the FT synthesis process as being of very high quality, due to a very low aromaticity and zero Sulphur content. Of special interest is the diesel fuel fraction because it requires a little processing from FT crude and has desirable characteristics, high centane number and burns cleanly in a compression ignition engine (El Shamy, 2004).



The characteristics of the crude will be affected by the operational conditions, so, since HTFT- reactor mainly produces olefins and smaller amount of paraffins this leads to high octane number compared to LTFT crude and conventional crude oil, the octane number describes the resistance of gasoline against knocking due to the presence of highly branched alkanes (Pondini, 2013). On the other side LTFT crude will have a better cetane number due to the high amount of linear paraffins and low aromatics which gives the diesel fuel better combustion quality during compression ignition (Pondini, 2013).

A number of possible processes for FT products are: wax hydrocracking, distillate hydrotreating, catalytic reforming, naphtha hydrotreating, alkylation and isomerization (Vander Laan, 1999).

The table 4 shows the products obtained from crude oil upgrade according to Vander Laan, 1999

Table 4: Products from crude oil upgrade Adapted from Vander Laan, 1999

Name	Synonyms	Components
Fuel gas	-	C <sub>1</sub> -C <sub>2</sub>
LPG	-	C <sub>3</sub> -C <sub>4</sub>
Gasoline	-	C <sub>5</sub> -C <sub>12</sub>
Naphtha	-	C <sub>8</sub> -C <sub>12</sub>
Kerosene	Jet fuel	C <sub>11</sub> -C <sub>13</sub>
Diesel	Fuel oil	C <sub>13</sub> -C <sub>17</sub>
Middle distillates	Light gas oil	C <sub>10</sub> -C <sub>20</sub>
Soft wax	-	C <sub>19</sub> -C <sub>23</sub>
Medium wax	-	C <sub>24</sub> -C <sub>35</sub>
Hard wax	-	C <sub>35+</sub>

### 2.2.5. Types of reactors

The FT reactor is highly exothermic, so rapid heat removal and temperature control are the major consideration in the design of suitable reactors in order to avoid undesirable increase methane production and catalyst damage (Subiranas, 2008). FT synthesis can be either carried out in a fixed bed, slurry phase or fluidized bed reactors

as described by Pondini, 2013. The tubular fixed bed and slurry reactors are used for LTFT to obtain long chain hydrocarbon with iron based or cobalt based catalyst (Subiranas, 2008).

The different technologies lead to variety of reactor designs:

- **Fixed bed multi-tubular reactor**

It was first developed in Germany after World War II, it operated at medium pressure and was run in once through mode, the preferred fixed reactor type is a multi-tubular, with the catalyst placed in the tubes and cooling medium (water) in the shell sides (Steynberg and Dry, 2004)

To achieve a high heat transfer, narrow tubes and a turbulent gas flow within the tubes are required, the syngas enters the reactor from the top at which also the feed water inlet and steam outlet is situated. At the bottom separated hydrocarbon waxes and shorter hydrocarbons stream which is still in gaseous state exits the reactor (Pondini and Erbert, 2013).

Multi-tubular fixed-bed reactors are simple to operate and can be used over a wide range of temperature. There is no problem separating liquid products from the catalyst. The main disadvantages of this reactor type are described by Subiranas, 2008 as being the following:

- i) High capital cost;
- ii) Scale-up is mechanically difficult;
- iii) It is not possible to replace the catalyst during operation;
- iv) High pressure drops (0.3-0.7 MPa), this last disadvantage is coupled with high gas compression costs.

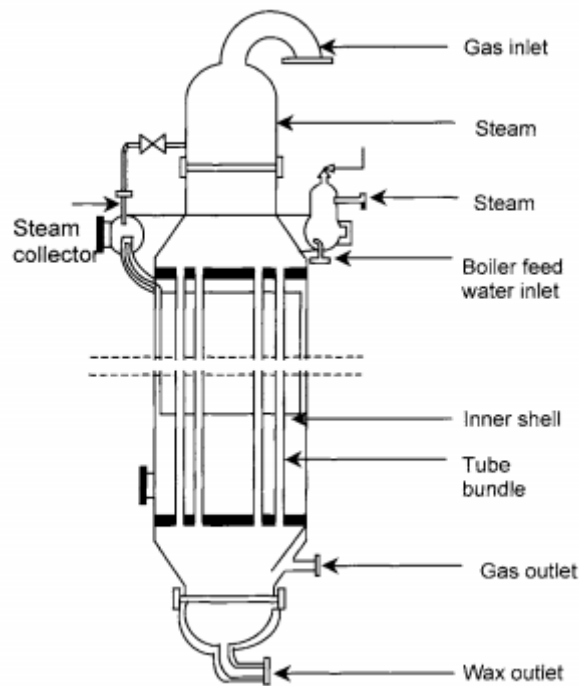


Figure 3: Multi-tubular fixed bed reactor from Steynberg and Dry 2004

- **Slurry reactor**

Different sizes of slurry reactors were tested in the 1950's and 1960's by Germany, England and USA, this system, was considered to be suitable for production of wax at low temperature FT operation since the liquid wax itself would be a medium where the finally divided catalyst is suspended (Steynberg and Dry, 2004)

The syngas is entering from the reaction bottom after passing a gas distributor it enters the slurry bed, in which the solid catalyst is suspended and dispersed in a liquid with high thermal capacity. The syngas bubbles through the slurry phase in which a heat exchanger is installed. The product gas exits through the reactor to where the catalyst and wax mixture is exiting the reactor on the side. The advantage of this technology is the low operation cost due to lower catalyst consumption and lower pressure drop within the reactor (Pondini and Erbert, 2013)

The main difficulty with the commercial application is the separation of the wax product from the catalyst. (Subiranas, 2008)

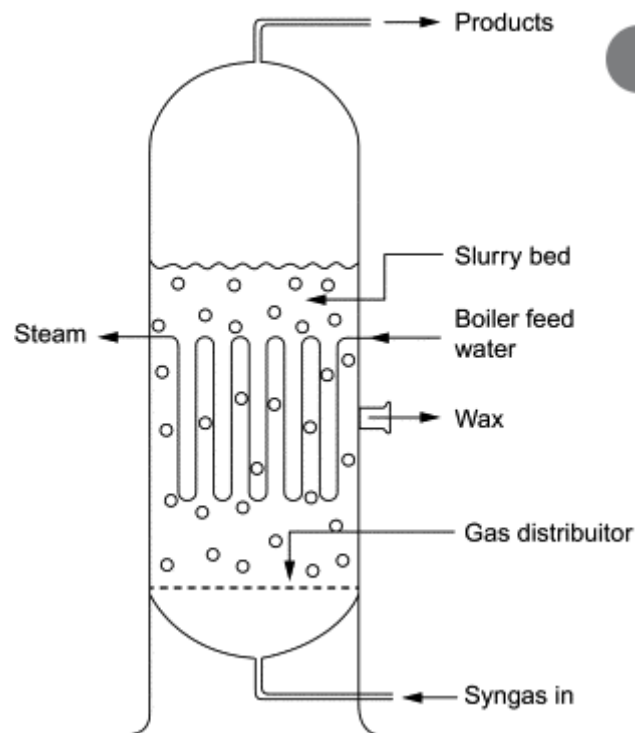


Figure 4: Slurry bed reactor from Steynberg and Dry 2004

- **Circulating fluidized bed**

The circulating fluidized bed technology was mainly used by Sasolburg in South Africa at the Secunda Complex. The syngas enters the reactor from the bottom and gets in contact with the solid catalyst (Pondini and Erbert, 2013). Subiranas, 2008 describes that HTFT synthesis is operated in a Circulating fluidized bed when the necessary products are alkenes and/or straight run fuels.

The necessary amount of catalyst is controlled by a slide valve. The syngas catalyst mixture streams into the riser, in which the reaction takes part since it is important to maintain near isothermal conditions heat exchangers are installed within the riser (Pondini and Erbert, 2013). The gas stream afterwards exits the reactor at the top of cyclone whereas the aerated catalyst falls down within the standpipe and is recycled back into the inlet syngas stream.

Due to high temperature in the reactor, there are more chances of carbon deposition what reduces the catalyst lifetime further disadvantages include the bulky and complex design which makes the circulating fluidized bed reactor difficult to control and to scale up (Pondini and Erbert, 2013).

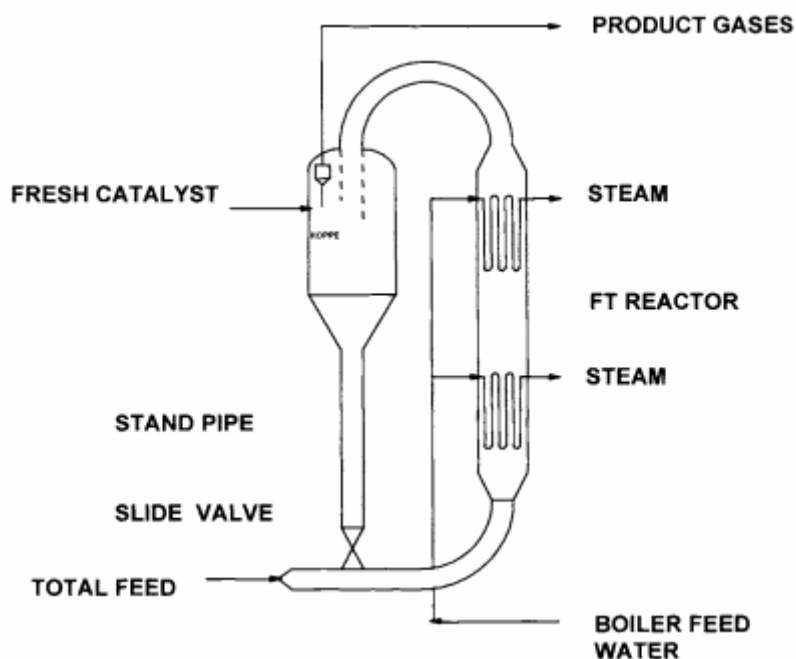


Figure 5: Circulating Fluidized Bed reactor from Steynberg and Dry 2004

### 2.2.6. Process catalyst

According to Steynberg and Dry 2004 only the metals Fe, Co, Ni and Ru have sufficiently high activities for hydrogenation of carbon monoxide for the FT synthesis. At low pressures, less than 100 bar, Ru produces much methane while at low temperatures and high pressure its selectivity is towards high molecular waxes (Vander Laan, 1999) however due to its scarcity and high price it is not used commercial applications.

Nickel has also high activity for FT but it has two major drawbacks, one is its high activity to methanation, so the yield for the desired long chain hydrocarbon is low, and also nickel forms volatile carbonyls resulting in the loss of metal at the operation temperature of the FT process (Steynberg and Dry, 2004).

One of the main advantages of iron-based catalyst is the low price when compared with other active metals (Pondini and Erbert, 2013), alkali promoted iron catalysts have been applied industrially for the FT, iron-based catalysts have high activity for water gas shift and high selectivity for olefins (Vander Laan, 1999).

Cobalt has 250 times higher hydrocarbon selectivity, therefore is applied to produce paraffins (Pondini and Erbert, 2013). This is the metal that offers higher yields and longest life time, the disadvantages are the high cost, so cobalt catalyst are viable for

natural gas-based FT processes for the production of middle distillate and high molecular weight products (Vander Laan, 1999). Cobalt catalysts are not inhibited by water resulting in higher productivity at high synthesis gas conversion (Vander Laan, 1999).

### 2.2.7. Process selectivity

Fisher Tropsch synthesis is kinetically controlled and follows a polymerization mechanism, in fact the CH<sub>2</sub> group polymerizes on the catalyst surface (Huve, 2017), the product selectivity of FT synthesis, can be described with the Anderson-Schulz-Flory statistical distribution (Huve, 2017). When considering the ideal case, the chain growth probability  $\alpha$  which can vary from zero (no chain growth), to one (infinite chain growth (Vander Laan, 1999). The range of  $\alpha$  is dependent on reaction condition and the type of catalyst: for Ru  $\alpha$  varies from 0.85-0.95, for Co  $\alpha$  varies from 0.7-0.8 and the value of  $\alpha$  for an Fe catalyst varies from 0.5 -0.7 (Vander Laan, 1999), for higher values of  $\alpha$  the product selectivity is shifted towards high chain products whereas at low  $\alpha$  values the selectivity tends to produce smaller molecules.

### 2.2.8. Product distribution

The products distribution in the Fischer-Tropsch synthesis is determined according to Anderson-Schultz-Flory (ASF) polymerization model, where the carbon number distribution of the product is a function of the chain growth probability ( $\alpha$ ) at the surface the catalyst (American Journal of chemistry and application,2018) and has the following mathematical expression (Castilho, 2017):

$$W_n = n(1 - \alpha)^2 \alpha^{(n-1)} \text{ Equation (27)}$$

Were

$W_n$ : is the Fraction in weight with n carbon atoms

n: is the number of carbon atoms in a chain

$\alpha$ : is the chain growth probability to pass from n to n+1

### 2.3. Cost estimation

Engineering is applied at many levels ranging from very crude back of envelop order-of-magnitude estimates to the reasonable precise estimates needed to get the money to proceed with buying equipment and constructing a plant, the most precise estimation strives to have an accuracy of  $\pm 10\%$  (Luyben, 2011).

According to Holmgren, 2015, methodologies used for cost estimation include:

- Divide plant into major process areas and subprocess including equipment size;
- Estimate base cost for the equipment by using literature or by consulting experts;
- Adjust the cost to the common time basis by using cost index;
- Adjust the equipment cost to the size of the design by scaling;
- Estimate total fixed capital cost using factors.

Another technique for cost estimates described by Luyben, 2011 consider the criterion of minimum total annual cost (TAC), pricing of feed stream and product is avoided. The total annual cost is the sum of the energy cost plus the annual cost of the capital investment using payback period:

$$TAC = \text{Energy cost} + \frac{\text{Capital installed cost}}{\text{Payback Period}} \quad \text{Equation (28)}$$

#### Equipment capital cost

The following equations extracted from Luyben, 2011 were designed to help to estimate installed capital cost, that is a cost of the equipment plus cost of installing it in the process, all the cost in US dollar and conventional carbon steel material of construction and modest pressure levels are assumed.

- **Vessels:**

Include reactors for chemical reactions and flash separators to separate liquids and vapors.

Separator vessels are commonly used in refinery, petrochemical plants to separate the vapor- liquid mixture. Flash drums separators are used to separate a vapor liquid mixture, and for design calculations it is normally assumed that the two phases are in equilibrium with one another. The vessel is adiabatic (no heat lost or

gained) and there is mass balance, heat balance and equilibrium (Mulyandasari *et al.*, 2015). In the figure 6 is shown a flash separator:

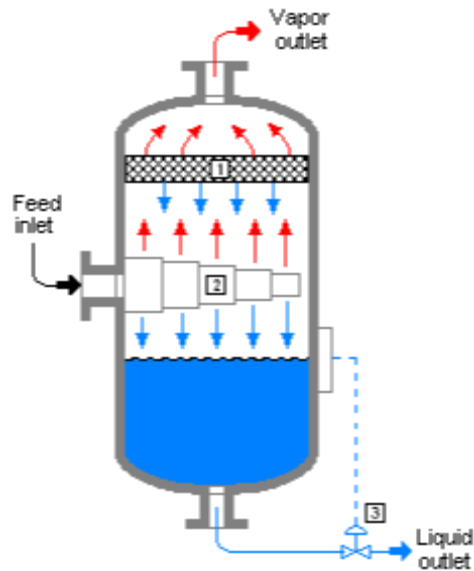


Figure 6: Flash separator

Source: Wikipedia.com

The size of reactors will be given by Coco simulator and the size of flash separators will be calculated by the following equations given by Luyben,2014:

$$V_{\max} \left( \frac{ft}{s} \right) = \frac{0.5}{\sqrt{\rho_v \left( \frac{lb}{ft^3} \right)}} \text{Equation (29)}$$

$$V \left( \frac{m^3}{s} \right) = \frac{\text{molar flow} \left( \frac{mol}{s} \right)}{\rho \left( \frac{mol}{m^3} \right)} \text{Equation (30)}$$

$$A(m^2) = \frac{V}{V_{\max}} \text{Equation (31)}$$

$$D = \sqrt{\frac{4 * V}{V_{\max} * \pi}} \text{Equation (32)}$$



$$\frac{L}{D} = 2 \text{ Equation (33)}$$

Where:

V: volumetric flow

$V_{\max}$ : vapor velocity

$\rho_v$ : density of vapor

A: area

D: diameter

L: length

$$\text{Capital cost} = 17640(D)^{1.066}(L)^{0.802} \text{ Equation (34)}$$

Where:

D is the diameter in m

L is the length in m

- **Heat exchangers:** are critical devices in every chemical plant, they are used to regulate efficient heat transfer from one fluid to another (Primo,2010). The most common type of heat exchanger used in the chemical industry is the shell-and- tube type, but there are other models that include (Hall,2012):
  - Finned tube;
  - Bare tube;
  - Plate-and-frame;
  - Spiral;
  - Plate coil.

The shell-and-tube heat exchanger has the lowest cost operation, especially when made of carbon steel, and can operate on the conditions of up to 650°C, 310 bar in the shell (Hall,2012).

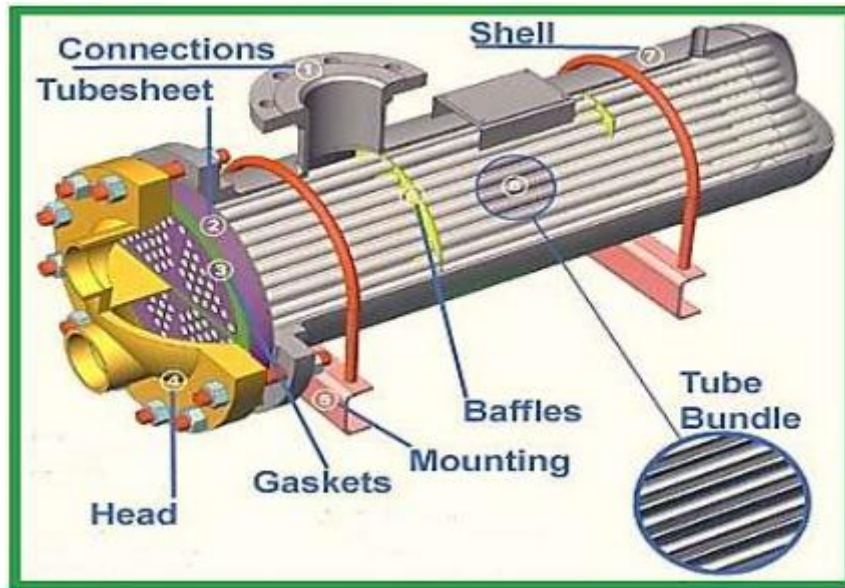


Figure 7: Heat Exchanger from Primo,2012

$$\text{Capital cost} = 7296(A)^{0.65} \text{ Equation (35)}$$

Where:

A is the area of heat exchanger in m<sup>2</sup>

The heat exchanger area can be calculated according to the following equation (Primo,2010):

$$A = \frac{Q}{U * \Delta T_m} \text{ Equation (36)}$$

Q: heat transfer rate (kJ/h)

U: overall heat transfer coefficient (kJ/h m<sup>2</sup>°C)

$\Delta T_m$ : log mean temperature difference °C

$$\Delta T_m = \frac{(T_1 - t_2) - (T_2 - t_1)}{\ln \left[ \frac{(T_1 - t_2)}{(T_2 - t_1)} \right]} \text{ Equation (37)}$$

T<sub>1</sub>: inlet tube side fluid temperature

T<sub>2</sub>: outlet tube side fluid temperature

t<sub>1</sub>: inlet shell side fluid temperature

t<sub>2</sub>: outlet shell side fluid temperature

In the table 5 is possible to see the values of overall heat transfer coefficient for different types of heat exchangers and cooling fluids

Table 5: Values of U (overall heat transfer coefficient) edited from Primo, 2010

<b>Typical Overall Heat Transfer Coefficients in Heat Exchangers</b>			
Type	Application and Conditions	U W (m <sup>2</sup> .K)	U Btu/(hr.ft <sup>2</sup> .°F)
Tubular, Heating or cooling	Gases at atmospheric pressure inside and outside tubes	5-35	1-6
	Gases at high pressure inside outside tubes	150-500	25-90
	Liquid outside (inside) and gas at atmospheric pressure inside (outside) tubes	15-70	3-15
	Gas at high pressure inside and liquid outside tubes	200-400	35-70
	Liquids inside and outside tubes	150-1,200	50-200
	Steam outside and liquid inside tubes	300-1,200	50-200
Tubular, condensation	Steam outside and cooling water inside tubes	1,500-4,000	250-700
	Organic vapors or ammonia outside and cooling water inside tubes	300-1,200	50-200
Tubular, evaporation	Steam outside and high-viscous liquid inside tubes, natural circulation	300-900	50-150
	Steam outside and low-viscous liquid inside tubes, natural circulation	600-1,700	100-300
	Steam outside and liquid inside tubes, forced circulation	900-3,000	150-500
	Cooling of water	600-750	100-130

Air-cooled heat exchangers	Cooling of liquid light hydrocarbons	400-550	70-95
	Cooling of tar	30-60	5-10
	Cooling of air or flue gas	60-180	10-30
	Cooling of hydrocarbon gas	200-450	35-80
	Condensation of low-pressure steam	700-850	125-150
	Condensation of organic vapors	350-500	65-90
Plate heat exchangers	Liquid to liquid	1,000-4,000	150-700
Spiral heat exchanger	Liquid to liquid	700-2,500	125-500
	Condensing Vapor to liquid	900-3,500	150-700

- **Compressors:** are devices used to increase pressure of a fluid (Cengel & Boles, 2005) and to move gases through ducts and pipes (Hall,2012), for oil and gas field (Hall,2012) recommends the use of screw compressor instead of reciprocating or centrifugal machines.

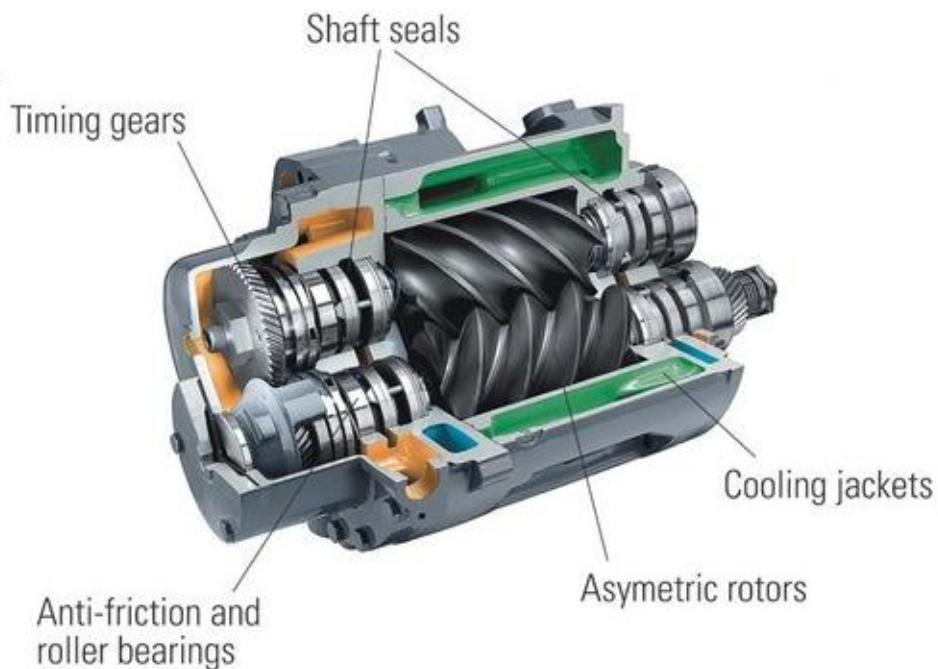


Figure 8: Air compressor from [www.kenyaengineer.co.ke](http://www.kenyaengineer.co.ke)

For a multistage compressor the work will be given by:

$$W = \left( \frac{x * n}{n - 1} \right) * P_1 V_1 \left[ \left( \frac{P_{x+1}}{P_1} \right)^{\left( \frac{n-1}{x*n} \right)} - 1 \right] \text{ Equation (38)}$$

$$\text{Capital cost} = \frac{(1293)(517.3)(3.11)(hp)^{0.82}}{280} \text{ Equation (39)}$$

Where:

x: number of stages

n: isentropic coefficient

P<sub>1</sub>: initial pressure in Pa

V<sub>1</sub>: initial volume in m<sup>3</sup>/s

W: work in J

- **Pumping, valves and piping:**

According to Luyben, 2011 the work of pumping liquid is usually small and the cost of a pump is much smaller than major vessels, so pumping cost can be neglected in conceptual design stage the same can be applied to valves and piping.

- **Energy cost** (Turton *et al.*,1998):

Low pressure steam 6 bar 160°C = USD7.78/GJ

Medium pressure steam 11 bar 184°C= USD8.22/GJ

High pressure steam 42 bar 254°C= USD9.88/GJ

- **Refrigeration** (Turton *et al.*,1998):

Chilled water 5°C returned at 15°C= USD4.43/GJ

Refrigeration at -20°C= USD7.89/GJ

Refrigeration at -50°C=USD13.11/GJ

- **Cooling water**

Colling is required in every plant, using a cooling medium a cooling medium (water, air or heat transfer fluid that is circulated through heat exchangers, coils and equipment jackets) (Hall,2012). Make up water is needed to increase some cooling water lost with evaporation, the following equations to calculate make up water were taken from Checalc.com/solved/ctmakeup.html (28<sup>th</sup> May 2021):

$$\text{Make up water} = \text{Evaporation loss} + \text{Drift loss} + \text{Blowdown} \text{ Equation (40)}$$

$$\text{Evaporation loss} = \frac{\left[0.85 * \left(\frac{1}{100}\right) * \Delta T\right]}{5.56} + \text{Circulation flow} \text{ Equation (41)}$$

$$\Delta T = 5.56^{\circ}\text{C}$$

$$\text{Circulation flow} \left(\frac{\text{m}^3}{\text{s}}\right) = \frac{\left[\frac{Q}{C_p(t_2 - t_1)}\right]}{\rho_w} \text{ Equation (42)}$$

From (Lienhard IV & Lienhard V, 2000),

$$\rho_w = 1 \frac{\text{kg}}{\text{m}^3} \text{ Equation (43)}$$

Drift loss varies from 0.1% to 0.2%

$$\text{Blowdown} = \frac{\text{Evaporation}}{(\text{cycles of concentration} - 1)} \text{ Equation (44)}$$

Cycles of concentration >1

### **Cost of manufacturing**

The elements that influence the manufacturing cost include (Turton *et al.*,1998):

1. Fixed capital investment (FCI);
2. Cost of operating labor (C<sub>OL</sub>);
3. Cost of utilities (C<sub>UT</sub>);
4. Cost of waste treatment (C<sub>WT</sub>);
5. Cost of raw material (C<sub>RM</sub>);

$$COM = 0.180 * FCI + 2.73C_{OL} + 1.23(C_{UT} + C_{WT} + C_{RM}) \text{ Equation (45)}$$

Depreciation is added separately:  $0.10*FCI$

- **Cost of operating labor**

According to Perry *et al.*, 1998 the labor requirement for a process, can be estimated by studying the equipment flowsheet and analyzing the various process steps. The annual labor cost can be estimated from the annual production applying the following equation:

$$\log_{10} Y = 0.783 * \log_{10} X + 1.252 + B \text{ Equation (46)}$$

Where:

Y: is the operating labor hours per ton per processing step

X: is plant capacity tons per day

B: is a constant having values of 0.132 when multiple units are used

- **Cost of utilities:**

Utilities are defined by Towler and Sinnott 2013, as the services needed in the operation of any production process. These services are normally supplied from a central site facility and include:

- Electricity;
- Fuel for fired heathery;
- Fluid for process cooling;
- Fluid for process heating;
- Process water;
- Compressed air;
- Inert gas supplies;

- **Cost of raw material**

Estimation of the cost of raw material and selling price of products, is usually source of too much more uncertainty (Luyben, 2011), but can be estimated by using prices listed in publications such as Chemical Market Report (CMR) (Turton *et al.*,1998).

- **Cost of treating liquid and solid**

As environmental regulation becomes more tighten the problem and costs associated with waste treatment of chemical streams increases. In recent years there has been a trend to try to reduce or eliminate the volume of waste produced with chemical processes through waste minimization strategies, that involve the utilization of alternative processes and technologies or using additional recovery steps in order to reduce or eliminate waste streams (Turton *et al.*,1998).

## **2.4. Summary**

Through the literature review done in the second chapter, is possible to see that the Fischer Tropsch is a process that has been present in the industry since the World War II and this process has been helping many countries to solve partially their problems regarding to fuel.

The Fischer Tropsch process has also helped countries to reduce their dependence in fuel importation and allows countries to explore and monetize their own resources.

It is important to realize that some gas to liquids plants were abandoned through time, what demonstrate that although is a good option to process natural gas, it might not be an easy one due to the complexity of the technology, and harshness of the process operation (high temperature and pressure).

Regarding to the cost estimation, two major references were used, Luyben, 2011 and Turton *et al.*,1998. These authors use equations associated to sizes of equipment or quantities of material to determine costs, so it is valid to use them as references for cost estimation even though they have more than 10 years.



### 3. Methodology

For the present study, three plants were simulated following the Fischer Tropsch process using COCO simulator and natural gas from Cabo Delgado Area1, to make the simulation on COCO Simulator, some variables were assumed and others were taken from literature all the variables of the simulation that include temperature, pressure, reactors size, amount of catalyst are on the appendix A.

The other point that has to be brought to attention is that, there is no data available regarding pressure and temperature of the gas coming from Cabo Delgado, so they were assumed to come at standard temperature and pressure, and compressors were used to increase the pressure and temperature to operational conditions.

The table 6 shows the composition of natural gas used for this simulation.

Table 6: composition of natural gas from Cabo Delgado from: G-A Development plant, 2017

Component	Mole %	Component	Mole %	Component	Mole %
N <sub>2</sub>	0.23	Methyl-cyclopentane	0.02	C10	0.01
CO <sub>2</sub>	0.34	Benzene	0.04	C11	0.00
H <sub>2</sub> S	0.00	Cyclohexane	0.00	C12	0.00
C1	96.86	C7	0.05	C13	0.00
N C2	1.49	Methyl-cyclohexane	0.03	C14	0.00
C3	0.56	Toluene	0.02	C15	0.00
i-C4	0.11	C8	0.01	C16	0.00
n-C4	0.11	Ethylbenzene	0.00	C17	0.00
i-C5	0.03	Meta/Paraxylene	0.00	C18	0.00
n-C5	0.02	Orto-xylene	0.00	C19	0.00
C6	0.03	C9	0.01	C20	0.00

The feed condition for the three plants was chosen to be as shown in the following table, plant 2 is 75% of plant 1 and the plant 3 is 50% of plant 1

Table 7: Plant feed condition

Feed	Plant 1	Plant 2	Plant 3
Natural gas (kmol/h)	1022	767	511
Air (kmol/h)	3,000	2,250	1,500
Hydrogen (kmol/h)	4,100	3,070	2,050
Water (kmol/h)	120	90	60

### 3.1. Process description

All the three plants have the same flow sheet, the one shown on the figure 10, and described here is from plant 1

The feed for the process is composed by natural gas, water, air and hydrogen. Natural gas at 1 bar and 25 °C is compressed in 4 stages up to 24 bar and 98°C, is mixed with high temperature steam at 810°C and 25 bar to feed the pre-reformer where most of the aromatics and higher hydrocarbons C<sub>2</sub>-C<sub>10</sub> are converted into carbon oxides and hydrogen. A cooler is placed after the mixer to bring down the temperature of the mixed gases from 622°C to 450°C, the pre-reformer operates adiabatically at 24 bar. During the steam reformer reaction taking place in the pre-reformer the water gas shift and methanation reactions also take place so, it is necessary to have a small amount of hydrogen (120 Kmol/h) to help with the methanation reaction.

The clean natural gas and steam leaving the pre-reformer is mixed with air, to feed the autothermal reformer (ATR) to burn some methane and the remaining higher hydrocarbons (C<sub>2</sub>-C<sub>10</sub>) in order to avoid the formation of coke. The ATR is adiabatic and operates at 24 bar 697°C, burning 29% for methane and 99% of oxygen. After the ATR the mixture goes through a steam reforming where methane reacts with steam to form hydrogen and carbon monoxide.

The products leaving the steam reformer are cooled down from 1,000°C to 350°C, and then feed the Reverse Water Gas Shift where carbon dioxide and hydrogen are consumed in order to adjust the H<sub>2</sub>/CO ratio.

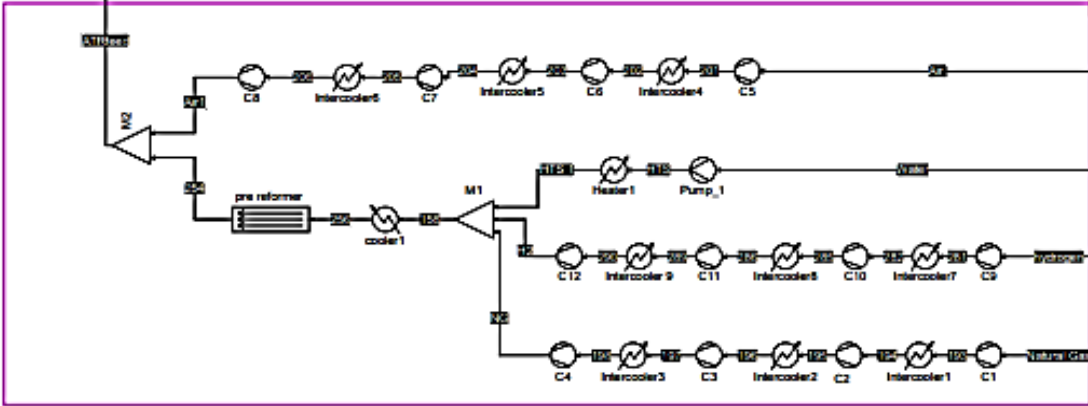
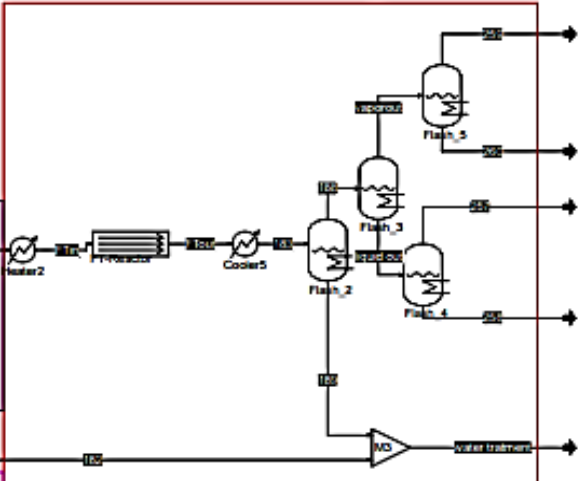
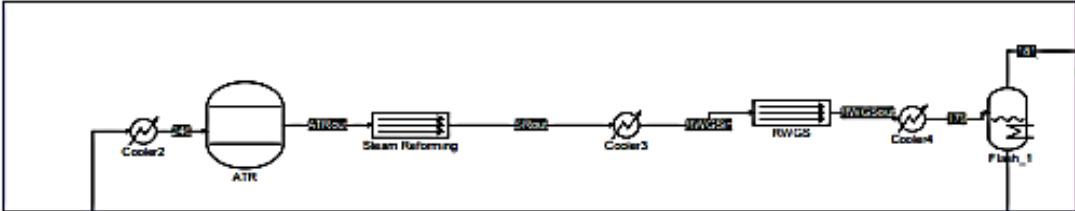
With the H<sub>2</sub>/CO ratio adjusted the products are cooled and sent to a flash separator (Flash\_1) to condensate and remove all the water before feeding the Fischer Tropsch reactor.

A mixture composed mainly of hydrogen and carbon monoxide enters the FTR at 220°C and the temperature in the reactor varies from 220°C to 223°C (temperature of the products leaving the reactor). The reactants enter in the FT reactor with a pressure of 23 bar, and as they move across the fixed bed reactor there is a pressure loss up to 18 bar. Products are cooled down to 100°C prior entering a flash separator to separate the liquid fuels from the gaseous fuels. In the Flash\_2 most part of the water formed in the Fischer Tropsch reaction is removed by reducing the product temperature to 95°C, and reused to cool down a hot stream. The gaseous stream leaving the Flash\_2 at 95°C and 18bar is sent to Flash\_3 where the liquid fuels are separated from gaseous fuels at 19°C and 18 bar. The Flash\_4 and Flash\_5 are used to reduce the pressure from 18 bar to 1 bar. The reactions taking place in each reactor, and the composition of the products leaving stream at the end of the process can be found in the appendix.

Figure 9: Flowsheet schematics

# Once Through FT

## Syngas Preparation



## Feed Preparation

- Air  
1 bar  
25°C  
3000kmol/h  
N<sub>2</sub>=79%  
O<sub>2</sub>=21%
- Water  
1 bar  
25°C  
4100kmol/h
- Hydrogen  
1 bar  
25°C  
120 kmol/h
- Natural Gas  
1 bar  
25°C  
1022kmol/h  
CH<sub>4</sub>=96.86%  
C<sub>2</sub>H<sub>6</sub>=1.40%  
C<sub>3</sub>H<sub>8</sub>=0.56%  
C<sub>4</sub>H<sub>10</sub>=0.11%  
C<sub>5</sub>H<sub>12</sub>=0.02%  
C<sub>6</sub>H<sub>14</sub>=0.03%  
C<sub>7</sub>H<sub>16</sub>=0.05%  
C<sub>8</sub>H<sub>18</sub>=0.01%  
C<sub>9</sub>H<sub>20</sub>=0.01%  
C<sub>10</sub>H<sub>22</sub>=0.01%  
i-C<sub>4</sub>H<sub>10</sub>=0.011%  
i-C<sub>5</sub>H<sub>12</sub>=0.03%  
C<sub>6</sub>H<sub>6</sub>=0.04%  
C<sub>7</sub>H<sub>8</sub>=0.02%  
C<sub>8</sub>H<sub>10</sub>=0.02%  
C<sub>9</sub>H<sub>12</sub>=0.03%

### 3.2. Summary

The simulation was made with COCO simulator, to give the idea of how the Fischer Tropsch plant would run in real life. It is important to understand that some of the variables were assumed in order to make the simulation work, so, it might have a deviation from the simulation to the reality, even though some values were taken from the literature.

In the pre-reformer, operating with a  $T_{in}$  of 450°C and a  $T_{out}$  of 490°C, it was possible to obtain a conversion of 95% to all the higher hydrocarbons being reformed in this unit. This conversion is important because it will prevent the formation of coke in the ATR during the next steps of the process.

In the ATR there are two reactions taking place, methane being burned with oxygen and methane reacting with steam to produce carbon monoxide and hydrogen, the overall conversion of methane is 99.8%.

The purpose of reverse water gas shift is to adjust the CO/H<sub>2</sub> ratio, by consuming carbon dioxide and hydrogen. In the entrance of the RWGS reactor, the CO/H<sub>2</sub> was 3, and at the end it reduced to 2.1 with a carbon dioxide conversion of 84%.

For the heart of the operation, the Fischer Tropsch reactor, the feed goes in at 220°C and leaves at 223°C. It was obtained a once through conversion of 64% for methane and 70% for H<sub>2</sub>.

## 4. Cost estimation

The cost estimation was done using correlations from Luyben (2011), Turton *et al.*, (1998) and some sites for salaries, raw material cost and some utilities cost necessary for the processes.

### 4.1. Raw material cost

The main raw material needed for the Fischer Tropsh is the natural gas, the cost was estimated from [www.nasdaq.com](http://www.nasdaq.com) (28<sup>th</sup> May 2021) where the price of natural gas was fixed at USD2.950/1,000ft<sup>3</sup>, and for hydrogen USD (2.5USD/kg-6.8USD/kg grey hydrogen from [www.sgh2energy.com](http://www.sgh2energy.com) -28<sup>th</sup> May 2021) with an average cost of 4.65USD/kg. For the present study, the annual cost of natural gas and hydrogen was considered constant for the calculation purposes. Even though hydrogen is being produced for the FT reaction, the hydrogen that is acquired here to be used in the pre-reformer for aromatics (benzene and toluene) hydrotreating. The raw material cost for the three plants simulated is shown in the table 8

Table 8: Raw material cost

Facility	Natural Gas (USD/year)	Hydrogen (USD/Year)
Plant 1	19,623,681.45	9,853,738.38
Plant 2	14,542,645.56	7,308,219.00
Plant3	9,811,840.46	4,926,888.90

### 4.2. Reactor and catalyst costs

The process has 4 reactors: a pre-reformer, a steam reformer, a reverse water gas shift reactor and the Fischer Tropsh reactor that is the most important reactor in all the process. Rector cost estimation was done using equation 34 that takes into account the length and the diameter of the reactors, the dimensions of the reactors were taken from Jess, 2009 and Zhang *et al.*, 2018. The catalyst cost was calculated consulting the site [www.alibaba.com](http://www.alibaba.com).

Reactors presenting the same cost have the same size (see table A6 of the appendix), the table 9 shows the cost of the reactors used in the simulation:

Table 9: Reactor cost estimation

<b>Reactor cost in USD</b>	<b>Plant 1</b>	<b>Plant 2</b>	<b>Plant 3</b>
Pre-Reformer	172,966.48	172,966.48	172,966.48
Steam Reformer	873,999.48	450,398.59	409,800.70
RWGS	989,014.13	767,331.76	767,331.76
FTR	628,833.83	551,988.30	499,269.49
Total	2,664,813.00	1,942,685.13	1,849,368.44

The table 10 shows the cost of the catalysts used in the reactors

Table 10: Catalyst cost estimation

<b>Catalyst cost USD</b>	<b>Plant 1</b>	<b>Plant 2</b>	<b>Plant 3</b>
Nickel catalyst (SR)	339,120.00	339,120.00	339,120.00
Nickel catalyst (PR)	565,200.00	565,200.00	565,200.00
Iron catalyst (RWGS)	317,105.00	317,105.00	317,105.46
Cobalt Catalyst (FTR)	402,640.94	402,640.94	402,640.94
Total	1,624,065.94	1,624,065.94	1,624,066.40

### 4.3. Heat Exchanger cost

The process has 5 coolers to cool down the hot streams and 9 intercoolers between the compressors, the cooling fluid used for all heat exchangers is water. The cost was estimated using the equation 35, the costs of the heat exchangers are presented in the table 11

Table 11: Heat Exchanger Cost Estimation

Plant	Heat exchanger cost USD
Plant 1	1,266,841.58
Plant 2	1,062,526.64
Plant 3	817,547.74

### 4.4. Compressor cost

Air, hydrogen and natural gas are compressed in 4 stages compressors up to the pressure of 24 bar, to compensate the pressure drop throughout the lines up to the Fischer Tropsch reactor. The Compressor cost was estimated from equation 39, for multistage compressors the work will be given by equation 38. In the table 12 is presented the cost of the compressors.

Table 12: Compressor Cost Estimation

Compressor (4 stages) cost in USD	Plant 1	Plant 2	Plant 3
Hydrogen	1,003,090.14	784,832.79	568,114.37
Natural gas	5,706,861.48	4,505,287.18	3,229,127.52
Air	14,014,829.91	11,107,532.19	7,936,824.61
Total	20,724,781.53	16,107,523.19	11,734,066.50



#### 4.5. Flash Separator cost

The process has 5 flash separators, the first one is used to remove water from the products coming from the reverse water gas shift reaction, the second reactor is also used to remove water coming from the Fischer Tropsch reactor, and the last three reactors are used to separate the gaseous fuels from liquid fuels. The flash separator cost was estimated according to the equation 34, and the flash size was calculated using equations from 29 to 33, the costs of flash separator are shown in the table 13.

Table 13: Flash Separator Cost

Flash cost in USD	Plant 1	Plant 2	Plant 3
Flash 1	698,115.96	536,687.84	336,587.29
Flash 2	429,145.81	309,616.24	196,658.24
Flash 3	362,225.35	254,558.9	157,818.98
Flash 4	17,714.33	10,486.63	6,083.51
Flash 5	305,833.75	239,434.74	145,757.94
Total	1,813,035.20	1,350,784.34	842,905.96

#### 4.6. Utilities cost

For this process utilities were considered cooling water, waste, process catalyst, and demineralized water to produce the steam. The utility cost was made using costs from some websites for the cost of catalysts, cost of water was taken from [www.aura.org.mz](http://www.aura.org.mz) estimated in 37MZN/ m<sup>3</sup>, what was converted to 0.6USD/m<sup>3</sup>

the utilities cost is shown in the table 14:

Table 14: Utility Cost Estimation

Utility (USD/year)	Plant 1	Plant 2	Plant 3
Cooling water (makeup water)	3,194,616,432.05	2,607,652,883.19	855,403,908.68
Water for steam	388,222,074.00	290,693,112.00	194,106,000.00
Total	3,582,838,506.05	2,898,345,995.19	1,049,509,908.68

#### 4.7. Energy cost

The ATR reactor cost is calculated as the cost of a fired furnace, taking into account the heat duty necessary to provide the large endothermic heat of reaction. The energy tax is estimated to be 3,99mt/kwh 17.78 USD/GJ from [www.edm.co.mz](http://www.edm.co.mz), this accessed on 14<sup>th</sup> June 2021, the energy cost is calculated for the fired reactor, compressors energy demand, heaters energy demand, water treatment plant for demineralized water.

The table 15 shows the cost of energy in the fired reactor calculated as the number of mols gas burned in the reactor

Table 15:Energy demand

Energy cost USD/year	Plant 1	Plant 2	Plant 3
Fired reactor	43,657,583.54	32,627,707.45	21,705,721.95
Compressor energy demand	8,630,695.06	6,067,923.73	4,268,075.52
Heater 2	3,339,017.87	2,522,255.33	1,655,426.37
Boiler (Heater 1)	47,742,338.46	35,748,531.48	23,871,169.23
Reverse Osmosis unit	67,285.21	50,463.91	33,642.6
Waste water treatment unit	34,764.02	26,073.02	17,438.08
RWGS Reactor Heating	1,722,253.81	1,245,158.64	977,104.65
Total	105,193,937.97	78,288,113.56	52,528,578.40

#### 4.8. Operating labor cost

Operating labor cost was estimated using equation (46), that estimates the operating labor hours per ton, the calculations were done according to the calculations made by Perry *et al.*, 1998.

The site [www.salay.com](http://www.salay.com) accessed on 14<sup>th</sup> June 2021 estimated an average salary for chemical plant operator in the oil/gas/mining industry of 83700MZN/month, what corresponds to 2790MZN/day, and is equivalent to 116.25 MZN/hour. The exchange rate MZN to USD on the 14<sup>th</sup> June 2021 was of 1USD corresponding to 62.36MZN, then, 116.25MZN/hour would correspond to approximately 2USD/hour.

The table 16 shows the costs of operating labor

Table 16: Operating labor cost

	<b>Plant 1</b>	<b>Plant 2</b>	<b>Plant 3</b>
Y(hours/ton)	1,588.06	1,376.47	1,064.65
Ton/year	82,624.25	68,845.65	49,589.96
Hourly wage (USD/hour)	2	2	2
Operating labour (USD/year)	262,425,337.74	189,528,141.10	105,592,843.35

#### 4.9. Total annual production

The total production of synthetic fuel was calculated considering the products leaving the FTR, the table 16 shows the products obtained including unconverted reactants and by products

Table 17: annual production

<b>Product</b>	<b>Plant 1</b>	<b>Plant 2</b>	<b>Plant 3</b>
Gas	9,279.23	7,855.77	5,659.66
LPG	13,417.41	11,157.22	8,036.41
Gasoline	29,975.40	24,925.96	17,953.87
Diesel	26,104.9	21707.47	15,635.64
Heavy(C <sub>20+</sub> )	3,847.33	3199.23	2,304.37
Total metric tons/year	82,624.25	68,845.65	49,589.96
<b>Byproduct/Unconverted (metric tons/year)</b>	<b>Plant 1</b>	<b>Plant 2</b>	<b>Plant 3</b>
Water	137,560.27	112,526.17	78,669.99
Nitrogen	582,157.73	438,557.54	291,078.71
Carbon monoxide	89,004.62	52,343.125	33,378.015
Carbon dioxide	19,304.013	16,834.922	2,238.858
Hydrogen	10,699.266	6,134.8524	2,559.3211

#### 4.10. Total cost

The total costs were calculated using equation 28 for the total annual cost and equation 45 for the cost of manufacturing. Regarding the cost equipment for demineralization of water, for steam boiler and waste water treatment, was consulted from [www.Made-in-china.com](http://www.Made-in-china.com) and the specification of the equipment are shown in the appendix.

The total cost is presented as the total annual cost, and the cost of each equipment for the process, in the table 18 is presented the total cost estimation

Table 18: total cost estimation

<b>Annual cost (USD/Year)</b>	<b>Plant 1</b>	<b>Plant 2</b>	<b>Plant 3</b>
Raw Material	29,477,464.83	21,850,864.56	14,738,729.36
Catalyst	1,624,065.94	1,624,065.94	1,624,066.40
Utilities	3,582,838,506.05	2,898,345,995.19	1,049,509,908.68
Energy	105,193,937.97	78,288,113.92	52,528,578.40
Operating labor	262,425,337.74	189,528,141.10	105,592,843.35
<b>Total</b>	<b>3,981,559,312.53</b>	<b>2,189,637,180.35</b>	<b>1,223,994,126.19</b>
<b>Equipment cost (USD)</b>	<b>Plant 1</b>	<b>Plant 2</b>	<b>Plant 3</b>
Reactor	2,664,813.92	1,942,685.13	1,849,368.44
Heat Exchanger	1,266,841.58	1,062,526.64	817,547.74
Flash Separator	2,069,631.25	1,620,337.45	842,905.96
Compressor	20,724,781.53	16,397,652.19	11,734,066.50
Steam producer (Boiler)	150,000.00	150,000.00	150,000.00
Demineralized water equipment	1,200,000.00	900,000.00	600,000.00
Waste water treatment unit	260,000.00	195,000.00	130,000.00
<b>Total</b>	<b>28,336,068.28</b>	<b>22,268,201.41</b>	<b>16,123,888.64</b>

The total annual cost and cost of manufacturing calculated are shown in the table 19

Table 19: Cost of manufacturing

	<b>Plant 1</b>	<b>Plant 2</b>	<b>Plant 3</b>
Total Annual Cost (USD/year)	116,263,360.19	87,334,91330	59,527,274.35
Cost of Manufacturing (USD/year)	5,180,497,221.01	4,124,974,247.09	1,608,009,196.52
Depreciation (USD/year)	11,626,336.01	8,733,491.33	5,952,727.43
Cost of Manufacturing +Depreciation (USD/year)	5,192,123,557.01	4,133,707,738.42	1,613,961,923.95
10% accuracy (USD/year)	5,192,123,557.01 ±519,212,355.70	4,133,707,773.84 ±413,370,773.84	1,613,961,923.95 ±161,396,196.40
(Cost of manufacturing)/(annual production) USD /kg	62.84	60.04	32.55
Cooling demand kJ/kg	-12,481.00	-13,333.00	-10,397.00

## 5. Results and Discussions

In this chapter all the obtained results are explained, justified and compared to what exist in the literature. So, the discussion regarding the cost will be concerned with the values obtained, and the products distribution. Since the three plants have the same trend regarding the product distribution, then only the plant 3 will be discussed and analyzed, and also because it is the plant that presents the lowest costs.

### 5.1. Product distribution and selectivity

The main byproduct of the FT reaction is presented to be water, analyzing the products leaving the FTR of the plant 3, it is possible to see the effect of air in the products, since air is made of oxygen and nitrogen and for the process only oxygen is needed to burn hydrocarbons. This huge presence of inert in the product, reduces the possibility of recycling of unconverted reactants and also having more nitrogen and water leaving the reactor makes the process unattractive. As seen in the table one, some GTL plants were abandoned, and this product profile could be a reason, since most of the product is water than the synthetic fuel itself.

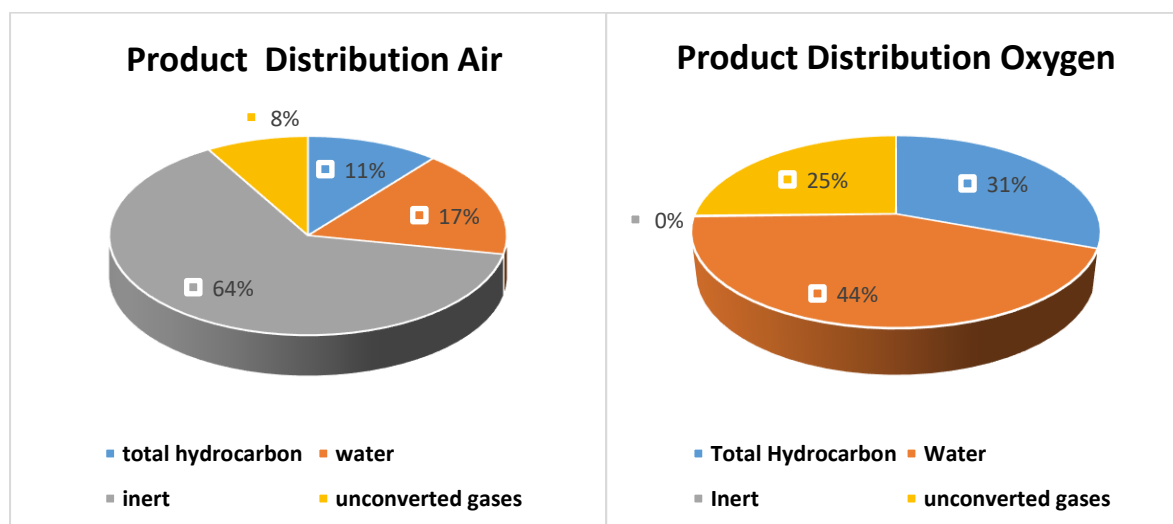


Figure 10:Product distribution

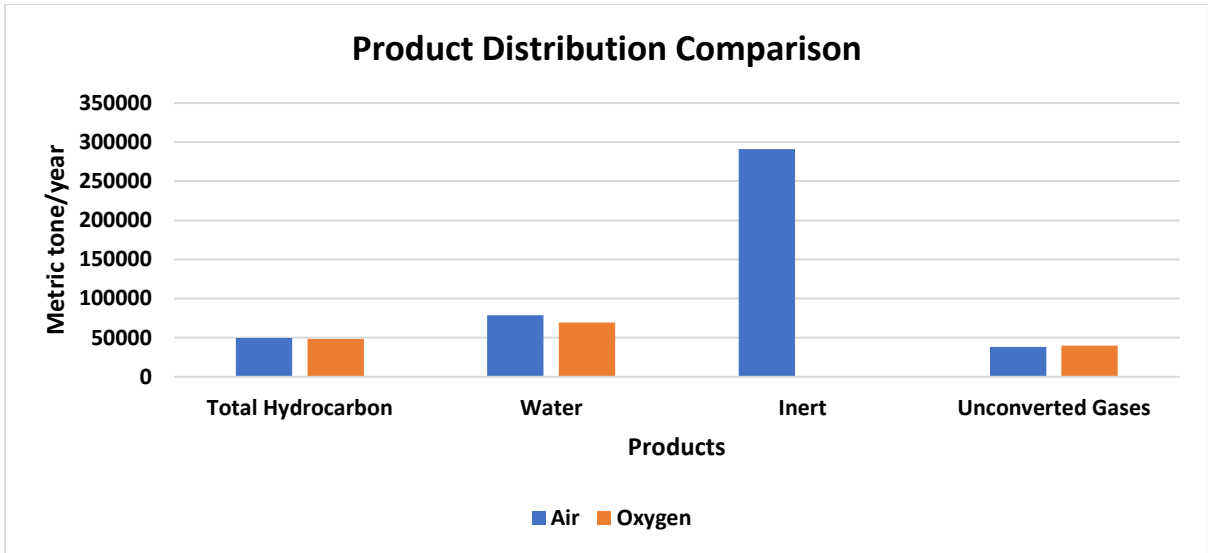


Figure 11: Product distribution comparison

Paying a closer attention to the hydrocarbon’s selectivity, the simulation shows 73% selectivity towards C<sub>5+</sub> hydrocarbons, while Jess, (2009) had a selectivity of 80% toward C<sub>5+</sub>.

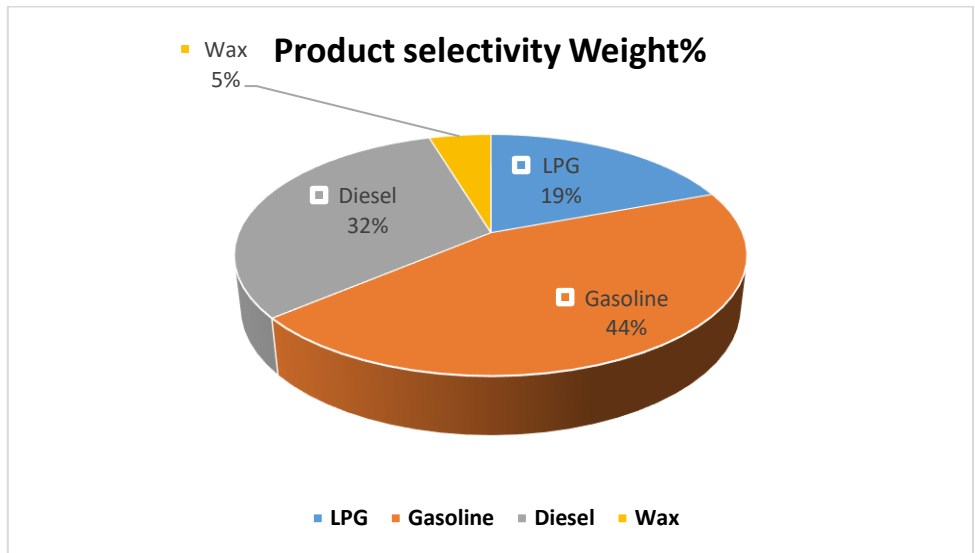


Figure 12: Product Selectivity



The annual demand and stockage capacity in the year of 2016 shown by CIP (Centro de Integridade Publica) was:

Table 20: Annual Demand in 2016

Product	Demand (m <sup>3</sup> )	Demand (metric ton)	Stockage (m <sup>3</sup> )	Stockage (metric ton)
Diesel	1,136,000	954,000	545,000	458,000
Gasoline	400,000	256,000	219,000	140,000
A <sub>1</sub> Jet	125,000	103,000	72,000	59,000
Total	1,661,000	1,312,000	836,000	657,000

Comparing with the annual production only with one reactor (49,589.96ton/year) so, it will not be possible to satisfy the demand only with one reactor.

As for example according to Steynberg and Dry, by 2004 Sasol was with 5 Multi-tubular Arge reactors with 3m of diameter, 2,050 tubes, 5cm ID, with a capacity of 500barrel/day and Shell-Bintulu was operating with 4 multi-tubular reactors with 7m of diameter and each reactor with a capacity of 8,000barrel/day each reactor.

## 5.2. Raw material

The cost of natural gas was estimated with a constant price, but the natural gas as well as hydrogen price might oscillate from month to month. It is important to understand that the hydrogen that is being acquired here is for hydrotreating of the aromatic present in the natural gas.

According to EIA, natural gas prices are function of market supply and demand, so increasing in natural gas supply will result in lower natural gas prices and a decrease in supply tend to lead to higher prices. On the other side increase in demand generally leads to high prices and decreases in demand tend to lead to lower prices.

Other factor that can affect the cost of natural gas is how far or close it is from the facility because pipelines and compressors to transport the gas will affect the cost.

There are several qualities of hydrogen in the market, the one used here for simulation purposes was the grey hydrogen, produced from natural gas for cost control purposes.

Although there is hydrogen on the final products and the recycling would contribute to the reduction of cost, the amount of nitrogen on the products will lower the partial pressure of the reactants and the products and as the net effect lower this ratio resulting in a lower conversion (Van Steen *et al.*, 2017).

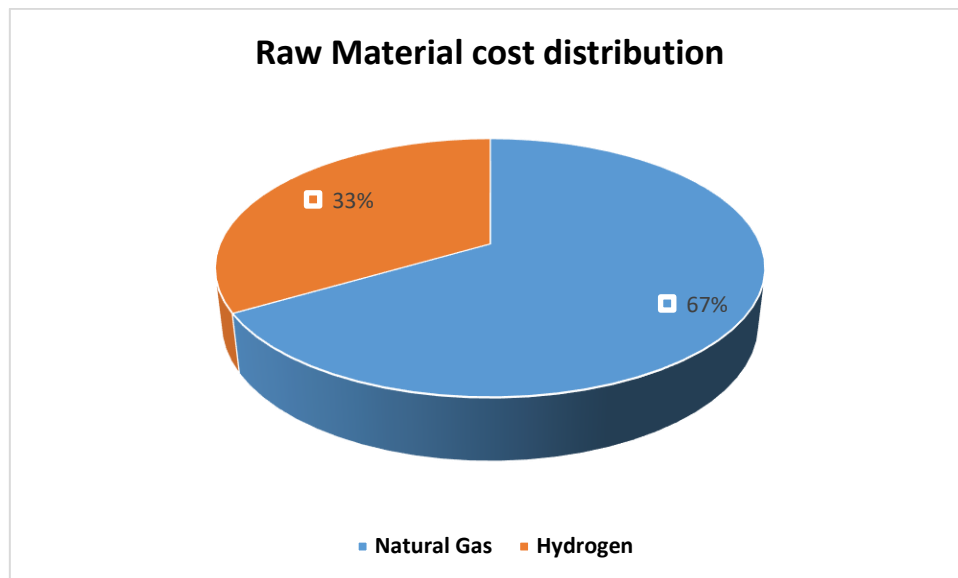


Figure 13: Raw material cost distribution

### 5.3. Reactor cost

According to the equation presented by Luyben, 2011 for the calculation of the cost of vessels, is dependent of the diameter and the length of the reactor. Looking closely to Fischer Tropsch reactor and reverse water gas shift reactor they have the biggest length and consequently the higher costs.

It is important to understand that, the bigger the reactor the higher the conversions, but then the cost of reactor will increase since cost will be affected by the length and diameter of the reactor. Other parameter that is affected by the size of reactor is the pressure drop as the longer the reactor the higher will be the pressure drops, and more compressors will be needed at the beginning in other to compensate the pressure loss.

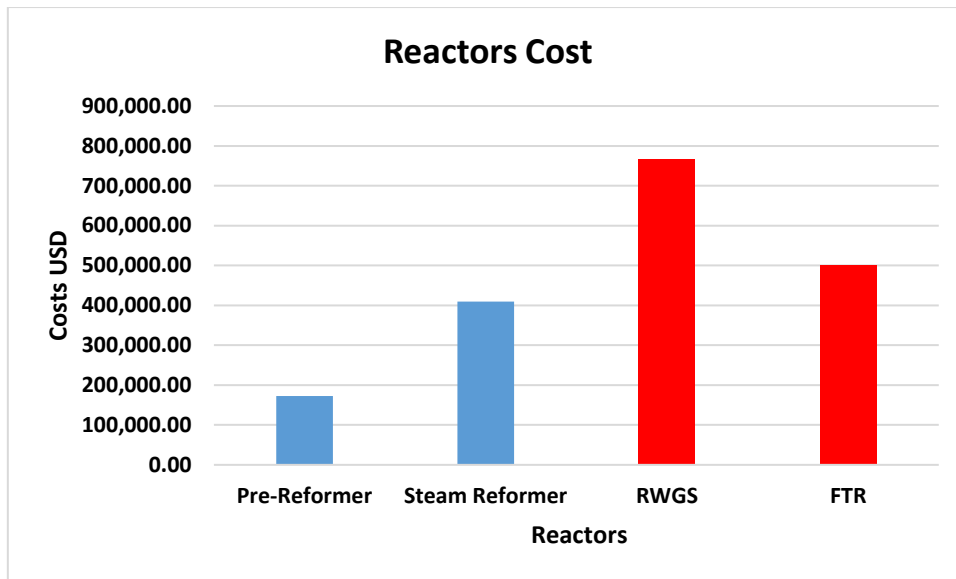


Figure 14 Reactor Cost

The cost of the catalyst was calculated taking into account the catalyst loading of each reactor, and the lifetime of catalysts considered was one year, the pre-reformer reactor does not have cooling tubes, so it has more volume to be filled with catalysts, presenting the highest cost of catalyst.

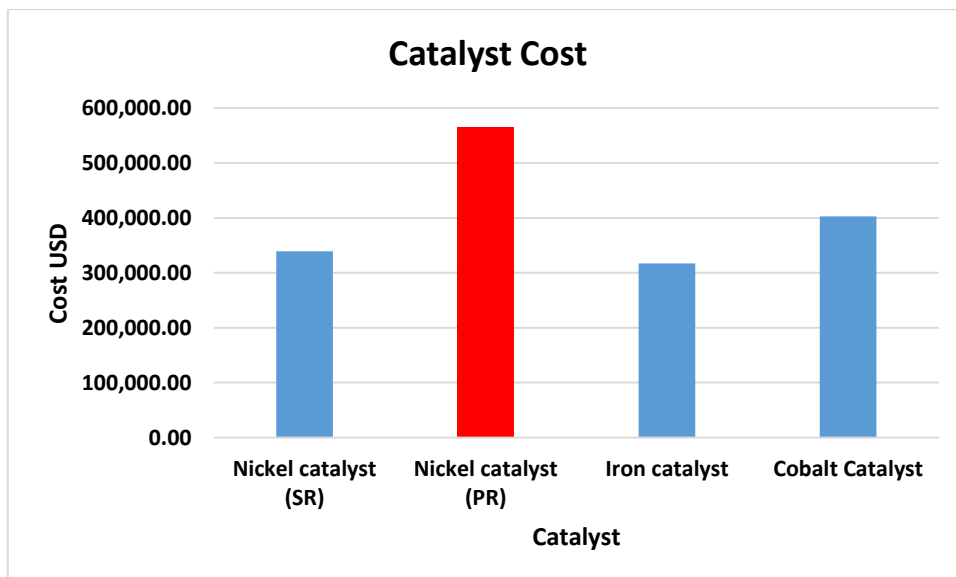


Figure 15: Catalyst cost

## 5.4. Heat Exchanger cost

The cost of the heat exchanger will be influenced by the area of heat exchanging. The area of the heat exchanger will be determined by the heat transfer coefficient, the amount of heat to be exchanged, and the difference in temperature between the two streams.

Regarding the intercoolers they can be water cooled or air cooled, but air as coolant has a low heat transfer coefficient when compared to water, although on the other side air is cheaper than water but low heat transfer coefficient will lead to bigger areas and consequently expensive heat exchanger.

The heat exchangers associated with higher costs, are coolers where there is a water condensation taking place (Cooler2, Cooler4, Cooler5).

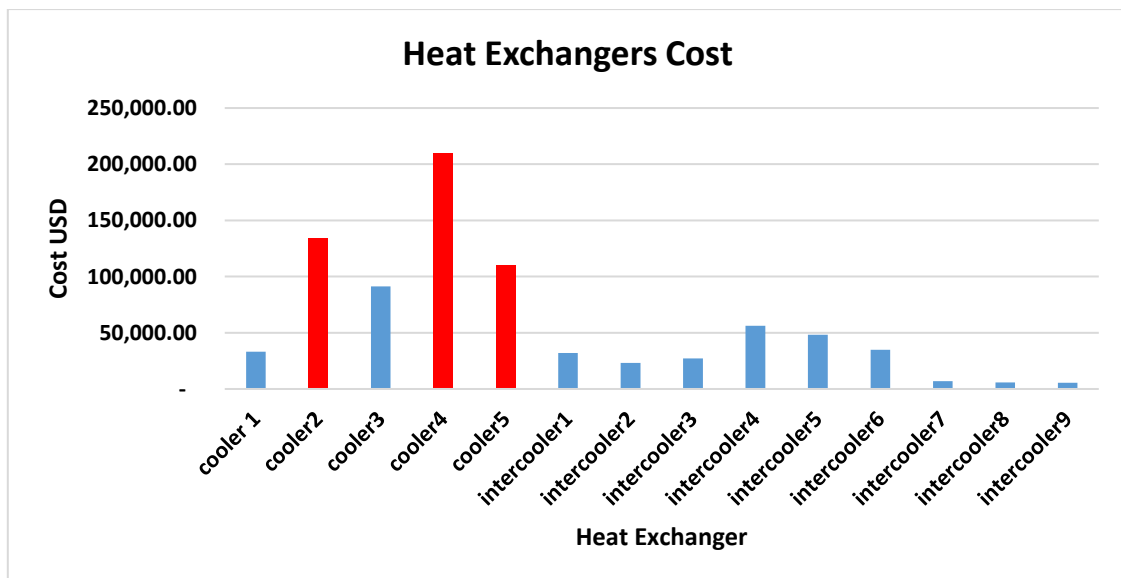


Figure 16: Heat Exchanger Cost

## 5.5. Compressor Cost

Although the Natural gas, Hydrogen and Air are compressed in four stages, the cost of the compressors will vary from gas to gas. The cost of the four stage compressors will be affected by the volume of gas to be compressed, the higher the volume the higher the work (hp) to be exerted in order to compress the gas.

The four-stage air compressor is the one that presents the higher cost, due to the huge amount of air (3000kmol/h) to be compressed, air has 79% nitrogen, and on the process, nitrogen is an inert, so the other option would be to use an air separation unit,

to ensure only oxygen is compressed and it would reduce the cost of compressors. But the cost of air separation unit was estimated in 47.7 million dollars by Tesch & Morosuk, 2019 what would make the process even more expensive.

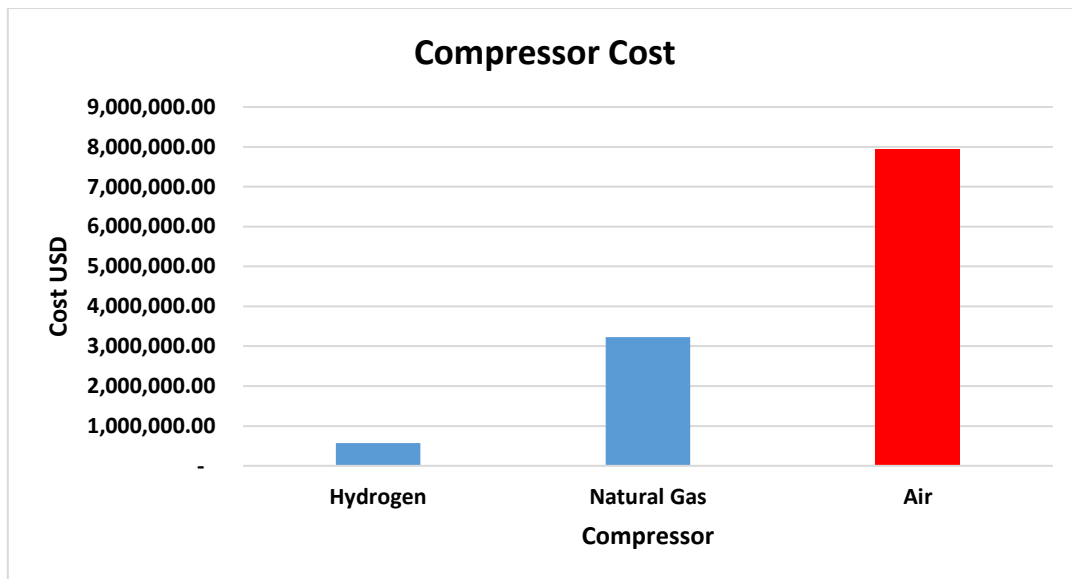


Figure 17: Compressor Cost

### 5.6. Flash separator cost

The flash separator cost is calculated taking into account the diameter and the length of the vessel, these variables (length and diameter) are calculated according to the flow of the vapor to be separated. The flash1 is located after the reverse water gas shift reactor and separates the huge flow 4,869.38kmol/h, so it presents the higher cost comparatively to other flash separators that deal with lower flow rate.

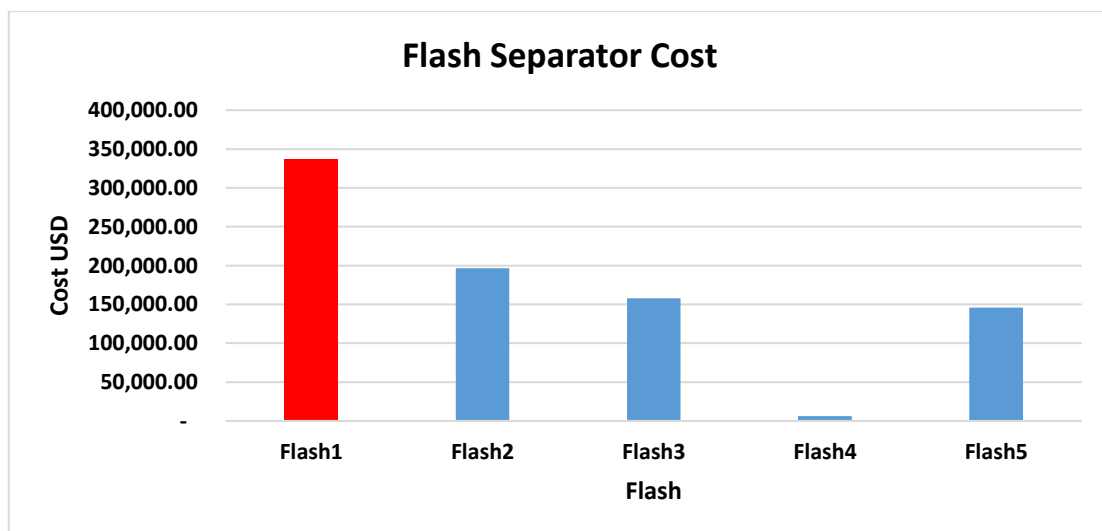


Figure 18: Flash Separator Cost

## 5.7. Utilities Cost

To calculate the cost of utilities were considered the costs of, cooling water, deionized water for steam generation and catalyst.

Regarding the cooling water it can be recirculated in order to avoid fresh cooling water streams what would become more expensive.

The most expensive utility is cooling water, that is needed for intercooling in compressors, coolers between reactors and the Fisher Tropsch reactor that is highly exothermic reaction and demands huge amount of cooling. To control cooling costs cooling water can be cooled down and recirculated. The high-pressure steam, that is needed for the steam reformer, this cost can be controlled by reutilizing the water generated by the processes, with a rigorous treatment before recycling the water in the system to avoid reactants build up.

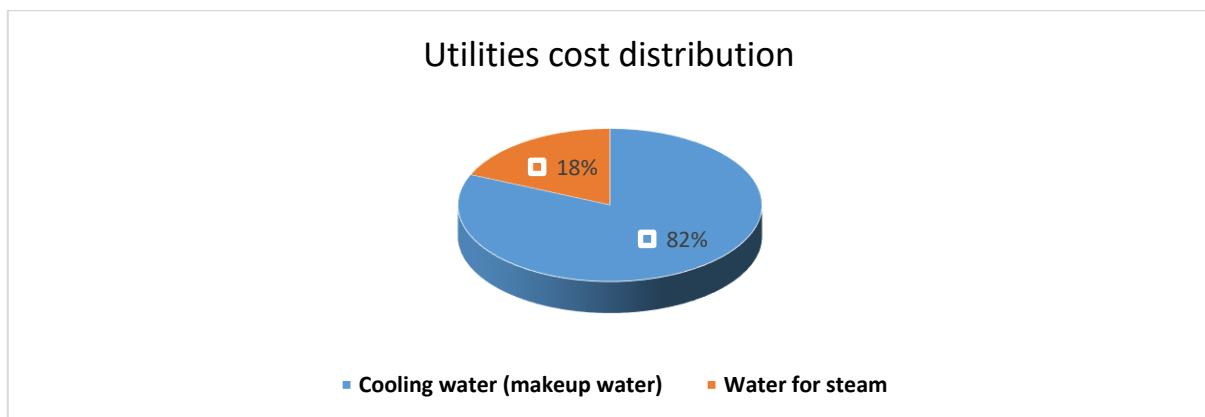


Figure 19: Utilities distribution

## 5.8. Waste water treatment

Waste water treatment is considered water coming from the flash separators, so this water contains some hydrocarbons, so according to Dutta *et al* (2015) hydrocarbons can be separated and combusted and the waste water can be used to handle other hot streams.

## 5.9. Energy cost

The energy cost was calculated only taking into account the fired reactor, the compressor energy demand and the heaters energy demand, the energy demand of the waste water treatment unit and demineralization unit. The energy on the fired reactor will be affected by the quantity of hydrocarbons to be burnt on the fired reactor, and the energy demand on the compressor will be affected by the volume of gas and the temperature of gas to be compressed. Compress a cool gas will require less energy than to compress hot gas.

Heater 1 is used for heating water, from liquid phase to transform it into steam at 809°C, for the steam reformer process. So, this phase changing consumes a huge amount of energy. Heat integration would be needed to take advantage of exothermic processes taking place in the plant to heat up the water, what would contribute to reduce the cost of energy demand.

The compressors C5 and C6 are responsible for compressing air in the first two stages, in the ATR only oxygen will be needed and as air is 79% nitrogen and 21% oxygen it means that only 21% of the 1,500kmol/h compressed are useful.

Compressing big quantities of gas, requires higher amounts of energy to operate the compressor, another possibility to control this energy cost is to use only oxygen so, it would reduce the amount of gas to be compressed. But the cost of air separation unit was estimated in 47.7 million dollars by Tesch & Morosuk, 2019 what would make the process even more expensive. The Compressor C1 is on the first stage to compress natural gas, to compress a gas for the first time it is also required high energy demand. The waste water treatment unit and demineralization unit present the lowest energy demand since the motor of both units has small consumptions (15.55kW and 30kW respectively)

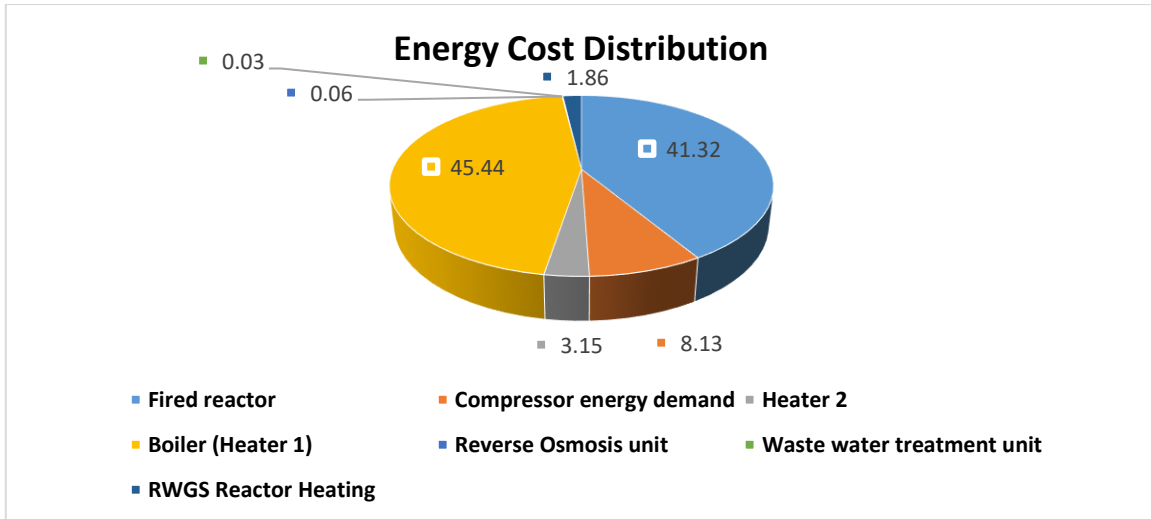


Figure 20: Energy Cost

### 5.10. Equipment cost distribution

Regarding the cost distribution for equipment, compressors represent 72.77% of the total cost of equipment, due to the fact that many compressors are needed to increase the pressure of the gas from 1 bar to 24 bar and compensate pressure loss during the process.

It is important to understand that the initial conditions (temperature and pressure) of the gas were assumed, because they are unknown, so, probably less compressors would be needed.

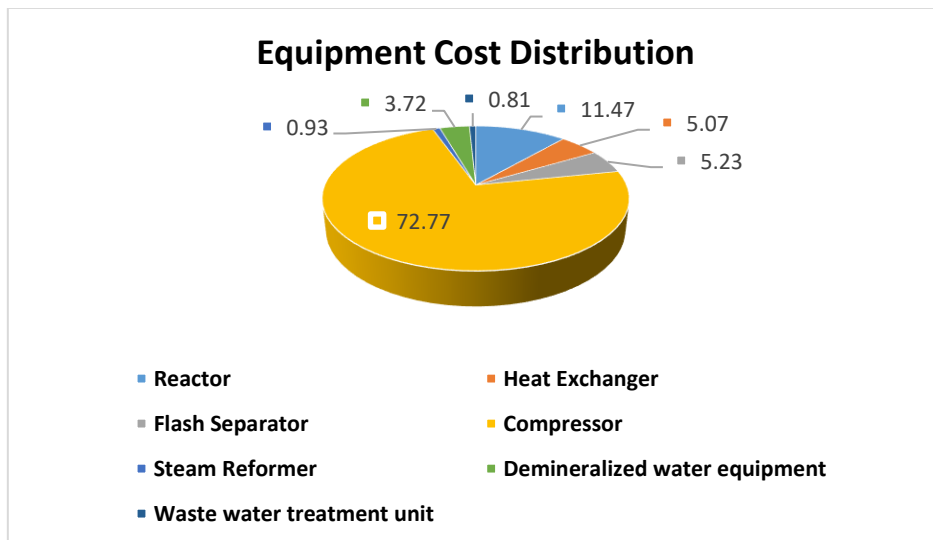


Figure 21: Equipment cost distribution



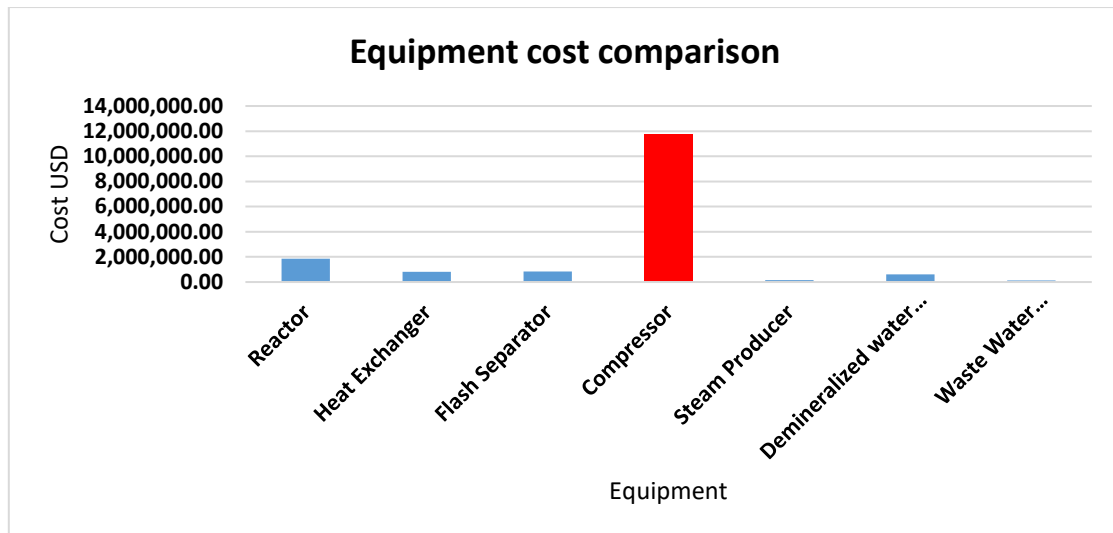


Figure 22 : Equipment cost comparison

### 5.11. Cost of manufacturing estimation

The cost of manufacture was estimated in  $5,192,123,557.01 \pm 519,212,355.70$  USD/year for plant 1,  $4,133,707,738.42 \pm 413,373,773.84$  USD/year for plant 2 and  $1,613,961,923.95 \pm 161,396,196.40$  USD/year for an annual production of 82,624.25 ton/year for plant 1; 68,845.65 ton/year for plant 2 and 49,589.96 ton/year for plant 3.

Small scale gas to liquid plant was estimated in 2013 by Glebova to be in 100 millions dollars, and big scale gas to liquid were estimated in 1.6 billion dollars (Glebova, 2013).

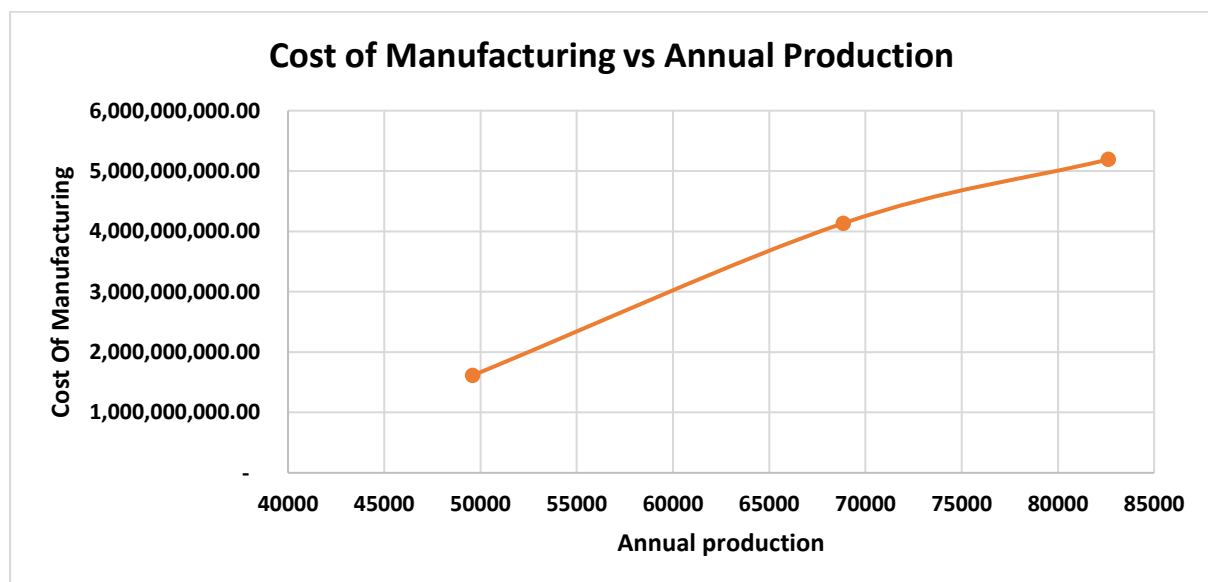


Figure 23: Cost of Manufacturing Vs Annual Production

## **6. Conclusions and Recommendations**

In this chapter, the conclusions, limitations and recommendations for future researches are presented.

### **6.1. Conclusions**

After simulating the three plants, and performing the cost calculation it is possible to see that only the plant 3 has the lowest cost of manufacturing, to compete with the importation cost, but it is higher when compared to the importation cost.

The simulations performed also shown that the quantity of fuel obtained only with one train of reactors will not be possible to satisfy the needs of all the market, so it would be necessary to increase the number of reactors and other equipment what affect directly on the costs.

The simulation was only concerned with the production of synthetic crude oil, so the final product was not upgraded and this cost was not considered in the calculations, then the upgrade of the final product would increase the values obtained.

For GTL facilities, is not possible to benefit of scale economy, because it was possible to realize that the bigger the plant the higher the operation cost.

Using air instead of oxygen make the plant less expensive but affects the quantity of the fuel as 76% of the gaseous stream is nitrogen. Having a huge amount of nitrogen also has an impact on the possibility of recycling unconverted hydrogen and carbon monoxide, since 9% of hydrogen and 8% of Carbon monoxide are present on the final product, but the attempt to recycle these gases would result in the introduction of inert gases in the process.

### **6.2. Limitations**

The major limitation faced mainly in the presentation of the results, because it was not possible to compare the values obtained with the values available in the literature since they are outdated.

Other limitations were related to unavailability of information from the gas wells coming from Cabo Delgado.

### **6.3. Recommendations**

So, FTGTL for the production of synthetic fuels using natural gas and air shown to be an unattractive option or application for the gas of Cabo Delgado since it presented higher costs of manufacturing to lower product demand when compared to the process of fuel importation then for future researches development it is recommended to study the feasibility and cost of manufacturing of other GTL processes that might be obtained by the processing of natural gas, such as:

- gas to methanol;
- gas to di-methyl-ether;
- gas to olefins;
- gas to gasoline.

The economic study of process such as the production of ammonia for example would give application to the huge amount of nitrogen that remained as inert in the final product for the present study.

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## **APPENDIX**



## Process assumptions

Table A1: Assumptions made

Component/system	Unit	
<b>General</b>		
Property model		Peng Robinson
Ambient temperature	°C	25
Ambient pressure	Bar	1
<b>Compressors</b>		
Isentropic efficiency	%	75
<b>Heat Exchangers</b>		
Counter current		
Effectiveness	-	0.9
<b>Pre-Reformer</b>		
PFR (Adiabatic)		
Length	m	4
Diameter	m	3
Tubes	-	0
Catalyst	Kg/m <sup>3</sup>	1,000
Void	-	0.4
Particle diameter	m	0.004
Heat transfer coefficient	w/m <sup>2</sup> /k	0
<b>ATR</b>		
Fixed-conversion-reactor		
Adiabatic		
Combustion		
O <sub>2</sub> /C ratio		0.63
C2 conversion	%	100
C3 conversion	%	100
C4 conversion	%	100
iC4 conversion	%	100
iC5 conversion	%	100

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C6 conversion	%	100
Cycle-C6 conversion	%	100
MCP conversion	%	100
MCH conversion	%	100
C7 conversion	%	100
C8 conversion	%	100
C9 conversion	%	100
C10 conversion	%	100

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### **Steam Reformer**

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#### **PFR**

Tube temperature	°C	1,000
H <sub>2</sub> O/CH <sub>4</sub> ratio	-	6.3
Length	m	12
Diameter	m	6
Tubes	-	2,000
Tube diameter	m	0.03
Particle diameter	m	0.003
Void	-	0.4
Catalyst	Kg/m <sup>3</sup>	1,000
Heat transfer coefficient	w/m <sup>2</sup> /k	500

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#### **RWGS**

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#### **PFR**

Tube temperature	°C	650
Length	m	15
Diameter	m	6
Tubes	-	2,000
Tube diameter	m	0.03
Particle diameter	m	0.004
Void	-	0.65
Catalyst	Kg/m <sup>3</sup>	1,603
Heat transfer coefficient	w/m <sup>2</sup> /k	500

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**FTR**

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PFR

H <sub>2</sub> /CO ratio	-	2.037
Catalyst density	Kg/m <sup>3</sup>	100
Void fraction	-	0.4
Number of tubes	-	2,000
Length	m	20
Diameter	m	3
Tube diameter	m	0.046
Particle diameter	m	0.004
Heat transfer coefficient	w/m <sup>2</sup> /k	800
LTFT	°C	220
Linear paraffins		C1-C29

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**Reactions Constants values**

Table A2: Reaction constants and Arrhenius kinetics parameters

Reaction	Constant	k <sub>0i</sub> mol/(kgcat.s)	E <sub>ai</sub> (kJ/mol)
1	k <sub>1a</sub>	8.11* 10 <sup>5</sup> bar <sup>2</sup>	86
1	k <sub>1b</sub>	6.82* 10 <sup>5</sup> bar <sup>2</sup>	86
2	k <sub>2</sub>	1.17* 10 <sup>15</sup> bar <sup>0.5</sup>	240.1
3	k <sub>3</sub>	2.81* 10 <sup>14</sup> bar <sup>0.5</sup>	243.9

From: Arpornwichanop and Wasuleewan, 2010

Table A3: Reaction equilibrium constants

Reaction	Constant	$K_{0i}$	$\Delta H_i$ (J/mol)
1	-	-	-
1	-	-	-
2	$K_{eq2}$	$5.75 \cdot 10^{12}$	11,476
3	$K_{eq3}$	$7.24 \cdot 10^{10}$	-4,639

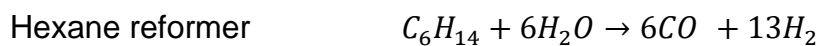
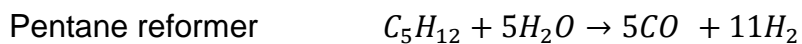
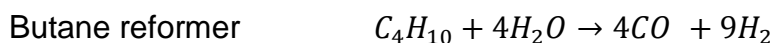
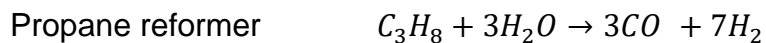
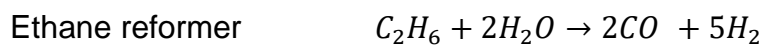
From: Arpornwichanop and Wasuleewan, 2010

Table A4: Van't Hoof parameters for species adsorption

Constant	$K_{0i}$	$\Delta H_{ads,i}$ (j/mol)
$K^{c_{CH_4}}$	$1.26 \cdot 10^{-1} \text{bar}^{-1}$	-27.23
$K^{c_{O_2}}$	$7.81 \cdot 10^{-7} \text{bar}^{-1}$	-92.80
$K_{CH_4}$	$6.65 \cdot 10^{-4} \text{bar}^{-1}$	-38.28
$K_{CO}$	$8.23 \cdot 10^{-5} \text{bar}^{-1}$	-70.65
$K_{H_2}$	$6.12 \cdot 10^{-9} \text{bar}^{-1}$	-82.65
$K_{H_2O}$	$1.77 \cdot 10^{-5}$	88.68

From: Arpornwichanop and Wasuleewan, 2010

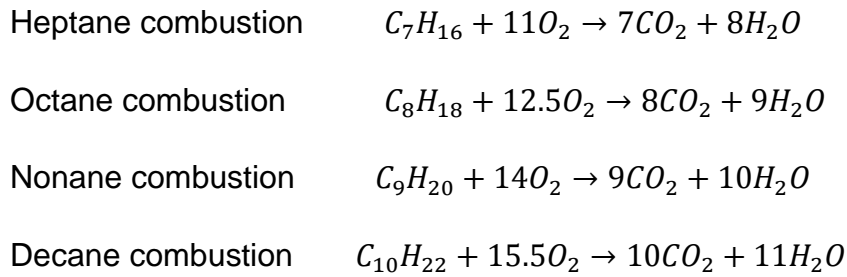
**Reaction taking place at the pre-reforming unit:**



Heptane reformer	$C_7H_{16} + 7H_2O \rightarrow 7CO + 15H_2$
Octane reformer	$C_8H_{18} + 8H_2O \rightarrow 8CO + 17H_2$
Nonane reformer	$C_9H_{20} + 9H_2O \rightarrow 9CO + 19H_2$
Decane reformer	$C_{10}H_{22} + 10H_2O \rightarrow 10CO + 21H_2$
Benzene reformer	$C_6H_6 + 6H_2O \rightarrow 6CO + 9H_2$
Toluene reformer	$C_7H_8 + 7H_2O \rightarrow 7CO + 11H_2$
Isobutane reformer	$i - C_4H_{10} + 4H_2O \rightarrow 4CO + 9H_2$
Isopentane reformer	$i - C_5H_{12} + 5H_2O \rightarrow 5CO + 11H_2$
Methylcyclopentane	$C_6H_{12} + 6H_2O \rightarrow 6CO + 12H_2$
Methylcyclohexane	$C_7H_{14} + 7H_2O \rightarrow 7CO + 14H_2$
Methanation	$CO + 3H_2 \rightarrow CH_4 + H_2O$
Water Gas Shift	$CO + H_2O \rightarrow CO_2 + H_2$

### **Combustions of hydrocarbons taking place at ATR1:**

Methane combustion	$CH_4 + O_2 \rightarrow CO_2 + 2H_2O$
Ethane combustion	$C_2H_6 + 3.5O_2 \rightarrow 2CO_2 + 3H_2O$
Propane combustion	$C_3H_8 + 5O_2 \rightarrow 3CO_2 + 4H_2O$
Butane combustion	$C_4H_{10} + 6.5O_2 \rightarrow 4CO_2 + 5H_2O$
Isobutane combustion	$iC_4H_{10} + 6.5O_2 \rightarrow 4CO_2 + 5H_2O$
Pentane combustion	$C_5H_{12} + 8O_2 \rightarrow 5CO_2 + 6H_2O$
Isopentane combustion	$iC_5H_{12} + 8O_2 \rightarrow 5CO_2 + 6H_2O$
Hexane combustion	$C_6H_{14} + 9.5O_2 \rightarrow 6CO_2 + 7H_2O$
Cyclohexane combustion	$C_6H_{12} + 9O_2 \rightarrow 6CO_2 + 6H_2O$
MCH combustion	$C_7H_{14} + 10.5O_2 \rightarrow 7CO_2 + 7H_2O$



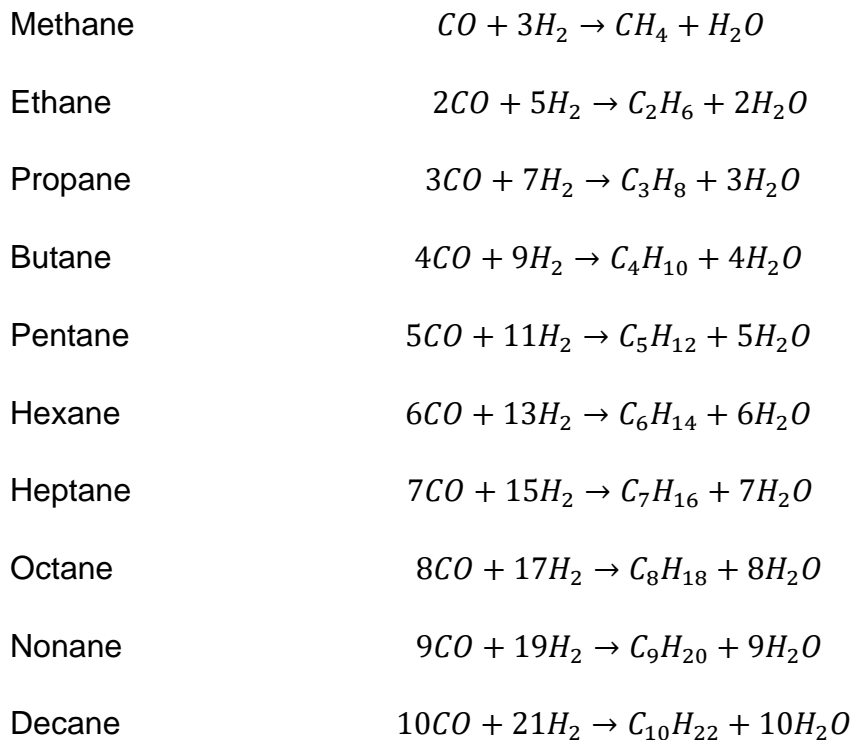
### Reactions taking place at steam reformer



### Reaction taking place at RWGS:



### Reactions taking place at FTR



Undecane	$11CO + 23H_2 \rightarrow C_{11}H_{24} + 11H_2O$
Dodecane	$12CO + 25H_2 \rightarrow C_{12}H_{26} + 12H_2O$
Tridecane	$13CO + 27H_2 \rightarrow C_{13}H_{28} + 13H_2O$
Tetradecane	$14CO + 29H_2 \rightarrow C_{14}H_{30} + 14H_2O$
Pentadecane	$15CO + 31H_2 \rightarrow C_{15}H_{32} + 15H_2O$
Hexadecane	$16CO + 33H_2 \rightarrow C_{16}H_{34} + 16H_2O$
Heptadecane	$17CO + 35H_2 \rightarrow C_{17}H_{36} + 17H_2O$
Octadecane	$18CO + 37H_2 \rightarrow C_{18}H_{38} + 18H_2O$
Nonadecane	$19CO + 39H_2 \rightarrow C_{19}H_{40} + 19H_2O$
Eicosane	$20CO + 41H_2 \rightarrow C_{20}H_{42} + 20H_2O$
Heneicosane	$21CO + 43H_2 \rightarrow C_{21}H_{44} + 21H_2O$
Docosane	$22CO + 45H_2 \rightarrow C_{22}H_{46} + 22H_2O$
Tricosane	$23CO + 47H_2 \rightarrow C_{23}H_{48} + 23H_2O$
Tetracosane	$24CO + 49H_2 \rightarrow C_{24}H_{50} + 24H_2O$
Pentacosane	$25CO + 51H_2 \rightarrow C_{25}H_{52} + 25H_2O$
Hexacosane	$26CO + 53H_2 \rightarrow C_{26}H_{54} + 26H_2O$
Heptacosane	$27CO + 55H_2 \rightarrow C_{27}H_{56} + 27H_2O$
Octocosane	$28CO + 57H_2 \rightarrow C_{28}H_{58} + 28H_2O$
Nonacosane	$29CO + 59H_2 \rightarrow C_{29}H_{60} + 29H_2O$

## Cost estimation

The cost calculation shown here is for plant 1 but plant 2 and plant 3 follow the same procedures

### Raw material cost

$$\frac{2.95USD}{28.3m^3} \text{ Equation A1}$$

Natural gas density varies from 0.7kg/m<sup>3</sup>-0.9kg/m<sup>3</sup>

$$\rho_{Ng} = 0.8 \frac{kg}{m^3} \text{ Equation A2}$$

$$28.3m^3 * 0.8 \frac{kg}{m^3} = 22.64kg \text{ Equation A3}$$

$$\frac{2.95USD}{22.64kg}$$

Estimated annual cost

$$\frac{2.95USD}{22.64kg} * 150,603,440 \frac{kg}{year} = 19,377,553.92 \frac{USD}{year} \text{ Equation A4}$$

Hydrogen cost

$$\frac{4.55USD}{1kg} * 2,119,093.2 \frac{kg}{year} = 9,853,783.38 \frac{USD}{year} \text{ Equation A5}$$

### Reactor Cost

$$FTR = 17,640 * 3^{1.066} * 20^{0.802} = 628,833.82USD \text{ Equation A6}$$

$$SR = 17,640 * 6^{1.066} * 12^{0.802} = 873,999.47USD \text{ Equation A7}$$

$$Pre - Reformer = 17,640 * 3^{1.066} * 4^{0.802} = 172,966.48USD \text{ Equation A8}$$



$$RWGS = 17,640 * 6^{1.066} * 14^{0.802} = 989,014.13USD \text{ Equation A9}$$

### Heat Exchanger Cost

$$Cooler1 = 7,296 * 20.58^{0.65} = 52,098.39 \text{ Equation A10}$$

$$Cooler2 = 7,296 * 195.37^{0.65} = 224,979.23 \text{ Equation A11}$$

$$Cooler3 = 7,296 * 97.53^{0.65} = 143,226.92 \text{ Equation A12}$$

$$Cooler4 = 7,296 * 349.42^{0.65} = 328,292.43 \text{ Equation A13}$$

$$Cooler5 = 7,296 * 112.80^{0.65} = 157,429.36 \text{ Equation A14}$$

$$Intercooler1 = 7,296 * 19.37^{0.65} = 50,086.31 \text{ Equation A15}$$

$$Intercooler2 = 7,296 * 11.77^{0.65} = 36,231.76 \text{ Equation A16}$$

$$Intercooler3 = 7,296 * 15.70^{0.65} = 43,693.77 \text{ Equation A17}$$

$$Intercooler4 = 7,296 * 46.33^{0.65} = 88,286.70 \text{ Equation A18}$$

$$intercooler5 = 7,296 * 36.65^{0.65} = 75,811.11 \text{ Equation A19}$$

$$intercooler6 = 7,296 * 22.22^{0.65} = 54,760.63 \text{ Equation A20}$$

$$intercooler7 = 7,296 * 1.83^{0.65} = 10,806.32 \text{ Equation A21}$$

$$intercooler8 = 7,296 * 1.44^{0.65} = 9,247.41 \text{ Equation A22}$$

$$intercooler9 = 7,296 * 1.26^{0.65} = 8,478.63 \text{ Equation A23}$$

### Compressor Cost

Hydrogen four stage compressor

$$W = \left( \frac{4 * 1.41}{1.41 - 1} \right) * 100,000Pa * 0.826 \frac{m^3}{s} * \left[ \left( \frac{240,000Pa}{100,000Pa} \right)^{\left( \frac{1.41-1}{4*1.41} \right)} - 1 \right]$$

$$= \frac{295,534.85J}{s} \text{ Equation A24}$$

$$295,534.85 \frac{\text{J}}{\text{s}} * 0.001341 \text{hp} = 396.32 \text{hp Equation A25}$$

Natural gas four stage compressor

$$W = \left( \frac{4 * 1.32}{1.32 - 1} \right) * 100,000 \text{Pa} * 7.026 \frac{\text{m}^3}{\text{s}} * \left[ \left( \frac{240,000 \text{Pa}}{100,000 \text{Pa}} \right)^{\left( \frac{1.32-1}{4*1.32} \right)} - 1 \right]$$

$$= \frac{2,462,693.55 \text{J}}{\text{s}} \text{ Equation A26}$$

$$2,462,693.55 \frac{\text{J}}{\text{s}} * 0.001341 \text{hp} = 3,302.52 \text{hp Equation A27}$$

Air four stage compressor

$$W = \left( \frac{4 * 1.4}{1.4 - 1} \right) * 100,000 \text{Pa} * 20.64 \frac{\text{m}^3}{\text{s}} * \left[ \left( \frac{240,000 \text{Pa}}{100,000 \text{Pa}} \right)^{\left( \frac{1.4-1}{4*1.4} \right)} - 1 \right]$$

$$= \frac{7,366,351.64 \text{J}}{\text{s}} \text{ Equation A28}$$

$$7,366,351.4 \frac{\text{J}}{\text{s}} * 0.001341 \text{hp} = 9,878.44 \text{hp Equation A29}$$

## Flash Operator

Flash1

$$V_{\max(ft/s)} = \frac{0.5}{\sqrt{0.4014 \text{lb}/\text{ft}^3}} = \frac{0.789 \text{ft}}{\text{s}} \text{ Equation A30}$$

$$0.789 \frac{\text{ft}}{\text{s}} * 0.3048 \frac{\text{m}}{\text{s}} = 0.24 \frac{\text{m}}{\text{s}} \text{ Equation A31}$$

$$V_L = \frac{2,704.33 \text{ mol/s}}{352 \text{ mol/m}^3} = 7.68 \frac{\text{m}^3}{\text{s}} \text{ Equation A32}$$

$$A = \frac{7.68 \text{m}^3/\text{s}}{0.24 \text{m/s}} = 32 \text{m}^2 \text{ Equation A33}$$

$$D = \sqrt{\frac{32 \text{m}^2 * 4}{\pi}} = 6.4 \text{m} \text{ Equation A34}$$

$$L = 6.4 \text{m} * 2 = 12.8 \text{m} \text{ Equation A35}$$

## Flash2

$$V_{max(ft/s)} = \frac{0.5}{\sqrt[2]{0.824 \text{lb/ft}^3}} = \frac{0.55 \text{ft}}{\text{s}} \text{ Equation A36}$$

$$0.55 \frac{\text{ft}}{\text{s}} * 0.3048 \frac{\text{m}}{\text{s}} = 0.168 \frac{\text{m}}{\text{s}} \text{ Equation A37}$$

$$V_L = \frac{1,212.62 \text{ mol/s}}{537.66 \text{ mol/m}^3} = 2.26 \frac{\text{m}^3}{\text{s}} \text{ Equation A38}$$

$$A = \frac{2.26 \text{m}^3/\text{s}}{0.168 \text{m/s}} = 13.42 \text{m}^2 \text{ Equation A39}$$

$$D = \sqrt{\frac{13.42 \text{m}^2 * 4}{\pi}} = 4 \text{m} \text{ Equation A40}$$

$$L = 4 \text{m} * 2 = 8 \text{m} \text{ Equation A41}$$

## Flash3

$$V_{max(ft/s)} = \frac{0.5}{\sqrt[2]{0.902 \text{lb/ft}^3}} = \frac{0.526 \text{ft}}{\text{s}} \text{ Equation A42}$$

$$0.526 \frac{\text{ft}}{\text{s}} * 0.3048 \frac{\text{m}}{\text{s}} = 0.16 \frac{\text{m}}{\text{s}} \text{ Equation A43}$$

$$V_L = \frac{1,011.44 \text{ mol/s}}{586.67 \text{ mol/m}^3} = 1.72 \frac{\text{m}^3}{\text{s}} \text{ Equation A44}$$

$$A = \frac{1.72 \text{m}^3/\text{s}}{0.16 \text{m/s}} = 10.8 \text{m}^2 \text{ Equation A45}$$

$$D = \sqrt[2]{\frac{10.8 \text{m}^2 * 4}{\pi}} = 3.7 \text{m} \text{ Equation A46}$$

$$L = 3.7 \text{m} * 2 = 7.4 \text{m} \text{ Equation A47}$$

#### Flash4

$$V_{\max(ft/s)} = \frac{0.5}{\sqrt[2]{1.119 \text{lb/ft}^3}} = \frac{0.473 \text{ft}}{\text{s}} \text{ Equation A48}$$

$$0.473 \frac{\text{ft}}{\text{s}} * 0.3048 \frac{\text{m}}{\text{s}} = 0.144 \frac{\text{m}}{\text{s}} \text{ Equation A49}$$

$$V_L = \frac{44.73 \text{ mol/s}}{741.78 \text{ mol/m}^3} = 0.06 \frac{\text{m}^3}{\text{s}} \text{ Equation A50}$$

$$A = \frac{0.06 \text{m}^3/\text{s}}{0.144 \text{m/s}} = 0.418 \text{m}^2 \text{ Equation A51}$$

$$D = \sqrt[2]{\frac{0.418 \text{m}^2 * 4}{\pi}} = 0.73 \text{m} \text{ Equation A52}$$

$$L = 0.73 \text{m} * 2 = 1.46 \text{m} \text{ Equation A53}$$

#### Flash5

$$V_{\max(ft/s)} = \frac{0.5}{\sqrt[2]{1.12 \text{lb/ft}^3}} = \frac{0.472 \text{ft}}{\text{s}} \text{ Equation A54}$$

$$0.472 \frac{\text{ft}}{\text{s}} * 0.3048 \frac{\text{m}}{\text{s}} = 0.144 \frac{\text{m}}{\text{s}} \text{ Equation A55}$$

$$V_L = \frac{966.7 \text{ mol/s}}{739.95 \text{ mol/m}^3} = 1.306 \frac{\text{m}^3}{\text{s}} \text{ Equation A56}$$

$$A = \frac{1.306 \text{m}^3/\text{s}}{0.144 \text{m/s}} = 9.072 \text{m}^2 \text{ Equation A57}$$

$$D = \sqrt{\frac{9.072 \text{m}^2 * 4}{\pi}} = 3.4 \text{m} \text{ Equation A58}$$

$$L = 3.4 \text{m} * 2 = 6.8 \text{m} \text{ Equation A59}$$

## Utilities Cost

Table A5: Cooling Water

	m <sup>3</sup> /s	m <sup>3</sup> /h
Cooler1	28.26	101,742.55
Cooler2	114.96	413,856.81
Cooler3	159.97	575,901.26
Cooler4	234.88	845,583.53
Cooler5	32.32	116,377.30
InterCooler1	3.99	14,384.94
InterCooler2	3.28	11,825.09
InterCooler3	1.19	4,300.37
InterCooler4	13.50	48,629.56
InterCooler5	6.18	22,278.15
InterCooler6	5.54	19,951.40
InterCooler7	0.54	1,950.37
InterCooler8	0.33	1,198.67
InterCooler9	0.18	673.47
	Total	2,178,653.54

$$\text{Circulation flow} = 2,178,653.54 \frac{\text{m}^3}{\text{h}} \text{ Equation A60}$$

$$\text{Evaporation loss} = \frac{\left[0.85 * \left(\frac{1}{100}\right) * 5.56\right]}{5.56} * 2,178,653.54 \frac{m^3}{h} \text{ Equation A61}$$

$$\text{Evaporation loss} = 18,518.55 \frac{m^3}{h} \text{ Equation A62}$$

$$\text{Drift loss} = \frac{0.2}{100} * 2,178,653.54 \frac{m^3}{h} \text{ Equation A63}$$

$$\text{Drift loss} = 4,357.30 \frac{m^3}{h} \text{ Equation A64}$$

$$\text{Blowdown} = \frac{18,518.55}{(4 - 1)} \frac{m^3}{h} \text{ Equation A65}$$

$$\text{Blowdown} = 6,172.82 \frac{m^3}{h} \text{ Equation A65}$$

$$\text{Make up water} = 18,518.55 \frac{m^3}{h} + 4,357.30 \frac{m^3}{h} + 6,172.82 \frac{m^3}{h} \text{ Equation A66}$$

$$\text{Make up water} = 29,048.71 \frac{m^3}{h} \text{ Equation A67}$$

$$\text{Make up water} = 697,169.13 \frac{m^3}{\text{day}} \text{ Equation A68}$$

$$\text{Make up water} = 254,466,733.4 \frac{m^3}{\text{year}} \text{ Equation A69}$$

Nickel Catalyst

$$\begin{aligned} & 3.14 * \frac{(0.03m)^2}{4} * 12m * 2,000 \text{ tubes} * \frac{1,000kg}{m^3} * \frac{20USD}{kg} \\ & = 339,120.00 \frac{USD}{\text{year}} \text{ Equation A70} \end{aligned}$$

Nickel Catalyst

$$3.14 * \frac{(0.03m)^2}{4} * 4m * \frac{1,000kg}{m^3} * \frac{20USD}{kg} = 565,200.00 \frac{USD}{\text{year}} \text{ Equation A7}$$

## Cobalt Catalyst

$$3.14 * \frac{(0.046m)^2}{4} * 20m * 2,000tubes * \frac{101kg}{m^3} * \frac{100USD}{kg}$$
$$= 402,640.00 \frac{USD}{year} \text{ Equation A72}$$

## Iron Catalyst

$$3.14 * \frac{(0.03m)^2}{4} * 12m * 2,000tubes * \frac{1,603kg}{m^3} * \frac{10USD}{kg}$$
$$= 317,105.00 \frac{USD}{year} \text{ Equation A73}$$

## Energy cost

### Fired reactor

$$energy\ cost = 2.45 * \frac{10^{12}J}{year} * \frac{USD17.78}{1,000,000,000J} = \frac{43,657,583.54USD}{year} \text{ Equation A77}$$

### Compressor Energy Demand

$$energy\ cost = 6.45 * \frac{10^{13}J}{year} * \frac{USD17.78}{1,000,000,000J} = \frac{1,146,909.18USD}{year} \text{ Equation A78}$$

$$energy\ cost = 2.33 * \frac{10^{13}J}{year} * \frac{USD17.78}{1,000,000,000J} = \frac{414,322.24USD}{year} \text{ Equation A79}$$

$$energy\ cost = 1.29 * \frac{10^{13}J}{year} * \frac{USD17.78}{1,000,000,000J} = \frac{231,137.70USD}{year} \text{ Equation A80}$$

$$energy\ cost = 9.59 * \frac{10^{12}J}{year} * \frac{USD17.78}{1,000,000,000J} = \frac{170,543.56USD}{year} \text{ Equation A81}$$

$$energy\ cost = 2.03 * \frac{10^{14}J}{year} * \frac{USD17.78}{1,000,000,000J} = \frac{3,607,307.90USD}{year} \text{ Equation A82}$$

$$energy\ cost = 8.80 * \frac{10^{13}J}{year} * \frac{USD17.78}{1,000,000,000J} = \frac{1,565,998.55USD}{year} \text{ Equation A83}$$

$$\text{energy cost} = 4.35 * \frac{10^{13}J}{\text{year}} * \frac{\text{USD}17.78}{1,000,000,000J} = \frac{774,557.39\text{USD}}{\text{year}} \text{ Equation A84}$$

$$\text{energy cost} = 2.68 * \frac{10^{13}J}{\text{year}} * \frac{\text{USD}17.78}{1,000,000,000J} = \frac{476,898.38\text{USD}}{\text{year}} \text{ Equation A85}$$

$$\text{energy cost} = 8.14 * \frac{10^{12}J}{\text{year}} * \frac{\text{USD}17.78}{1,000,000,000J} = \frac{144,793.79\text{USD}}{\text{year}} \text{ Equation A86}$$

$$\text{energy cost} = 2.91 * \frac{10^{12}J}{\text{year}} * \frac{\text{USD}17.78}{1,000,000,000J} = \frac{51,783.82\text{USD}}{\text{year}} \text{ Equation A87}$$

$$\text{energy cost} = 1.56 * \frac{10^{12}J}{\text{year}} * \frac{\text{USD}17.78}{1,000,000,000J} = \frac{27,792.95\text{USD}}{\text{year}} \text{ Equation A88}$$

$$\text{energy cost} = 1.05 * \frac{10^{12}J}{\text{year}} * \frac{\text{USD}17.78}{1,000,000,000J} = \frac{18,650.05\text{USD}}{\text{year}} \text{ Equation A89}$$

Heater energy demand

$$\text{energy cost} = 2.68 * \frac{10^{15}J}{\text{year}} * \frac{\text{USD}17.78}{1,000,000,000J} = \frac{47,742,338.6\text{USD}}{\text{year}} \text{ Equation A90}$$

$$\text{energy cost} = 1.87 * \frac{10^{14}J}{\text{year}} * \frac{\text{USD}17.78}{1,000,000,000J} = \frac{3,339,017.87\text{USD}}{\text{year}} \text{ Equation A91}$$

## Equipment Specification

### Steam Boiler

5-75t/h high efficiency circulating fluidized bed steam boiler

Function: Steam boiler, oil boiler, hot air boiler

Fuel: coal, oil, gas, electricity

Water circulation: natural circulation

### Automatic demineralized water filter with reverse osmosis system

Model: T-20

Outcome capacity: 20ton/h



Motor power: 30kw

Membrane 8040

Entrance diameter: 60mm

Size(LxWxH)(mm): (3,000x1,800x2,000)

### **Multiphase Dissolved air flotation for oil and water treatment**

Model: GDXF-100

Capacity: 100m<sup>3</sup>/h

Size (LxWxD)(m): (9x3.6x2.1)

Total power: 15.55kw

Table A6: Equipment size

Reactor size (LxD)(m)	Plant 1	Plant 2	Plant 3
Pre-reformer	4x3	4x3	4x3
Steam reformer	12x6	9x4	8x4
RWGS	14x6	13x5	13x5
FTR	20x3	17x3	15x3
Heat Exchangers area (m <sup>2</sup> )	Plant 1	Plant 2	Plant 3
Intercooler 1	19.4	14.6	9.7
Intercooler 2	11.8	8.8	5.9
Intercooler 3	15.1	11.3	7.6
Intercooler 4	46.3	34.9	23.2
Intercooler 5	36.7	27.6	18.3
Intercooler 6	22.2	16.7	11.1
Intercooler 7	1.8	1.3	0.9
Intercooler 8	1.4	1.1	0.7
Intercooler 9	1.3	0.9	0.6
Cooler 1	20.6	15.4	10.3
Cooler 2	175.2	133.8	88.4
Cooler 3	97.5	73.2	48.8
Cooler 4	349.4	264.1	174.76

Cooler 5	112.6	92.4	64.6
Flash separator size (LxD)(m)	Plant 1	Plant 2	Plant 3
Flash 1	12.8x6.4	9.3x4.6	7.2x3.6
Flash 2	8x4	8x4	5.4x2.7
Flash 3	7.4x3.7	7.4x3.7	4.8x2.4
Flash 4	1.5x0.75	1.5x0.75	0.84x0.42
Flash 5	6.8x3.4	6.8x3.4	4.6x2.3
Compressor (hp)	Plant 1	Plant 2	Plant 3
Hydrogen	396.3	293.8	198.1
Natural gas	3,302.5	2,475.3	1,649.1
Air	9,878.4	7,439.6	4,937.9

Table A7: Cooling and Heating needs

<b>Fisher Tropsh Reactor cooling demand</b>			
	Plant1	Plant 2	Plant3
Q(kJ/year)	-2.015*10 <sup>12</sup>	-1.650*10 <sup>12</sup>	-1.031*10 <sup>12</sup>
Cooling water(m <sup>3</sup> /year)	5,074,895,355.29	4,156,804,462.93	1,298,384,320.78
Cost (USD/Year)	3,981,559,312.53	2,607,652,883.19	855,403,908.68
<b>Reverse Water Gas Shift Reactor heating demand</b>			
	Plant 1	Plant 2	Plant 3
Q (kJ/year)	9.69*10 <sup>10</sup>	7.00*10 <sup>10</sup>	5.50*10 <sup>10</sup>
Cost (USD/year)	1,722,253.81	1,245,158.64	977,104.65