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Diesel Production Using Gas to liquid Technology

إنتاج الديزل باستخدام تقنية (تحويل الغاز الطبيعي إلى سوائل هيدروكربونية)

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الأيـة :

قَالَ ٱللَّهُ تَعَالَىٰ
﴿٣١﴾ ٱللَّهُ ٱلَّذِى خَلَقَ
ٱلسَّمَٰوَٰتِ وَٱلْأَرْضَ وَأَنزَلَ مِنَ ٱلسَّمَآءِ مَآءً فَأَخْرَجَ بِهِۦ مِنَ
ٱلثَّمَرَٰتِ رِزْقًا لَّكُمْ ۖ وَسَخَّرَ لَكُمُ ٱلْفُلْكَ لِتَجْرِىَ فِى ٱلْبَحْرِ
بِأَمْرِهِۦ ۖ وَسَخَّرَ لَكُمُ ٱلْأَنْهَٰرَ ﴿٣٢﴾

سُورَةُ إبراهِيم

Dedication

We would be honored to dedicate this project to our parents, the two persons who gave the tools and values necessary for us to be where we are standing today, to all brothers, sisters, friends, teachers, colleagues, relatives, and anyone who assisted advised, and supported us and our project.

Acknowledgment

We would like to our full gratitude and appreciation to Eng. Sarah Ahmed Yassin for providing us the opportunity to work under her supervision, and we also express our gratitude to the Department of Transport and Refining Engineering for assistance to us on the completion of this research, also the our gratitude to Khartoum University, Department of Chemical Engineering, Last but not least to our families, all our lecturers, friends & collogues for encouragement and kind support when we needed it most.

Abstract:

A few years ago, the consumption of diesel fuel in Sudan increased, while the diesel production from our domestic refineries are insufficient to overcome the shortage of the local diesel demand, the project aims at devising a new method to produce in quantities that will cover the shortage in the market and deigned GTL unit.

Gas to Liquid (GTL) is a technology in which natural gas is converting in to crude oil i.e. Mixture of complexes hydrocarbon, we can also use coal and biomass for feed stock.

In the currently situation it is one of the alternative source of energy which can produce transportable fuel at economical rate an also environmentally clean fuel.The material and energy balance was calculated by HYSYS Software program, the size of Fisher Tropsch fixed bed reactor and the quantity of catalyst used were calculated, and produce sufficient quantities of diesel were obtained to cover local market demand.

التجـــــريد:

في الاعوام السابقة زاد الطلب علي الديزل في السودان بنسبة عالية وما تنتجه المصافي المحلية لا تكفي لتغطية الطلب . يهدف المشروع الي ابتكار طريقة جديدة لانتاج الديزل بكميات تكفي تغطية النقص في السوق وتصميم وحدة GTL.

(GTL) هي التكنلوجيا التي يتم فيها تحويل الغاز الطبيعي الى النفط الخام اي الى خليط من المركبات الهيدروكربونية . يمكن استخدام اشياء اخرى غير الغاز الطبيعي لكي تستخدم ك feed مثل ال , coal وال biomass . في الوقت الحالي يعد هذا المصدر احد مصادر الطاقة البديلة التي يمكن ان تنتج وقودا قابلا للنقل بسعر اقتصادي وهو ايضا يعد وقود نظيف بيئيا.

تم حساب موازنات المادة والطاقة عن طريق برنامج الهايسيس وتم حساب حجم مفاعل فيشر-تروبش وكمية العامل الحفاز المستخدم وتم الحصول علي كميات ديزل تكفي لتغطية الطلب في السوق.

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Symbol content

symbol	Description	unit
F_A	**Molar flow rate**	**mole/time**
W	**Catalyst Wight**	**kg**
N_A	**Number of mole**	**mole**
r'_A	**Rate of reaction**	**Mole/volume/time**
P_{H_2}	**Partial pressure of hydrogen**	**atm**
P_{CO}	**Partial pressure of CO**	**atm**
K	**Rate of reaction constant**	$\frac{Kmole}{Kgcat.min.atm^{1.5}}$
T	**Temperature**	°F
C_A	**Concentration of A**	**Mole/volume**
y_{H_2}	**Mole fraction**	
P_t	**Total pressure**	**ATM**
V	**Volume of Reactor**	m^3
V_B	**Bed volume**	m^3
ρ_{cat}	**Catalyst density**	Kg/m^3

Chapter 1

Introduction

1.1 Introduction:

In the early stage of oil and gas production, natural gas was only treated as unwanted product. So, the natural gas was burned and this has related in loses of millions dollar each day. Now days, people around the world start to realize that natural gas has it commercial value and can bring profits to this industry. Then come this Gas-to-Liquid Technology that been used worldwide now days.

Gas to liquid (GTL) technology converts natural gas – the cleanest-burning fossil fuel into high quality liquid products that would otherwise be made from crude oil. These products include transportation fuels, motor oils and the ingredients for everyday necessities like plastics, detergents and cosmetics.

GTL products are colorless and odorless. They contain almost none of the impurities – Sulphur, aromatics and nitrogen – that are found in crude oil.

Natural gas is abundant, versatile and affordable. GTL production can help countries with natural gas resources grow their economies as new gas supplies come on-stream to satisfy growing global demand for liquid products.

GTL is a refinery process to convert natural gas or other gaseous hydrocarbons into longer-chain hydrocarbons, such as gasoline or diesel fuel.

The motivation for GTL is to produce liquid fuels, which are more readily transported than methane. Methane must be cooled below its critical temperature of -82.3 °C in order to be liquefied under pressure. Because of the associated cryogenic apparatus, LNG tankers are expensive, not to mention potentially dangerous. Methanol is a conveniently handled combustible liquid.

Using gas-to-liquids processes, refineries can convert some of their gaseous waste products (flare gas) into valuable fuel oils, which can be sold as is or blended only with diesel fuel. The World Bank estimates that over 150 billion cubic meters (5.3×1012 cu ft.) of natural gas are flared or vented annually, an amount worth approximately $30.6 billion Gas-to-liquids processes may also be used for the economic extraction of gas deposits in locations where it is not economical to build a pipeline. This process will be increasingly significant as crude oil resources are depleted.

1.2 Methane-rich gases are converted into liquid synthetic fuels Two general strategies exist:

- **Direct partial combustion** of methane to methanol.
- **Fischer-Tropsch** like processes that convert methane into hydrogen and carbon monoxide (Synthesis), and convert syngas into (Synthesis Crude).

1.3 problem statement

A few years ago, the consumption of diesel fuel in Sudan increased, while the diesel production from our domestic refineries are insufficient to overcome the shortage of the local diesel demand, which has forced the government to supply diesel from outside the country so to solve this problem we submitted this project as dissertation of GTL unit design this unit is aimed to produce suitable quantities of diesel fuel which enhance the diesel production by using the GTL technology.

1.4 Objective:

The objectives of the research are:

- Optimum Design for GTL unit according to the characteristics of the Sudanese natural gas.
- Production of diesel with high quality.

Chapter 2

Literature Review

2.1 Natural gas:

Natural gas is a combustible, gaseous mixture of simple hydrocarbon compounds, usually found in deep

underground reservoirs formed by porous rock. Natural gas is a fossil fuel composed almost entirely of methane, but does contain small amounts of other gases, including ethane, propane, butane and pentane. Methane is composed of a molecule of one carbon atom and four hydrogen atoms.

Natural gas is a fossil fuel used as a source of energy for heating, cooking, and electricity generation. It is also used as a fuel for vehicles and as a chemical feedstock in the manufacture of plastics and other commercially important organic chemicals. Fossil fuel based natural gas is a non-renewable resource

2.1 Definitions of GTL:

Gas to liquids (GTL) is a refinery process to convert natural gas or other gaseous hydrocarbons into longer-chain hydrocarbons, such as gasoline or diesel fuel. Methane-rich gases are converted into liquid synthetic fuels either via direct conversion-using non-catalytic processes that convert methane to methanol in one step-or via syngas as an intermediate, such as in the FT, Mobil, and syngas to gasoline plus processes. It shares many similarities with indirect coal liquefaction that full breaks down coal into hydrogen and carbon that can be reassembled into H-C-chains of a desired length. (Mikael, 2013)

2.2 The Benefits of GTL:

1. Reduction in harmful emissions including Nitrogen Oxides (NOx), Particulate Matter (PM), Carbon Monoxide(CO), and unburnt hydrocarbons (HC's). Quantifiable benefits vary significantly depending on many factors, such as engine size, age, industry, etc.

2. Ease of use so there is No need for engine modifications, new infrastructure or vehicle investment it can be used as a direct replacement for conventional diesel fuels in heavy and light-duty engines.

3. GTL Fuel has a longer shelf life than conventional diesel as it is FAME-free with no bio content and with a CFPP below -20˚C. As it will mix with gas oil, there is no need to clean tanks first and that why it's better in storage.

4. The fuel offers improved levels of safety, handling and storage characteristics due to a higher flash point. As a non-toxic, odorless fuel, GTL Fuel has a low hazard rating because all molecules are paraffinic.

5. It provides a better starting performance in cold conditions due to a higher cetane number and a low cold filter plugging point (the temperature at which diesel starts to wax).

2.3 Advantages of GTL:

1. In the aspect of environment, this technology produces much more environment friendly product. GTL diesel product has almost zero Sulphur, low aromatics, a high cetane number and lower density compared to refinery diesel. It also can be used as blend stock to improve the quality of larger quantities of standard diesel in the markets where strict specifications are demand.

2. GTL also is beneficial at the area where non-flaring policy for associated gas used. This technology also has no greater impact on global warming.

System used in GTL to compare to a crude oil refinery system produces lower amount of carbon dioxide emissions and GHG.

2.4 Green House Gases:

Greenhouse gases trap heat in the atmosphere, which makes the earth warmer by absorbing and emitting radiant energy within the thermal infrared range. Increasing greenhouse gasses emissions cause the greenhouse effect. The prime forcing gases of the greenhouse effect are: carbon dioxide (CO2). Methane (CH4), nitrous oxide(N2O) and fluorinated gases. They are caused by human activity and some are naturally occurring, GHGs absorb infra-red radiation and trap heat in the atmosphere, therapy enhancing the natural greenhouse effect defined as global warming.

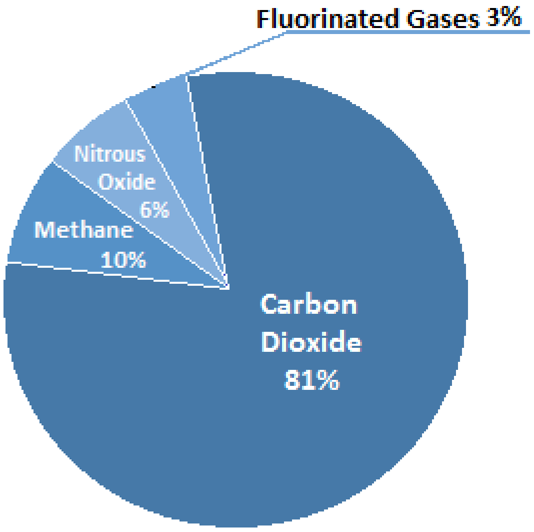


Figure 1.2U.S. Greenhouse gas emissions in 2016

2.5 Previous study:

The FT process discovered in Germany by Franz Fischer and Hans Tropsch in the 1920. During World War II, first time coal is converted to liquid transport fuels in Germany. But after the war FT process were disconnected due to easy availability of petroleum. Oryx is the first full time scale modern GTL production facility in the world.

Prof. Franz Fischer

Dr. Hans Tropsch

- 1902 Sabatier and Sanderson report that methane is formed from CO and hydrogen over Ni and Co catalysts.
- 1908 Orlov finds ethane from synthesis gas over $NiPd$ catalysts.
- 1913 BASF patent for "Preparation of a liquid oil from synthesis gas", Co and Os catalysts.
- 1924 Fischer and Tropsch report about the preparation of hydrocarbons over an Fe catalyst, the catalyst deactivates rapidly.
- 1936 The first 4 plants are commissioned (200,000 t/year capacity), Pichler finds that by increasing the pressure to 15 bar, the lifetime of the catalyst increases
- 1944 Nine plants and a total of 700,000 tons/year; Co catalyst (Co, ThO_2, MgO, Kieselguhr)
- 1955 Sasol I starts (combination of fixed and fluid bed reactors).

- **Pichlers et al., (1967)** experimentally worked on organ metallic complexes. They studied that carbide are intermediate in chain growth process of Fischer Tropsch reaction. When carbide is interacting with CO then oxygenates are formed. However, when methylene is interacting with carbide then organ metallic are formed Hinder Mann et al.
- **1994 Shell starts operating plant in Malaysia (SMDS process).**
- **Van der Laan et al., (1994**) reviewed the overall kinetics and reaction mechanism of Fischer–Tropsch (FT) process. It is concluded that the development of rate equations for the Fischer Tropsch Synthesis should be based on realistic mechanistic schemes. The proposed Fischer Tropsch kinetic equations on iron catalysts show inhibiting effects of CO_2 and H_2O, dependent on the Water Gas Selectivity activity. The product distribution of the FTS shows significant deviations from the Anderson–Schulz–Flory distribution on iron, cobalt, and ruthenium catalysts. The chain-length dependency of the olefin-to paraffin ratio can hardly be due to diffusion effects only.
- **LiuQuan et al., (1998)** discussed the dynamics behavior of the Fisher Tropsch fixed bed reactor. They concluded that most effective parameter for the determination of performance of reactor are the pre exponential kinetic constant and radial heat transfer parameter. The wall temperature has much effect than feed temperature. Also they found that steady state conversion down as the feed temperature decline.
- **Gerard et al., (1999**) analyzed the reaction kinetics of FT reaction in the gas-slurry system. They also focused on the side reaction like the water gas shift reaction. The main aim was to described the reaction mechanisms of gas-solid system. The results show that reaction rates of the FT synthesis depend on the H_2/CO feed ratios. It is directly proportional to ratio of H_2/CO in feed. The water gas shift reaction rate is also lower at these low

H_2/CO ratios due to complete occupation of the Water Gas Shift catalyst sites.

- **Yi-Ning wang &yuang-yuang, (2003)** simulated one dimensional heterogeneous model for fixed bed with recycle stream for Fischer Tropsch Synthesis process. The simulation results show that the increase of tube diameter is unfavourable to increase of over all yields of C5+products and allowable diameter less than 60mm in their cases. Increasing of coolant temperature suppresses the C5+ yield however it increases the conversion of CO. They take the assumption that gasses are ideal in nature.
- **Marvast et al., (2004)** modelled a 2 D packed bed Fischer –Tropsch reactor packed with Fe-HZSM5 catalyst .They studied effect of operating parameter on the selectivity of products and calculated the optimum condition for pilot plant to be operated in the Research Institute of Petroleum Industry (RIPI).They concluded that a better performance of reactor system is achieved by applying a feed with a H_2/CO ratio of 0.8.they also analyzed that Increasing in tube diameter having no effect on selectivity and yield of products.
- **Yang et al., (2004)** studied detailed kinetics of the Fischer-Tropsch synthesis over an industrial Fe-Mn catalyst in a fixed-bed reactor under the conditions [temperature, 540-600 K; pressure, 1.0-3.0 MPa; H_2/CO feed ratio, 1.0-3.0; space velocity, (1.6-4.2) 10-3 Nm^3kg of $catalyst^{-1}s^{-1}$]. Reaction rate equations were derived on the basis of the Langmuir-Hinshelwood-Hougen-Watson type models for the Fischer-Tropsch reactions and the water-gas-shift reaction. They also optimize the kinetic parameters, with a genetic algorithm approach and second optimization with the conventional Levenberg-Marquardt method.
- **Ali Adel Nader, (2004)** simulated a mathematical models of slurry bed reactor that is conducted in GTL process, and studied the effect of the design parameters, hydrodynamics parameters, and reaction kinetics on

transport processes. They found that the Cobalt catalyst shows higher conversion value of about (0.9) than that of the Iron catalyst (0.78). Therefore, Cobalt catalyst is the best option for the Fischer-Tropsch Synthesis due to the high conversion, and low water gas shift activity compared with Iron catalyst. For Cobalt catalyst the favourable ratio for syn gas conversion is about 2, while for Iron catalyst it is around of 1.5 to 1.7.

- **Botes et al., (2005)** studied the combination of an alkali-promoted iron-based Fischer–Tropsch catalyst and an acidic co-catalyst (HZSM-5) i.e. bifunctional catalyst for syngas conversion to hydrocarbons in a fixed reactor. It was found that the addition of HZSM-5 to the Fischer–Tropsch process improved both the selectivity and the quality of the gasoline product fraction. But at the same time selectivity of low value paraffin's was very high. So, we didn't get longer chain of carbon i.e. gasoline, diesel. So, the commercial application of a bifunctional process became difficult.
- **2005 - Several large GTL processes under construction. (Burtron H. Davis, 2006).**
- **Bartholomew et al., (2006)** compared cobalt catalyst and Fe catalyst. They used cobalt at the place Fe catalyst in FT process. they found that Iron (Fe) catalyst having lower cost but it has lower life and less selectivity. Catalyst have not the same activity throughout the process with the time its activity is decreases due to coke deposits, sulphur poisoning and variable operating condition. So the catalyst regeneration is required with the time. Cobalt having higher activity than Iron due to readsorption of oefin on catalyst is higher.
- **Sehab iague et al. (2008)** modelled a slurry bed reactor which having capacity of 10000bbl/day and simulated with Neural Network. The main aim of the project was to optimize the operating condition of reactor. They found that optimize value of composition of feed at the ratio of H_2/CO is equal to 2. They also reputed the effect of operating condition.

- **Buping Bao, (2008)** worked on thermal pinch analysis to reduce the losses of whole GTL plant. They integrated heat engine with Heat Exchanger Network and calculated the amount of losses that can be recovered for power generation and improve the efficiency of overall plant. They worked on the case study of GTL plant which having capacity of 1.16 bbl/day. They calculated optimum condition of process and they worked on economic analysis and reported that under current market prices tos sustain of GTL plant, the production capacity should be at least 68,000 BPD to make profit.
- **Robert et al., (2008)** compared slurry bubble column and fixed-bed reactors with monolith reactors on the basis of productivity per unit catalyst by mathematical modelling. The main aim to study the catalyst activity losses due to mass and heat transfer resistance and analyzed which reactor is better on the basis of catalyst activity period. The results come from the simulation show that a microstructure reactor is the best than slurry bubble column reactor and at last monolith reactor. The order of this reactor on the basis of productivity per unit of catalyst volume followed is same. The fixed-bed reactor has low catalyst specific productivity due to severe mass transfer resistances.
- **Shah Hosseini et al., (2009)** simulated the 2D model of fixed bed Fischer –Tropsch reactor and studied the hydrodynamics of reactor. They also studied the effect of parameter like particle diameter, bed void age, fluid velocity and bed length on pressure drop. They concluded that lower pressure drop in the reactor can be obtained by increasing diameter of tube and by decreasing the velocity of fluid. Rahim pour et al., (2009) proposed a model of two reactors in which one is fixed bed reactor and other is fluidized bed reactor. both the reactor is combined to form Fischer tropsch products. In the fixed bed reactor water are used as coolant are used. And fluidized bed gas is used for that. In this combined reactor process the

membrane was used to production of hydrogen by which we can used this produced hydrogen in the feed so that we can get optimum value of H_2/CO in feed. Results showed gasoline yield is more in the above combination of Fischer Tropsch reactor were obtained. Beside its they also found decrease in formation of carbon dioxide along the fluidized bed reactor.

- **Philippe et al., (2009)** investigated the effects of operating conditions like velocity temperature, composition on the selectivity and yield of product. The main aim of the project was to study catalyst properties like thermal conductivity of catalyst, specific heat on the operation of reactor and yield of product. They found that thermal properties become effective when the velocity of fluid is low or large diameter tube are used. Because in large dense structure thermal properties having less effect.
- **Irani et al., (2011)** developed a 2-D CFD model of fixed bed reactor for Fischer Tropsch. They used saturated steam as coolant to maintain wall temperature of reactor. hydrodynamics, chemical reaction, non-ideality of the mixture, heat and mass transfer in the reactor. They also studied effect of parameter. The model assumptions are that they consider gasses are ideal and homogeneous model. They got Good agreement of simulation results with the pilot experimental data. The result showed that when they maintain the flow rate of coolant equal to 25–250 g.min–. they got better maintained of wall temperature and they found optimum temperature of wall is equal to 573 K.
- **Miroliaei et al. (2012)** simulated the Fischer Tropsch reaction in in a fixed bed reactor using CFD. The model of fixed bed reactor was eulerian model. AT first they validated the model and then study the effect of parameter. The main aim of this investigation was to study product selectivity. It they found that selectivity of product can be increased by increasing the temperature of feed and coolant. (Kamar, 2014)

2.6 Industry:

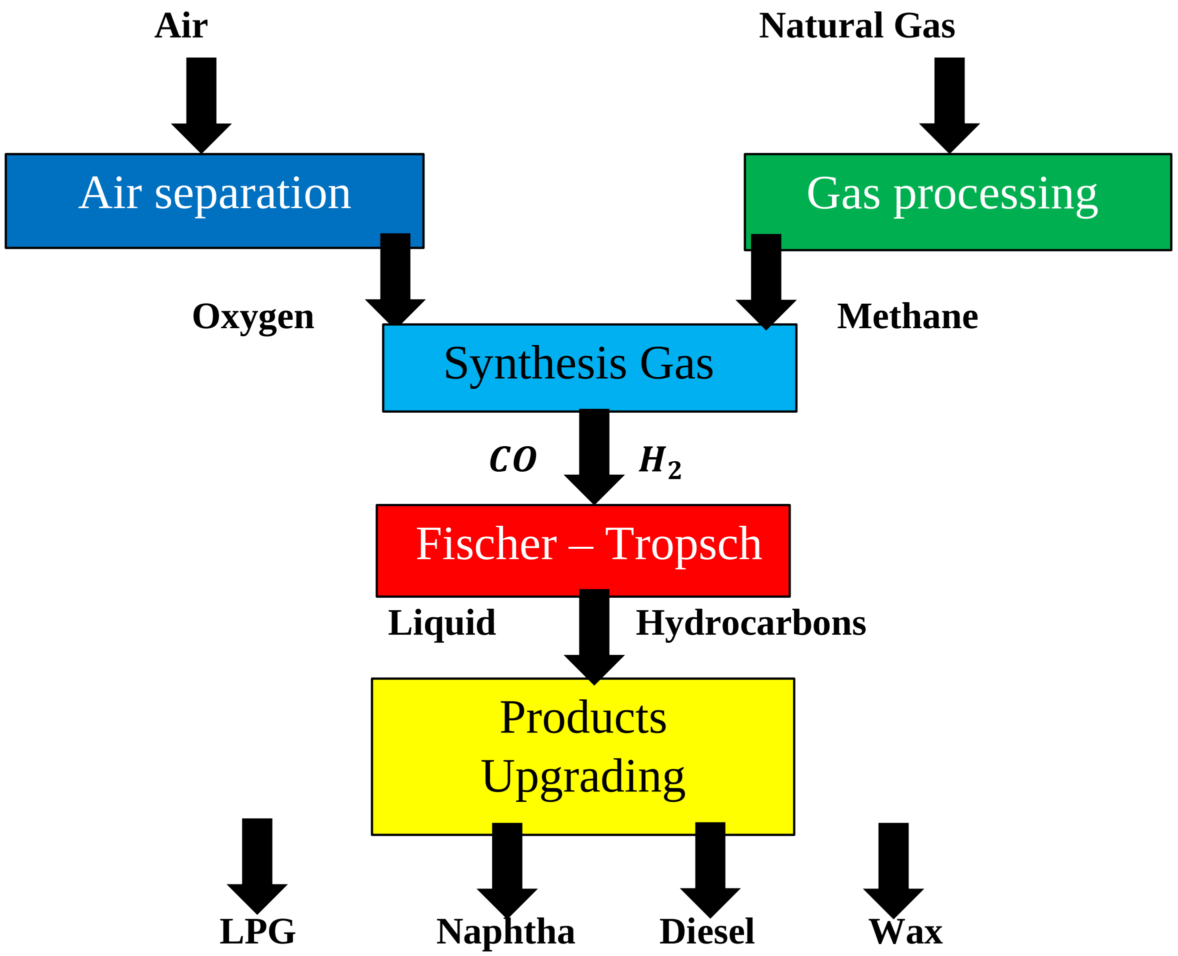
Table 1.2list of company’s participated in fischer-tropsch (van der laan et al..,1999)

company	Synthesis gas preparation	FT reactor	Capacity (bbl/day)	Catalyst
Exxon	CPO (O_2)	slurry	200	Co
Renatech	PO with O_2, SR, ATR	slurry	235	Fe
Sasol	Coal gasification	fluidized	111,000	Fe, Co
Shell	Po with O_2	fixed	12,500	Co
Syntroleum	ATR with air	fixed	200	Co

Where:

- **CPO ≫ Catalytic Partial Oxidation.**
- **SR ≫ Steam Reforming**
- **ATR ≫ Auto Thermal Reforming.** (Kamar, 2014)

2.7 GTL Process Steps:



Overall process scheme Fischer-Tropsch

2.7.1 Air separation unit.

Cryogenic separation of air is used to obtain oxygen with a purity of approximately 99.8%.

2.7.2 Feed gas processing:

I.Desulfurization:

To prevent catalyst poisoning in subsequent steps, it is imperative for the gas to be free of contaminants, especially Sulfur compounds. In addition, the separation of valuable NGL from the raw feedstock is important. At the end of the feed Gas processing step, greater than **99%** of sulfur and LPG is recovered**.**

- **There are three steps in the desulfurization of natural gas:**

a. using an amine treatment step to remove H_2S and CO_2

b. Conversion of H_2S into elemental sulfur.

c. Adsorption.

II. Remove NGL:

In this assembly, NGL such as LPG and condensate are separated.

III. Trace component removal:

Organic chlorine and mercury contaminants in natural gas are removed by adsorbents. (Remans, 2008)

2.7.3 The Synthesis Gas:

In the latter half of the nineteenth century, complete gasification of coke was achieved commercially by means of cyclic gas generator in which the coke was alternately blasted with air to provide heat and steam to generate "**Blue Water Gas**", a name given to the gas because it formed from steam and burned with blue flame [4]. The discovery of blue gas is attributed to Fontana in 1780, who proposed making it by passing steam over incandescent carbon. The blue gas was composed of about 50 % H_2 (Howard, 2013)

The name "**Blue Water Gas**" of the mixture $CO$and H_2 was changed to "**Synthesis Gas"** or "**Syngas**", a name which is given to mixtures of gases in suitable properties for the production of synthesis products without adding further reactants. Synthesis gas is composed primarily of carbon monoxide and hydrogen, and it is an odorless, colorless and toxic gas. Its specific gravity depends to percent of hydrogen and carbon monoxide content, and will burn flameless when introduced to air and temperature of

574℃. Synthesis gas can be used as a fuel to generate electricity or steam or used as a basic chemical building block for a large number of uses in the petrochemical and refining industries. It is also utilized as a source of hydrogen for production of methanol, ammonia and hydrogen delivery in gas treating operations and even as fuel.

➢ Main Methods of Producing Synthesis Gas:

1. Gasification.
2. Partial Oxidation (PO).
3. Steam Reforming (SR).
4. Auto thermal Reforming(ATR).

➢ Autothermal Reforming (ATR)

In this project we use ATR method to obtained Syngas, because This process is a combination of the above two processes (PO and SR) in a single step. The benefits are a lower reaction temperature, lower oxygen assumption, and an H_2/CO ratio of 2:1 that is ideally suited for the Fischer-Tropsch synthesis.

2.7.4 Fischer-Tropsch synthesis

Fischer-Tropsch synthesis is a process that the syngas is converted into crude oil its means mixture of hydrocarbon. That why its product is called syncrude. After that by conventional refinery process to get useful hydrocarbon like Fuel gas, LPG, Gasoline, Naphtha, Kerosene, Diesel, Middle distillates, Soft wax, Medium wax, Hard wax. In syncrude composition is mainly depended on operating temperature. The FTS process divided in to two part according to operating temperature:

I. low temperature Fischer–Tropsch (LTFT) process, operated at 200–250℃,

II. High temperature Fischer–Tropsch (HTFT) process, operated at 300–350 ℃

we can have analyzed that if we required lighter product we have to used higher operating temperature (HTFT) process. because at higher temperature cracking reaction become very fast. So, according to product requirement we can used operating condition and get required product composition depend on temperature

that lighter component gets from HTFT and heavier component get from LTFT. So, according to product requirement we can use LTFT and HTFT (Kamar, 2014).

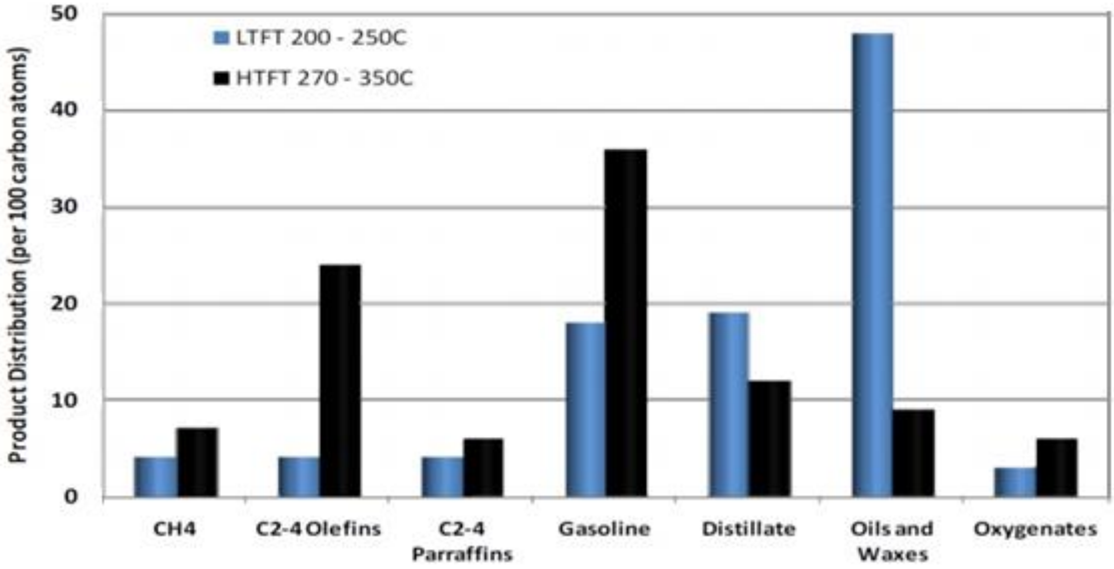


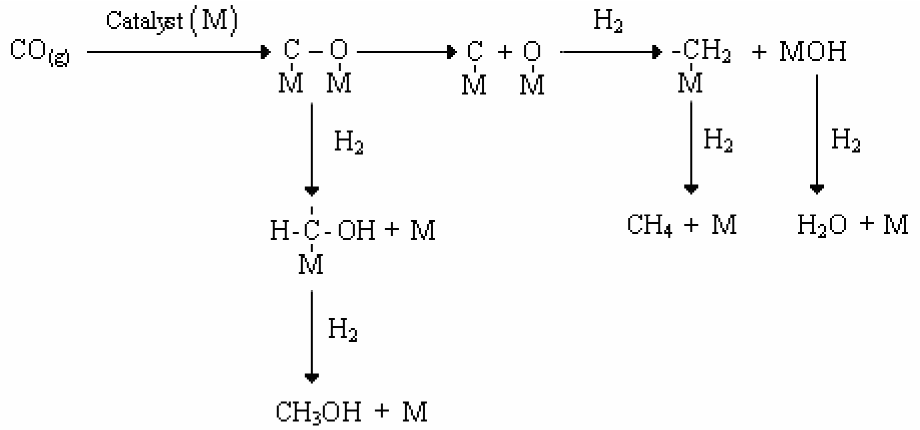
Figure 2.2 Comparison between LTFT and HTFT

2.7.4.1 Mechanism of Fischer-Tropsch Reaction.

The exact mechanism (alsharge, 2006) of Fischer - Tropsch reaction is very complicated, not well defined, and subject of much debate. In order to establish a possible mechanism of the reaction, we define the reaction starting materials to be CO, H_2 a catalyst site denoted as M, and dual catalyst sites denoted by MM. The observed C1 products are defined as CO_2, CH_4, CH_3OH, andH_2OThe mechanism maybe divided into at least three major steps:

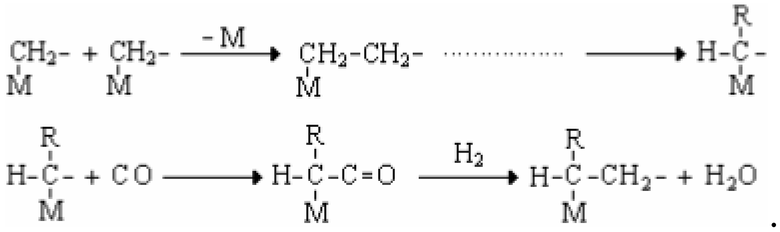
1. Initiation or C1 compound formation by:

- CO adsorption on metal catalyst surface (M).
- $C-O$ bond breakage.
- Sequential hydrogenation of the carbon species to form C_1.



2. Hydrocarbon chain growth by:

Successive insertion of the C1 building blocks to form high molecular hydrocarbons.

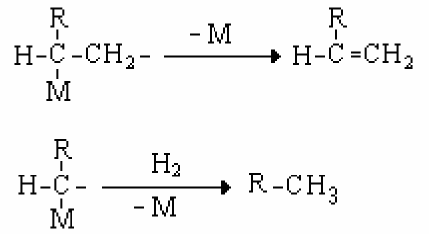


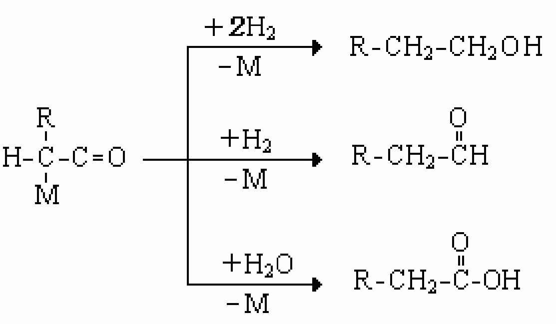
3. Chain termination by:

- Hydrogenation and desorption of saturated species.

- Desorption of unsaturated surface species.

- Hydrogenation, hydrolysis, and desorption of oxygenated species.





2.7.4.2 Fischer-Tropsch catalysts:

The Fischer-Tropsch catalysts are Iron (Fe), Ruthenium (Ru), Nickel (Ni) and Cobalt (Co). In industry mainly Fe and Co are used. Iron catalysts are used in FT process in fused and precipitated form. From table (2.2) we can have analyzed that in Fe catalyst coking reaction is fast So its life time is very short. but its having cost is lower than CO catalyst. But in Co catalyst yield is higher than Fe catalyst. In CO catalyst higher linear paraffinic chain is formed. (Kamar, 2014)

Table 2.2 comparison between Cobalt and Iron Catlyst.

Iron (Fe)	Cobalt (Co)
Short life (limited to eight weeks)	Longer life (over five years)
Low cost	Expensive (exotic promoters)
Generally preferred for coal-based syngas	Generally preferred for natural gas-based syngas
Precipitated / fused	Supported (AL_2O_3, SiO_2, TiO_2))
Syngas ratio $\left(\frac{H_2}{CO}\right) = 1.5$	Syngas ratio $\left(\frac{H_2}{CO}\right) = 2$
By product((H_2/CO)/steam)	By product (H_2O/steam)

2.7.5 Products upgrading:

Syngas formation and then Fischer tropsch synthesis on syngas produced crude oil i.e mixture of complex hydrocarbon that is called syncrude .After that Conventional refinery processes like : atmospheric distillation, vacuum distillation ,cracking, wax hydrocracking, distillate hydrotreating, catalytic reforming, naphtha hydrotreating, alkylation and isomerization is used for separation of required product. Hydrocracking is preferably used to convert the wax into lighter distillates with shorter chain length and lower boiling points. It uses fixed-bed reactors and suitable catalysts. FT products are less pollutant than conventional refinery process products. Hydrogen is supplied either with PSA purity or as pure hydrogen made from a slip stream of syngas. Hydrogenation is applied to the naphtha to saturate straight-run product streams. Fractionation Liquid effluent from the hydrocracking / isomerization block is heated and then distilled. The separate products are withdrawn, cooled and sent to their storage tanks. When we compare GTL product with the refinery product we find that middle distillate in GTL product having higher percentage and of good quality Shone Figure 3.2. (Kamar, 2014)

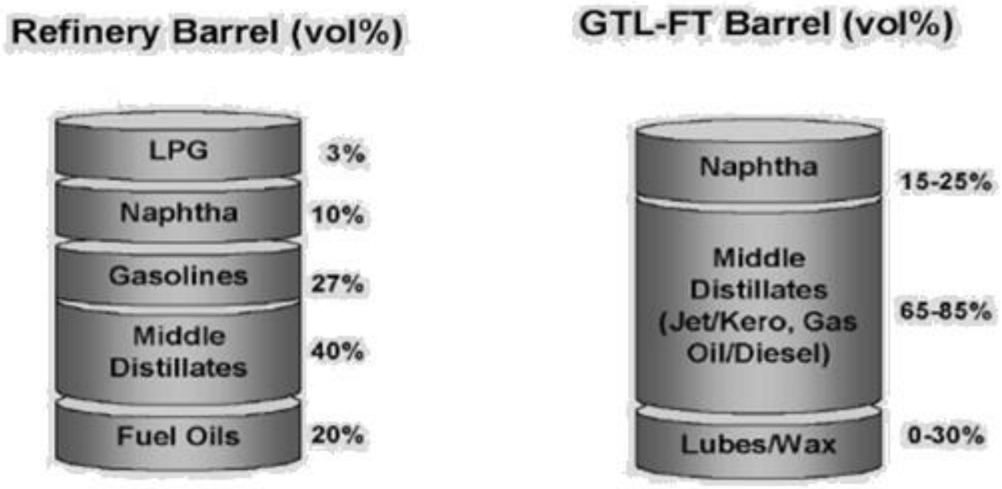
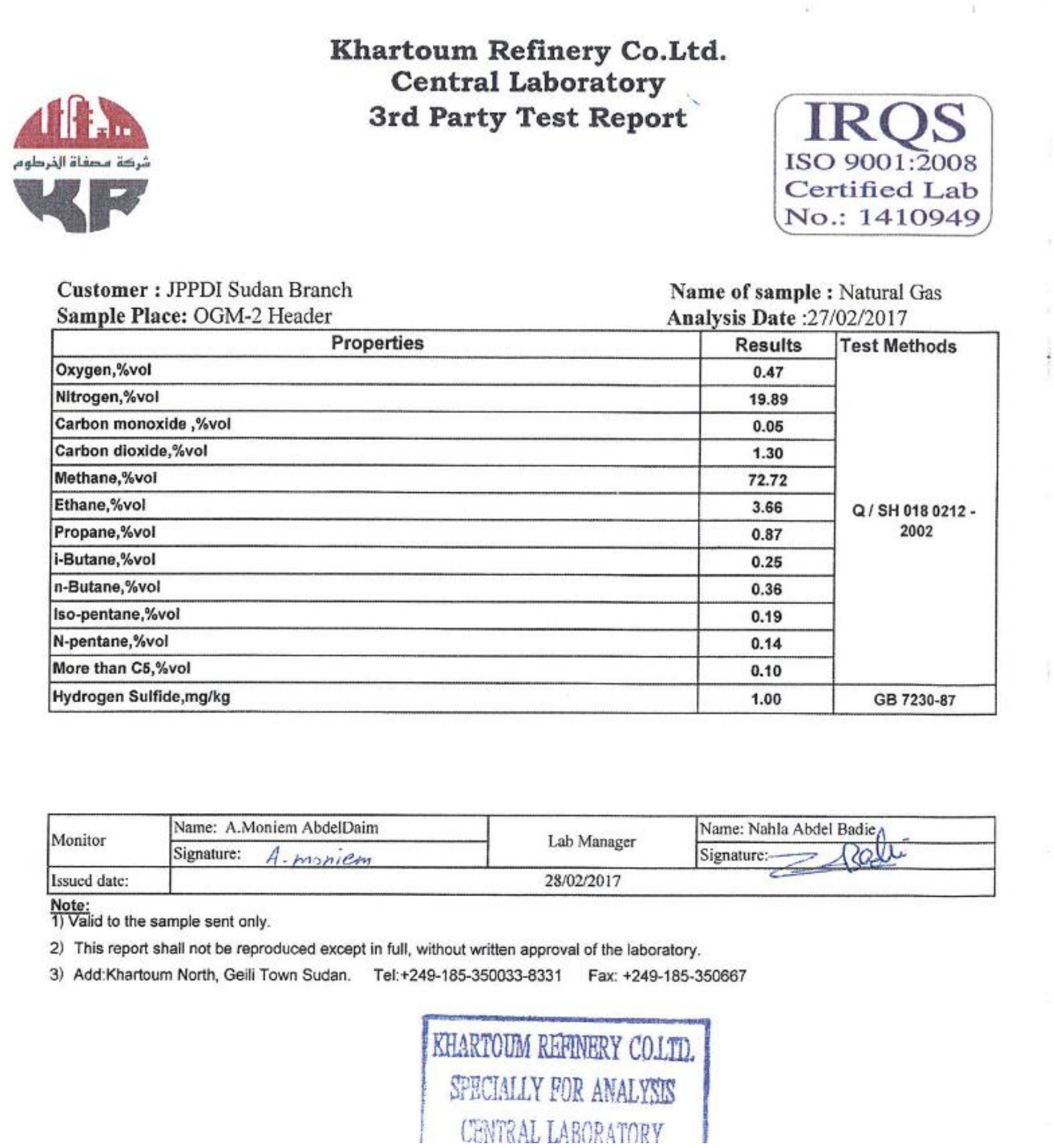


Figure 3.2 deference in Products Yild between GTL & Crude oil Refinery

Chapter 3

Methodology

3.1 The main feed steam (Natural gas) data from OGM-2 Header.



شركة مصفاة الخرطوم

Khartoum Refinery Co.Ltd.
Central Laboratory
3rd Party Test Report

IRQS
ISO 9001:2008
Certified Lab
No.: 1410949

Customer : JPPDI Sudan Branch
Sample Place: OGM-2 Header

Name of sample : Natural Gas
Analysis Date :27/02/2017

Properties	Results	Test Methods
Oxygen,%vol	0.47	Q / SH 018 0212 - 2002
Nitrogen,%vol	19.89	
Carbon monoxide ,%vol	0.05	
Carbon dioxide,%vol	1.30	
Methane,%vol	72.72	
Ethane,%vol	3.66	
Propane,%vol	0.87	
i-Butane,%vol	0.25	
n-Butane,%vol	0.36	
Iso-pentane,%vol	0.19	
N-pentane,%vol	0.14	
More than C5,%vol	0.10	
Hydrogen Sulfide,mg/kg	1.00	GB 7230-87

Monitor	Name: A.Moniem AbdelDaim	Lab Manager	Name: Nahla Abdel Badie
	Signature: A. moniem		Signature:
Issued date:	28/02/2017		

Note:
1) Valid to the sample sent only.
2) This report shall not be reproduced except in full, without written approval of the laboratory.
3) Add:Khartoum North, Geili Town Sudan. Tel:+249-185-350033-8331 Fax: +249-185-350667

KHARTOUM REFINERY CO.LTD.
SPECIALLY FOR ANALYSIS
CENTRAL LABORATORY

3.2 Case study:

Diesel production has high quality and low gaseous emissions, in quantities suitable according to the LTFT method in ASPENHYSIS V8.8 simulators.

3.3 Aspen HYSYS process simulator:

Aspen HYSYS® is AspenTech's process modeling tool for steady-state simulation, design, performance monitoring, optimization, and business planning for the oil and gas production, gas processing, and petroleum refining industries. Aspen HYSYS is built upon proven technologies, and more than 30 years of experience supplying process simulation tools to the oil and gas and refining industries. It provides an intuitive and interactive process modeling solution that enables engineers to create steady-state models for plant design, performance monitoring, troubleshooting, operational improvement, business planning, and asset management. (Aspen HYSYS sofwere simlation , v8.8)

3.4 Process description:

The GTL process consist of three main steps:

3.4.1 Syngas Generation it contains six equipment (pre-reformer reactor, Auto thermal reformer, tow phase separator, tow heaters and one cooler).

3.4.2 Syncrude Generation it contains (Fischer Tropsch Reactor PFR, tow phase separator, cooler, recycle and three phase separator).

3.4.3 Products upgrading it consist mainly fractionator.

Before thesis steps natural gas is treated from any impurities such as sulfides, NLG, Trace component and any impurities that lead to the poisoning of the catalyst. The Clean feed is then fed to a syngas generation unit, first rise the feed temperature to desert temperature 455℃ and introduced feed with steam at 252℃ into pre-reforming unit to convert higher hydrocarbons into methane and syngas according **Pre-reforming reaction**.

The product temperature from pre reformer rise to 650℃ and then injected with oxygen at 200℃ by (2 to 1) oxygen to natural gas to prevent soot formation in ATR reactor, the synthesis gas is produced according to **Auto Thermal Reforming reaction** the synthesis gas produced from ATR reactor is cooled to 38℃ to separate the water (by product) quantities from the synthesis gas by tow phase separator Recycle light hydrocarbons from Fischer Tropsch reactor to pre-reformer feed The syngas is heated to 210℃ for the reaction of Fischer Tropsch. According to reaction, syngas is converted to syncrude, which is composed of a mixture of heavy hydrocarbons and water the reaction occurs in the presence of the catalytic, the reaction depends on the catalyst type as well as the conditions of the reactor, and the process conditions, The output from the Fischer Tropsch reactor is then inserted into tow phase and three phase separator to separate the produced water with syncrude, after cooling to a temperature of 38℃ All contaminated water is collected and sent to the water treatment, unit and the syncrude goes to The third phase of the GTL process is the product upgrading process, where the same operations are done in the refineries.

in this project has been used splitter equipment to facilitate the calculations.

3.5 Reaction chemistry:

3.5.1 Pre reforming reactions:

$$C_2H_6 + 2H_2O \longrightarrow 5H_2 + 2CO \quad (3.1)$$

$$C_3H_8 + 3H_2O \longrightarrow 7H_2 + 3CO \quad (3.2)$$

$$iC_4H_{10} + 4H_2O \longrightarrow 9H_2 + 4CO \quad (3.3)$$

$$nC_4H_{10} + 4H_2O \longrightarrow 9H_2 + 4CO \quad (3.3)$$

$$iC_5H_{12} + 4H_2O \longrightarrow 9H_2 + 4.501CO \quad (3.4)$$

$$nC_5H_{12} + 4.441H_2O \longrightarrow 6H_2 + 5CO \quad (3.5)$$

$$CO + 3H_2 \longrightarrow H_2O + CH_4 \quad (3.7)$$

$$CO + H_2O \longrightarrow CO_2 + H_2 \quad (3.8)$$

3.5.2 Auto Thermal Reforming reactions (ATR):

$$CH_4 + 1.5O_2 \longrightarrow CO + 2H_2O \quad (3.9)$$

$$CH_4 + H_2O \longrightarrow CO + 3H_2 \quad (3.10)$$

$$CO + H_2O \longrightarrow CO_2 + H_2 \quad (3.11)$$

3.5.3 Fischer-Tropsch reaction:

$$2.028H_2 + CO \longrightarrow 0.01H_2O + 0.009CH_4 + 0.008C_2H_6 + 0.007C_3H_8 + 0.007C_4H_{10} + 0.006C_5H_{12} + 0.005C_6H_{14} + 0.005C_7H_{16} + 0.005C_8H_{18} + 0.004C_9H_{20} + 0.004C_{10}H_{22} + 0.003C_{11}H_{24} + 0.003C_{12}H_{26} + 0.003C_{13}H_{28} + 0.003C_{14}H_{30} + 0.002C_{15}H_{32} + 0.002C_{16}H_{34} + 0.002C_{17}H_{36} + 0.002C_{18}H_{38} + 0.002C_{19}H_{40} + 0.001C_{20}H_{42} + 0.012C_{30}H_{62} + H_2O$$

(3.12)

3.6 Martial balance:

3.6.1 Introduction

The general form quoted for a mass balance is The mass that enters a system must, by conservation of mass, either leave the system or accumulate within the system. Mathematically the mass balance for a system without a chemical reaction is as follows.

$$Input = Out\,put + Accumulation \qquad \textbf{(3.13)}$$

Strictly speaking the above equation holds also for systems with chemical reactions if the terms in the balance equation are taken to refer to total mass, i.e. the sum of all the chemical species of the system.

In the absence of a chemical reaction the amount of any chemical species flowing in and out will be the same; this gives rise to an equation for each species present in the system.

However, if this is not the case then the mass balance equation must be amended to allow for the generation or depletion (consumption) of each chemical species.

Some use one term in this equation to account for chemical reactions, which will be negative for depletion and positive for generation. However, the conventional form of this equation is written to account for both a positive generation term (i.e. product of reaction) and a negative consumption term (the reactants used to produce the products).

Although overall one term will account for the total balance on the system, if this balance equation is to be applied to an individual species and then the entire process, both terms are necessary.

This modified equation can be used not only for reactive systems, but for population balances such as arise in particle mechanics problems. The equation is given below; note that it simplifies to the earlier equation in the case that the generation term is zero. (Himmelbau, 1967)

$$\boldsymbol{Input + Generation \ = Out\ put + Accumulation + Consumption} \quad \textbf{(3.14)}$$

3.6.2 Natural gas feed:

Table 3.3 Natural gas Composition

O_2	0.0047	CO	0.013	nC_4H_{10}	0.0036
CH_4	0.7272	C_2H_6	0.0366	iC_5H_{12}	0.0019
N_2	0.1989	C_3H_8	0.0087	nC_5H_{10}	0.0014
CO_2	0.0005	iC_4H_{10}	0.0025		

3.6.2.1 Assumption:

- Feed of natural gas free from $\boldsymbol{H_2S}$.
- The oxygen needed is obtained from an air separation unit.
- Feed flow rate assumed $\boldsymbol{7000\ Kgmole/hr}$.

3.6.3 Overall martial balance:

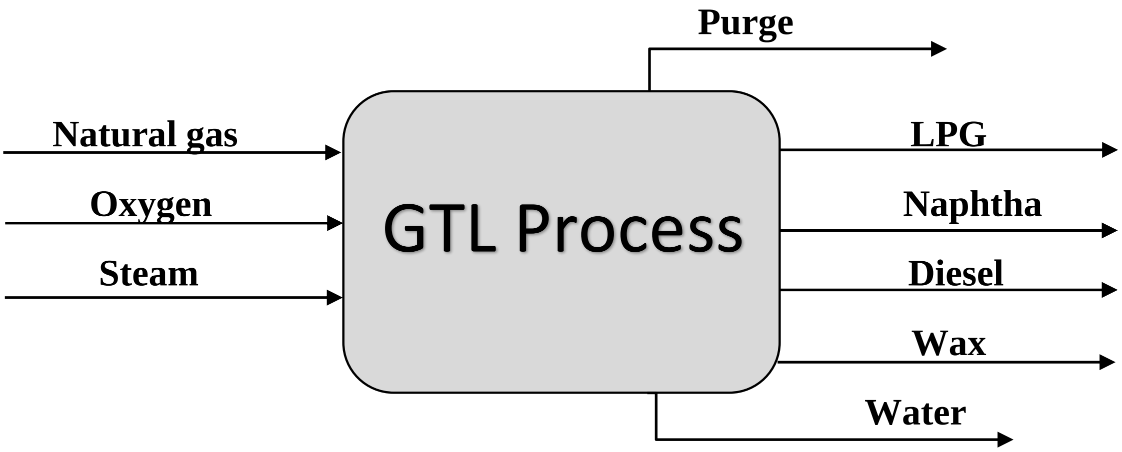


Figure 4.3 over all martial balance

Inlet martial streams

Table 4.3 Overall Inlet martials streams

Streams	**Quantities** $\mathbf{Kg}/\boldsymbol{hr}$
Natural gas	**139100**
Oxygen	**57648**
Steam	**121600**
Total	**318348**

Outlet martial streams

Table 5.3 Overall Outlet martials streams

Streams	**Quantities** $\boldsymbol{Kg/hr}$
Waste	**0.0000**
Waste water	**169840**
LPG	**1085**
Naphtha	**14461**
Diesel	**24571**
Wax	**25035**
Purge	**83356**
Total	**318348**

3.6.4 Syngas generation unit:

3.6.4.1 Heater

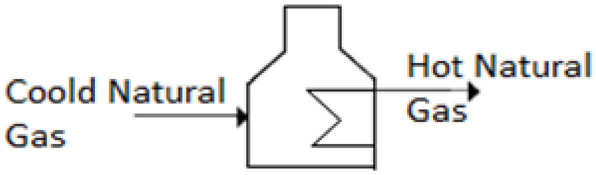
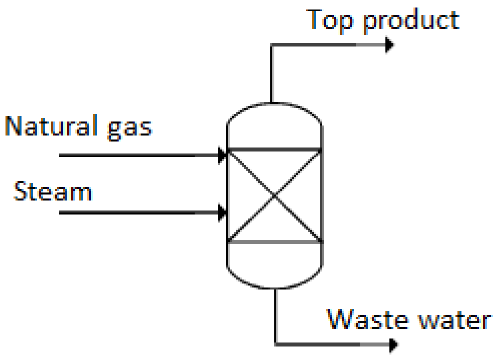


Table 6.3 Matral balance aronund heater (1)

Compounds	Cold natural gas Kg/h	Hot natural gas Kg/h
O_2	1053.80	1053.80
CH_4	39041.5	39041.5
N_2	154.200	154.200
CO_2	2551.54	2551.54
H_2O	0.00000	0.00000
CO	81746.5	81746.5
C_2H_6	7711.62	7711.62
C_3H_8	2688.20	2688.20
iC_4H_{10}	1018.20	1018.20
nC_4H_{10}	1466.20	1466.20
iC_5H_{12}	960.570	960.570
nC_5H_{10}	707.787	707.787
Total	139100.1	139100.1

3.6.4.2 Pre reformer reactor:



Inlet feeds

Table 7.3 Pre reformer inlet streames Matrial balance

Streams	Quantities Kg/h
Natural Gas	**139100.2**
Steam	**57648.32**

Outlet streams

Table 8.3 Pre reformer Outlet streames Matrial balance

Components	**Top Product** Kg/h	**Bottom Product** Kg/h
O_2	**1053.80**	**0.0000**
CH_4	**39041.5**	**0.0000**
N_2	**405.471**	**0.0000**
CO_2	**0.14474**	**0.0000**
H_2O	**59076.1**	**0.0000**

CO	95433.0	0.0000
C_2H_6	2.059642	0.0000
C_3H_8	1.5e-004	0.0000
iC_4H_{10}	2.1e-008	0.0000
nC_4H_{10}	1466.2	0.0000
iC_5H_{12}	3.2e-021	0.0000
nC_5H_{10}	1.0e-021	0.0000
H_2	270	0.0000
Total	**196748.3**	**0.0000**

3.6.4.3 ATR Reactor:

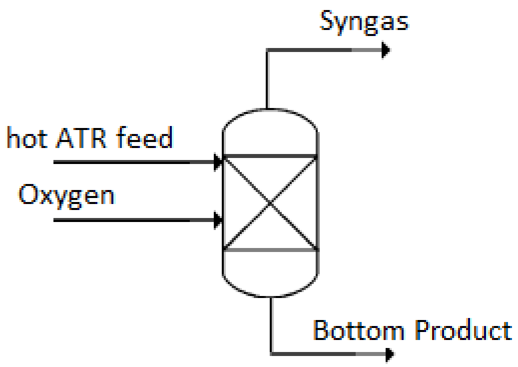


Table 9.3 Matrial balance around ATR reactor

Components	Hot ATR Feed Kg/h	Oxygen Kg/h	Syngas Kg/h	Bottom product Kg/h
O_2	1053.8	121600	1.4e-007	0.000
CH_4	39041.5	0.00000	39041.54	0.000
N_2	405.5	0.00000	30089	0.000
CO_2	0.145	0.00000	147611	0.000

H_2O	59076	0.00000	77941	0.000
CO	95433	0.00000	70.27	0.000
C_2H_6	2.060	0.00000	2.06	0.000
C_3H_8	1.5e-004	0.00000	1.5e-004	0.000
iC_4H_{10}	2.1e-008	0.00000	2.1e-008	0.000
nC_4H_{10}	1466.2	0.00000	1466.2	0.000
iC_5H_{12}	3.23e-021	0.00000	0.000	0.000
nC_5H_{10}	1.e-021	0.00000	0.000	0.000
H_2	269.93	0.00000	22126	0.000
Total	**196748.1**	**121600**	**318000**	**0.000**

3.6.4.4 Tow Phase separator:

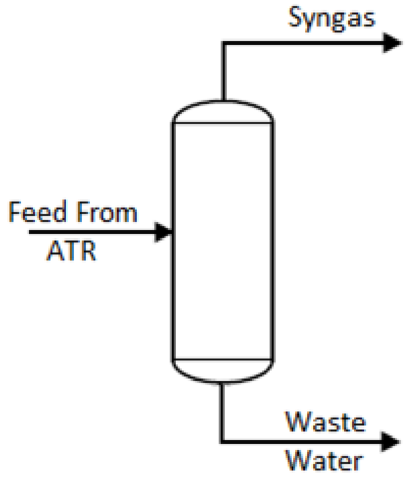


Table 10.3 material balance around tow phase separator (1)

Components	Syngas Kg/h	Syngas to F.T Kg/h	Water Kg/h
O_2	1.4e-007	1.4 e-007	3.8e-012
CH_4	39041.54	39038.8	2.7

N_2	30089	30019	69.5
CO_2	147611	147609	1.2
H_2O	77941	895.8	77045
CO	70.27	70.2	5.31e-006
C_2H_6	2.06	2.1	4.e-009
C_3H_8	1.5e-004	1.5e-004	2.79e-015
iC_4H_{10}	2.1e-008	2.17e-008	1.2e-021
nC_4H_{10}	1466.2	1466.28	1.4e-010
iC_5H_{12}	0.000	0.00000	0.000
nC_5H_{10}	0.000	0.0000	0.00
H_2	22126	22125.8	0.24329
Total	318000	241227	77118.64

3.6.5 Syncrude Generation unit:

3.6.5.1 Fischer Tropsc (Fixed bed Reactor):

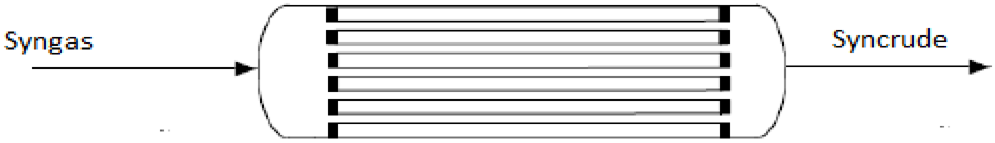


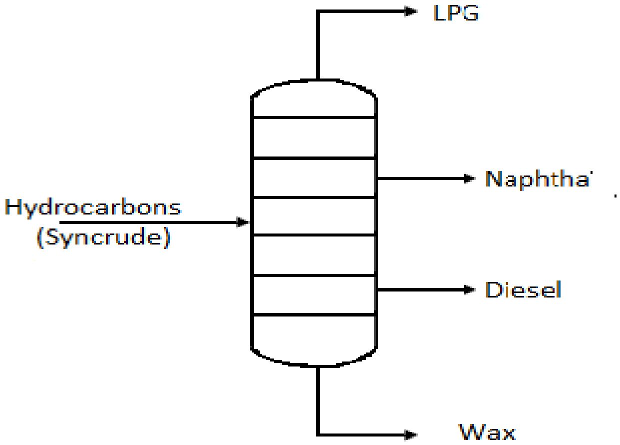
Table 11.3 Material balance around Fischr- Troepech

Components	Syngas Kg/h	Syncrude Kg/h
O_2	1.4 e-007	0.0000
N_2	39038.8	194559.72
CO_2	30019	146348.4
CO	147609	40269.6

H_2O	895.8	92290.00
CH_4	70.2	4317
C_2H_6	2.1	6565
C_3H_8	1.5e-004	8119
iC_4H_{10}	2.17e-008	0.00
nC_4H_{10}	1466.28	14149.7
iC_5H_{12}	0.00000	0.000
nC_5H_{10}	0.0000	7852
H_2	22125.8	5160
C_6H_{14}	0.0000	5534.9
C_7H_{16}	0.0000	3797.3
C_8H_{18}	0.0000	3437.6
C_9H_{20}	0.0000	2766.9
$C_{10}H_{22}$	0.0000	2926.45
$C_{11}H_{24}$	0.0000	2365.01
$C_{12}H_{26}$	0.0000	2559.17
$C_{13}H_{28}$	0.0000	2760.54
$C_{14}H_{30}$	0.0000	2966.75
$C_{15}H_{32}$	0.0000	2117.05
$C_{16}H_{34}$	0.0000	2256.3
$C_{17}H_{36}$	0.0000	2396.36
$C_{18}H_{38}$	0.0000	2535.68
$C_{19}H_{40}$	0.0000	2675.45
$C_{20}H_{42}$	0.0000	1407.61
$C_{30}H_{62}$	0.0000	25143.56
Total	**241227**	**587277.1**

3.6.5 Product upgrading unit:

3.6.5.1 Fractionator column:



Inlet feed

Table 12.3Fractionator column inlet streams mass flow

Components	Syncrude Kg/h
O_2	0.0000
N_2	144.7
CO_2	642.42
CO	34.93
H_2O	8.693
CH_4	7.59
C_2H_6	46.6
C_3H_8	167.51
iC_4H_{10}	0.000
nC_4H_{10}	830.8
iC_5H_{12}	0.000
nC_5H_{10}	1186.5

H_2	**2.0151**
C_6H_{14}	**1840.6**
C_7H_{16}	**2172.6**
C_8H_{18}	**2697.7**
C_9H_{20}	**2503.12**
$C_{10}H_{22}$	**2812.6**
$C_{11}H_{24}$	**2329**
$C_{12}H_{26}$	**2542.54**
$C_{13}H_{28}$	**.27543**
$C_{14}H_{30}$	**2964**
$C_{15}H_{32}$	**2116.3**
$C_{16}H_{34}$	**2256.0**
$C_{17}H_{36}$	**2395.8**
$C_{18}H_{38}$	**2535.6**
$C_{19}H_{40}$	**2675.4**
$C_{20}H_{42}$	**1407.6**
$C_{30}H_{62}$	**25143.5**
Total	**64218.42**

Out let streams

Table 13.3Fractionator column outlet streams mass flow

Components Kg/h	LPG Kg/h	Naphtha Kg/h	Diesel Kg/h	Wax Kg/h
O_2	0.0000	0.0000	0.0000	0.0000
N_2	144.7	0.0000	0.0000	0.0000
CO_2	642.42	0.0000	0.0000	0.0000
CO	34.93	0.0000	0.0000	0.0000
H_2O	8.693	0.0000	0.0000	0.0000
CH_4	7.59	0.0000	0.0000	0.0000
C_2H_6	46.6	0.0000	0.0000	0.0000
C_3H_8	167.51	0.0000	0.0000	0.0000
iC_4H_{10}	0.000	0.0000	0.0000	0.0000
nC_4H_{10}	830.8	830.8	0.0000	0.0000
iC_5H_{12}	0.000	0.000	0.0000	0.0000
nC_5H_{10}	1186.5	1186.5	0.0000	0.0000
H_2	2.0151	2.0151	0.0000	0.0000
C_6H_{14}	0.0000	1840.6	0.0000	0.0000
C_7H_{16}	0.0000	2172.6	0.0000	0.0000
C_8H_{18}	0.0000	2697.7	0.0000	0.0000
C_9H_{20}	0.0000	2503.12	0.0000	0.0000
$C_{10}H_{22}$	0.0000	2812.6	0.0000	0.0000
$C_{11}H_{24}$	0.0000	0.0000	2329	0.0000
$C_{12}H_{26}$	0.0000	0.0000	2542.54	0.0000
$C_{13}H_{28}$	0.0000	0.0000	.27543	0.0000

$C_{14}H_{30}$	**0.0000**	**0.0000**	**2964**	**0.0000**
$C_{15}H_{32}$	**0.0000**	**0.0000**	**2116.3**	**0.0000**
$C_{16}H_{34}$	**0.0000**	**0.0000**	**2256.0**	**0.0000**
$C_{17}H_{36}$	**0.0000**	**0.0000**	**2395.8**	**0.0000**
$C_{18}H_{38}$	**0.0000**	**0.0000**	**2535.6**	**0.0000**
$C_{19}H_{40}$	**0.0000**	**0.0000**	**2675.4**	**0.0000**
$C_{20}H_{42}$	**0.0000**	**0.0000**	**1407.6**	**0.0000**
$C_{30}H_{62}$	**0.0000**	**0.0000**	**0.0000**	**25143.5**
Total	**3071.758**	**14045.94**	**23976.54**	**25143.5**

3.7 Energy balance:

3.7.1 introduction:

The concept of energy conservation as expressed by an energy balance equation is central to chemical engineering calculation, similar to mass balance studied previously, a balance on energy is crucial to solving many problems, general equation can be written for the conservation of energy: (Himmelbau, 1967)

Energy out + Consumption + Accumulation = Energy in + Generation

(3.15)

Energy Imbalance = (total flow of outlet streams) - (total flow of inlet streams)

(3.16)

3.7.2 Overall energy balance:

Table 14.3 Overall Energy balance

Inlet streams	Energy flow KJ/h	Out let streams KJ/h	Energy flow KJ/h
$Q_{Natural\ gas}$	- 4.298e+008	Q_{waste}	0.000
$Q_{Heater(1)}$	1.348e+008	$Q_{cooler(1)}$	1.174e+009
Q_{steam}	- 8.551e+008	$Q_{Fixed\ bed\ Reac}$	8.025e+008
Q_{oxygen}	1.958e+007	$Q_{cooler(2)}$	3.798 e+008
$Q_{Heater(2)}$	2.233e+008	$Q_{Waste\ water}$	-2.646 e+009
$Q_{Heater(3)}$	1.492e+008	Q_{LPG}	-6.560e+006
$Q_{Heater(4)}$	6.704 e+007	$Q_{Naphtha}$	-2.587e+007
$Q_{Comp(1)}$	1.928e+007	Q_{Diesel}	-3.082e+007
		Q_{Wax}	-3.123 e+005
		Q_{Purge}	-3.181e+008
Q_{Total}	-6.717e+008	Q_{Total}	-6.715e+008

3.8 Process design:

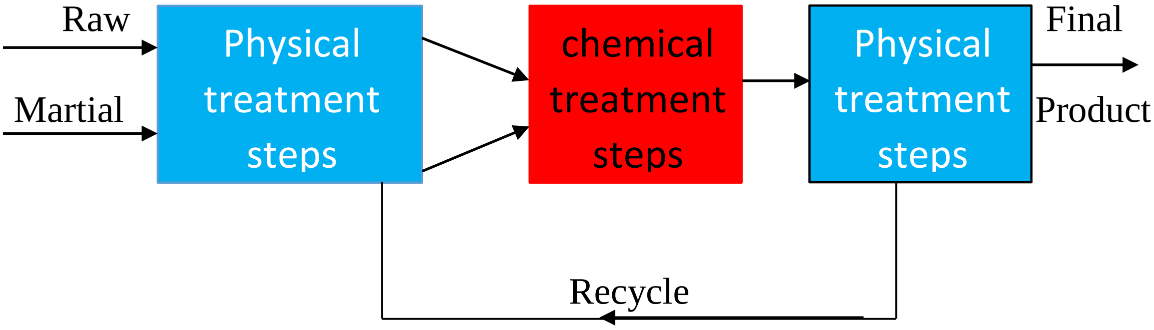
3.8.1 Introduction:

3.8.1.1 Importance of Reactor Design:

Every industrial chemical process is designed to produce economically a desired product from raw materials through a succession of treatment steps.

The raw materials undergo a number of physical treatment steps to put them in the form in which they can be reacted chemically, then they pass through the reactor.

The products of the reaction must then undergo further physical treatment-separations, purifications, etc.-for the final desired product to be obtained



The reactors part is the heart of almost all chemical processes.

3.8.1.2 Reactor Design Considerations:

In searching for the optimum design, it is not just the cost of the reactor that must be minimized.

One design may have low reactor cost, but the materials leaving the unit may be such that their treatment requires a much higher cost than alternative designs. Hence, the economics of the overall process must be considered. (HS, 2005)

3.8.2 Fischer-Tropsch reactor (the hart of GTL technology):

FT reaction is very exothermic in nature. So, the temperature is one of the very sensitive operating parameter. (Kamar, 2014)

3.8.2.1 Fischer Tropsch reactors commercially used:

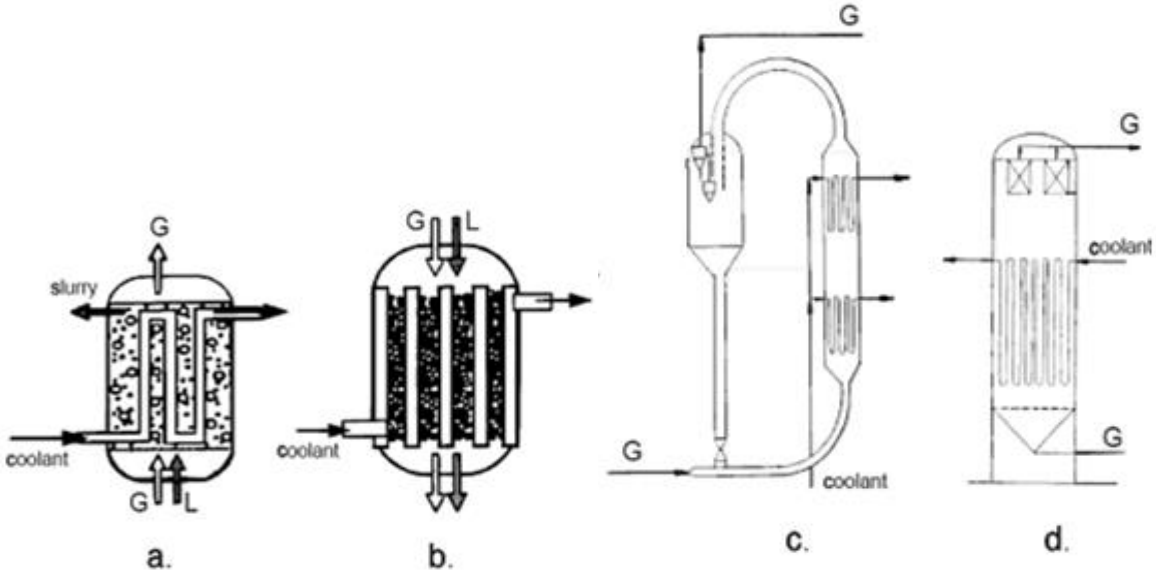


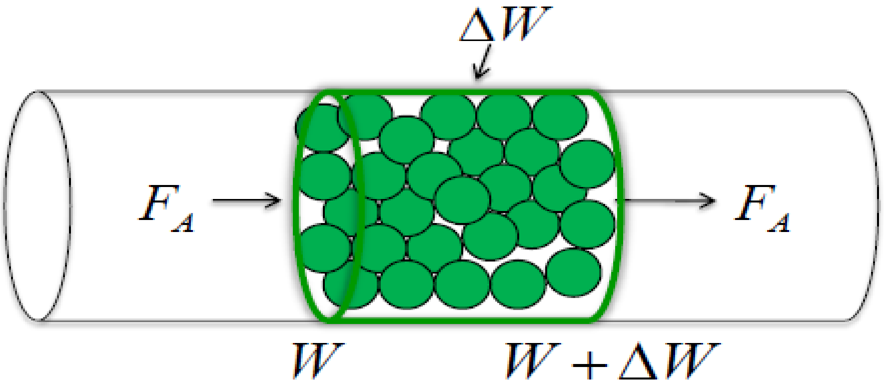
Figure 5.3 Type of Fischer - Tropsch Reactors

a. **slurry phase reactor.**
b. **Multi tubular fixed-bed reactor.**
c. **circulating fluidized bed reactor.**
d. **fluidized bed reactor with internal cooling.**

In our work we will be using fixed bed reactor because it’s a relatively simple design and, **because uses LTFT**, and its suitable for $\mathbf{200-250}$**℃,** and product from it large amounts of paraffin hydrocarbons and wax martials, and **High quality diesel** compare with other reactors used.

3.8.3 Multi tubular Fixed-bed Reactor design:

3.8.3.1 Calculation the of catalyst: (HS, 2005)



Mole balance equation :

$$In - Out + Genration \ = Accumulation \qquad (3.17)$$

$$F_A(w) - F_A(w + \Delta w) + r'_A \Delta W = \frac{dN_A}{dt} \qquad (3.18)$$

Study state

$$\frac{dN_A}{dt} = 0 \qquad (3.19)$$

$$\lim_{\Delta w \to 0} \frac{F_A\big|_{(W+\Delta w)} - F_A\big|_W}{\Delta W} = r'_A \qquad (3.20)$$

Rearrange

$$\frac{dF_A}{dW} = r'_A \qquad (3.21)$$

Design equation of packed bed reactor as function in conversation

$$\frac{dx}{dW} = \frac{-r'_A}{F_{A_0}} \qquad (3.22)$$

The integral form to find catalyst Wight

$$W = F_A \int_0^X \frac{dx}{-r'_A} \qquad (3.23)$$

The reaction rate low is the function in the partial pressure

$$-r'_A = f(CO) * q(H_2) \qquad (3.24)$$

For Fisher Tropsch reaction, at our desired operating conditions and catalyst rate of reaction can be calculated from this relation.

$$-r'_A = \frac{k\, P_H^{0.5}}{1 + \alpha P_{H_2}}\, P_{CO} \qquad (3.25)$$

Reaction equation

$$61H_2 + 30CO \quad \rightarrow C_{30}H_{62} + 30\, H_2O \quad (3.26)$$

Assume Rate of reaction K_1 at temperature

$\mathbf{500}$°F $=\mathbf{1.116}\frac{Kmole}{Kgcat.min.atm^{1.5}}$

Calculate K_2at temperature 431.34°F

$$\frac{K_1}{K_2} = \frac{T_1}{T_2} \qquad (3.27)$$

$$\gg\ K_2 = \frac{1.116 * 431.34}{500} = 0.963 \frac{Kmole}{Kgcat.min.atm^{1.5}}$$

The partial pressure of CO is approximately $= 1\ atm$ So that the reaction rate became

$$-r'_A = \frac{k\, P_H^{0.5}}{(1 + \alpha P_{CO}\ )} \qquad (3.28)$$

$$C_A = C_{A_0} \frac{(1 - X)}{(1 + \varepsilon X)} \qquad (3.29)$$

- **Assume that no change in reactor volume then ε = 0.**

$$C_A = C_{A_0}(1 - X) \qquad (3.30)$$

$$RTC_A = RTC_{A_0} \qquad (3.31)$$

$$\gg\ P_{H_2} = P_{H_{2\,0}}(1 - X) \qquad (3.32)$$

The ratio of $CO : H_2 = \frac{61}{30} = 2.034$

$$y_{H_2} = \frac{Moles\ of\ H_2}{Total\ Moles} \qquad (3.33)$$

$$= \frac{2.034}{3.034} = 0.67$$

P$_t$ = 29.61atm

$$P_{H_{2\,0}} = y_{H_2} * P_t \qquad (3.34)$$

$$P_{H_{2\,0}} = 0.67 * 29.61 = 19.8387atm$$

$$P_{H_2} = P_{H_{2\,0}}(1 - X) = 19.8387(1 - x)$$

Combine:

$$W = F_{H_{2\,0}} \int_0^X \frac{(1 + \alpha P_{H_2})dx}{k\, P_{H_2}^{0.5}} \qquad (3.35)$$

From reaction data $\alpha = 1.753$

$$W = 13021.86 \int_0^{0.843} \frac{(1 + (1.753 * (19.8387 * (1 - x))))dx}{0.963 * (19.8387 * (1 - x))^{0.5}}$$

$$W = 69674.5Kg$$

3.8.3.2 Catalyst data:

Table 15.3 Catlyst data

Particle diameter	**1.000e-003** $\boldsymbol{m}$
Particle Sphericity	**1.000**
Solid density	**6000** $\boldsymbol{Kg/m^3}$
Bulk Density	**3300** $\boldsymbol{Kg/m^3}$
Solid Heat Capacity	**250** $\boldsymbol{KJ/(Kg.}$℃$)$

3.8.3.3 Volume of Reactor:

I.Reactor volume = $\frac{\boldsymbol{Volume\ of\ catlyst}}{\boldsymbol{1-Procity\ of\ catlyst\ bed}}$ $(\mathbf{3.35})$

$$\boldsymbol{V = \frac{W}{\rho_C(1-\varphi)} = \frac{69674.5}{6000*(1-0.45)} = 21.11m^3}$$

II.Bed volume = $\boldsymbol{V_B = \frac{W_{cat}}{\rho_{cat}}}$ $(\mathbf{3.36})$

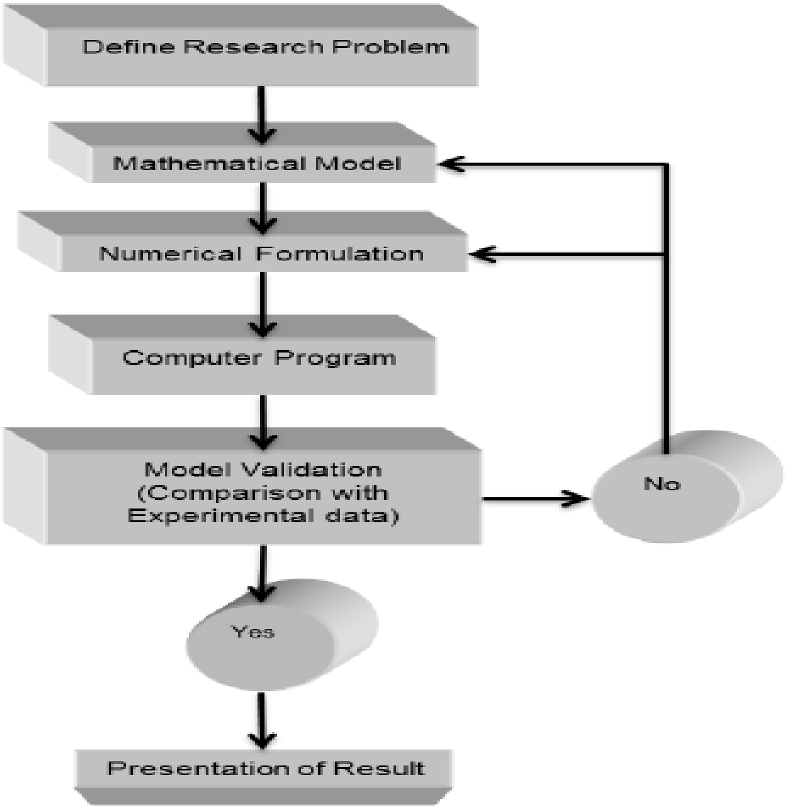
$$\boldsymbol{= \frac{69674.5}{6000} = 11.612m^3}$$

Reactor volume comparison between manual calculation and aspen HYSYS:

	Manual	**Aspen Hysys**
Volume	**21.11** $\boldsymbol{m^3}$	**21.12** $\boldsymbol{m^3}$

Chapter 4

Results and Discussion



4.1 Result:

Inlet martial streams:

Table 16Quantaties of inlet streames

Streams	Quantities Kg/hr
Natural gas	139100
Oxygen	57648
Steam	121600
Total	318348

Outlet martial streams:

Table 17 Quantaties of outlet streames

Streams	Quantities in Kg/hr
Waste	0.0000
Waste water	169840
LPG	1085
Naphtha	14461
Diesel	24571
Wax	25035
Purge	83356
Total	318348

4.2 Discussion:

4.2.1 Discussion amount of diesel production:

It was found that the amount of diesel to be reached $\mathbf{575.35}\ \boldsymbol{tonne/day}$ Sudan consume $\mathbf{850}\ \boldsymbol{tonne/day}$, daily production of diesel from Khartoum Refinery Company (KRC) Approximately $\mathbf{430}\ \boldsymbol{tonne/day}$, so **139100** $\boldsymbol{Kg/hr}$ From methane enough to cover the shortage of diesel in the local market , **knowing that the proven reserves of the two countries (Sudan, and south Sudan) are estimated at 3 trillion cubic feet, gas extraction is limited and most of it is burned in the Air or reinjected**

into wells. It is estimated that Sudan has burned about 11.8 billion cubic feet of west (Anon., 10 may 2015)

4.2.2 Effect of feed Fischer Tropsch (Fixed bed Reacter)

H_2/CO ratio:

This ratio is very important as it should be taken into account because it directly effects in the amount of diesel produced. In this study, the ratio H_2/CO was **2.03** which is suitable as feed gas to the diesel producing LTFR reactor.

4.2.3 Effect of Temperature:

Temperature is the most important parameter to be considered when designing the reactor. As temperature increases the FT reaction favors shorter alkanes and as temperature decreases the FT reaction favors longer alkanes.

In this research we aim to produce diesel so we use the **LTFT (210-221.8**℃**)** method because it produces larger quantities of diesel than HTFT method.

Chapter 5

Conclusion and Recommendation

5.1 Conclusion:

Clearly the GTL technology and GTL plant as one of the solutions to increase energy resources and improve the Sudan economic. also this technology plays effective role toward environment impact upgrade The specifications of the GTL products and the clean fuels are very similar, especially with the regard to the emissions of the harm pollutants. Therefore, these two kinds of fuels can help in covering some of the world demands for road fuels.

5.2 Recommendation:

1. It is very important to pay more attention to the Gas to Liquids (GTL) technology especially Sudan which has adequate amounts of natural gas because this industry can provide additional incomes to these countries, as well as creating more job opportunities.

2. It is also important to encourage establishing joint factories between the GTL industry and other kinds of industries. Because its depend on the refinery facility in operation.

3. More research can give better benefits and efficiency.

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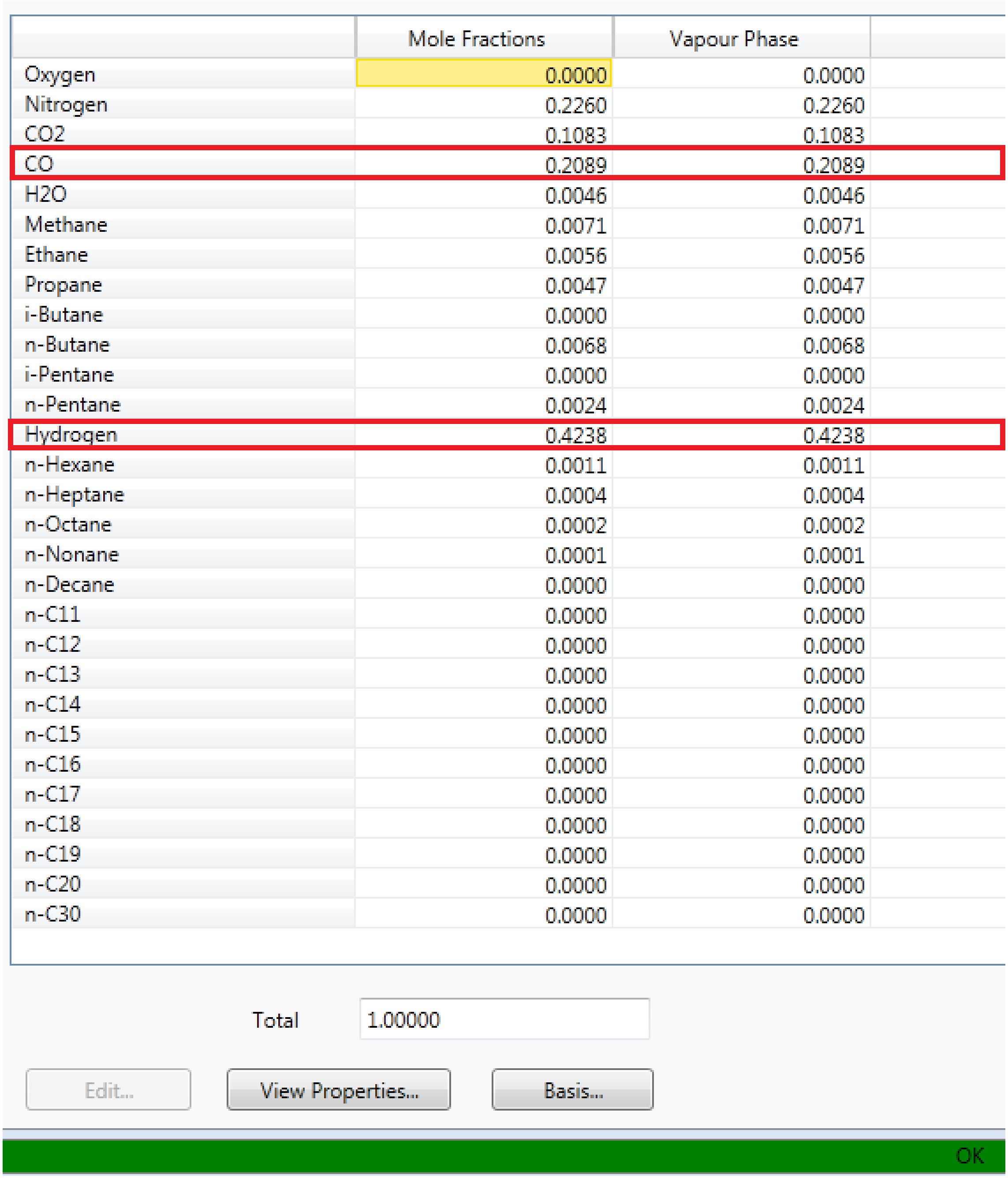
Appendix:

1. H_2/CO **Ratio:** $= \frac{0.4238}{0.2089} = 2.028$



	Mole Fractions	Vapour Phase
Oxygen	0.0000	0.0000
Nitrogen	0.2260	0.2260
CO2	0.1083	0.1083
CO	0.2089	0.2089
H2O	0.0046	0.0046
Methane	0.0071	0.0071
Ethane	0.0056	0.0056
Propane	0.0047	0.0047
i-Butane	0.0000	0.0000
n-Butane	0.0068	0.0068
i-Pentane	0.0000	0.0000
n-Pentane	0.0024	0.0024
Hydrogen	0.4238	0.4238
n-Hexane	0.0011	0.0011
n-Heptane	0.0004	0.0004
n-Octane	0.0002	0.0002
n-Nonane	0.0001	0.0001
n-Decane	0.0000	0.0000
n-C11	0.0000	0.0000
n-C12	0.0000	0.0000
n-C13	0.0000	0.0000
n-C14	0.0000	0.0000
n-C15	0.0000	0.0000
n-C16	0.0000	0.0000
n-C17	0.0000	0.0000
n-C18	0.0000	0.0000
n-C19	0.0000	0.0000
n-C20	0.0000	0.0000
n-C30	0.0000	0.0000

Total 1.00000

figure 6.6 Ratio between Hydrogen to Oxygen

2.

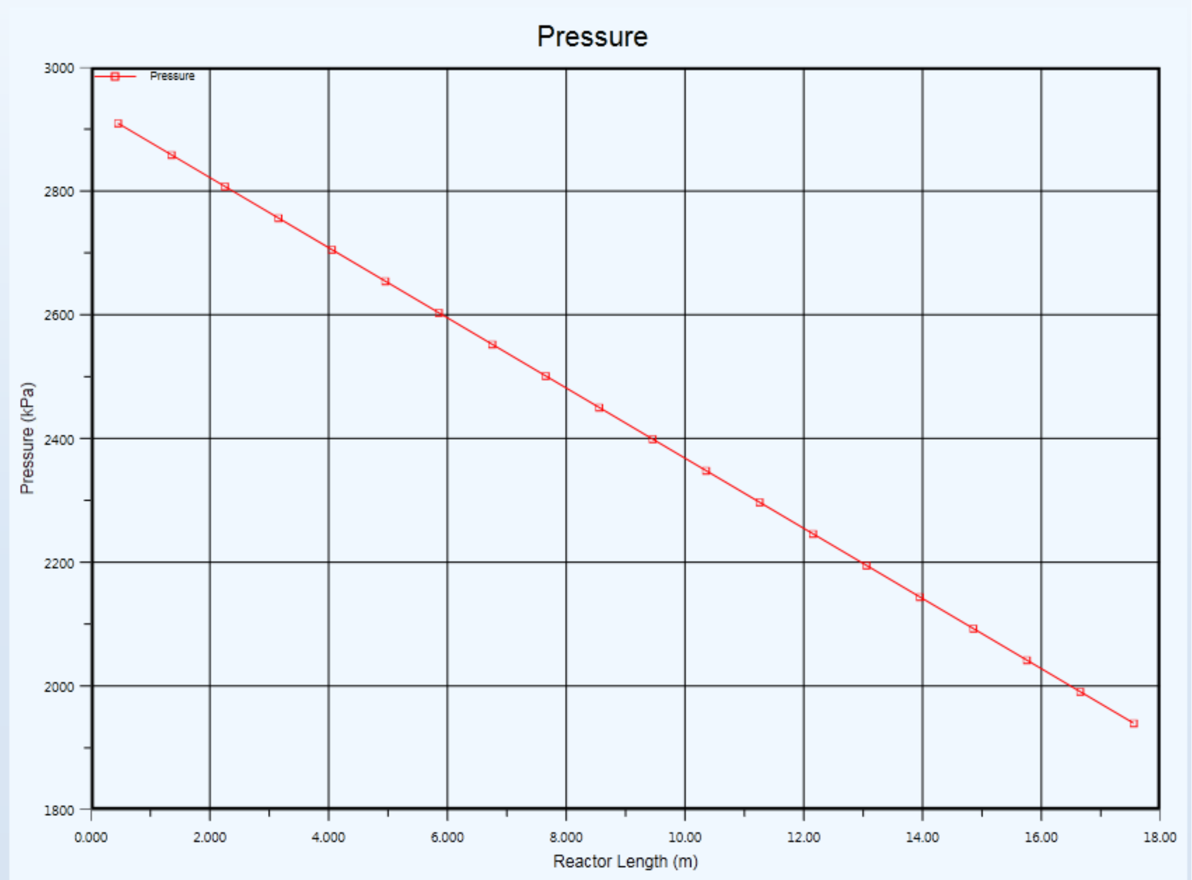


figure 7.6 (pressure VS length) **Fischer-Tropsch** reactor

3.

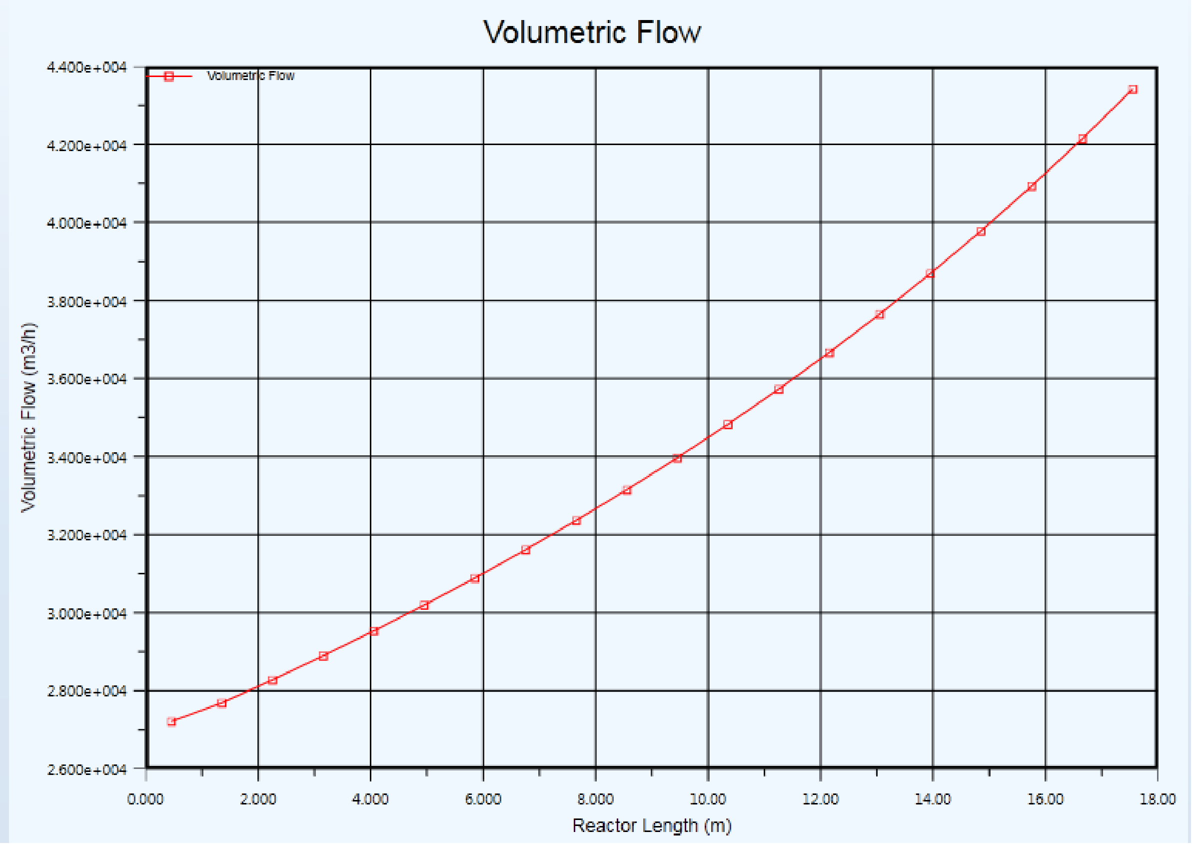


Figure 8.6 (Volumetric flow VS length) Fischer-Tropsch reactor