University of Fort Hare

Faculty of Science and Agriculture

DEVELOPMENT OF A BENCH SCALE SINGLE BATCH BIOMASS TO LIQUID FUEL FACILITY

By

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Declaration

I declare that this thesis entitled "Development of a Bench Scale Single Batch Biomass to Liquid fuel facility," is the result of my own research except as cited in the references. It is being submitted for the Degree of Master of science in Chemistry to the University of Fort Hare, Alice. The dissertation has not been accepted for any other degree and is not concurrently being submitted in candidature of any other degree.

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Abstract

The research described in this dissertation was motivated by the global demand for energy that is not dependent on coal, oil, natural gas and other non-renewable fossil fuels. The technology used in this project is related to the use of biomass to produce a viable alternative to conventional sources of fuel. A bench scale biomass to liquid (BTL) facility was built and tested. This produced results confirming the feasibility of the BTL process. The findings of the pilot study outlined in this dissertation justified the conclusion that the next step will be to expand the capacity and productivity of the BTL pilot plant to an industrial scale.

Biomass comes from a variety of renewable sources that are readily available. In this case, the material used in the fixed bed biomass gasification facility to generate wood gas was agricultural and forestry waste, such as straw and wood chips. The gasifier had the capacity to produce up to 10 cubic metres/hr of gas with a carbon monoxide and hydrogen content of between 20–40% by volume, when it was operated at ambient pressure and with air as the oxidizer. The gas, produced at a temperature above 700º C, was cooled in a quench/water scrubber in order to remove most of the mechanical impurities (tars and water-soluble inorganic particles), condensed and dried with corn cobs before being compressed in cylinders at over 100 bar (g) for use in the Fischer-Tropsch Synthesis (FTS).

The syngas was subjected further to a series of refining processes which included removal of sulphur and oxygen. The sulphur removal technology chosen entailed applying modified activated carbon to adsorb H_2S with the help of hydrolysis in order to convert organic sulphur impurities into H_2S which reduced the sulphur content of the gas to less than 5 ppbv.

Supported cobalt catalyst (100 grams), were loaded into a single-tube fixed bed FT reactor with an inner diameter of 50 mm. The reactor was fitted with a heating jacket through which, heated oil ran to cool the reactor during a normal reaction occurring at < 250 ºC, while nitrogen was used in the heating jacket during reduction, which occurred at temperatures up ~ 350 ºC. The FTS reaction was carried out at different pressures and temperatures.

Liquid and wax products were produced from the facility. The properties of the liquid and solid hydrocarbons produced were found to be the same as FT products from other feed stocks, such as natural gas and coal.

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List of abbreviations

BTL	biomass to liquid
FTS	Fischer-Tropsch Synthesis
UNFCCC	United Nations Framework Convention on Climate Change
RDF	refuse-derived fuel
WGS	Water gas shift
LTFT	low-temperature FT
HTFT	high-temperature FT
CFB	circulating fluidized bed reactor
FFB	fixed fluidized bed reactor
SAS	Sasol Advanced Synthol
CTL	coal to liquid
ASF	Anderson, Schultz and Flory distribution
GC	gas chromatograph
FPD	flame photometric detector
GTL	gas to liquid
TPR	temperature programmed reduction
BET	Isotherm of Brunauer Emmett and Teller
TCD	Thermal conductivity detector
FID	Flame ionisation detector
UHP	Ultra High Pure

UMC	United Microelectronics Corporation

Chapter1: Introduction

1.1 Background

1.1.1 Severe energy and environmental problems

Since the start of the Industrial Revolution, liquid fuels and chemical products, largely based on oil, have been used in ever-increasing quantities and demand. Over the past century, the developed world has enjoyed cheap and abundant energy supplies through the adoption of a fossil energy economy. The 1900s have been declared the ‘‘Petroleum Century’’, but this has both positive and negative connotations (Crocker, 2010). On the positive side, one can say that the rapid development of the whole industrialized world and the growth of national and personal wealth were made possible by the extravagant use of petroleum. It is the negative side that is apparent in the twenty-first century, when the whole world has to confront two urgent problems: a diminishing supply of fossil energy and environmental threats directly related to the use of these fuels.

This creates a dilemma. On one hand, because industrial and economic development depends on energy, the demand for power continues to rise. Figure 1.1 shows the world market in energy use (International Energy Outlook, 2010). From the figure, it can see that liquid fuels represent the world’s most heavily-utilized source of energy, and that the demand is increasing. On the other hand, the over-exploitation of fossil fuels has inevitably resulted in a global energy crisis. It has been reported that at the current rate of oil extraction and use, the world's proven recoverable oil reserves will be exhausted by 2050 (British Petroleum, 2008). Another cause for concern is the volatile political situation in the Middle East (the world's largest supplier of oil) and the rapid development of the global economy; the prices of crude oil continue to rise. There is a general consensus in the international community that the era of cheap oil is over.

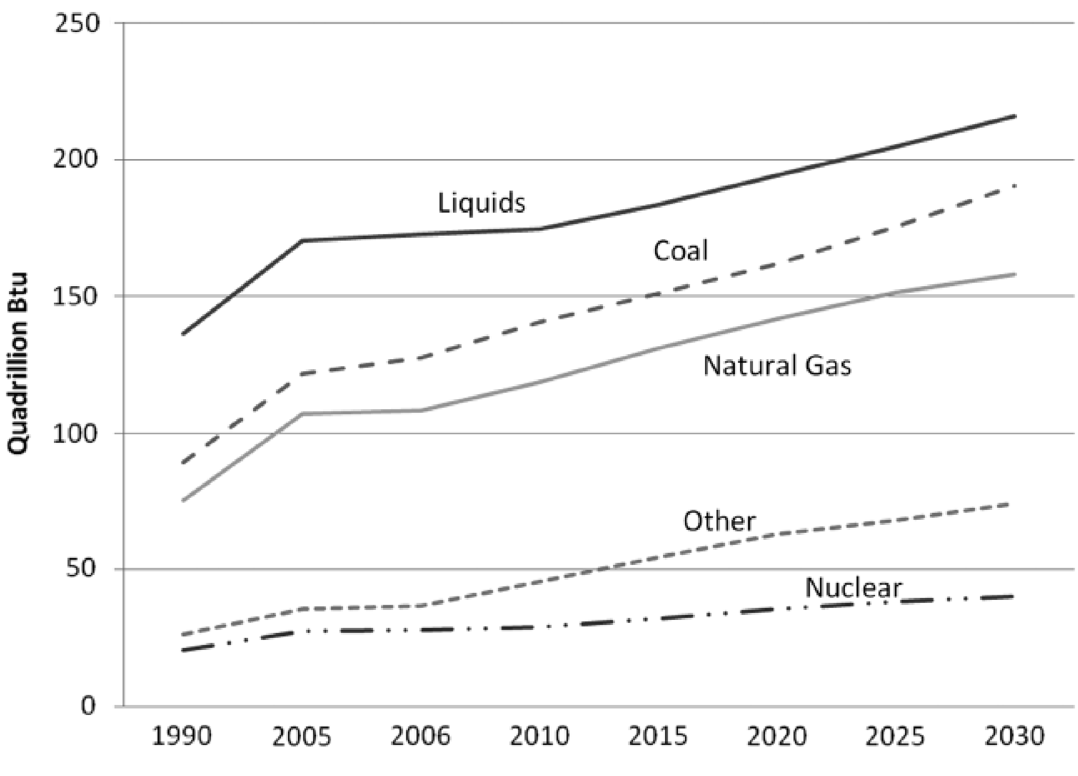

Figure 1.1 World market energy uses by type (International Energy Outlook, 2010)

At the same time, the large-scale use of fossil energy causes huge damage to the natural environment. According to Ni et al. (2010), among the most serious of the environmental problems caused by fossil energy are the following:

- greenhouse effect;
- acid rain;
- destruction of the ozone layer;
- atmospheric particulate matter pollution;
- damage to ecological systems; and
- spillage

1.1.2 The development and utilization of renewable energy

As result of the over-exploitation of fossil fuels and all the problems resulting from their use, researchers around the world are actively seeking sources of renewable energy. The term ‘renewable’ refers to energy that can be regenerated, to distinguish it from non-renewable resources’, which will run out.

Renewable resources include wind power, solar, geothermal and biomass energy.

- **Solar energy**

Solar energy generally refers to the use of sunlight radiation energy to generate electricity. The total solar energy absorbed by the Earth's atmosphere, oceans and land masses is approximately 3,850,000 EJ per year (Philibert, 2005). Solar technology has been widely characterized as passive and active ways to capture, convert and distribute sunlight (Hermann, 2006).

However, solar energy has disadvantages (Philibert, 2005; Hermann, 2006):

1. There no power supply at night, thus requires energy storage, which is still under development to meet the need;
2. It is not practicable to areas in which sunshine is of short duration; and
3. The life span of solar panels is short

- **Geothermal energy**

Geothermal energy is the energy generated and stored in the Earth. It is the energy that determines the temperature of matter. This type of energy occurs in the Earth's crust, and originates, in part (20%), from the original formation of the planet and mostly (80%) from the radioactive decay of minerals (How Geothermal Energy Works, 2012; Turcotte & Schubert, 2002).

The only disadvantage of geothermal energy is that extraction of this energy requires advanced technology (Turcotte & Schubert, 2002).

- **Wind power**

Wind power is the conversion of wind energy into a useful form of energy. For example, wind turbines can be used to make electrical power, windmills for mechanical power, and wind pumps for water pumping or drainage. Wind power is abundant, renewable, widely distributed, and the energy produced is clean (Gipe, 1989).

The disadvantages of this method of producing energy are (Gipe, 1989):

1. Wind power is difficult to store, and hence it is unstable and unreliable during generation;
2. Wind farms require a great deal of land; and
3. Wind machines are very noisy, therefore a great number of them working together create a deafening amount of noise

- **Biofuels**

Biomass, the material from which biofuel is made, originates in living species like plants and animals. It is formed as soon as a seed sprouts or an organism is born. Unlike the material used for fossil fuel, biomass does not take millions of years to develop. The most significant advantage of biofuels is that they reduce carbon dioxide emissions. Plants use sunlight through photosynthesis to metabolize atmospheric carbon dioxide, which enables them to grow. Animals eat food from biomass in order to survive and thrive. Fossil fuels do not reproduce themselves whereas biomass does, which is the reason the latter is considered renewable (Almeida, 2008; Demirbas, 2009).

1.2 Motivation and rationale

Theoretically, biomass synthetic oil can use any form of carbon source as raw material. These sources include: agricultural waste such as straw, rice husks, animal manure, and sawdust, timber processing byproducts, branches and leaves. As the carbon inside the raw materials comes from carbon dioxide in the atmosphere, the whole process of making synthetic fuel from biomass can be considered “carbon-neutral” (Crocker, 2010), although in practice, there are still a number of residual greenhouse gas emissions in the process.

Fischer-Tropsch synthesis (FTS) is an efficient technological technique to convert synthesis gas ($CO+H_2$) into liquid fuel. Currently, FTS is mainly used in the coal and gas liquefaction industries. However, coal and natural gas, being non-renewable resources, is likely to become depleted in the near future. This is why scientists are turning to renewable biomass as a possible alternative source of fuel.

The synthetic oil produced from biomass is of high quality (Williams, Larson & Jin, 2006). The aromatic content in synthetic oil is very low, and it has good combustion properties (Metz, 2007). It is also cleaner than conventional petroleum, since its emissions are less harmful to the environment (Crocker, 2010). Researchers carrying out a life cycle assessment reported by the International Energy Agency (2001) that full-cycle greenhouse gas emissions can be reduced by 90% when synthetic oil is used in a vehicle, when compared with the emissions from conventional fossil fuels (Fulton, 2001). Another advantage of using biomass derived synthetic oil is that, owing to the technological characteristics of the BTL process, the oil contains very little sulphur. The sulphur content of conventional fuels is now subject to increasingly stringent regulation, which means that the industries that produce them have to carry out desulphurization processes are becoming very expensive.

Currently, almost all biomass waste is being burnt, which is not only wasteful but causes great damage to the environment. This waste can be put to use, as a new and sustainable source of material for the BTL process. As the demand for synthetic fuels grows, so does the importance of biomass waste to the future of bio-energy development.

1.3 The aim and objectives

The major aim of this project is to design and establish a low-cost bench scale BTL facility in order to demonstrate possibility and appropriateness of the BTL process.

Objectives:

- to choose the best method that is most appropriate technology for biomass gasification, gas cleaning and FTS for a bench scale operation;
- to investigate the best manner to undertake the whole BTL process;
- to characterize the syncrude product; and
- to optimize the bench scale process

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Chapter 2: Literature review

2.1 Biomass gasification

2.1.1 Definition of Biomass

Generally, biomass is the organic matter relating to all direct and indirect use of green plant photosynthesis. It includes animals, microorganisms and their excretion of metabolites, with the only exceptions being vegetation that is fossilized (What is the BIOMASS? 2007). However, it is difficult to find a precise definition that is widely accepted. One of them, which is contained in the UNFCCC (United Nations Framework Convention on Climate Change, 2005), is relevant here:

Biomass means non-fossilized and biodegradable organic material originating from plants, animals and micro-organisms. This shall also include products, by-products, residues and waste from agriculture, forestry and related industries as well as the non-fossilized and biodegradable organic fractions of industrial and municipal wastes. Biomass also includes gases and liquids recovered from the decomposition of non-fossilized and biodegradable organic material.

Biomass, therefore, comprises not only all organic material, but their residues. Common sources of biomass are (Basu, 2010):

- ***Agricultural**:* Food grain, bagasse (crushed sugarcane), corn stalks, straw, seed hulls, nutshells, and manure from cattle, poultry, and hogs;

- ***Forest:*** Trees, wood waste, wood or bark, sawdust, timber slash, and mill scrap;
- ***Municipal:*** Sewage sludge, refuse-derived fuel (RDF), food waste, waste paper, and yard clippings;
- ***Energy-processing:*** Poplars, willows, switch grass, alfalfa, prairie bluestem, corn, and soybean, canola, and other plant oils; and
- ***Biological***: Animal waste, aquatic species, biological waste

2.1.2 Biomass gasification

Thermochemical conversion of biomass can take four forms as: combustion, pyrolysis, gasification and liquefaction. Gasification of biomass as an efficient and clean use of energy can play many important roles in the industry, providing heat, electricity and fuel for transport (Qin et al., 2004). It also offers advantages over the direct use of biomass. The paragraphs below describe some of the benefits of gasification (Liu, Zhuang & Xia, 1999).

- The main sources of raw materials suitable for gasification are timber and wood processing residues, fuel wood, agricultural byproducts, including board, wood chips, twigs, straw, rice husks, and corn cobs. All of these wide ranges of raw materials are cheap and readily available.
- Because biomass contains a high percentage of volatile components, and has low

ash content, hence it is the ideal material for gasification. The conversion efficiency from biomass to syngas in gasifiers is generally more than 70%.

- The gas generated by the gasification process is combustible; easy to use and clean (in other words it has no harmful effects).

2.1.3 The process of biomass gasification

The reaction for biomass gasification is very complex, because there are a number of differing types of gasifier processes, reaction conditions, kinds of gasifying agent, different characteristics of the raw materials, and pulverization of granules. All these affect the reaction process. However, even under different conditions, biomass gasification essentially follows a similar process, which is illustrated schematically in Figure 2.1 below (Basu, 2010).

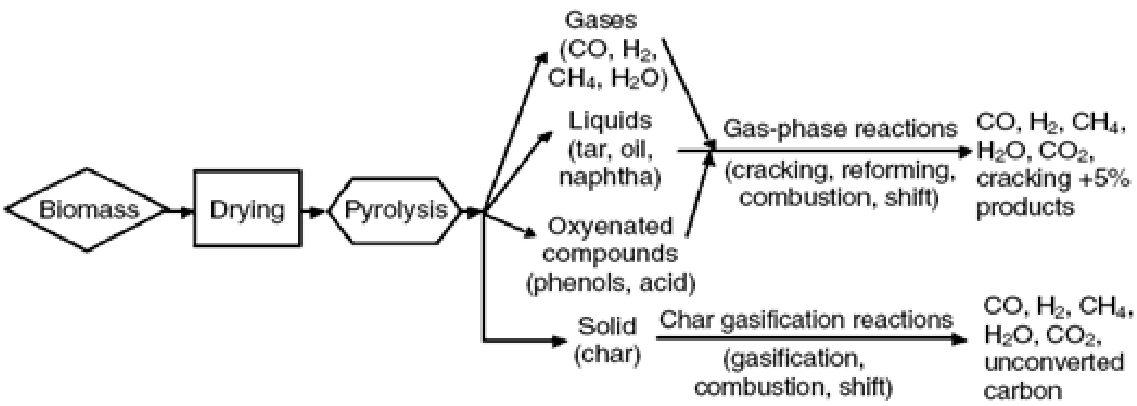

Figure 2.1 Typical biomass gasification processes (Basu, 2010)

There are four steps in the process: preheating and drying; pyrolysis; char gasification and reduction. Although these processes can be modelled into a series, the boundary between them is not very clear (Basu, 2010; Zheng, Shao & Li, 2010).

a) ***Heating or drying:*** After entering the gasifier, the surface moisture is released from biomass by the heat (200-300 °C). This is the primary drying stage.

b) ***Pyrolysis:*** When the temperature is increased to 300 °C or more, pyrolysis reaction begins. Between 300-400 °C, biomass can release about 70% of volatiles, which include water vapour, H_2, CO, CH_4, tars and other hydrocarbons.

c) ***Char gasification (oxidization):*** The char remaining after pyrolysis reacts with the introduction of oxidizing gas, and releases a great deal of heat, with temperatures rising as high as 1000–1200 °C. This supports bio-drying, pyrolysis and the subsequent reduction reaction simultaneously.

d) ***Reduction:*** During the reduction process, oxygen is non-existent. The combustion products and steam from the oxidization layer react with the char in the reduction layer in order to produce H_2 and CO. These gases and the volatile composition of the combustible gas comprise syngas.

This description covers the entire process of converting solid biomass to fuel gas.

In the gasifier, biomass and oxygen partially react to obtain crude syngas. The main reactions involved are listed in Table 2.1 (Higman & Van der Burgt, 2008; Klass, 1998; Ahrenfeldt, 2005).

Table 2.1 Typical Gasification Reactions (Higman & Van der Burgt, 2008; Klass, 1998; Ahrenfeldt, 2005) at 25 °C

Reaction Type
Carbon Reactions
R1 (Boudouard) $C + CO_2 \leftrightharpoons 2CO$
R2 (water-gas or steam) $C + H_2O \leftrightharpoons CO + H_2$
R3 (hydrogasification) $C + 2H_2 \leftrightharpoons CH_4$
R4 $C + 0.5\ O_2 \rightarrow CO$
Oxidation Reactions
R5 $C + O_2 \rightarrow CO_2$
R6 $CO + 0.5O_2 \rightarrow CO_2$
R7 $CH_4 + 2O_2 \leftrightharpoons CO_2 + 2H_2O$
R8 $H_2 + 0.5\ O_2 \rightarrow H_2O$
Shift Reactions
R9 $CO + H_2O \leftrightharpoons CO_2 + H_2$

However, as already noted, the whole gasification process is thermochemically complex. It can be affected by several factors, such as the many side reactions also occurring at the same time.

2.1.4 Type of gasifier

The gasifier is the core piece of equipment in any biomass gasification system. This is because it is within the gasifier that the reactions that produce synthesis gas occur.

There are three types of gasifier as: moving/fixed bed; fluidized bed; and the entrained-flow models (Li et al., 2011). Each of these has its own advantages and disadvantages. Table 2.2 offers a comparison of the characteristics of the three gasifier types.

Table 2.2 Comparison of some Commercial Gasifiers (Basu, 2006; Higman & Van der Burgt, 2003)

Parameters	Fixed/Moving Bed	Fluidized Bed	Entrained flow
Feed size	<51 mm	<6mm	<0.15mm
Tolerance for fines	Limited	Good	Excellent
Tolerance for coarse	Very good	Good	Poor
Exit gas temperature	450-650	800-1000	>1260
Feedstock tolerance	Low-rank coal	Low-rank coal and excellent for biomass	Any coal including caking but unsuitable for biomass
Oxidant requirements	Low	Moderate	High
Reaction zone temperature	1090 °C	800–1000 °C	1990 °C

Steam requirement	High	Moderate	Low
Nature of ash produced	Dry	Dry	Slagging
Cold-gas efficiency	80%	89%	80%
Application	Small capacities	Medium-size units	Large capacities
Problem areas	Tar production and utilization of fines	Carbon conversion	Raw-gas cooling

Each type of gasifier can be further subdivided into specialized functions, as shown in Figure 2.2 (Higman & Van der Burgt, 2003).

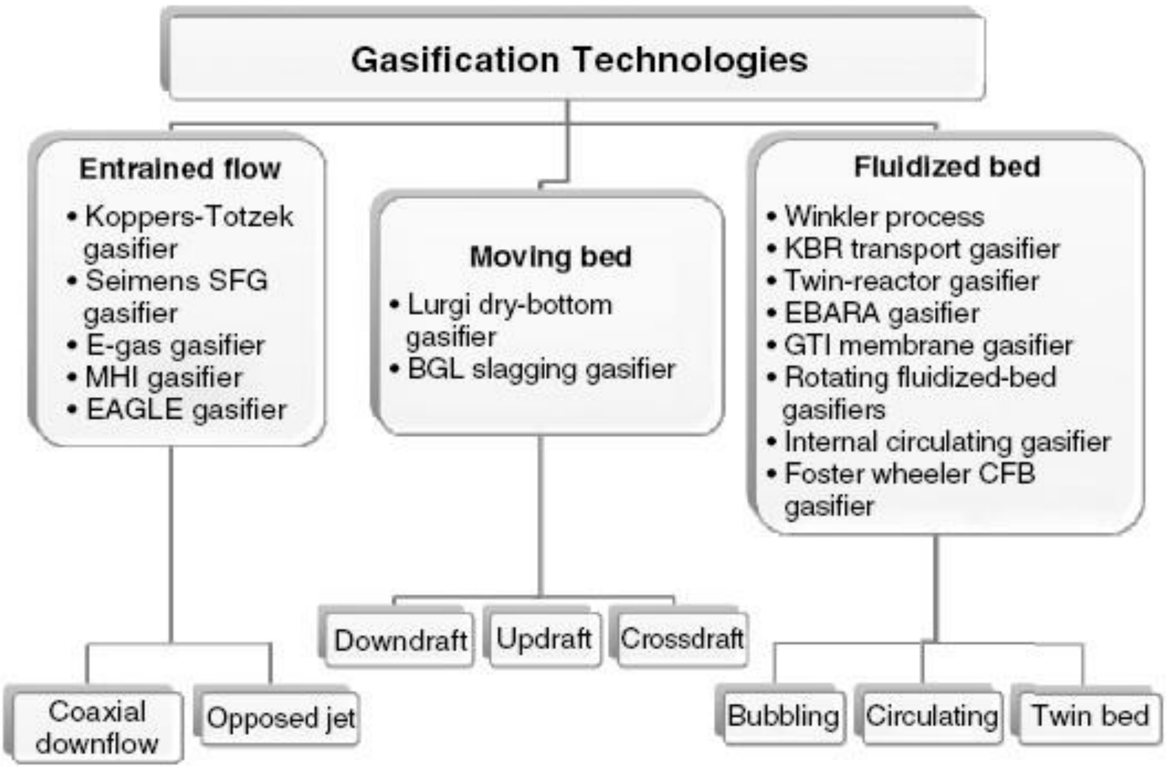

Figure 2.2 Gasification technologies and their commercial suppliers

(Higman & Van der Burgt, 2003).

2.1.5 Syngas purification

Biomass gasification produces not only combustible gas, but other products that include ash, moisture and tar.

During the reaction, most of the ash falls into the ash space down the draft of the fixed bed gasifier. The small amount of fine dust that remains is removed at the same time as the tar. The syngas contains a certain amount of water vapour, which condenses into water when the hot syngas is cooled in the transfer pipeline. Generally, the treatment of moisture and ash in the production of synthesis gas is relatively simple. However, this is not the case when it comes to removing the tar generated in the biomass gasification process, from the syngas. The composition of the tar is very complicated. Analysis has identified more than 200 different components. Milne et al. (1998) listed the main components of tar, as shown in Table 2.3 below.

Table 2.3 Typical Composition of Tar (Milne, Abatzoglou & Evans, 1998)

Component	**Weight**
Benzene	37.9%
Toluene	14.3%
Other 1-ring aromatic hydrocarbons	13.9%
Naphthalene	9.6%
Other 2-ring aromatic hydrocarbons	7.8%
3-ring aromatic hydrocarbons	3.6%

4-ring aromatic hydrocarbons	0.8%
Phenolic compounds	4.6%
Heterocyclic compounds	6.5%
Other	1.0%

According to Liu et al. (2000), syngas containing tar has the following negative effects:

a) tar condenses into liquid at low temperatures, and this tends to plug the gas pipelines with water and ash;

b) it is difficult to combust tar completely, and burning it will produce carbon particles that can cause serious damage to the gas utilization equipment; and

c) gas retaining tar after combustion is harmful to humans health

It follows that tar should be removed before we use the syngas.

The current methods of removing tar, which follow different principles, can be divided into two categories: the physical and the thermo-chemical (Liu et al., 2000; Sun & Jiang, 2006).

The physical method, which includes washing and filtration, does not actually remove the tar, but merely transfers it from the gas phase to the condensed phase. It therefore does not really solve the tar problem. However, while this method has shortcomings, it is widely used in the gasification and gas purification processes.

The thermochemical method induces a series of chemical reactions that convert macromolecules of the tar into small molecules of syngas under certain conditions. The thermochemical method does not only remove the tar from syngas (in so doing, eliminating the hidden danger of equipment damage and environmental pollution caused by tar), but also recycles most of the energy formerly contained in the tar. Data reported by Zhang (2003) shows that the tar product of gasification generally contains 5–15% of the total energy of the syngas. The thermochemical method allows most of the energy in the tar to be recovered.

All of the available methods (and they are many) of removing tar from syngas have advantages and disadvantages. When selecting the method to be used, one must consider the cost, as well as the possible environmental hazards.

2.2 Fischer -Tropsch synthesis (FTS)

FTS is a process that converts synthesis gas into long carbon chain hydrocarbons by means of a metal catalyst. The pioneers of the process are Franz Fischer and Hans Tropsch, of the Kaizer Wilhelm Institute for Coal Research in Germany. In 1923, they proved CO hydrogenation over Fe, Co or Ni catalysts at 180–250°C and atmospheric pressure produces a mixture of linear hydrocarbons (Anderson, 1984).

2.2.1 Fischer -Tropsch synthesis reactors

In the ninety years since the introduction of FTS, many types of commercial reactor have been developed for use with the FTS. Most of them can be classified as falling within two categories: low-temperature FT technology (LTFT) and high-temperature FT technology (HTFT) (Chronis, 1999; Dry & Steynberg, 2004; Ngwenya, 2003). HTFT synthesis can produce environmentally-friendly gasoline, diesel fuel, solvent oil and olefin by FTS operated at a high temperature (300–350 ºC and at 20 bars). LTFT synthesis, on the other hand, takes place at a low temperature (200–240 ºC). Its main product is paraffin that can be processed into a special wax or hydrocracked/isomerized in order to produce high-quality diesel (Chronis, 1999; Dry & Steynberg, 2004; Dry, 1981; Espinoza et al., 1999).

2.2.1.1 Fixed bed reactor (ARGE)

The classical fixed bed reactor, referred to as an ARGE, was developed by Ruhrchemir in collaboration with Lurge. Fixed bed reactors are usually employed in the LTFT process, and used to produce wax and middle distillates. The first commercial ARGE reactor in South Africa became operational in 1955. The diameter of a SASOL ARGE reactor is 3000 mm, and it comprises 2052 tubes that are 12m in length and 50mm in inner diameter, and are packed with extrusion-iron catalyst. The operational conditions of this reactor are 225 ºC and 26 Mpa (Chronis, 1999; Dry & Steynberg, 2004; Ngwenya, 2003; Espinoza et al., 1999; Jager & Espinoza, 1995).

Usually, the radial temperature difference of a multi-tube fixed-bed reactor is about 2–4 ºC, while the axial temperature difference of the reactor is 15–20 ºC (Dry, & Steynberg, 2004; Sasol: 50 years of innovation). The reactor can never be allowed to operate over the highest limits of these reaction temperatures because the coke will cause the catalyst to break down and the reaction tube to clog. It may even become necessary to replace the catalys (Espinoza et al., 1999). A schematic diagram of a multi-tube fixed bed reactor is shown in Figure 2.3.

Advantages

The main advantages of a fixed bed reactor are the following (Chronis, 1999; Ngwenya, 2003; Dry, 1981; Dry, 1982; Dry, 1996; Bartholomew, 1991):

- it is easy to operate;
- the separation of catalyst and liquid product is uncomplicated;
- if a small amount of H_2S is absorbed by the upper portion of the catalyst, the other parts of the catalyst will not be affected;
- no catalyst attrition occurs;
- scaling-up is easy; and
- it operates at a low temperature to yield products that cover a wide range of molecular masses

Disadvantages

The ARGE type of reactor has some shortcomings (Dry & Steynberg, 2004; Ngwenya, 2003; Dry, 1981; Dry, 1982; Dry, 1996; Bartholomew, 1991):

- temperature control is difficult;
- the high gas velocity flowing through the catalyst bed results in a significant drop in pressure, which raises the cost of gas compression;
- the loading and unloading of catalyst is a very troublesome task; and
- the pressure drop of up to 0.7 MPa from top to bottom of the inner tube places considerable stress on it, which makes it necessary for them to be thick-walled and of large diameter, hence expensive requirement

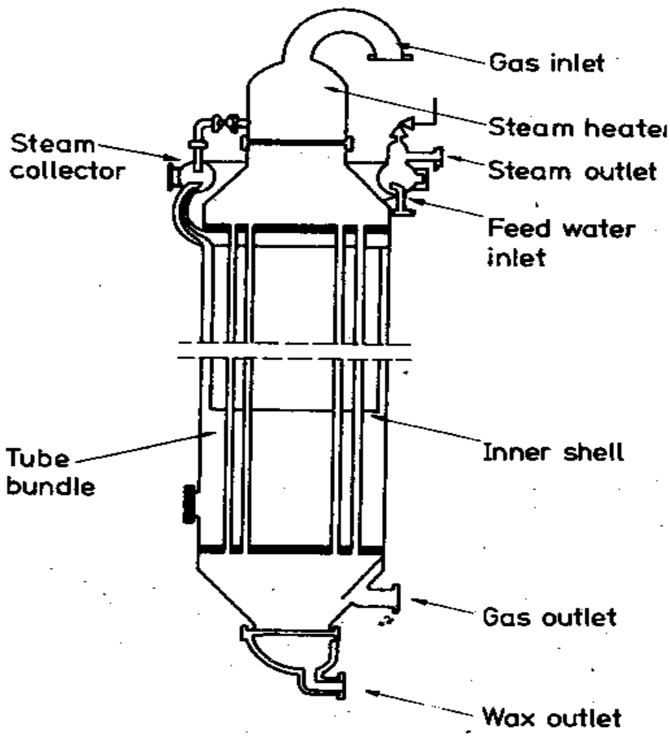

Figure 2.3 Multi-tube fixed bed reactor (ARGE) (Dry, 1981)

2.2.1.2 Slurry bed reactor

A slurry bed reactor uses feed gas as the power source of the reaction, and an inert solvent, in which the catalyst is suspended, as the carrier. When the reaction is carried out in a slurry bed, the gas bubbles through the liquid (slurry) layer of suspended fine solid particles bring about a gas–liquid–solid phase reaction. The heat generated by the reaction can be removed in two ways: by circulating the slurry through external heat exchangers; or by using heat exchangers immersed directly in the slurry bed (Dry & Steynberg, 2004; Dry, 1981). A slurry bed reactor for FTS was successfully designed and commissioned at Sasol in 1993 (Dry & Steynberg, 2004; Ngwenya, 2003; Dry, 1981; Sasol: 50 years of innovation). Figure 2.4 shows the structure of a slurry bed reactor.

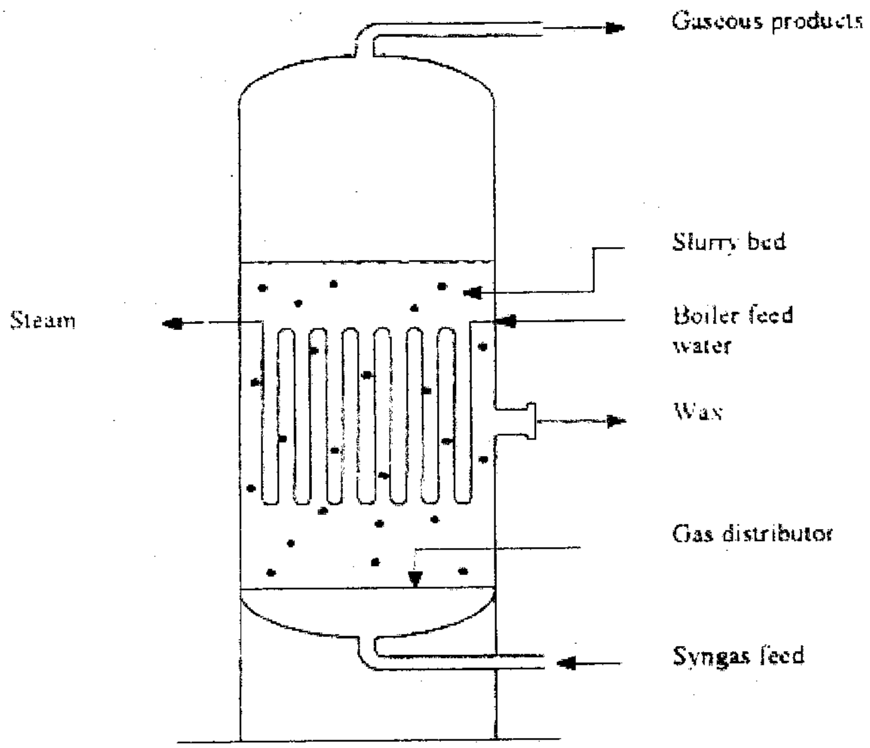

Figure 2.4 Slurry bed reactor (Dry, 1981)

Advantages

The slurry bed reactor offers a number of positive features (Chronis, 1999; Ngwenya, 2003; Dry, 1981):

- it is simple to load and unload the catalyst;
- it has good heat transfer properties, and the reaction temperature is uniform;
- it has a wide range of H_2:CO ratio applications;
- it does not require strict operating conditions;
- it uses a small amount of the catalyst very effectively; and
- it has a simpler structure than the other types of reactor, and consequently has the lowest capital cost per unit volume

Disadvantages

The disadvantages of using slurry bed reactors can be summarized as follows (Chronis, 1999; Dry & Steynberg, 2004; Ngwenya, 2003; Dry, 1981):

- it is not easy to separate the solid catalyst from the liquid product;
- it is difficult to scale up, therefore any scaling up needs to be carefully planned;
- information concerning the true residence time required by the reactants is not readily available, which makes the determination of the residence time difficult; and
- it operates in a narrow gas velocity range

2.2.1.3 Fluidized bed reactor

There are two types of fluidized bed reactor, the circulating fluidized bed reactor (CFB) and the fixed fluidized bed reactor (FFB). The most significant difference between them is that the catalyst is carried with the fast-moving gas in a CFB reactor, while in an FFB reactor, the entire catalyst layer remains stationary, with the airflow passing through it (Ngwenya, 2003; Dry, 1981).

The circulating fluidized bed reactor was developed by the American Kellogg Company. Sasol built a much larger version of the CFB in 1955 (Dry, 1981; Lu, Hoffer & Guczi, 1992) at Sasol I. The inner diameter of this reactor is 2.3m and the height is 46m. After many revisions, this reactor, named Synthol, ran successfully for 50 years. In 1980 and 1982, Sasol set up 16 Synthol reactors, which can produce 7500 barrels of oil per day, at its plants Sasol II and Sasol III (Dry, 1981; Lu, Hoffer & Guczi, 1992; Sasol: 50 years of innovation).

Since separating the catalyst particles from the tailgas is very difficult in a CFB, Sasol developed a fixed fluidized bed reactor (FFB), named Sasol Advanced Synthol (SAS) reactor. When compared with a commercial CFB reactor, the SAS reactor has similar selectivity and greater conversion capability (Sasol: 50 years of innovation). Simple schematic diagram of a FFB reactor and a CFB reactor are shown in Figure 2.5.

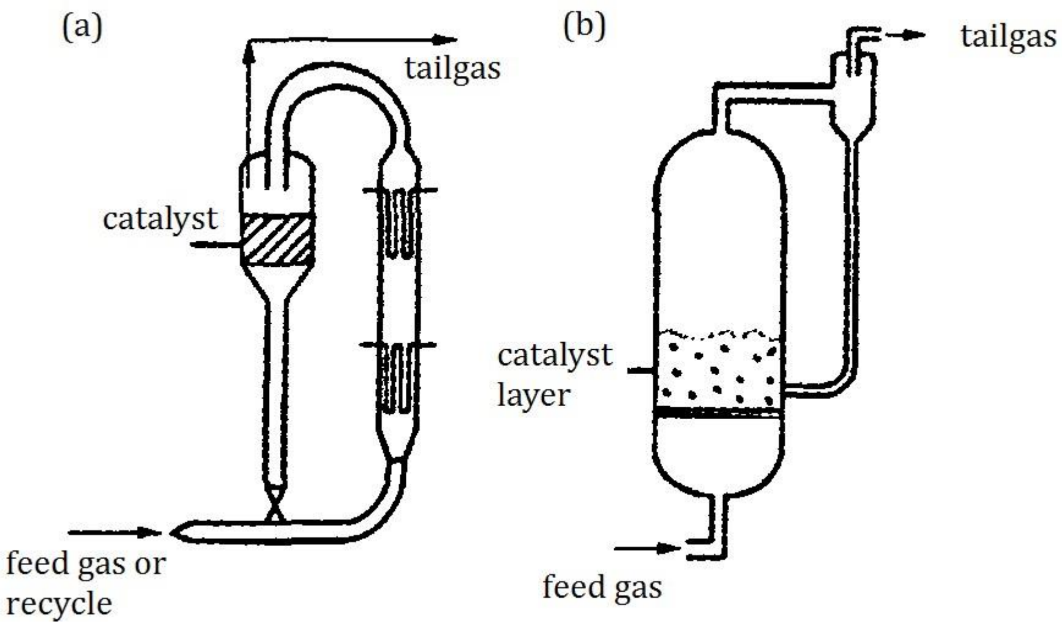

Figure 2.5 (a) Circulating fluidized bed reactor; (b) fixed fluidized bed reactor (Okabe et al., 2009)

Advantages

The benefits of using a CBF reactor are (Ngwenya, 2003; Dry, 1981; Bartholomew, 1991; Xu & Zuo, 2008; Okabe et al., 2009):

- the cost of gas compression is low, because of the lower pressure drop;
- it has excellent temperature control;
- it is easy to load and unload the catalyst;
- the catalyst can be replaced during running time; and
- it has no diffusion limitations

Disadvantages

Despite its strong points, the CFB reactor has some shortcomings (Dry & Steynberg, 2004; Ngwenya, 2003; Dry, 1981; Xu & Zuo, 2008; Musanda, 2008):

- its operation is complicated;
- because it is difficult to separate the catalyst and the products, an expensive special device is required to aid separation;
- scaling up must be carefully planned; and
- there is considerable attrition of the reactor walls, owing to the high line speed of the catalyst particles

2.2.2 Fischer-Tropsch synthesis catalyst

The use of a catalyst is one of the key technologies of the Fischer-Tropsch reaction, because it plays crucial role in product selectivity and the conversion rate of the reactants. The Fischer-Tropsch reaction has been widely used in industry for more than 90 years, during which period a great deal of research has been devoted to identifying the capabilities of different catalysts.

Almost all of the researchers in FTS technology believe that the catalysts used should mainly belong to group VIII metals, such as Fe, Co, Ni and Ru. However, in order to improve the activity, stability and selectivity of the catalyst, they recommend that auxiliary components, such as metal oxides or salts, should be added to the metal selected (Chronis, 1999; Dry, 1981; Musanda, 2008; Ott, Fleisch & Delgass, 1979; Reuel & Bartholomew, 1984). At present, most of the literature on the subject categorizes FT catalysts as divisible into four groups:

Ru-based; Ni-based; Co-based; and Fe-based

The evaluation of catalysts, especially those intended for industrial products, entails a comprehensive comparison of their relative prices and performance. Fe and Co catalysts are the most commonly used, commercially. Throughout the history of FTS technology used in industrial production, Fe-based catalysts have been widely chosen because of their low cost (Anderson, 1984; Chronis, 1999; Dry & Steynberg, 2004; Ngwenya, 2003; Dry, 1981; Anderson, Storch & Golumbic, 1984). However, Co-based catalysts have recently attracted a great deal of attention, because of their greater stability and their capacity to produce wax at low temperature and low pressure (Anderson, 1984; Ngwenya, 2003; Adesina, 1996). Table 2.4 shows the relative prices of the types of catalyst used in FTS.

Table 2.4 the relative prices of metals used in Fischer -Tropsch synthesis (Chronis, 1999)

Metal	Relative price (1999)
Fe	1
Ni	160
Co	1200
Ru	41200
Rh	660000

2.2.2.1 Co-based catalyst

The active phase of cobalt in FTS is the reactive cobalt metal. Because cobalt is expensive, engineers often add small amounts of the precious metals: Pt, Ru and Re in order to improve the catalyst's performance (Bertole, Mims & Kiss, 2004; Chu, 2007; Storsæter et al., 2005). Since the water produced in FT does not affect the activity of cobalt, a Co-based catalyst has good FT performance at higher conversion. The main product of catalysis by cobalt is linear paraffins, but CH_4 selectivity increases significantly at high temperatures (Khodakov, Chu & Fongarland, 2007; Iglesia, 1997). As cobalt-based catalysts are vulnerable to sulphur poisoning, their application in coal to liquid (CTL), FT synthesis has been greatly limited (Chronis, 1999; Ngwenya, 2003; Khodakov, Chu & Fongarland, 2007).

2.2.2.2 Fe-based catalyst

A Fe-based catalyst is a good choice in respect of its adaptability to changes in the reaction conditions and the synthesis gas components, or alterations made to control the reaction product selectivity. By adjusting the additives to Fe-based catalysts or the reaction temperature, engineers can obtain high selectivity of different products, such as: light olefins, gasoline fractions, heavy hydrocarbons and oxygen-containing organic compounds (Chronis, 1999; Dry, 1981; Dry, 1982). However, as iron is the catalyst for the water gas shift reaction, Fe-based catalysts used in FTS will produce great amounts of CO_2 (Ngantsoue-Hoc et al., 2002; Yang et al., 2006).

2.2.2.3 Ni-based catalyst

Nickel also has catalytic activity for FTS, but Ni-based catalysts produce large amounts of methane. Furthermore, under FT reaction conditions, the amount of Ni in the catalyst will reduce; because the formation of nickel carbonyl is the gas phase (nickel carbonyl is a gas at 43 °C) (Chronis, 1999; Ngwenya, 2003; Dry, 1981; Storsæter et al., 2005; Chen et al., 1991). Therefore it is difficult to apply Ni-based catalysts industrially.

2.2.2.4 Ru-based catalyst

Ruthenium is known as the highest-activity FTS catalyst. It has the best carbon chain growth probability and the best CO conversion (Chronis, 1999; Ngwenya, 2003). However, the high price and limited reserves of ruthenium limit its industrial application, considerably. Recent studies show that a Ru-based catalyst can maintain a high activity under high water pressure and in an oxide-containing atmosphere, which indicates that it may, in the future, have a role to play in the BTL process (Okabe et al., 2009; Simonetti wt al., 2007).

2.2.3 Fischer -Tropsch synthesis chemistry

The FTS reaction gives rise to a number of different products, such as: paraffins, olefins and alcohol. The chemistry involved can be expressed by following equations (Anderson, 1984; Dry, 1981; Dry, 1990; Rao, Ramachandran & Balasubramanian, 1961):

Paraffins: $(2n+1)\ H_2 + n\ CO \rightarrow C_nH_{2n+2} + n\ H_2O$

Olefins: $2n\ H_2 + n\ CO \rightarrow C_nH_{2n} + n\ H_2O$

Alcohols: $2n\ H_2 + n\ CO \rightarrow C_nH_{2n+1}OH + (n-1)\ H_2O$

Some side reactions that occur during the FT process can be condensed into the following equations as well (Dry, 1981; Bartholomew, 1991; Dry, 1990; Stoop, & Van der Wiele, 1986):

WGS reaction: $CO + H_2O \rightarrow CO_2 + H_2$

Boudouard reaction $2\,CO \rightarrow C + CO_2$

Catalyst oxidations/reduction a. $M_xO_y + y\,H_2 \rightarrow y\,H_2O + x\,M$

b. $M_xO_y + y\,CO \rightarrow y\,CO_2 + x\,M$

Bulk carbide formation $y\,C + x\,M \rightarrow M_xC_y$

2.2.4 Fischer-Tropsch product spectrum

FTS is a complex catalyzed polymerization reaction because of the number of products that are formed during the synthesis. Anderson, Schultz and Flory (referred to as ASF) proposed a kinetic model that is currently used to describe the product distribution for FTS (Anderson, 1984; Dry, 1981; Dry, 1982; Dry, 1996). The relationship between the weight of the hydrocarbon products, the carbon number and the chain growth probability can be expressed in the following equations:

(1) $$\frac{Wn}{n} = (1-\alpha)^2\alpha^{n-1}$$

(2) $$\ln\left(\frac{Wn}{n}\right) = 2\ln(1-\alpha) + (n-1)\ln\alpha$$

(3) $$\alpha = \frac{Rp}{Rp-Rt}$$

Where:

Wn =the weight fraction of hydrocarbon product containing n atoms

N =the carbon number

α = the chain growth probability

Rp = the rate of chain propagation

Rt = the rate of chain termination.

2.3 Biomass to liquid fuels

Although biomass can be used in its raw form as a resource, the best way to utilize the biomass is by converting it to liquid fuel, because the low density and high water content of biomass. Recently, many researchers have focused on finding economical and efficient methods of changing the solid biomass to liquid fuels. Figure 2.6 shows the different routes by which biomass can be converted to liquid (Crocker, 2010; Huber & Dumesic, 2006).

In the figure, it can be observed that there are three main pathways to BTL (Behrendt et al., 2008; West et al., 2009; Carlson, Vispute & Huber, 2008; Srokol et al., 2004):

1. Biomass is gasified into syngas. After pretreatment to remove tars and other impurities, syngas can be catalytically converted to hydrocarbons or to alcohols.
2. Direct thermochemical conversion processes are used to convert biomass into raw bio-oil. Following this, through hydrotreating or zeolite updating, the bio-oil is converted to liquid fuel.
3. Enzymes, acid- or base-catalyzed hydrolysis are used to decompose the sugar polymers in the biomass into their constituent monomers. These sugars can then be fermented into alcohols.

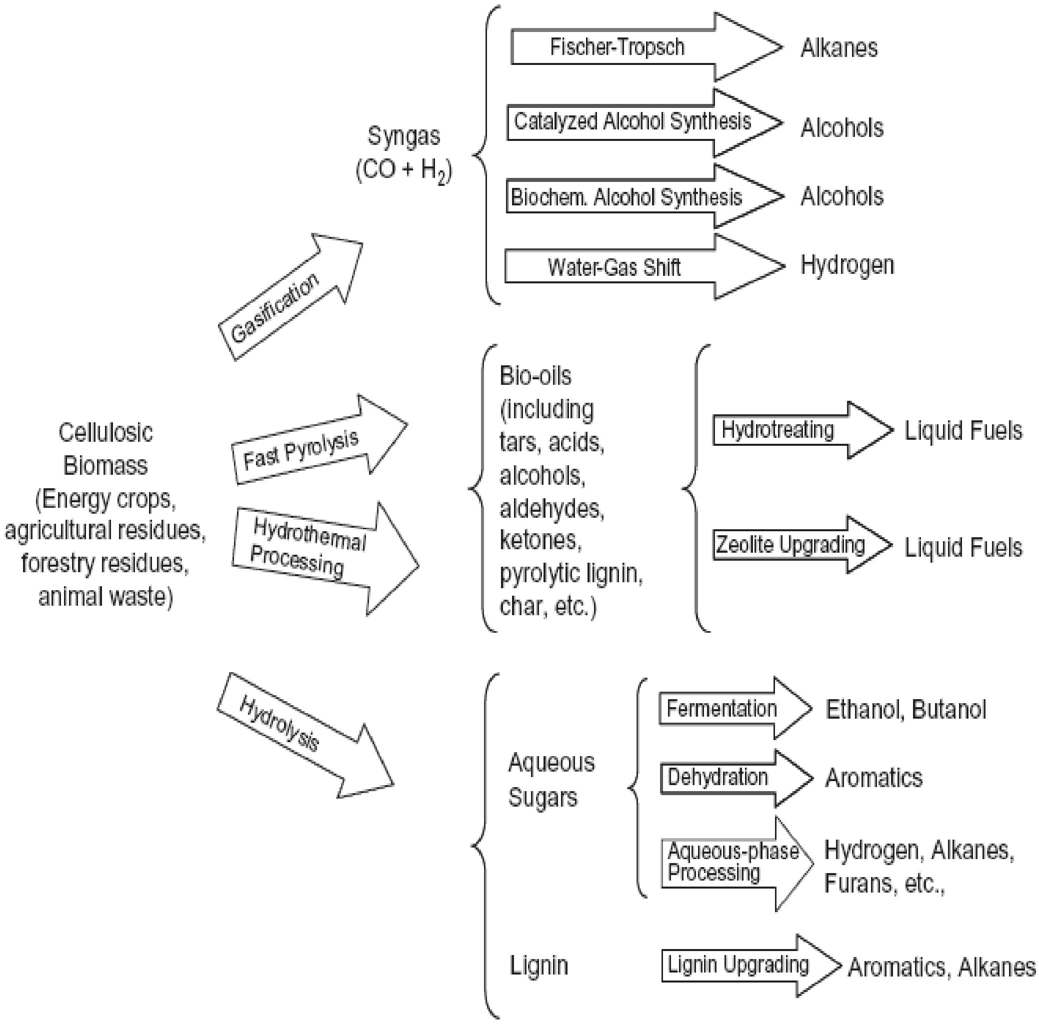

Figure 2.6 Summary of the pathways for cellulosic biomass conversion to liquid fuels (Crocker, 2010)

The world’s first commercial BTL plant with FT route, utilizing the Choren Carbo-V® Process, was constructed in Frieberg, Saxony (Swain, Das & Naik, 2011). However, on the 9th of February, 2012 Choren's biomass gasification technology was sold to Linde Engineering, Dresden. This company will further develop the Choren Carbo-V® technology used to produce syngas (European Biofuels Technology Platform, 2011). Figure 2.7 shows the process of BTL used in Choren.

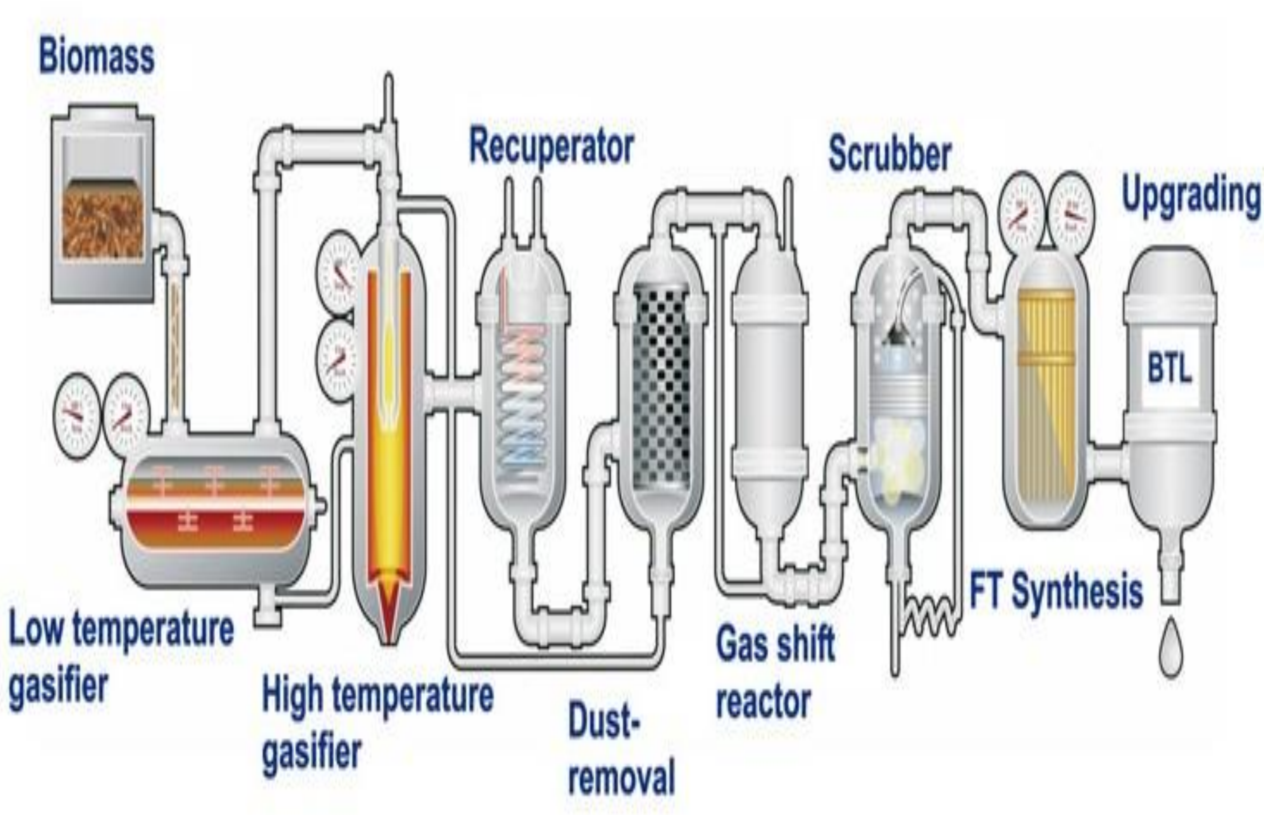

Figure 2.7 the process used by the Choren commercial BTL (European Biofuels Technology Platform; 2011)

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Chapter 3: Biomass gasification and syngas purification

3.1 Introduction

As the syngas that forms the feed for FTS comes from the biomass gasification process, the latter can be described as the first step in the conversion of biomass to liquid fuels. The composition of biomass can comprise many substances apart from agricultural and forestry wastes, such as: garbage, sewage and waste paper (Basu, 2010; UNFCCC, 2005). However, each type of raw material differs in physical properties and chemical composition. It is therefore important to the integrity of the experiments that one source of biomass that can be used consistently for gasification throughout the entire project, is selected.

The gasification process takes place in the gasifier (Basu, 2006; Liu, Zhuang & Xia, 1999; Higman & Van der Burgt, 2003). After decades of development, many types of gasifier are now available. In this project, which focuses on a bench scale BTL technology, the required gasifier was one that not only produced a suitable quantity of gas, but also a gas quality that complied with the requirements of FTS.

Another consideration was that the syngas resulting from the biomass gasification process inevitably contains impurities (Liu et al., 2000), such as tars, ash and inorganic matter. These must be removed since the syngas is compressed, because they affect the performance of the catalysts. Oxygen (which is contained in the air feed) and sulphides also interfere with the effectiveness of the catalysts. It is, therefore, necessary to ensure that the amount of these undesirable elements in the syngas used for FTS is minimal, and is not allowed to rise above a certain level. It is also the requirement of the compressor, to remove O_2.

This chapter describes the whole process of biomass gasification, including the selection of raw materials and the gasifier, syngas purification before compression, and the additional deep purification process necessary to remove oxygen and sulphides.

3.2 The gasifier and gasification

The gasifier is the core piece of equipment in any biomass gasification system. In the high-temperature conditions of a gasifier, biomass is broken down into small molecules, which are then converted into syngas (which contains CO, H_2 and other components). This syngas is the feed for FTS. Various types of gasifier produce gas containing different proportions of the above components, which in turn have an enormous impact on the results (that is, the products) of FTS. This explains why selecting the appropriate gasifier is vital to any research involving gasification.

For a bench scale BTL, the gasifier must have the following properties:

- ease of operation;
- low cost;
- low tar content after gasification; and
- scale small enough to match the FTS

Gasification carried out in a fluidized bed gasifier is very rapid, and produces a higher quantity of syngas than a fixed bed reactor (Wang et al., 1997; Li et al., 2004). However, in comparison with a fixed bed gasifier, the structure of a fluidized bed gasifier is more complex, and its operation is relatively difficult. Moreover, the cost of a fluidized bed gasifier is too high to be practicable in a bench scale BTL facility. For these reasons, it was decided that a fluidized bed gasifier was not suitable for the project. Another consideration was that the syngas from an updraft fixed bed gasifier has more tar content than that formed by the downdraft fixed bed version (Kunii & Levenspiel, 1999). In addition, it is easy to load a biomass for downdraft gasifier. Consequently, an atmospheric pressure fixed downdraft biomass gasifier was chosen forth is study.

The major equipment parameters of the gasifier selected for this study is specified in Table 3.1. Figure 3.1 shows the structure and outward appearance of the gasifier.

Table 3.1 Major parameters of the gasifier

Diameter	600mm
Height	2000mm
Lording	50kg
Gas production rate	$10m^3/hr$

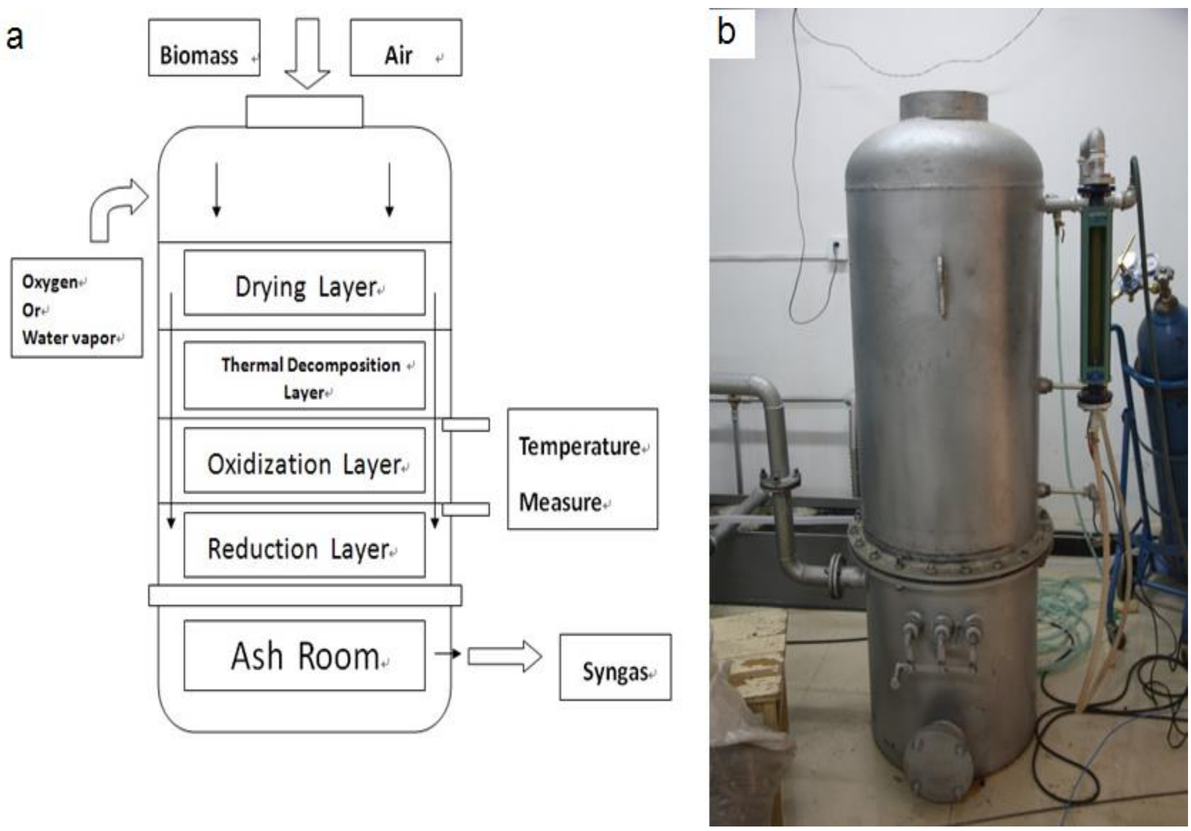


Figure 3.1(a) Schematic diagram of the gasifier and (b) Photograph of the gasifier

The inner layer of this gasifier is the reaction zone, while the outer layer comprises the insulation, which is filled with firebrick. The insulation layer, not only conserves the high temperature of the reaction zone, but it is also able to reduce the temperature of the outer wall of the gasifier. The feed opening is at the top, while the bottom of the furnace connects to the ash room. The grate, which is cast in high-temperature heat-resistant steel, is sufficiently heat-resistant in order to contain the internal temperature without damage. The advantages of this type of gasifier are as follows (Basu, 2010; Higman & Van der Burgt, 2003):

- it is smaller in scale than any other types of gasifier capable of producing enough syngas to support FTS;
- the technology of the design has matured;
- it is easy to operate; and
- it is less expensive than other types of gasifier

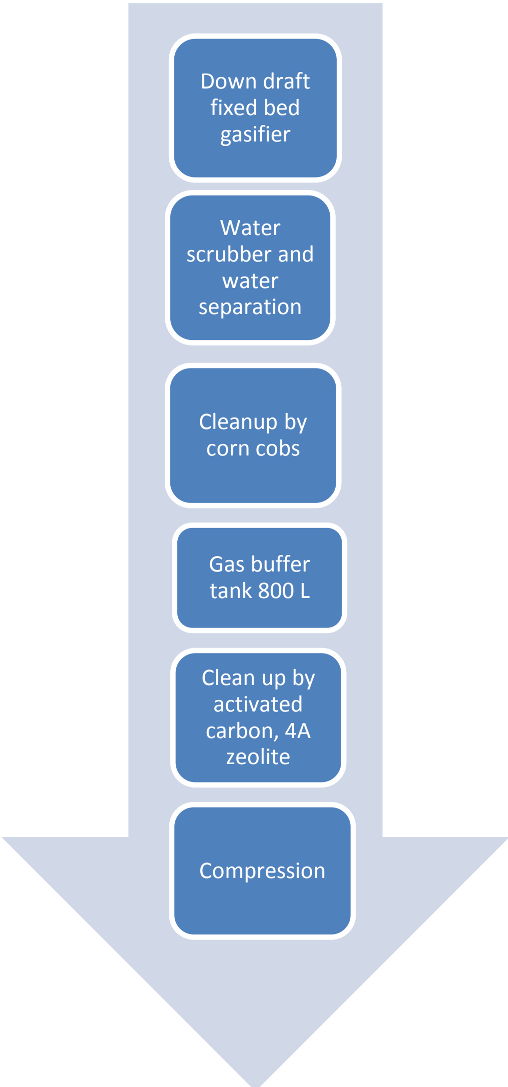
Although an atmospheric pressure fixed downdraft biomass gasifier has some shortcomings, for example the low temperature inside the gasifier restrains the quantity of syngas production, and produces more ash than excepted. This was the model chosen to be used for the experiments in biomass gasification described in this dissertation. Its salient advantages were the ease of operation and low cost.

3.3 Syngas purification before compression

As previously noted, since the gas leaving the gasifier contains some impurities, such as tar, ash and water vapour, it must be purified before undergoing compression. In this study, the gas purification process included washing in order to remove tar;

moisture separation; physical adsorption of impurities; and storage in a gas buffer tank, where solid impurities were removed and zeolite was used to dry the gas. A flowchart for the purification process is shown in Scheme 3.1, and Figure 3.2 shows the purification equipment.

The diameter of the water scrubber is 300 mm and the height is 2000 mm. The syngas leaving the gasifier at a temperature of over 700°C is cooled in this facility, which



Scheme 3.1 The sequence of purification of syngas before compression

Figure 3.2 Photographs of purification equipment

also removes most of the solid impurities, tars, and water-soluble inorganic particles. When this method is compared with the catalytic cracking method of removing tar, water washing is not as efficient, and the water consumption is higher. However, this method is simpler, and can be carried out without additional labour (Wang et al., 1997), which explains the decision that getting rid of tar by the water washing method was better suitable for the research programme.

After water-washing and water separation, the syngas is cooled to room temperature. Most of the tar and ash in the syngas will have been removed by the water-washing process. Thereafter the gas is fed into a dryer filled with corn cobs. These have good physical adsorption capacity; hence they are able to reduce the remaining amounts of tar, ash and other inorganic impurities.

After this secondary purification, the syngas is stored in a gas buffer tank, which is sealed by water. The diameter of the buffer tank is 500 mm, and its capacity is sufficient for 0.8$m^3$of syngas. The water in the buffer tank separates the last solid impurities from the gas, after which 4A zeolite is used to remove moisture from the syngas.

The next step was gas compression. The compressor used has a rated pressure of 15 MPa, and it can compress 8 m^3 of gases per hour. In our experiments, the pressure in the cylinders was over 10 MPa, and the content volume of each cylinder was 40 L.

3.4 Selection and pretreatment of biomass

3.4.1 Biomass selection

Theoretically, almost all organic biomass can be used as raw material for synthesis gas. However, the major target of the programme was to design and establish a low-cost bench scale BTL facility in order to demonstrate the process of converting biomass to liquid. Consequently, considerations of expense and ready availability were crucial in selecting a suitable source of biomass as the raw material for gasification. When compared with other kinds of biomass, agricultural and forestry wastes, these renewable materials, are the most commonly used in gasification in order to produce conventional fuels. There is another advantage since the gasification of these types of waste has been developed into a relatively matured gasification technology. Agricultural and forestry wastes were therefore chosen as the raw materials for this experimental study.

Table 3.2 Comparison of ultimate analysis of some agricultural and forestry wastes (Basu, 2010; Boley & Landers, 1969; Bowerman, 1969; Tillman, DA 1978; Wen et al., 1974)

Fuel	**C (%)**	**H (%)**	**N (%)**	**S (%)**	**O (%)**	**Ash (%)**
Maple	50.6	6.0	0.3	0	41.7	1.4
Douglas fir	52.3	6.3	9.1	0	40.5	0.8
Douglas fir (bark)	56.2	5.9	0	0	36.7	1.2
Redwood	53.5	5.9	0.1	0	40.3	0.2
Redwood (waste)	53.4	6.0	0.1	0.1	39.9	0.6
Rice straw	39.2	5.1	0.6	0.1	35.8	19.2
Rice husk	38.5	5.7	0.5	0	45.4	1.0
Sawdust	47.2	6.5	0	0	45.4	1.0
Paper	43.4	5.8	0.3	0.2	44.3	6.0

Table 3.2 sets out the ultimate analysis of some agricultural and forestry wastes that provide a point of reference (Basu, 2010; Boley & Landers, 1969; Bowerman, 1969;

Tillman, DA 1978; Wen et al., 1974). From the table, it is easy to see that the carbon and hydrogen content of woody biomass is higher than that of herbaceous biomass. Carbon and hydrogen in the raw materials have a direct effect on the CO and H_2 contents of the syngas; and CO and H_2 as reactants, play a key role in the FTS reaction. For these reasons, a woody waste was selected as the source of raw material most appropriate for the project.

3.4.2 Pretreatment of biomass

3.4.2.1 Drying of materials

When the moisture in the material is greater than a certain value (approximately 70%), the combustion reaction cannot occur. (Basu, 2010) Such large moisture content also prevents the reduction (gas-producing) reaction, which relies on the heat provided by the combustion reaction. Thus, before gasification, the woody biomass must be dries. Generally, provided the amount of moisture in the biomass is less than 15%, this will ensure that the operation of the downdraft gasifier is economical and also reliable (Basu, 2010).

3.4.2.2 Material crushing and reshaping

When the components of the woody waste are too large (diameter: 20-50 mm) (Wang et al., 2004), feeding the waste directly into the gasifier can cause “bridging”, which means that the contact area between the feedstock and the gasifying agent is smaller, and the resultant reaction is incomplete. This in turn results in a localized high temperature in the furnace, which can damage the flame retardant coating (Han, 1994). In order to avoid bridging, the wood was crushed and reshaped. Figure 3.3 shows the reshaped biomass used in the experiment.

The research study carried out by Han Z. (1994) points out that the particle size of biomass material has a considerable effect on the gasification process. From the perspective of chemical kinetics, a smaller particle size can increase the reactive surface area of the material. The greater the reaction surface, the more heat exchange occurs in the diffusion process, creating a considerably rapid and complete gasification reaction. However, the particle size of the biomass feed cannot be too small, because that will cause a pressure drop.

Figure 3.3 the crushed and compressed biomass used in this study

In addition, uniformity of particle size is a major factor in the airflow distribution. This is because an uneven distribution of large particles in the bed will result in irregular areas of resistance that in turn will lead to local patches of intense combustion (Wang et al., 2004). The high temperatures will cause the gasification layer to move up or sinter to form the localized spots of excessive heat. In order to avoid this occurrence, it was ensured that the ratio of maximum and minimum particle size of the material was not more than eight (Basu, 2006). In Figure 3.3, it can be seen that the pre-compressed particles of biomass are of similar size.

3.5 Experiment and results

This section describes a gasification experiment carried out using the equipment and materials described in the section above.

3.5.1 Experimental procedure

Before ignition

In the preparatory stage (before ignition), confirmation that the gasification section was sealed (i.e., no leaking was apparent) was required in the whole gasification system, and that the in- and out-flow functions of the water scrubber were working normally. It was necessary to check that the fan was functioning properly.

Ignition

The first step involves inserting a number of corn cobs into the gasifier and then adding some burning newspaper in order to ignite them. After that, the fan would be switched on, thus modifying the air flow rate to a suitable speed.

Once the combustion in the furnace was stable, the woody biomass was fed in and the feed port was closed. The next task was to test the gas components and prepare for compression when the flame of the burner was steady.

3.5.2 The effect of changing the conditions of gasification

During the process, the biomasses react with the gasifying agent in the gasifier. Through a series of complex oxidation–reduction reactions, a crude synthesis gas product was obtained. The main equations involved can be expressed as follows:

$$C_mH_nS_{r+m/2} + O_2 \rightarrow mCO + (n/2-r)H_2 + rH_2S$$

$$CO + H_2O \rightarrow H_2 + CO_2$$

These reactions occur at atmospheric pressure and a temperature of between 800–900 °C. They can produce CO, H_2, CO_2, H_2O, CH_4 and a small amount of COS and H_2S in the syngas. Table 3.3 shows the components of the syngas produced in the first run, to be used in the BTL setup.

From Table 2.6, it can be seen that the components of syngas produced by a downdraft gasifier are relatively stable. The H_2/CO ratio of this syngas ranges from 0.8–1.2, and the total sulphur content was less than 28 ppmv. However, the high oxygen content of around 2% was still a big problem because it did not only affect the catalyst in FTS, but also increased the risk of the cylinder explosion. Moreover, the H_2 and CO contents are lower than anticipated.

Table 3.3 Components of syngas in the first run (GC condition: Hold at 50 ºC for 4 min, heat to 180 ºC at 5 ºC /min, hold at 180 ºC for 4 min)

	CH_4 %	**C_2H_4 %**	**C_2H_6 %**	**N_2 %**	**CO %**	**CO_2 %**	**O_2 %**	**H_2 %**	**Total %**	**H_2/CO**	**H_2S ppmv**	**COS ppmv**	**Total S Ppmv**
1	5.3	0.5	0.4	50	10.5	7	2.3	12.2	89	1.16	21	5	26
2	4.3	0.5	0.2	54.1	11.1	13.5	2.2	9.9	96	0.89	6.8	1.7	8.5
3	5.6	0.6	0.3	52.4	13.9	7	1.8	11.8	94	0.85	1.3	1.3	2.6
4	5.8	0.6	0.2	49.7	10.3	8.2	1.8	11.8	90	1.14	0.5	4	4.5
5	4.9	0.5	0.2	55	12	11.2	2.3	10.3	97	0.86	5.6	2.2	7.8
6	6.9	0.8	0.4	52.2	12.7	10.6	2.4	12.1	101	0.95	3.5	3.5	6.9

3.5.3 The effect of air input

During earlier experiments, it was found that the feed rate of the gasification agent influences the components of the end product (the synthesis gas). It was therefore necessary to control the rotation speed of the fan in order to adjust the rate at which the air (the gasification agent) is fed. Table 3.4 shows the changes in the main components of syngas that can be achieved by modifying the rotation speed of the fan.

Table 3.4 Components of syngas at different air flow rates

Air flow rate (m^3/hr)	**H_2 (%)**	**CO (%)**	**N_2 (%)**	**O_2 (%)**
15.75	10.3	9.866	53.11	1.75
18	11.75	11.11	54.06	2.1
20.25	12.08	12.05	52.09	1.96
22.5	15.33	14.48	49.16	1.32
24.75	16.98	13.22	48.24	0.85
27	15.57	13.45	50.83	0.7

Table 3.4 shows that the oxygen content decreased as the rotation speed of the fan increased, and that the H_2 and CO content of the syngas reached a maximum of 55 and 50r/sec, respectively. The most suitable H_2/CO ratio for FTS was 2: therefore, when the H_2/CO and oxygen contents are compared as set out in the table, it follows that syngas produced at the air flow rate of 24.75m^3/hr was the most appropriate for FTS. Figure 3.4below shows the variation in different gas components caused by the variations in the air flow rate graphically.

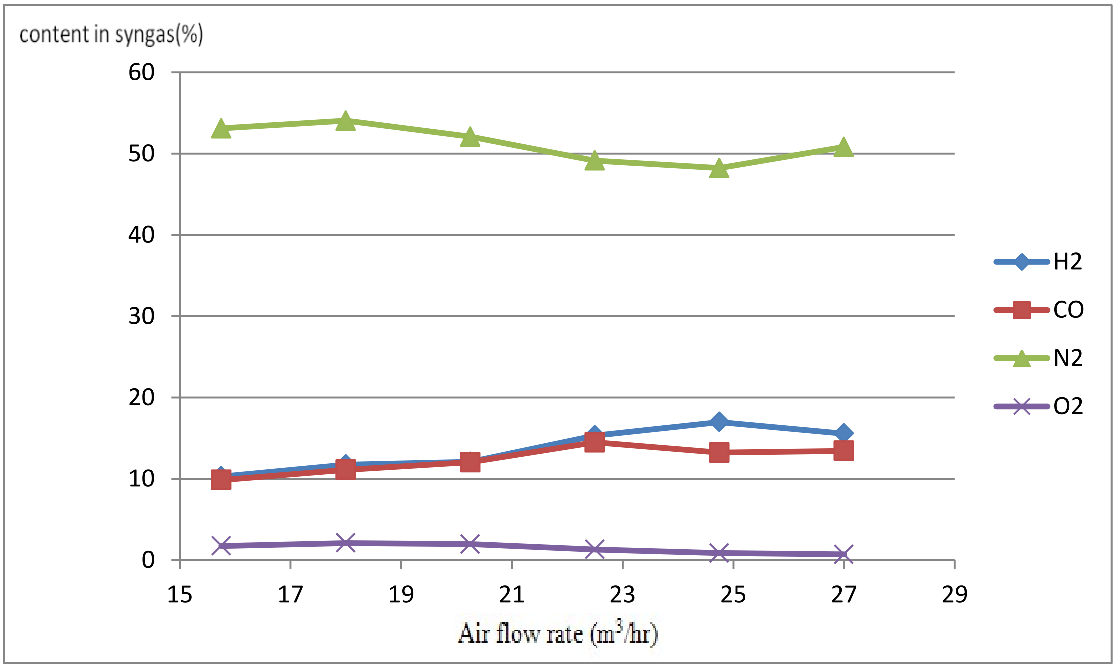


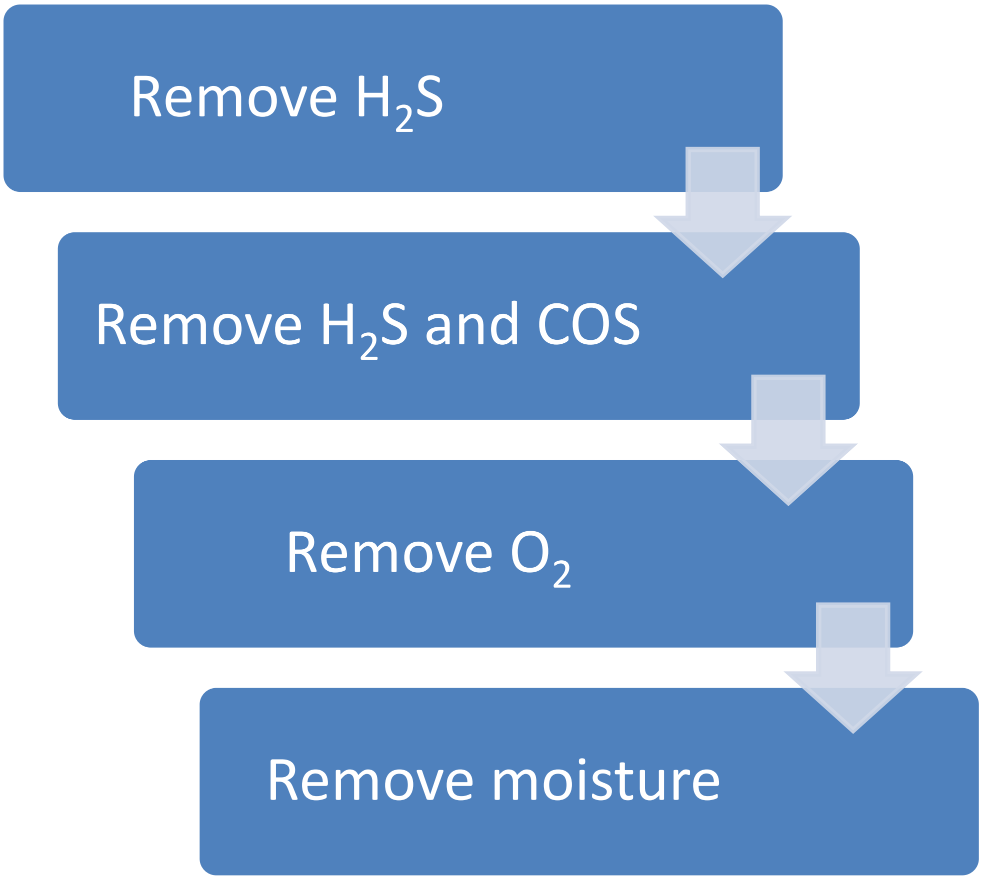
Figure 3.4 Changes in gas content with different air flow rates

3.6 Removal of sulphur and oxygen from the syngas

Since the synthesis gas in the cylinders has undergone preliminary purification, the tar and mechanical and inorganic impurities in the gas have been removed. However, in order to meet the conditions required for FTS, the gas was subjected to "deep purification", which mainly comprised of desulphidation and deoxygenization.

Sulphide is the most common cause of catalyst poisoning. An extremely small amount of sulphur can lead to catalyst deactivation, which nullifies the experiment. Oxygen, on the other hand, renders the catalyst used for FTS inactive. High oxygen content in the synthesis gas represents a huge threat to the experimental result.

Scheme 3.2 shows the flowchart of the deep purification carried out during this study.



Scheme 3.2 Deep purification stages before syngas can be used for FTS

Rectisol, a Linde/Lurgi-developed acid gas removal process that uses methanol as a separation agent, has become the most widely-used method for removing sulphur (Wang, Zheng & Zhang, 2010). However, this process is not quite suitable for small-scale production. For the current experiment, a fixed-bed gas purification process was chosen to remove the sulphide by using modified activated carbon, which through adsorption is able to reduce the sulphide content to less than 5 ppb.

A gas chromatograph (GC) is to measure the sulphide content of the syngas before and after the sulphur removal process. This made it possible to assess the effectiveness of the desulphurization. The GC was fitted with a flame photometric detector (FPD) with a detection limit of 5 ppbv.

The removal of the oxygen was carried out according to the reaction $2H_2+O_2 \rightarrow 2H_2O$ with a 506HT-supplier deoxidation catalyst. This is a palladium-semiconductor catalyst. The advantages of using it are as follows (Deoxidization catalyst 506HT):

- High catalytic activity.
- No activation regeneration, first used without pretreatment.
- High-temperature (650 degrees Celsius), not ablation (450 degrees Celsius) highest congener product.
- High strength, not pulverization

In the final stage, moisture is removed by 4A zeolite at ambient temperature.

Figure 3.5 shows the structure of the desulphurizer, deaerator and drier. The photograph in Figure 3.6 shows their appearance.

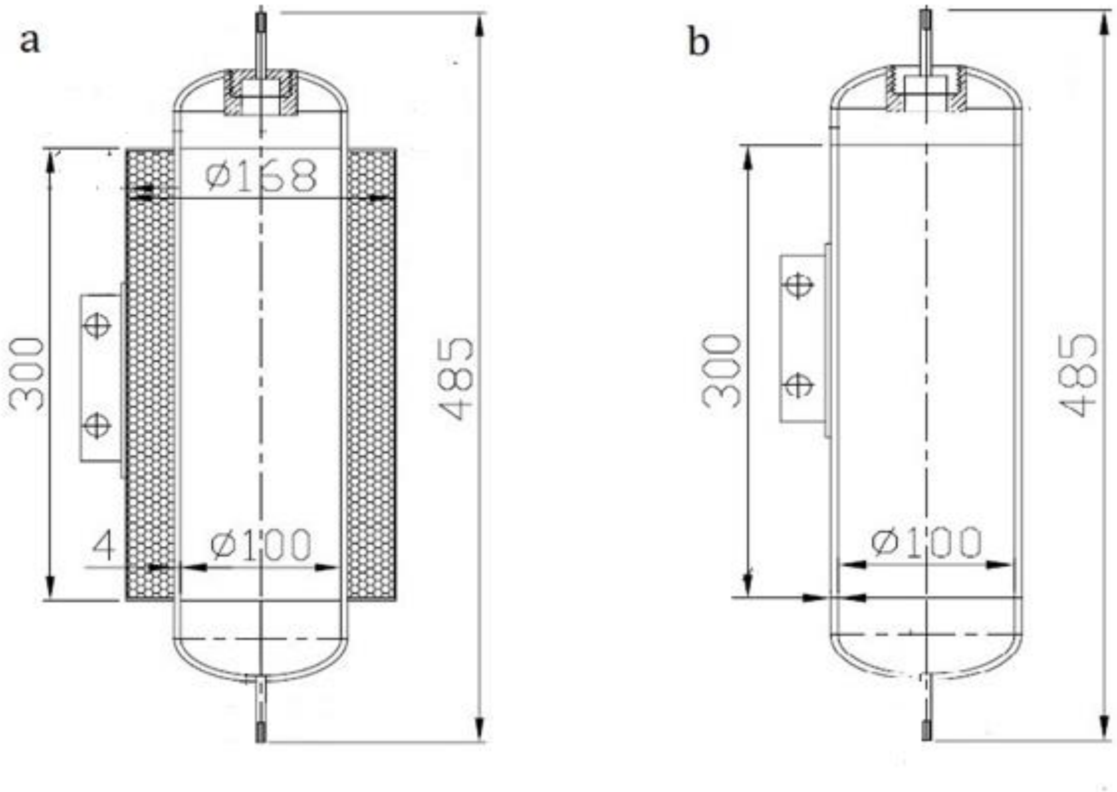


Figure 3.5 a) The structure of desulphurizer and deaerator; b) the structure of dehydrator

Figure 3.6 Thesetup of the desulphurizer, deaerator and dehydrator

Table 3.5 compares the gas content of the syngas before and after deep purification. From the table, it is observable that the sulphide has been reduced to an undetectable level (less than 5ppbv), and that the O_2 content is considerably lower than before.

Table 3.5 Results before and after deep purification

before deep purification												
CH_4 %	**C_2H_4 %**	**C_2H_6 %**	**N_2 %**	**CO %**	**CO_2 %**	**O_2 %**	**H_2 %**	**Total %**	**H_2/CO**	**H_2S ppmv**	**COS ppmv**	**total S ppmv**
5.9	0.6	0.3	51.6	9.7	7.0	1.9	11.5	88.7	1.18	1.3	1.3	2.6
After deep purification										**ppbv**	**ppbv**	**ppbv**
7.2	1.1	0.1	61.8	12.0	5.5	0.9	12.0	100.6	1.00	<5	<5	<5
6.6	0.9	0.1	54.6	10.9	18.5	0.8	11.5	104.1	1.06	<5	<5	<5
6.0	1.0	-	51.2	9.9	23.9	0.7	9.9	102.9	1.00	<5	<5	<5

3.7 Conclusion

A downdraft fixed bed gasifier with a10 m^3/hr gas production capacity was built for the research described in this dissertation. If 50 kg of raw materials are fed to this gasifier, it can run continuously for between 6–8 hours, and produces about 50 Nm^3 of synthesis gas, which is equivalent to converting 1 kg of biomass to 1 Nm^3 of qualified syngas. According to the estimates, if the gasifier is in an uninterrupted operation over a long period, it should be possible to obtain 2 Nm^3 per kg of biomass.

In this experimental project, the water washing method was used to remove tars, ash and other impurities, followed by a deep purification process that prepared the syngas to be fed into the FT reactor, by reducing the sulphide and oxygen in the gas to a minimal level. Following this process, the sulphide content was lower than the GC detection limit (5 ppbv) and the oxygen content was below 1%. The syngas analysis of data on the other components showed the H_2 content was between 10–17%, and gave a similar reading for the CO content of between 10–15%. At this stage, the syngas was suitable for use in FTS.

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Chapter 4: The bench scale FT reactor and catalyst

4.1 Introduction

Ever since the FTS process was discovered in 1923, the types of reactors best suited for this process have been the subject of continuous research (Anderson, 1984; Vosloo, 2001). Many types of reactors have been investigated, and variations in reactor design have been developed. At the same time, researchers have also studied the catalysts used in FTS, in order to determine their physicochemical properties and selectivity. At present, the most successful commercial FTS reactors can be divided into three categories: fixed-bed, slurry bed and fluidized bed reactors (Dry, 1981; Espinoza et al., 1999; Ngwenya, 2003).

Although FT synthesis technology is sufficiently developed for industrial production in the areas of coal to liquid (CTL) and gas to liquid (GTL) technology, the commercial use of biomass as raw material for FTS, is in its infancy. The bench scale BTL facility, which is proposed in this study, is a key step towards making BTL commercially viable. It follows that careful selection of the FT reactor and the catalyst is very important for the success of our programme.

The catalyst is one of the key components of the FT reaction. Currently, the catalysts for commercial FT synthesis are Fe-based and Co-based, although in order to improve their activity, stability and selectivity, chemical engineers and scientists frequently add small amounts of chemicals, such as metal oxides or salts to the basic catalyst (Dry, 1981; Musanda, 2008; Reuel & Bartholomew, 1984).

The focus of this chapter is the main structure of the reactor chosen for FTS, when performing BTL conversion and the catalysts used for this purpose.

The details of the structural characteristics of the reactor including its tube, its heating jacket, and the various systems for temperature measurement, product collection and product analysis, are discussed.

4.2 Design of the FTS reactor

The major aim of the research was to build a low-cost bench scale BTL facility in order to demonstrate the feasibility of generating fuels from biomass feed by means of FTS. In addition, it also intended to accumulate data on the process in order to provide a basis for scaling up the process to industrial level.

Earlier in this dissertation, the various types of FTS reactor were discussed. A single-tube fixed bed reactor was chosen for this research, because, when compared with other types of reactor, in terms of scaling up and operates, this kind of reactor is simpler in procedures (Dry, 1981; Bartholomew, 1991; Dry, 1982). This work also proposed to test the viability of a larger diameter (50 mm) single tube. The design objective of the laboratory set-up was that the reactor should be capable of an output rate of 100 g of liquid hydrocarbon a day when operating at the full scale. The original production capacity this project envisaged was 300 mmol CH_2/hr (100 g in 24hrs) in two or three stages. However, for budget reasons, these experiments were carried out in a single tube reactor only (with commensurate to 100 g per day)

4.2.1 The FTS reactor

4.2.1.1 Tube length

The whole FTS process comprises a series of several different reactors. 200 mmol CH_2/hr (68 g CH_2/d) was estimated as the highest liquid/wax production achievable by a single reactor. The catalyst activity proposed in this project was 4 mmol CH_2 (total) /g Cat/hr, and 2mmol CH_2 (liquid)/g Cat/hr with an assumed 50% liquid selectivity of hydrocarbon, which requires 100g of catalyst in the reactor. Since the density of the catalyst is about 0.7g/ml, it must occupy a volume of 150ml in the reactor tube. The inner diameter of the tube is 5cm.

The cross-sectional area is $S = \pi * (5 / 2)^2 = 19.625\ cm^2$.

The catalyst bed is situated at the centre of the reactor tube. The height of the catalyst layer is $H1 = 150 / 19.625 \sim 7.7$ cm. Owing to the large inner diameter of the reactor tube, the temperature distribution inside the tube must be measurable, which is why its inner volume must also accommodate four thermocouple channel. This means that the actual length of the catalyst layer H1 will be greater than 8 cm.

In order to ensure good gas distribution and stability of feed gas, eight times that of the diameter of the inner reactor tube is needed in the catalyst bed.

H2 = 8 * 5 = 40 cm

Thus, the total length of the reactor tube will be 2 * H2 + 8 ~ 90 cm.

4.2.1.2 Heating jacket

FTS is a highly exothermic reaction, and the catalyst must attain a certain temperature in order to become active. This requires that the reactor is preheated prior to the start of the reaction, and that it is able to remove the heat generated during the reaction. In this experimental programme, two methods were used to bring about heat exchange: the oil bath and the N_2 bath.

An oil bath keeps the reactor temperature as high as 250 ºC (although it is designed to have a limit of 300 ºC). Silicon oil, which is commercially available, can be safely used for this purpose. Its function is to preheat the bed before the reaction, and to remove the heat generated by the reaction during FTS. Hot oil is fed from the bottom of the reactor and removed from the top. In order to provide enough driving force, the temperature of the oil is set between 10–20 ºC lower than that of the feed gas. This process entails a double pipe heat exchanger. The thickness of the heating jacket is De = D2 - D1, where D2 is the inner diameter of the outer pipe, and D1 is the outer diameter of the inner pipe.

The density of the oil is about 1 g/ml, and the specific heat required for the silicon oil is 1.6 kJ/kg/K.

The highest total production rate of CH_2this project envisaged is 4mmol/g·Cat/hr. With a 100 g catalyst loading in a single tube, the highest CH_2 production rate will be 0.4mol/hr. The heat generated by the FT reaction is 165 kJ/mol (CH_2), which gives a reaction heat of 66 kJ/hr.

Heat to be removed: Q = 66 kJ/hr = 18 W

Driving force proposed: ΔT = 10 K

Lowest oil flow rate: $R_{oil} = Q / (\Delta T * 1600 J/kg/K)$ = 1.1 g/s = 4 kg/hr = 4 L/hr.

A N_2 bath was also used to keep the reactor temperature higher than 250–350 ºC. An electric heater is used to preheat the N_2 to the desired temperature. There are three of crawler ceramic heaters located in progressive sequence along the length of the outside of the heating jacket in order to maintain the temperature. Nitrogen is fed from the bottom of the reactor and removes the heat generated by the reaction. This allows the amount of heat generated by the reduction to be managed, and to maintain it at less than 1 W.

Driving force proposed: ΔT = 10 K.

Lowest N_2 flow rate: $R_N = 1 / (\Delta T * 29$ J/mol/K$)$ = 3.4 mmol/s = 5 ml/min.

4.2.1.3 The structure of the reactor tube and heating jacket

Table 4.1 lists the specifications of the reactor. Figure 4.1 shows the structure of the single tube fixed bed reactor, and the nozzle sizes are given in Table 4.2.

Table 4.1 Design specifications of the reactor

Requirements	Inner tube	Inner heating jacket
Medium	Catalyst, filler	N_2, oil
Operating temperature (ºC)	350(reduction)/ 250(reaction)	360/250
Operating pressure (MPa)	0.8/4.0	0.8/4.0
Design temperature (ºC)	375	380
Design pressure (MPa)	4.5	4.5
Volume (L)	1.96	/
Safety valve opening pressure (MPa)	4.2	/
Heat transfer area (mm^2)	/	125
Thickness of insulation (mm)	100	/

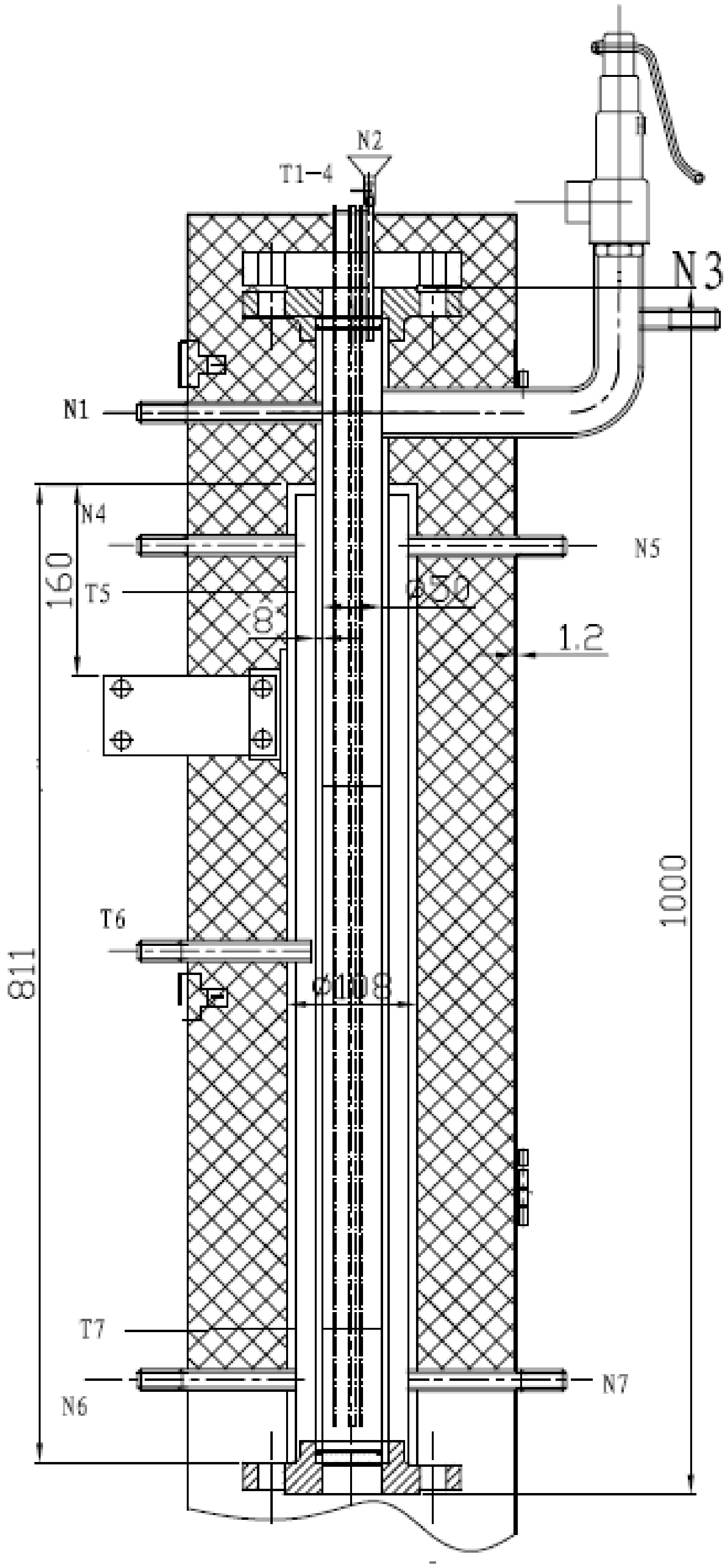

Figure 4.1 The structure of the reactor

Table 4.2 Nozzle Sizes (Nos. shown in Figure 4.1)

No.	Size	Connection	Function
N1	G 3/8	screw connection	Catalyst inlet
N2	G1/4	screw connection	Syngas inlet
N3	G1/4	screw connection	Pressure gauge connection
N4	G 3/8	screw connection	Oil outlet
N5	G 3/8	screw connection	N_2 outlet
N6	G 3/8	screw connection	N_2 inlet
N7	G 3/8	screw connection	Oil inlet

4.2.2 Temperature measurement

Since the FT reaction is strongly exothermic, temperature runaway can occur during the reaction. This causes, not only the failure of the whole process, but damages the catalyst. In addition, the large diameter of the reaction tube (50 mm) renders the heat transfer process and the temperature distribution in the inner reactor tube more complicated. It is, therefore, necessary to monitor the temperature by means of several temperature measurement points, so that the reaction can be easily and efficiently controlled.

There are three temperature measurement points in the tube wall between the reactor tube and the heating jacket. The location of these points is shown in Figure 4.1, where they are marked as T5, T6 and T7. The first, T5, is situated above the catalyst bed and beyond the oil outlet; T7 is located between the oil inlet and the catalyst bed. The T6 temperature point is to be found in the middle of the catalyst bed, to measure the temperature of the outer region of the catalyst bed. Because it can track the temperature distribution of the inner catalyst bed, this point provides invaluable data on heat transfer while the reaction is taking place.

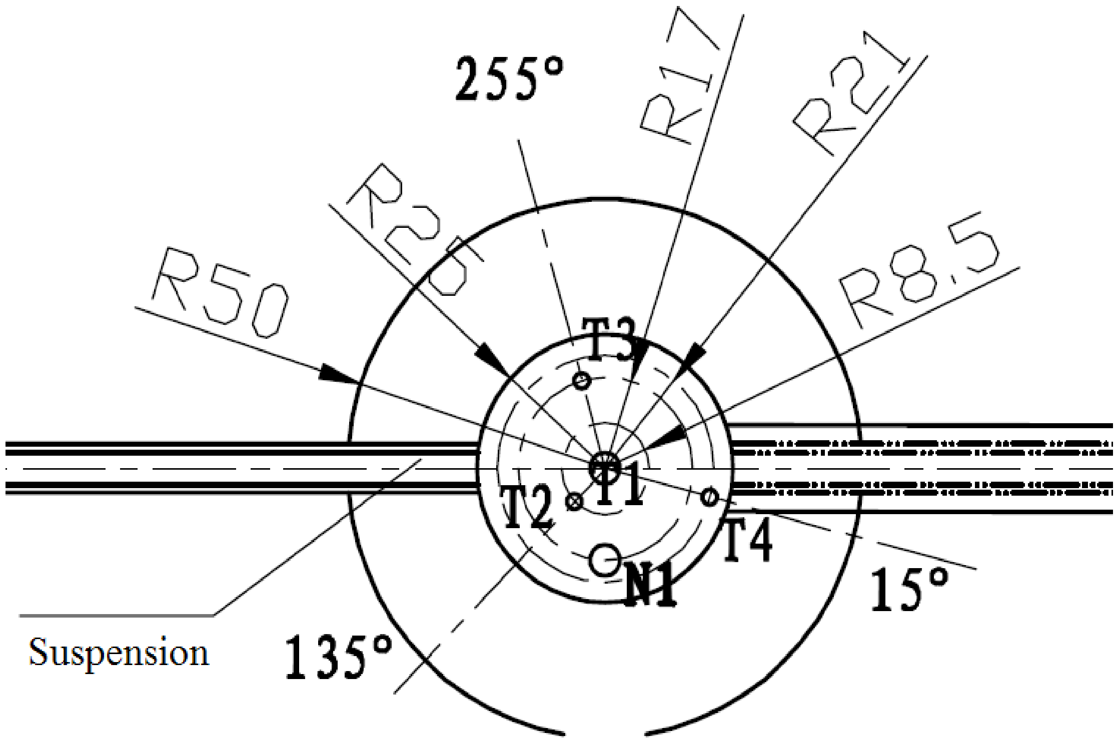

Figure 4.2 the reactor viewed from the top

FTS is also a heterogeneous reaction, since the catalysts are solid. The reactants are gas, while the products of the reaction are gas, solid and liquid (Reuel & Bartholomew, 1984). Mass- and heat- transfers occur simultaneously during FTS. It is an extremely complex process. To scale-up the BTL process to industrial level, it is very important to obtain data on the temperature of the inner tube of the reactor. This is provided by four thermocouple shields, about 1 m in length (allowing them to pass through the whole reactor), which are welded onto the top of the reactor. Figure 4.2 shows the distribution of these shields.

Shield T1 is located in the centre of reactor, R1 = 0, while T2, T3, T4 are grouped around T1. The distances between the shields and the centre are R2 = 8.5 mm, R3 = 17 mm and R4 = 21 mm, respectively. These thermocouple shields measure the temperature distribution in the radial direction. In order to measure the temperature distribution in the axial direction, the thermocouple can be pulled to different levels of the catalyst bed in order to investigate the temperatures at different heights in the reactor tube.

The diameter of the thermocouple shields T2–T7 is 2.5 mm, while that of shield T1 is 6 mm (because it is a multi-point thermocouple). The structure (a) and outward appearance (b) of a multi-point thermocouple is shown in Figure 4.3 below. T1 has four temperature measurement points. The first one is located at the top of catalyst bed, and the last one at the bottom. The four points are evenly distributed in the centre of the catalyst layer in the axial direction. In Figure 4.3a), Ln is L4, and Ln – L1 is the length of catalyst bed H1.

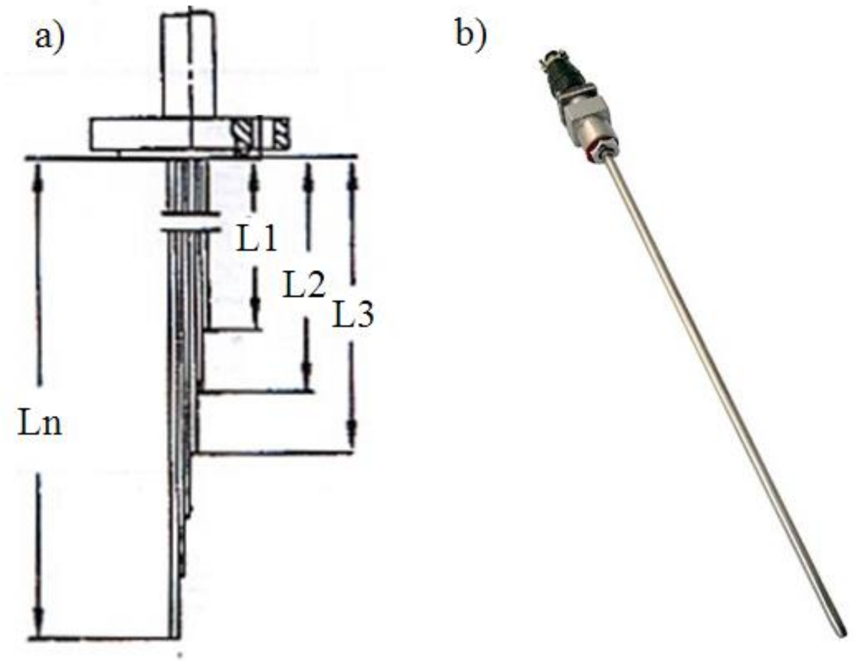

Figure 4.3 the inner structure and outward appearance of a multi-point thermocouple

4.2.3 Products collection

A number of products are formed during FTS. In general, these can be divided into three categories: gas, liquid and wax. The wax and liquid products (long chain hydrocarbons) are collected in the hot trap, while short chain hydrocarbon and water are collected in the cold trap.

4.2.3.1 Hot trap

The hot trap is directly connected to the bottom of the reactor by a flange. The size of the tubing is the same as that of the reactor tube (50 mm). It is heated by a crawler ceramic heater to 120 °C and the heater and hot trap are located in the insulation jacket.

The hot trap should be of sufficient size in order to store the wax accumulated during seven days of operation. As 100 g of liquid and wax is proposed as the reaction capacity in a single tube reactor per day, the largest amount of wax produced can be as high as 70 g. Therefore a week's operation will yield a maximum of 490 g wax products. To accommodate this amount, a 2L hot trap is needed.

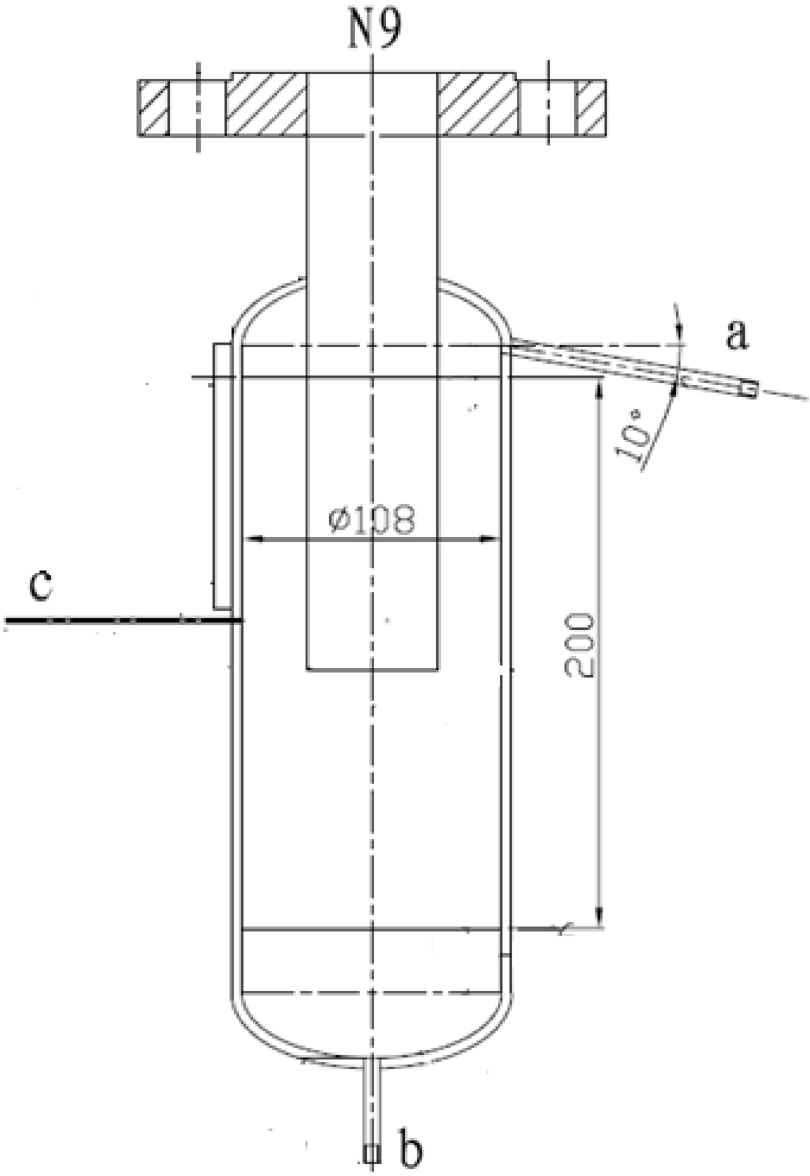

Figure 4.4 the structure of the hot trap

The structure of the hot trap used in this programme is shown in Figure 4.4. The connection labeled N9 is directly connected with the reactor tube. Pipe “a” is the outlet for tailgas, water vapour and short carbon chain liquid products. Pipe “b” is the outlet for wax and heavy oil products. Both pipes “a” and “b” are wrapped in a heating tape to maintain the temperature, preventing wax and liquid products that can block the pipes from condensing. For the same reason, the design of pipe “a” must include an incline to a certain angle. C is a thermocouple shield that measures the temperature of the wall of the hot trap.

4.2.3.2 Cold trap

The short carbon chain products and water are collected in the cold trap, which is connected with the hot trap by a size G 3/8 tube.

Like the hot trap, the cold trap must be able to store liquid for a week. As it can achieve a total product of 100 g liquid and wax per day, the highest amount of wax produced daily was 70 g per day, while the lowest production of light liquid is 30 g per day. One week operation can give a minimum of 210 g liquid products. Since the FTS reaction can be condensed to the equation:

$$2n\ H_2 + n\ CO \rightarrow (CH_2)_n + n\ H_2O$$

128 g/d H_2O is produced from the reaction every day. Seven days of operation can therefore produce 896 g of water. The cold trap is designed to have a 2 L capacity.

In order to condense the liquid product and water fully, a cryogenic cooling circulation system was used that feeds a 10% glycol solution from the bottom of the cooling jacket, and removes it from the top. This cooling circulation system can maintain the temperature of the whole cold trap at 0 ºC. Figure 4.5 gives the cross-sectional view of the cold trap.

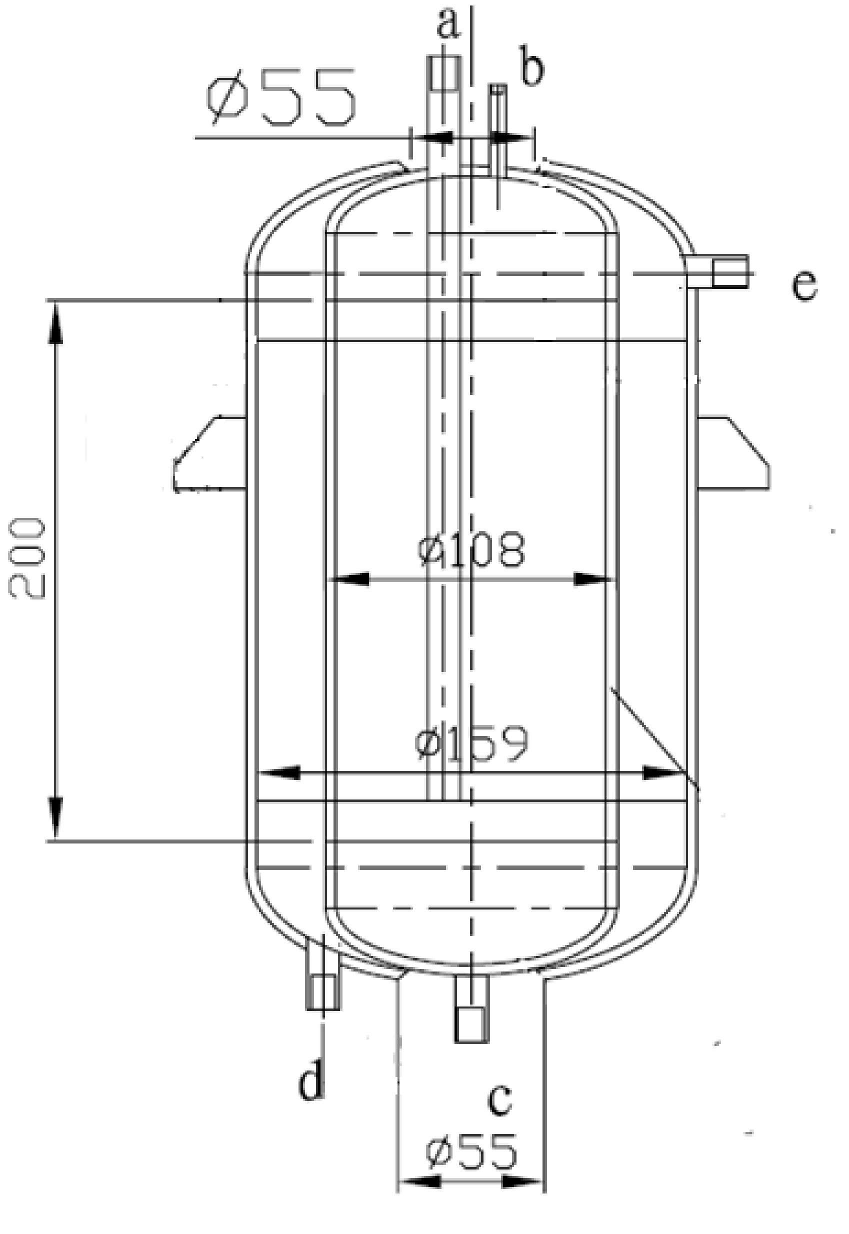

Figure 4.5 the structure of the cold trap

In the above figure, pipe “a” is shown as the conduit through which the liquid products, water vapour and tailgas enter the cold trap. In order to ensure full condensation, the pipe extends to the lower half of the cold trap. Pipe “b” is the inlet for mixed products, and pipe “c” is the outlet for water and light oil. The glycol solution is fed from pipe “d” and removed via pipe “e”.

Table 4.3 lists the design specifications of the product collectors.

Table 4.3 the technical characteristics of the hot and cold traps

Requirements	Hot trap	Cold trap	
	Inner tube	Inner tube	Inner cooling jacket
Medium	Wax, oil, tailgas	Oil, water, tailgas	10% glycol solution
Operating temperature (ºC)	350	350(reduction)/ 250(reaction)	0 - 15
Operating pressure (MPa)	4.0	0.8/4	0.15
Design temperature (ºC)	375	375	-5 - 40
Design pressure (MPa)	4.5	5	0.2
Volume (L)	2.2	2.2	/

4.3 The catalyst

Since this research project used biomass as raw material, the H_2 and CO content of the syngas produced is lower than the amounts normally found in FTS feed gas. It was, therefore, necessary to select a high-activity catalyst to compensate for the relatively low yield of liquid products. A catalyst that does not deactivate rapidly was also needed, because of the difficulty of loading and unloading the catalyst in a fixed bed reactor. Another consideration was that when compared with Fe-based catalysts, Co-based catalysts have virtually no catalytic activity for the water gas shift reaction under FTS reaction conditions (Ngantsoue-Hoc, 2002; Khodakov, Chu & Fongarland, 2007; Yang et al., 2006). For these reasons a Co-based catalyst was chosen in this experimental programme.

4.3.1 Catalyst preparation

For this project, a 15% Co supported on SiO_2 catalyst was used, which was prepared via the incipient wetness method (Bartholomew, 1991; Chronis, 1999). This consists of the dissolution of a metal salt in a volume of distilled H_2O sufficient to fill the pores of the support. For every 100g of catalyst prepared, 74.08g Co $(NO_3)_2$•$6H_2O$ was dissolved in 130ml distilled H_2O.This solution was absorbed by 85g of commercial SiO_2 at 50°C, after which the temperature was raised to 90°C at the rate of 5°C per hour. After three hours, the precursors of the catalyst were baked in a muffle furnace heated from room temperature to 400°C at a rate of 120°C per hour. The catalyst was ready for use after five hours. Figure 4.6 shows the apparel of the catalyst.

Figure 4.6 Co-based catalyst used in the project

4.3.2 Characterization

Characterization is the best method to understand the properties of a catalyst, since it enables the understanding of the impact of the different preparation and pretreatment methods for catalysts, which can in turn be used for many purposes, including the development of new catalysts.

However, because the main thrust of this research was to give a full experimental trial of the complete BTL process, the nature of the catalyst was not a primary focus. For the purposes of this project two methods were used, temperature programmed reduction and Brunauer–Emmett–Teller theory, in order to determine the basic properties of the catalyst.

4.3.2.1 Temperature programmed reduction (TPR)

Temperature programmed reduction (TPR) provides information on the interaction between different metal oxides (or metal oxides and the carrier) during the process of reducing a supported metal catalyst (Chorkendorff & Niemantsverdriet, 2007; Hurst et al., 1982). The TPR profile can show the hydrogen consumption of the catalyst oxide precursor during the reduction process, and therefore assist the researcher to select the most efficient reduction conditions.

In this research programme, TPR was used to measure the reducibility of the catalysts.

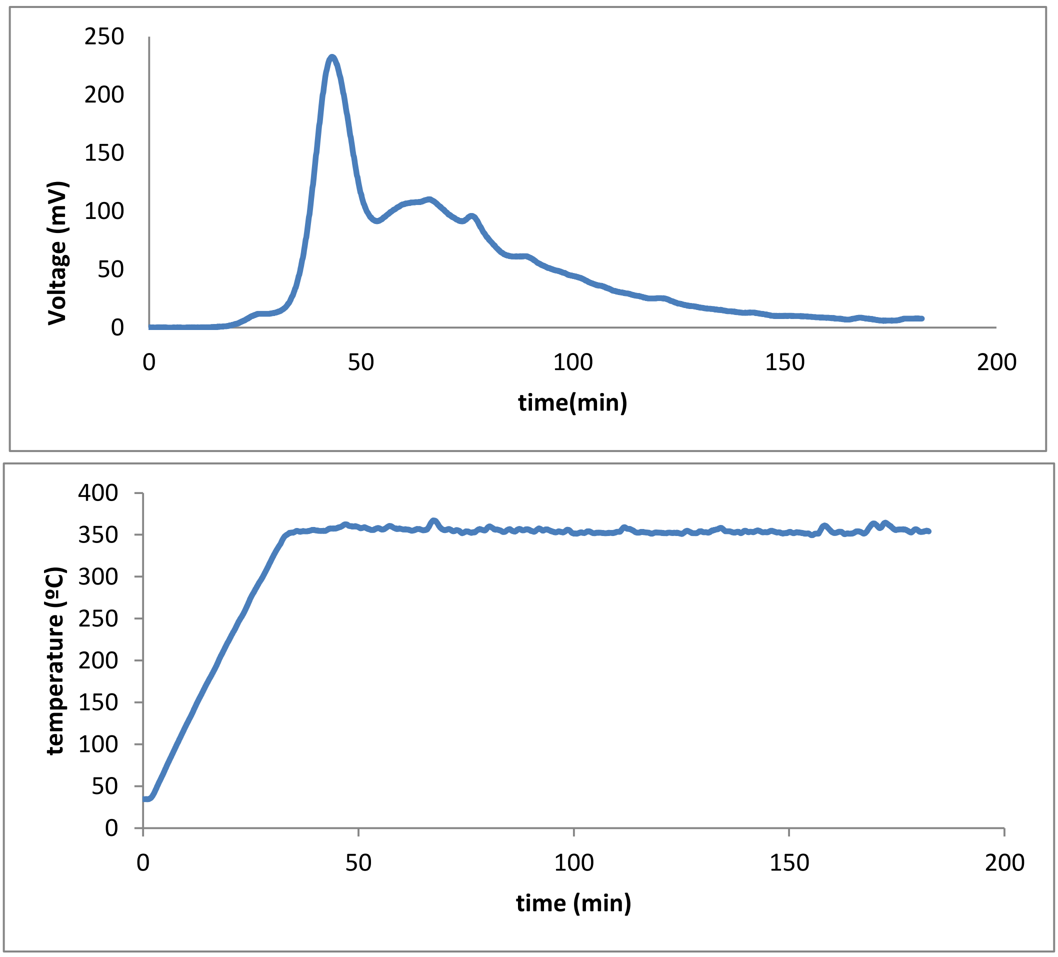

Figure 4.7 TPR profile of 15wt% Co/SiO_2

The TPR experiment was carried out with a Quantachrome CHEMBET 3000 unit.0.1044g of catalyst, which had been ground to powder, was placed in a quartz tubular reactor that had been fitted with a thermocouple for continuous temperature measurement. The reactor was heated in a furnace. Before the temperature programmed reduction test, the catalysts were flushed with high purity helium at 150 ºC for 30 minutes, in order to dry them before allowing the reactor to cool down to room temperature. After that, 10% H_2/Ar was fed to the reactor and the temperature was increased at a rate of 10 ºC /min from 35 to 350 ºC (at which it was held for 180 minutes). The gas flow rate through the reactor was controlled by three mass flow controllers and maintained at 5 ml/min. The computer recorded the H_2 consumption automatically. Figure 4.7 shows the TPR profile of 15 wt% Co/SiO_2.

In the Figure, the two major peaks appeared after the temperature had reached 350 ºC. In Duvenhage's research (1993), the first peak presents the reduction step of Co_3O_4 to CoO, and the next one is seen as the step of CoO to Co. This result, shown in Fig 4.6, indicates that reduction requires a sufficient amount of hydrogen and a sufficient long reduction time in the process of catalyst reduction at 350 ºC.

4.3.2.2 Brunauer–Emmett–Teller (BET)

The Brunauer–Emmet–Teller method is the basis of the scientific theory of particle surface adsorption. It is widely used in data processing instruments for testing the particle surface adsorption performance. For a supported metal catalyst, the BET method yields the total surface area of the support and metal components of the catalyst.

The specific surface areas and textures of the catalysts were determined by nitrogen physisorption according to the BET method, and with a Quantachrome Nova 2000e unit. The test for N_2 adsorption–desorption was conducted at 77.3 K (-196 ºC) on 0.1422 g of the catalyst. A sample of 15 wt% Co/SiO_2 was degassed at 200 ºC for six hours before the test began. The experimental results gave the BET surface areas in a relative pressure (P/P_0) range of between 0.05–0.22. The total pore volume was calculated from the amount of N_2 gas adsorbed at a relative pressure of 0.977. The results of the BET test are listed in Table 4.4.

Table 4.4 Texture of 15 wt% Co/SiO_2catalysts (BET)

	15 wt% Co/SiO_2
Size (mm)	0.5 – 1
BET surface area (m^2/g)	197
Pore volume (cm^3/g)	0.69
Average pore diameter (nm)	14.08

4.4 Product analysis

The composition of FTS products is very complex, but they comprise of mainly a straight-chain alkane, alkene, carbon dioxide and water. In this research study, the feed syngas was derived from biomass gasification, the components of which are also complicated. The engineer therefore requires analytical equipment that can test the full distribution of organic products from C1–C35, and inorganic reactants and products, such as: H_2, CO, CO_2 and O_2, in addition to the N_2 that results from the biomass gasification process.

In the research programme described in this dissertation, an online FULI GC 9790 and an online FULI GC 9790II were used to analyze the feed gas and the tail gas, three times a day. In the 9790II GC, an online TCD detector measures the inorganic gases CO, CO_2, O_2 and $N_2$and categorized the results in two columns, and analyzed the organic gases by means of an online FID detector. The online TCD detector in GC 9790 tests for hydrogen, and its offline FID detector analyzes the wax and liquid hydrocarbons.

4.4.1 Online products analysis

A three-way valve is used to connect the gas line tube and the two online GCs. The syngas and the tail gas are fed to the GC 9790II sampling loop through a heated line. The gas enters the GC column through the multiple sampling valves, while the temperature of the column oven is held constant at 50 ºC for four minutes. After that, the temperature is increased to 180 ºC at the rate of 5 ºC per minute, after which it remains at 180 ºC for four minutes. Figure 4.8 shows the flow chart obtained from the GC 9790II, which does not require a temperature-programmed process in order to detect H_2 in its online TCD. After the peaks of hydrogen and methane have appeared, the GC can be stopped, since this channel is only suitable for testing H_2. Table 4.5 gives detailed information on the columns and carrier gas obtained from the online detectors.

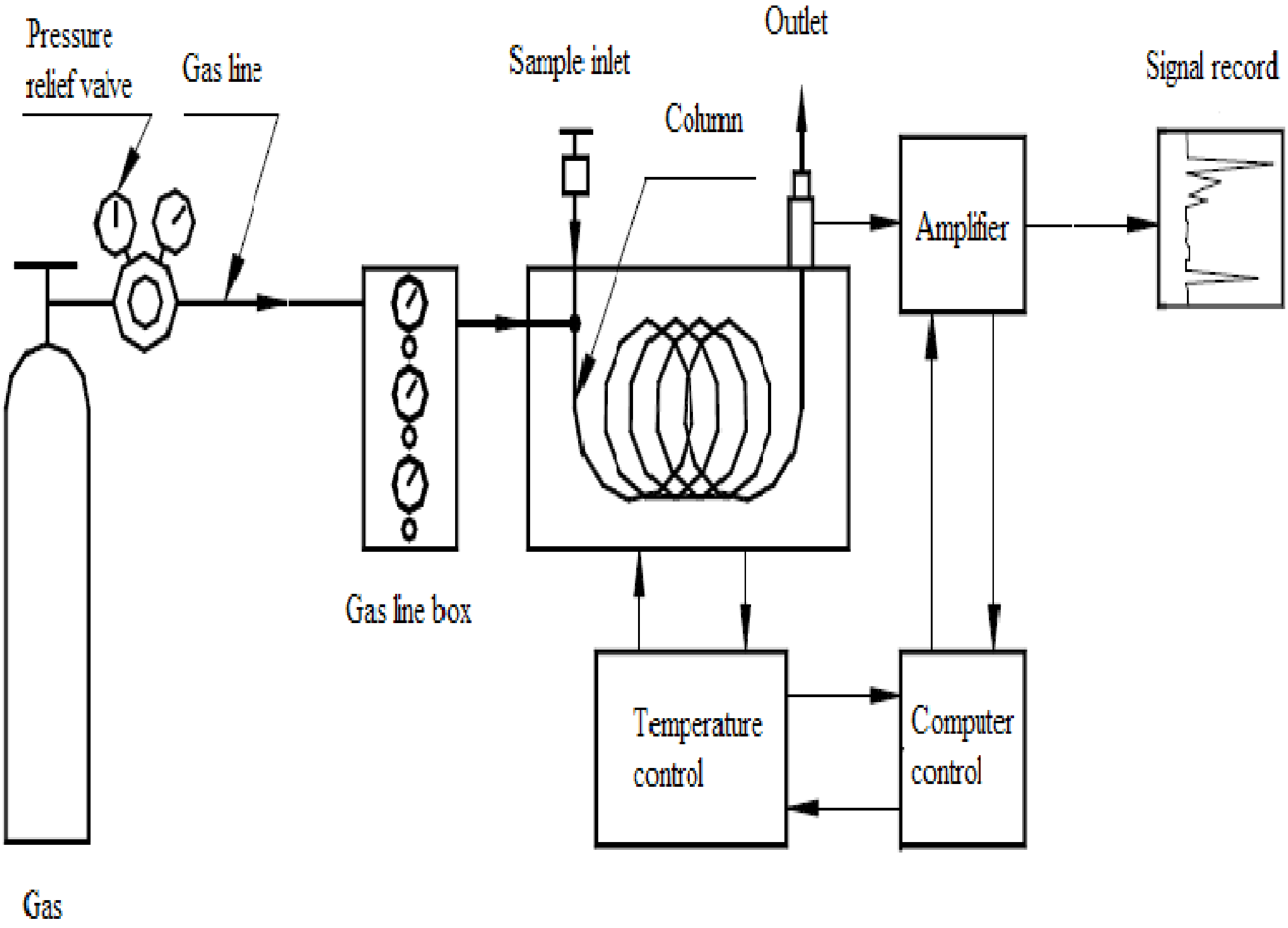

Figure 4.8 Flow chart of the GC’s structure

Table 4.5 Characteristics of the online GCs employed

GC 9790 II	
Detector A	FID detector, T = 150 ºC
Column A	Capillary column (KB-Al_2O_3/Na_2SO_4), 50m*0.32mm*10um, Max temperature: 200 ºC
Carrier gas	UHP He, P = 0.04 MPa
Oven temperature programmed	Hold at 50 ºC for 4 min, heat to 180ºC at 5ºC /min, hold at 180ºC for 4 min
Products analysis	C1 to C5
Detector B	TCD detector, T = 150 ºC
Column B	5A molecular sieve, 3m * 3mm * 2mm, Max temperature: 550 ºC
Column C	TDX-01porapack column, 1.5m * 3mm * 2mm, Max temperature: 250ºC
Flame gas	Air , P = 0.1 MPa; H_2, P = 0.1 MPa
Carrier gas	UHP He, P = 0.04 MPa
Oven temperature programmed	Hold at 50 ºC for 4 min, heat to 180ºC at 5ºC /min, hold at 180ºC for 4 min
Products analysis	Column B for inorganic gas (except H_2 and CO_2) Column C for CO_2
GC 9790	
Detector C	TCD detector, T = 150ºC
Column D	5A molecular sieve, 3m * 3mm * 2mm, Max temperature: 550 ºC
Carrier gas	UHP N_2
Oven temperature programmed	No need
Products analysis	H_2

4.4.2 Off-line products analysis

An off-line FID detector in the GC 9790 used a capillary column to measure the wax and liquid products (the long-chain hydrocarbons).The GC was connected to a computer that recorded the amplified signal from the detector. Ultra high purity nitrogen was used as a carrier gas. A 0.5μl sample was fed via syringe into the gas chromatograph which analyzed both the oil and wax products. In order to prevent the accumulation of long chain hydrocarbons in the column, the temperature of the GC was ramped at a rate of 5 ºC /min (Tijmensen et al., 2002). Detailed information concerning the offline GC is given in Table 4.6.

Table 4.6 Characteristics of the offline GC

GC 9790	
Detector D	FID detector, T = 150ºC
Column E	Capillary column (KB-PONA), 60m*0.25mm*0.5um, Max temperature: 350 ºC
Column F	Capillary column (KB-1), 60m*0.25mm*0.5um, Max temperature: 350 ºC
Flame gas	Air , P = 0.06MPa; H_2, P = 0.1 MPa
Carrier gas	UHP N_2
Oven temperature programmed	Heat from 50 to 330ºC at rate of 5ºC /min, hold at 330ºC for 45 min (liquid products) or 180 min (wax)
Products analysis	Liquid products (Column E), Wax (Column F)

4.4.2 Chromatogram

Figure 4.9 gives an example of an online GC chromatogram, while Figure 4.10 shows an offline chromatogram. However, it is pertinent to point out that in Figure 4.9 the running time was not 48 minutes as for Figure 4.11, but 33 minutes.

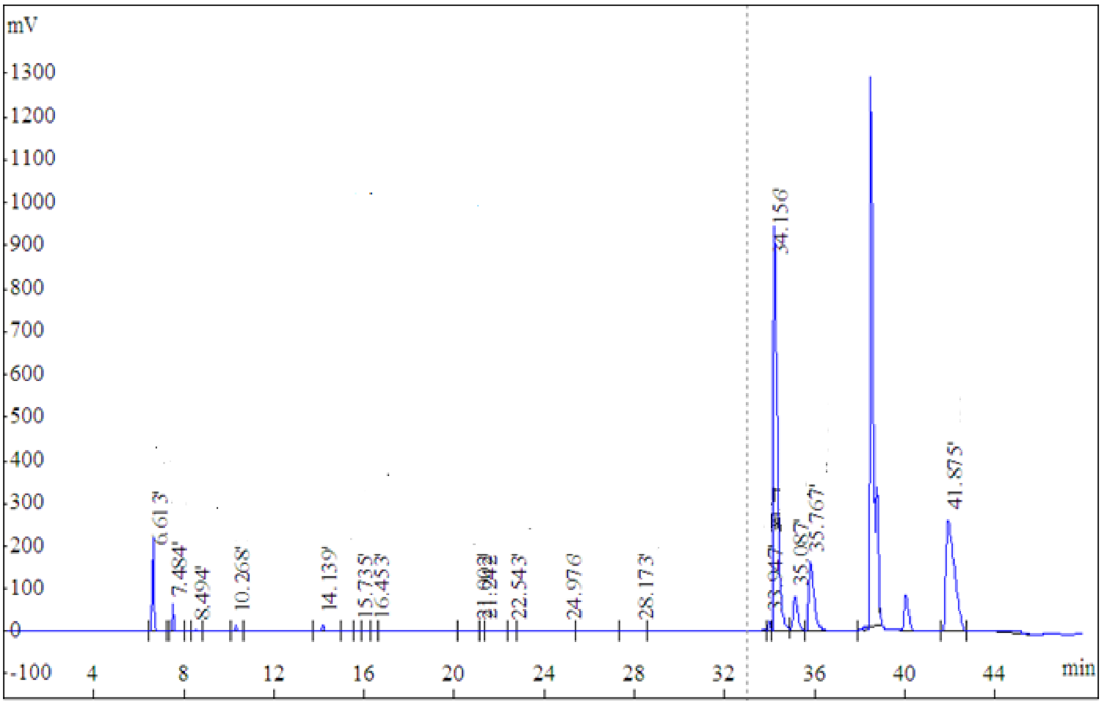

Figure 4.9 Online GC 9790II gas phase chromatogram of syngas

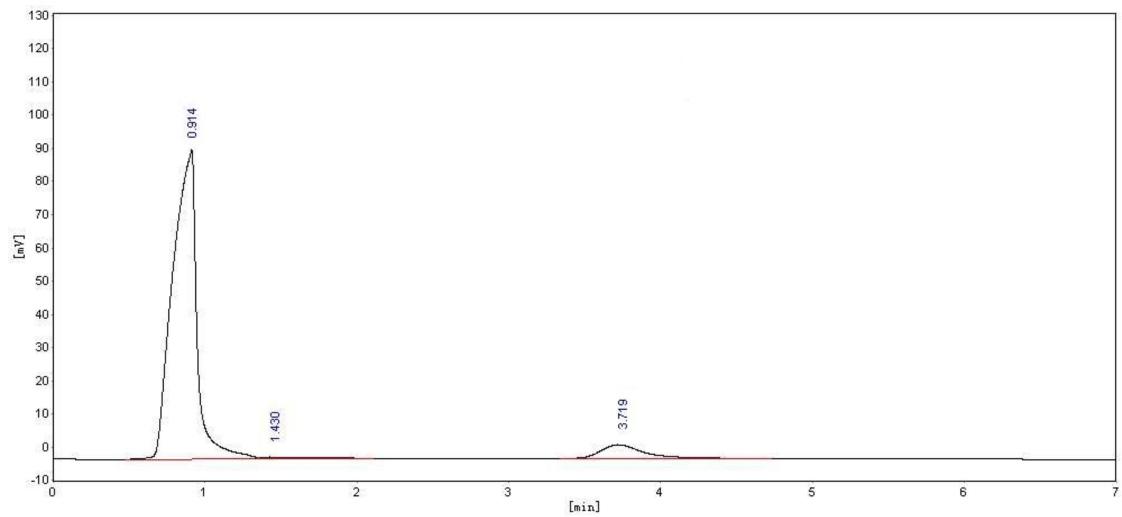

Figure 4.10 Online GC 9790 gas phase chromatogram of syngas

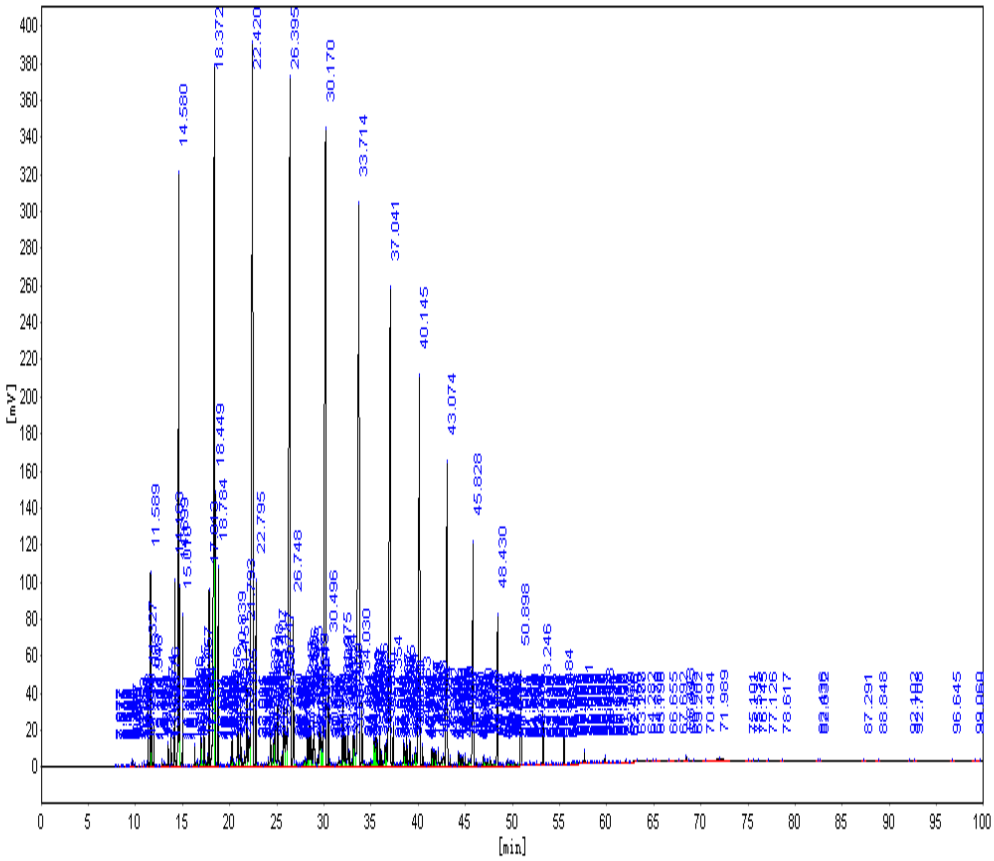

Figure 4.11 Offline GC data of oil collected in the cold trap

4.5 Tailgas power generation

In order to simplify the synthesis process and reduce costs, it was decided not to recycle the tailgas for use but to use feed gas instead. It was necessary to avoid discharging the tail gas into the atmosphere, because doing so would not only be wasteful, but also harmful to the environment. It was therefore decided that the most appropriate use of the tailgas would be to transform it into electricity by means of a gas generator. Recent studies have demonstrated that the synthetic United Microelectronics Corporation (UMC) process is superior to others involving the separate production of synthetic oil or separate power generation processes in terms of greater efficiency in the liquid fuel synthesis and power generation (Yu et al., 2010). It is likely to influence the development of a small-scale biomass synthetic oil production in the future. It is not demonstrated in this project since the scale is too small.

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Chapter 5: FT synthesis experiments and discussion of results

5.1 Introduction

As a consequence of the rapid depletion in the resources from which fossil fuels are made, many scientists are beginning to look for new types of liquid fuel. Already, many researchers have published reports indicating that biomass to liquid technology is an effective way to solve the combined problem represented by dwindling supplies of fuel and rising demand for petroleum (Zheng, Shao & Li, 2010; Klass, 1998; Qin et al., 2004).

FTS synthesis is a well-established technology that is already used by two companies, Shell and Sasol, on a commercial basis. European Biofuels Technology Platform (2011) and Aichenrig et al. (2008) proposed that fuel synthesized by the BTL process can be produced on an industrial scale.

The main focus of this chapter is a description of the BTL fuel process via FT synthesis, under different operating conditions. By examining the operating pressure, external heating temperature, syngas inlet flow rate, partial pressure of the reactants on the catalyst, and the operating performance of the FTS reactor, it can create a sufficient mass of data that will enable the optimization of the process and scale-up the capacity of the BTL facility in which the experiments were carried out.

5.2 Experiment

5.2.1 Catalyst reduction

The first step of the experiment was to load 100 grams of Co-based catalyst into the fixed bed reactor. Following the TPR result (see Chapter 4), the temperature was set at 320 °C and utilized UHP H_2 (99.99%) to reduce the catalyst. As a result of the large loading quantities of catalyst, $N_2$was introduced into this process as a buffer gas, and the total flow rate at 3 NL/min was maintained.

Figure 5.1is a graphical representation of the reduction temperature programme.

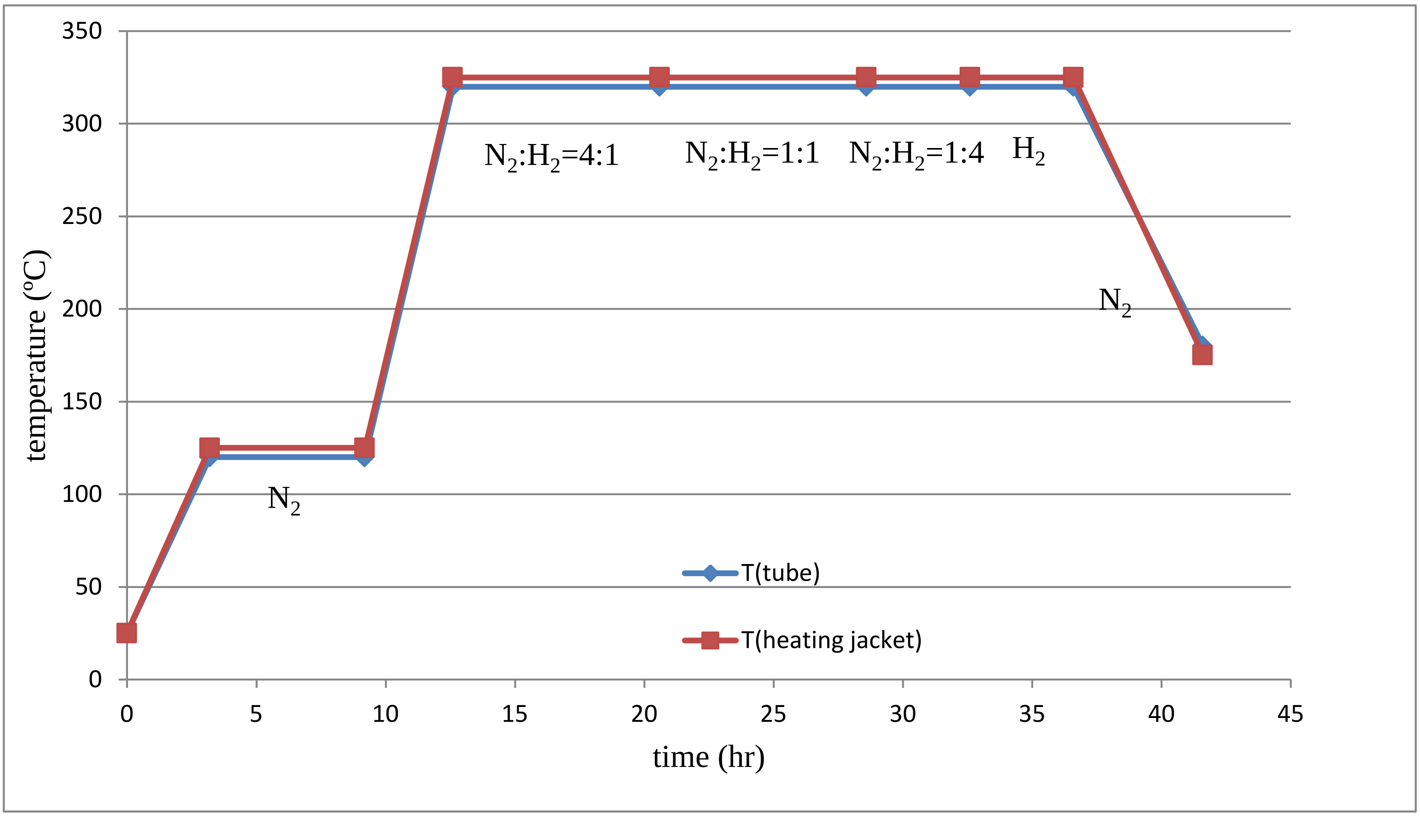

Figure 5.1 Reduction temperature programme

5.2.2 Catalyst activity

In order to test the performance of the catalyst in the reactor, FTS was conducted under a variety of reaction conditions, after which the calculated, compared and simulated experimental data obtained were analyzed. Although the results are discussed in Section 5.3, Table 5.1 below provides detailed information on the reaction conditions this project used.

Table 5.1 Reaction operating conditions

<table>
<tr><th>Gauge Pressure (bar)</th><th>Temperature (ºC)</th><th>Flow rate (NL/min)</th></tr>
<tr><td rowspan="11">25</td><td rowspan="3">180</td><td>0.75</td></tr>
<tr><td>1.5</td></tr>
<tr><td>3</td></tr>
<tr><td>185</td><td>0.75</td></tr>
<tr><td rowspan="7">190</td><td>0.75</td></tr>
<tr><td>1.05</td></tr>
<tr><td>1.5</td></tr>
<tr><td>1.5</td></tr>
<tr><td>1.3</td></tr>
<tr><td>0.8</td></tr>
<tr><td>0.9</td></tr>
<tr><td>25</td><td rowspan="6">190</td><td>0.87</td></tr>
<tr><td>20</td><td>0.88</td></tr>
<tr><td>16</td><td>0.87</td></tr>
<tr><td>11</td><td>0.87</td></tr>
<tr><td>6</td><td>0.87</td></tr>
<tr><td>0.5</td><td>0.87</td></tr>
<tr><td>16</td><td>195</td><td>0.87</td></tr>
</table>

		1.3
11	195	0.87
		1.62

5.3 FTS results and discussion

5.3.1 Influence of pressure on the FT reaction

Where all the other variables were constant, the influence of reaction pressure on the radial temperature profile can be seen in Figure 5.2 below. The effect of the reaction pressure on the temperature inside the tube is very obvious. As the pressure increases, so does the temperature at the hot spot of the bed and the trend extrapolates. The increase in the radial direction hotspot (highest temperature point almost at the middle of catalyst bed) temperature in the catalyst bed is between 0–15 ºC.

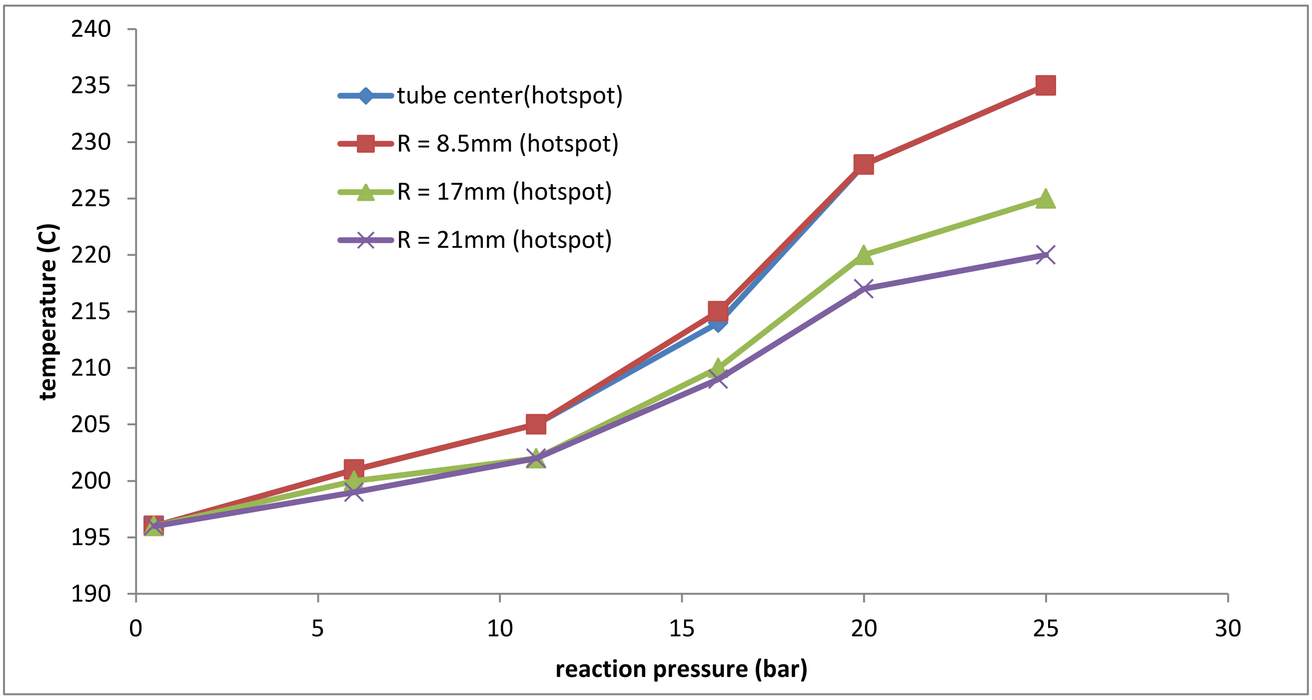

Figure 5.2 the effect of pressure on bed temperature

($T_{(out)}$ = 190 ºC, FR = 52.2 NL/hr)

Furthermore, the temperature in the lower portion of the catalyst bed also rises, as is shown in figure 5.3. Obviously, the overall temperature of the catalyst bed increased with the reaction pressure. Although the effective thermal conductivity of the catalyst bed was essentially constant, the temperature of catalyst bed was not. When the reaction pressure increased, the exothermic heat of reaction cannot be removed, consequently the amount of heat accumulated. Thus, the position of the hotspot appeared to have moved in the direction of the catalyst bed exit.

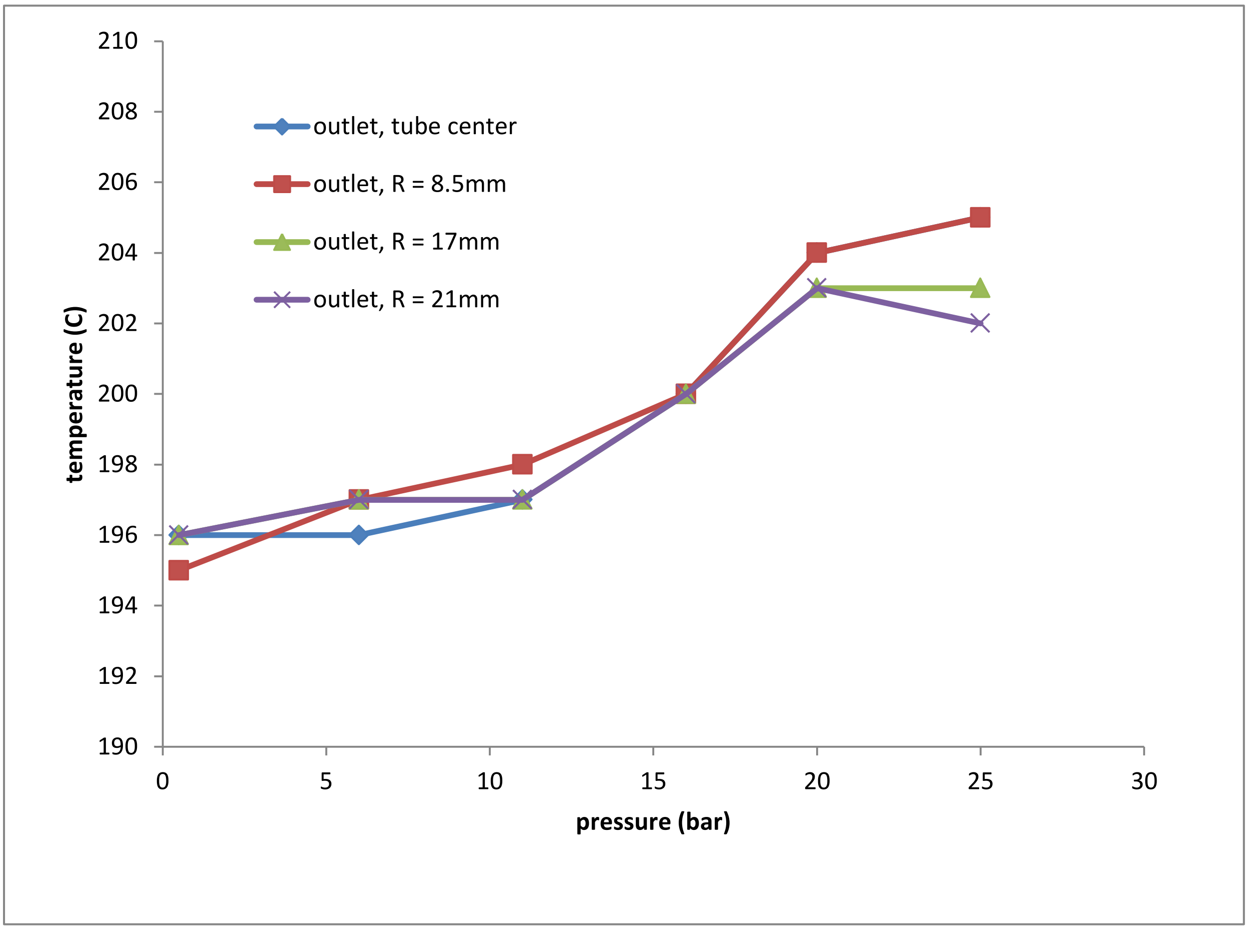

Figure 5.3 Temperature in the lower portion (the bottom) of the catalyst bed

($T_{(out)}$ = 190 ºC, FR = 52.2 NL/hr)

In general, the excessively high hotspot temperature of the catalytic bed can easily lead to the deactivation of the catalyst, which indicates that the operating pressure should be controlled in order to prevent deactivation of the catalyst.

The influence of reaction pressure on the conversion of the reactants can be seen in Figure 5.4. The conversion of CO and H_2 increased as the pressure rose, a phenomenon also reported by Chronis (1999). As the pressure in the tube increased while the flow rate of syngas into the reactor remained constant, the linear velocity of the syngas dropped, and the residence time of the reactants in catalysts bed increased. Thus, the general trend that can be detected is the CO hydrogenation activity and the CO and H_2 conversions improved in response to an increase in the reactor pressure.

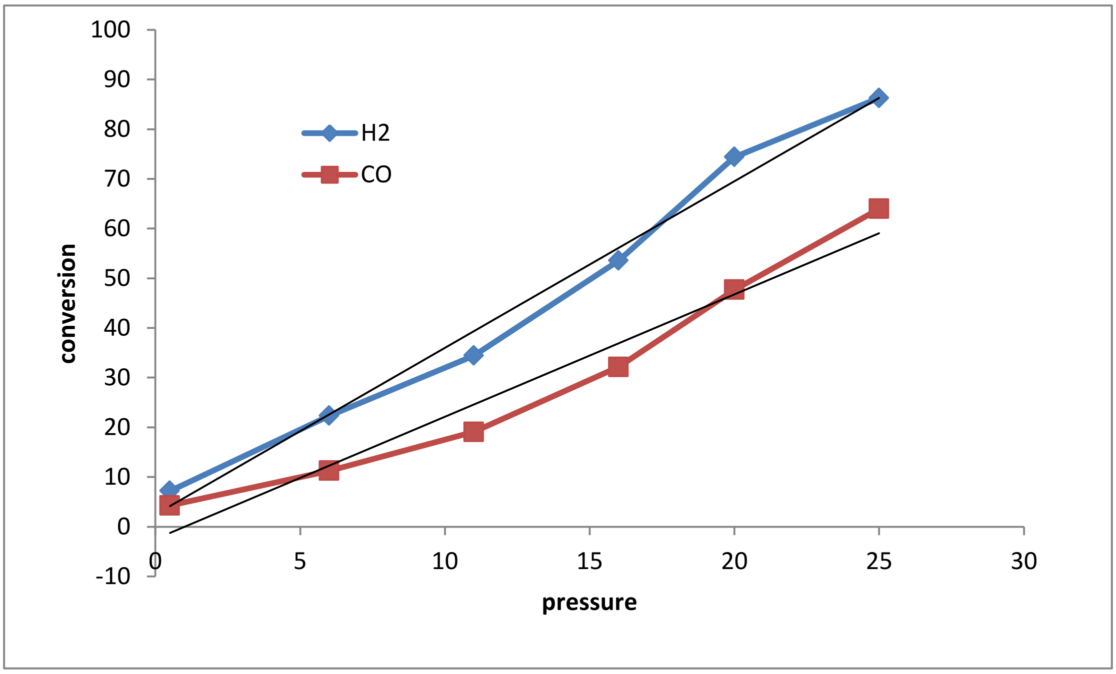

Figure 5.4 The effect of pressure on CO and H_2 conversion

($T_{(out)}$ = 190 ºC, FR = 52.2 NL/hr)

The experimental results also showed that by raising the reaction pressure, one can effectively improve FTS activity. However, a higher operating pressure will lead to a decreasing efficiency of removing heat (Wu, 2010). Moreover, there will be greater corresponding compression and operating costs associated with raising the reaction pressure. Engineers involved in BTL on a commercial scale should therefore consider the level of reaction pressure most appropriate to industrial use, in view of the cost factors.

5.3.2 Influence of external heating temperature on the FT reaction

This experiment used oil and N_2 as the cooling media that flows though the heating jacket from bottom to top, and the reaction temperature in the tube was controlled by adjusting the external heating temperature. The effect of the latter temperature on that of the inner tube is shown in Figure 5.5.

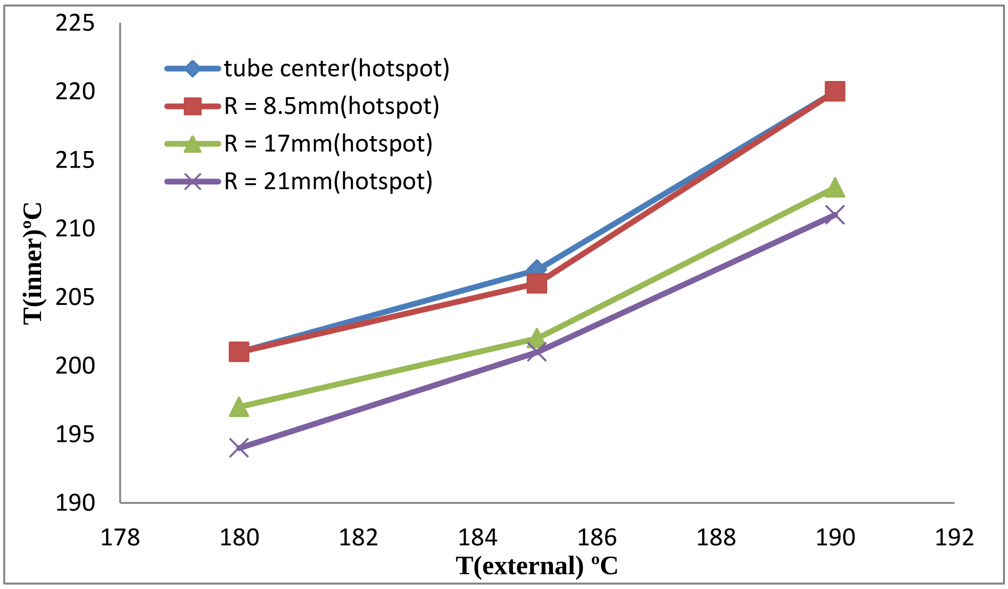

Figure 5.5 the effect of external heating temperature on the bed temperature

(P = 25 bar, FR = 45 NL/min)

As can be seen in the figure, when the external electric heating temperature rose from 180–190 ºC, the bed temperature increased as well. The temperature at the hot spot of the tube centre increased from 201–220 ºC. This caused the acceleration in the reaction rate, which in turn generated a significant amount of heat. Since the effective thermal conductivity of the catalyst bed was essentially constant, whereas heat generation was not, heat removal slowed down. This caused the temperature at the hot spot to increase. The most effective method of controlling the temperature in the catalyst bed is to adjust the external heating temperature.

Figure 5.6 below shows that the temperature in the lower portion (the bottom) of the catalyst bed also increased with an external heating temperature increased.

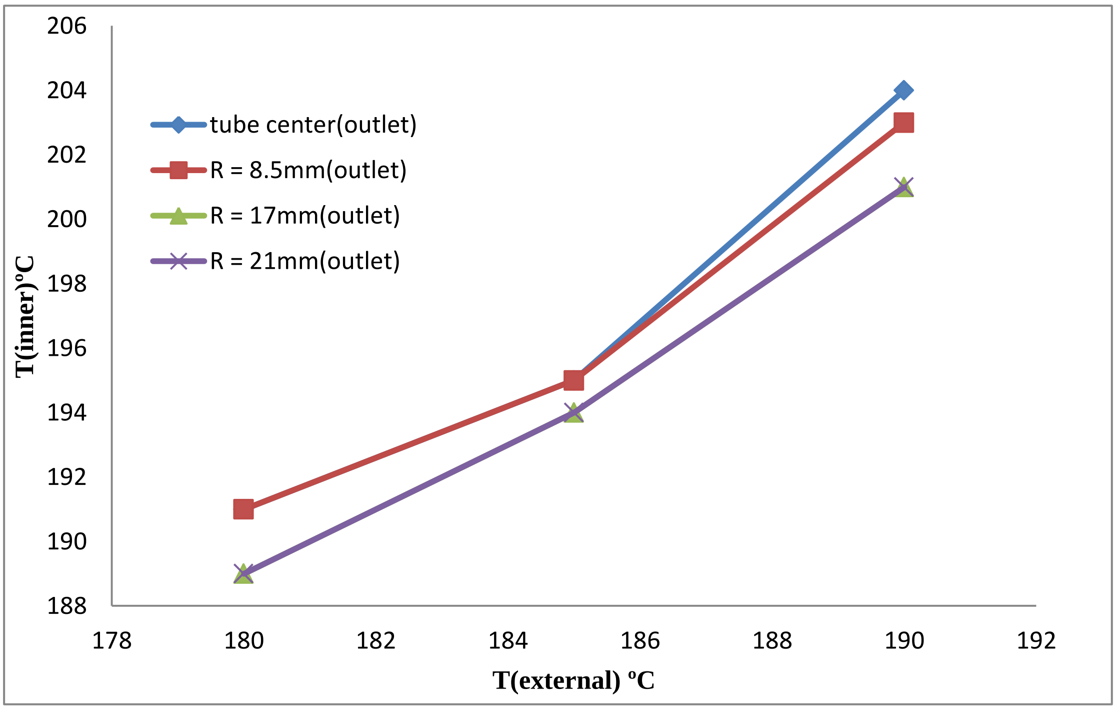

Figure 5.6 The effect of external heating on the temperature of the lower portion of the catalyst bed (P = 25 bar, FR = 45 NL/min)

As previously noted, the reaction temperature has a significant effect on the FT reaction activity.CO and H_2 conversion and the CO hydrogenation rate increased as the reactor temperature increased. As it can be seen in figure 5.7, the CO conversion increased with an increase in the external heating temperature.

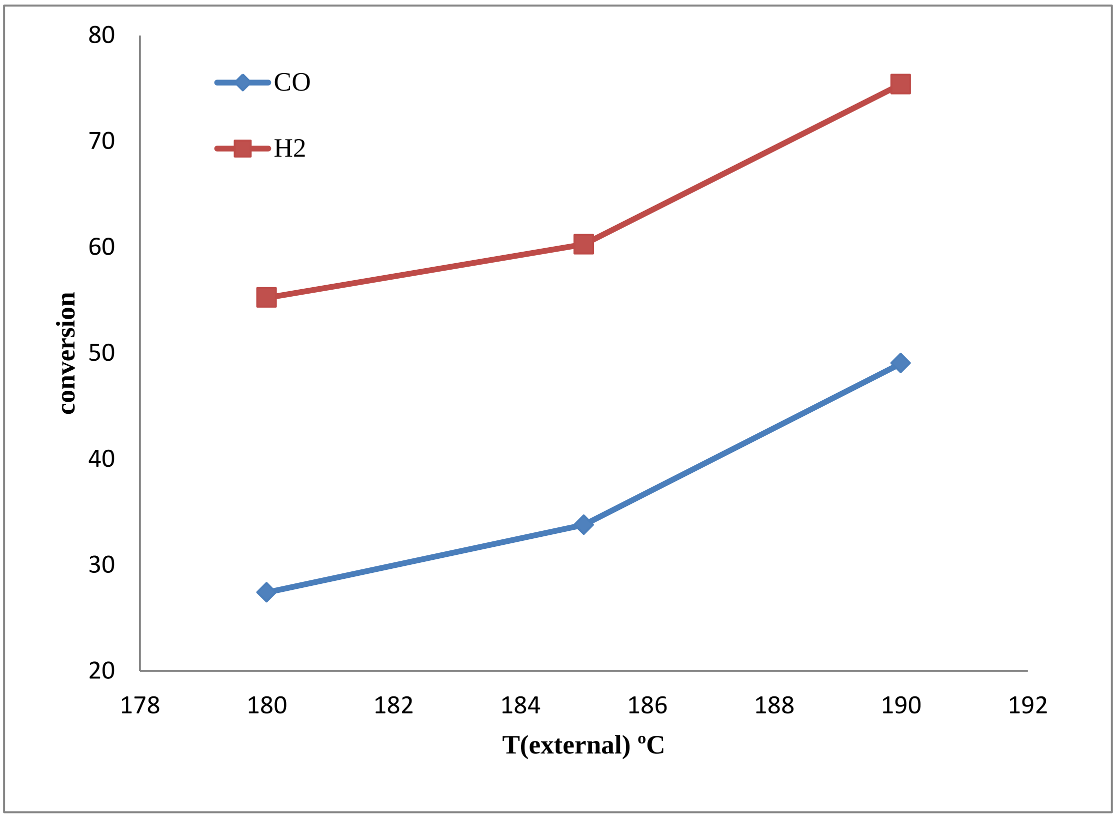

Figure 5.7 the effect of the external heating temperature on CO and H_2 conversion

(P = 25 bar, FR = 45 NL/min)

A high operating temperature augmented the dissociation of CO and also enhanced the rate of hydrogenation (Dry, 1982; Dry, 1986; Dry, 1981). However, it is well known that FT product distribution is sensitive to temperature, and that a low temperature favours long chains more than a high catalyst bed temperature, which reduces the yield of oil and wax (Chronis, 1999; Dixit & Tavlarides, 1983; Hurlbut, Puskas & Schumacher, 1996). Therefore, it may not be suitable for the project purposes to improve reactant conversion by increasing the external heating temperature: rather in order to ensure higher conversion, using a lower reaction temperature must be considered.

5.3.3 Influence of the flow rate on the FT reaction

When all the other operating conditions remain unchanged, increasing the feed gas flow rate increased the space velocity of the reaction, which decreased the residence time of the reactants in the catalyst bed and resulted in a lower conversion rate. At the same time, the unreacted gas removed heat, which caused the temperature at the hot spot of the catalyst bed to reduce. The effect of flow rate on the temperature of the inner tube is shown in Figure 5.8.

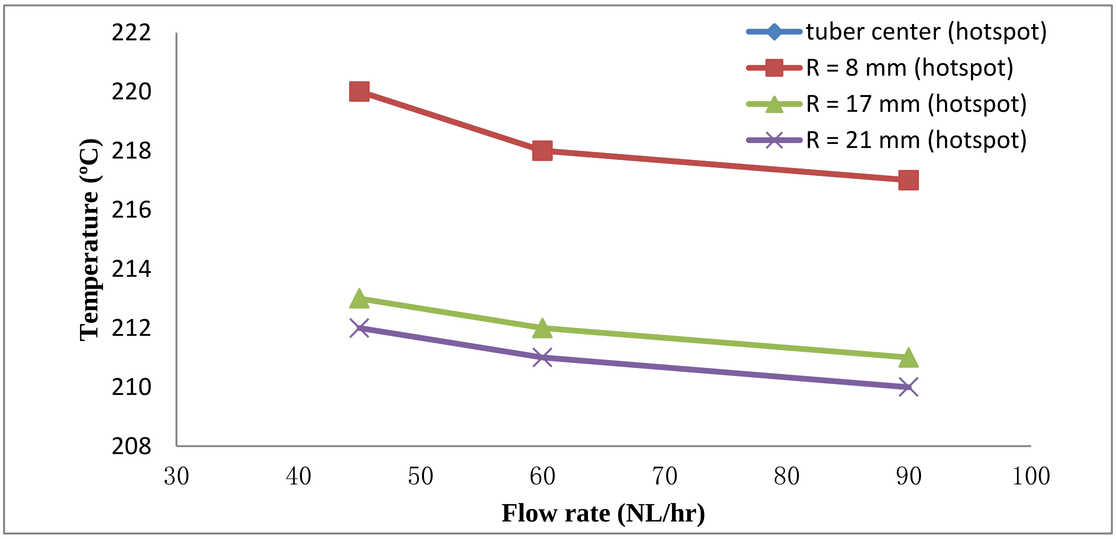

Figure 5.8 the effect of the feed flow rate on the bed temperature

(P = 25 bar, $T_{(out)}$ = 190 °C)

The dependence of hydrogenation activity and CO conversion on the inlet flow rate was illustrated in Figure 5.9. As can be seen, the CO conversion decreased as the inlet flow rate increased, in other words, the CO content in feed gas remained constant, while flow rate increased. As mentioned above, a low-temperature FTS reaction is beneficial to the formation of long chain carbon products. However, under this condition the reduced conversion of the reactants dominated in the reactor, therefore an excessive feed flow rate will limit the yield of reaction products.

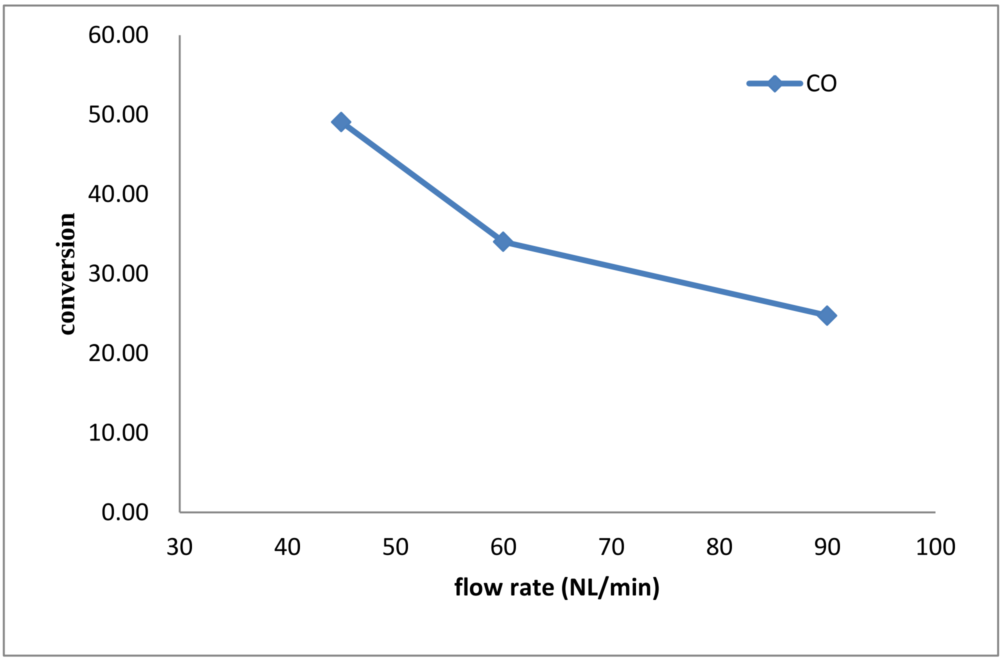

Figure 5.9 the effect of the feed flow rate on CO conversion

(P = 25 bar, $T_{(out)}$ = 190 ºC)

5.3.4 Influence of H_2 and CO partial pressure on the FT reaction

In the BTL process, the composition of syngas varies with the biomass material used to produce it. As the syngas is continuously collected from the gasifier, even when the same kind of biomass feed is used, there is a difference in the components and their proportion. At the same time, the partial pressure of H_2 and CO will have an enormous impact on the FTS reaction. No other gases similar to H_2 or CO were added to control the proportions of the syngas components in this experiment.

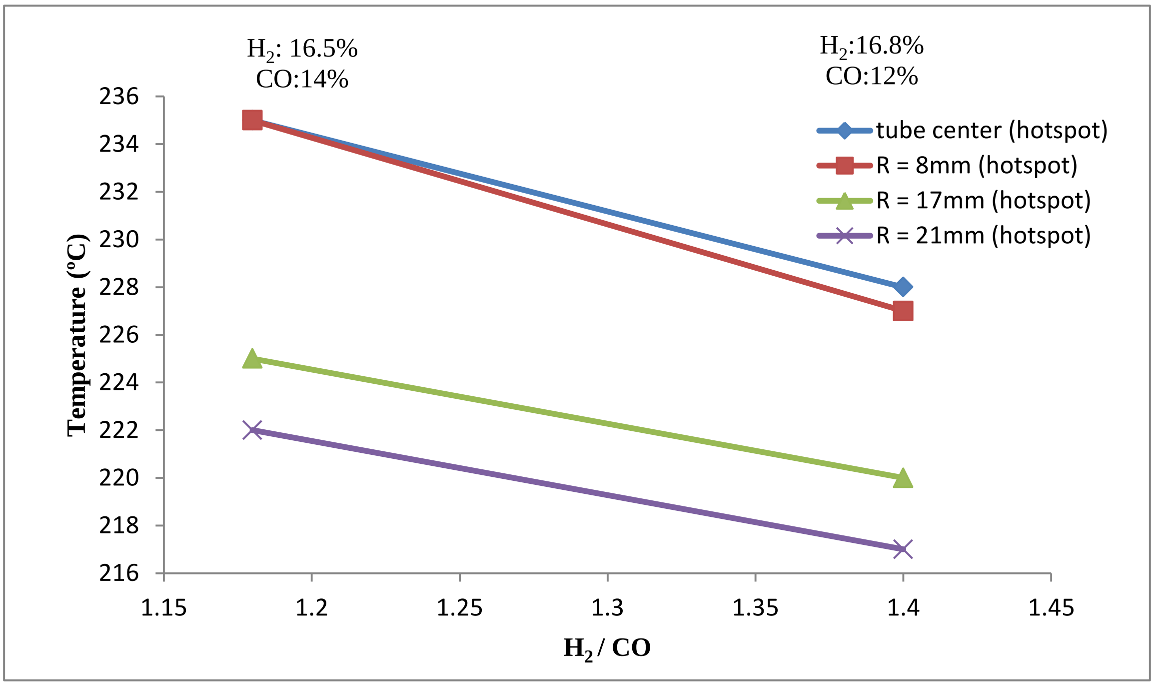

Figure 5.10 Effect of differences in partial pressure of reactants on inner tube temperature (P = 25 bar, $T_{(out)}$ = 190 ºC, Flow rate = 52.2 NL/min)

The effect of the differences in partial pressure of the reactants on inner tube temperature, where all other operating conditions remain unchanged, is shown in Figure 5.10. As can be seen, the partial pressure of H_2 remained essentially the same, while the partial pressure of CO was lowered. Since the partial pressure of the reactants in whole reaction system had dropped, the amount of product formed by the reaction was reduced. The heat produced by the reaction decreased, and have the temperature at the hotspot decreased. Thus, when an actual operation is under way, the engineer must be vigilant in order to monitor the changes in temperature in the catalyst bed, brought about by the change in the ratio of H_2 and CO, in order to prevent the occurrence of a temperature runaway.

Figure 5.11 shows the influence of the lack of uniformity in the partial pressure of reactants on catalyst activity and reactant conversion. The theoretical optimum ratio of H_2/CO for the FTS reaction is 2. In these experiments, the ratio of H_2/CO was less than 1.5. In Figure 5.11, it can be seen that the conversion of CO increased as its partial pressure decreased, while the conversion of H_2 was essentially constant. Therefore, controlling the ratio of H_2 and CO at close to 2 improves FTS reaction efficiency.

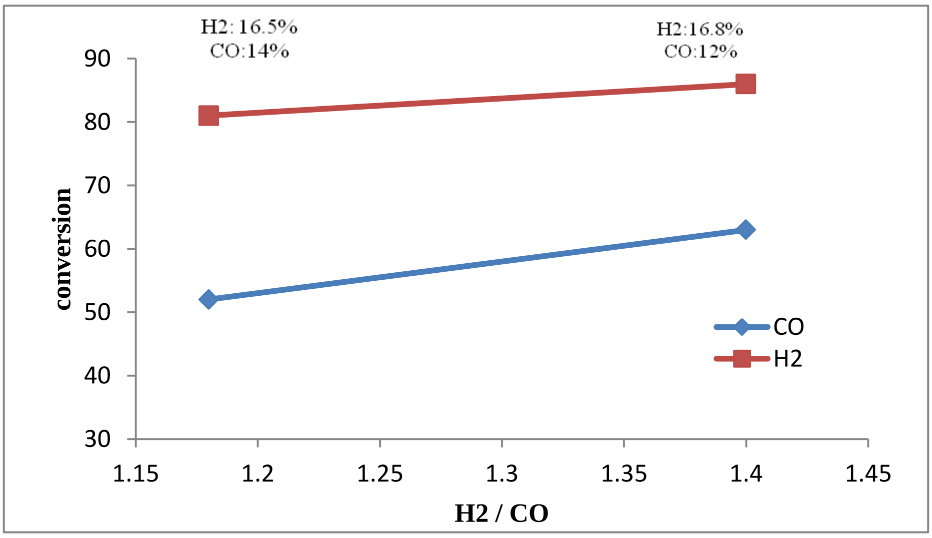

Figure 5.11 The effect of the partial pressure of CO and H_2 on reactant conversion

(P = 25 bar, $T_{(out)}$ = 190 ºC, Flow rate = 52.2 NL/min)

5.4 Reaction products

The products resulting from the experimental programme were not pure because this project didn’t carry out a distillation separation process. The condensed products formed at different stages can be characterized as light oil, heavy oil and wax.

Figure 5.12 Light oil

Figure 5.12 is a photograph of light oil, which was collected in the cold trap (4 ºC). The light oil is colourless or slightly yellow. This is possibly because of a small amount of the olefin content that has been oxidized by contact with oxygen. The chromatogram of light oil is shown in appendix A. From the chromatographic analysis it can be seen that the light oil consist mainly of carbon number C_6 and above (up to C_{25}), all of which are straight-chain alkanes. Most of the components are C_9. It can be observed that the contents of the components gradually decreased with an increase in the carbon number. The maximum detectable component is C_{25}. In addition, the light oil products contain a small amount of isomeric hydrocarbons, but because further detailed analysis was not conducted, their kind and content were not ascertained.

Figure 5.13 Heavy oil

Above, is a photograph of heavy oil, which is the liquid product, collected in hot trap (120 ºC). As can be seen, heavy oil is light yellow or yellow, and darker than the light oil. Moreover, heavy oil is more turbid than light oil. The reason might be the presence of a very small amount of catalyst. The chromatogram of heavy oil, which is shown in Appendix B, indicates that its carbon number is mainly straight chain alkanes of C_7 and above. However, most of these alkanes fall into the C_{16}–C_{18} range, and then with the increase in the number of carbon, contents of components gradually decreased, the maximum detectable component is C_{28}. Like light oil, heavy oil contains isomeric hydrocarbons, but in a smaller proportion than is found in the former.

Figure 5.14 wax

The wax, which was also collected in the hot trap, was white and solid at room temperature, as indicated in the photograph above. The chromatogram, which is shown in Appendix C, reveals that the wax is a straight chain alkane and its carbon number is generally above C_7. Most of these alkanes fall into C_{16} to C_{20} range. After C_{20}, as the carbon number increased, the proportion of the components gradually decreased, while the maximum detectable component is C_{40}. Comparing the wax with the liquid products, it was found that the amount of isomeric hydrocarbons contained in wax was markedly smaller. Theoretically, longer carbon chain hydrocarbon components are to be found in wax, and the quantity of the long carbon chain contents should be higher. This cannot be easily confirmed, probably because of the chromatographic settings being used.

It was possible to match the results of the chromatographic analysis of the three kinds of products with those published on other kinds of known FTS products, such as coal to liquid and natural gas to liquid (Anderson, 1984; Bartholomew, 1991; Dry & Steynberg, 2004; Yao, 2011). The agreement between these results and other workers proves that the biomass to liquid fuel process is feasible.

5.5 Estimating the efficiency of biomass to liquid technology

In this research, the FTS reaction was carried out under different operating conditions. To assess the efficiency of this process, operating conditions were chosen that resulted in the highest CO conversion. These conditions are set out in Table 5.2.

Table 5.2 the experiments achieving the best CO conversion results

Component	Conversion (%)
CO	61.87
H_2	85.66
Component	Selective (%)
CO_2	4.66
CH_4	8.46
C_2H_4	-2.52
C_2H_6	5.4
C_3H_6	-0.8
C_3H_8	2.83

From the table, it can be observed that the selectivity of C_2H_4 and C_3H_6 is negative. One possible reason is that the C_2H_4 and C_3H_6in the feed gas forms C_2H_6 and C_3H_8 by the hydrogenation process under these operating conditions. Another possibility is that some of the C_2H_4 and C_3H_6 may be absorbed by liquid products.

Under these operating conditions, the content of CO was 14.03% and its conversion was 61.87%. As calculated using equation 5.4, the selectivity of C_{5+} was 81%. During the biomass gasification process, 50 kg raw materials fed into the gasifier would enable it to run continuously for between six to eight hours, and produce about 50 $Nm^3$of syngas. It was therefore possible to calculate that the BTL fuel facility used in this research could produce 2.2 kg of liquid products and wax per 50 kg of raw biomass materials.

5.6 Conclusion

The pilot BTL facility successfully synthesized FT products such as FT wax and oil. The results of chromatographic analysis of the products are in agreement with those published on other types of FT synthesis, such as coal to liquid and natural gas to liquid. The equipment used for the BTL pilot facility operated reliably, and the heat transfer took place satisfactorily. This series of experiments provides a strong empirical basis on which to expand the scope and scale-up of the biomass to liquid fuel reactor.

In this research programme, the experimental BTL facility was used in this project to examine the effect of reaction pressure, heating jacket temperature, and feed gas flow rate and partial pressure of the reactants on the BTL fuel process. The findings can be summarized as follows.

1. As the reaction pressure increased, the temperature of the catalysts bed increased, as did the conversion of CO and H_2.

2. The most efficient way to control the temperature of the catalyst bed was to adjust the temperature of the external heating jacket. A higher external heating temperature improved the activity of the catalysts, and increased the conversion of reactants, but it easily caused the temperature to run away, which was not conductive to the formation of long carbon chain products.

3. As the reaction space velocity increased, the temperature of the catalyst bed and the conversion of the reactants reduced. This can be remedied by providing a sufficient amount of inlet feed gas in order to boost the yield of synthetic product.

4. In this experiment, the H_2/CO ratio was less than 1.5. The result obtained by controlling the ratio of H_2 and CO at close to 2 confirmed that this setting is effective in improving the FTS results.

According to the present calculations, the biomass to liquid fuel facility used in this research can produce 2.2 kg of liquid products and wax per 50 kg of raw biomass materials.

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Chapter 6: Conclusion

A bench scale BTL fuel facility was successfully set up and operated, resulting in the production of liquid fuel and Fischer-Tropsch wax. All the equipment functioned adequately well, and the high sensitivity of maximum temperature in the catalyst with changes in operating conditions was directly attributable to the large diameter of the tube.

The research project described in this dissertation entailed the setting up of a bench scale BTL fuel facility. The first stage comprised the researchers building a downdraft fixed bed gasifier capable of 10 m^3/hr gas production in order to carry out biomass gasification. When fed a 50 kg of raw material, the gasifier proved capable of running continuously for between six to eight hours, thereby producing about 50 $Nm^3$of synthetic gases.

The second stage comprised a number of refining processes: purification, desulphidation and deoxygenization that prepared the syngas for use in FTS. When these had been carried out, the sulphide content of the gas was lower than the GC detection limit (5 ppbv); the oxygen content was below 1%; the H_2 content was 10–17%; and the CO content was between 10–15%. At this stage, the syngas could be fed into the reactor.

For this experimental project, a single tube fixed bed FT reactor was used with an ID of 50 mm, a length of 900 mm and a catalyst bed of 100 mm. The diameter of this reactor tube was as large as those used on an industrial scale. The advantages of using a reactor tube of large diameter were cost saving on the purchase of the reactor, the benefit of being able to load a sufficient amount of catalyst for the reaction in one step, and the improved efficiency of heat removal. The latter is a feature that is particularly attractive, given that FTS is a highly exothermic reaction.

The amount of reaction activity obtainable in this facility was also investigated under different operating conditions. This made it possible for the author to analyze the effects of the variations in reaction pressure, heating jacket temperature, feed gas flow rate and partial pressure of the reactants on the BTL process. The results of these tests yielded information (discussed in Chapter 5) that will be invaluable in the next phase of the research, which will entail scaling up the process to industrial capacity.

For hydrocarbons with carbon chain lengths of between 5 to 46 carbon atoms (collectively referred to as C_{5+}) in the liquid fuel as it can be detected, a selectivity of over 81% was obtained and the conversion of CO and H_2 was over 61% and 86%, respectively, under the operating conditions of 3MPa, 220–240 °C. The flow rate of the feed gas was 52.2 NL/hr. In addition, when the pressure in the reactor (an important feature of the reaction) decreased to 0.5 bars, the conversion of CO and H_2 dropped to 4.3% and 7%, respectively. At these settings, the flow rate of the feed gas was 52.2

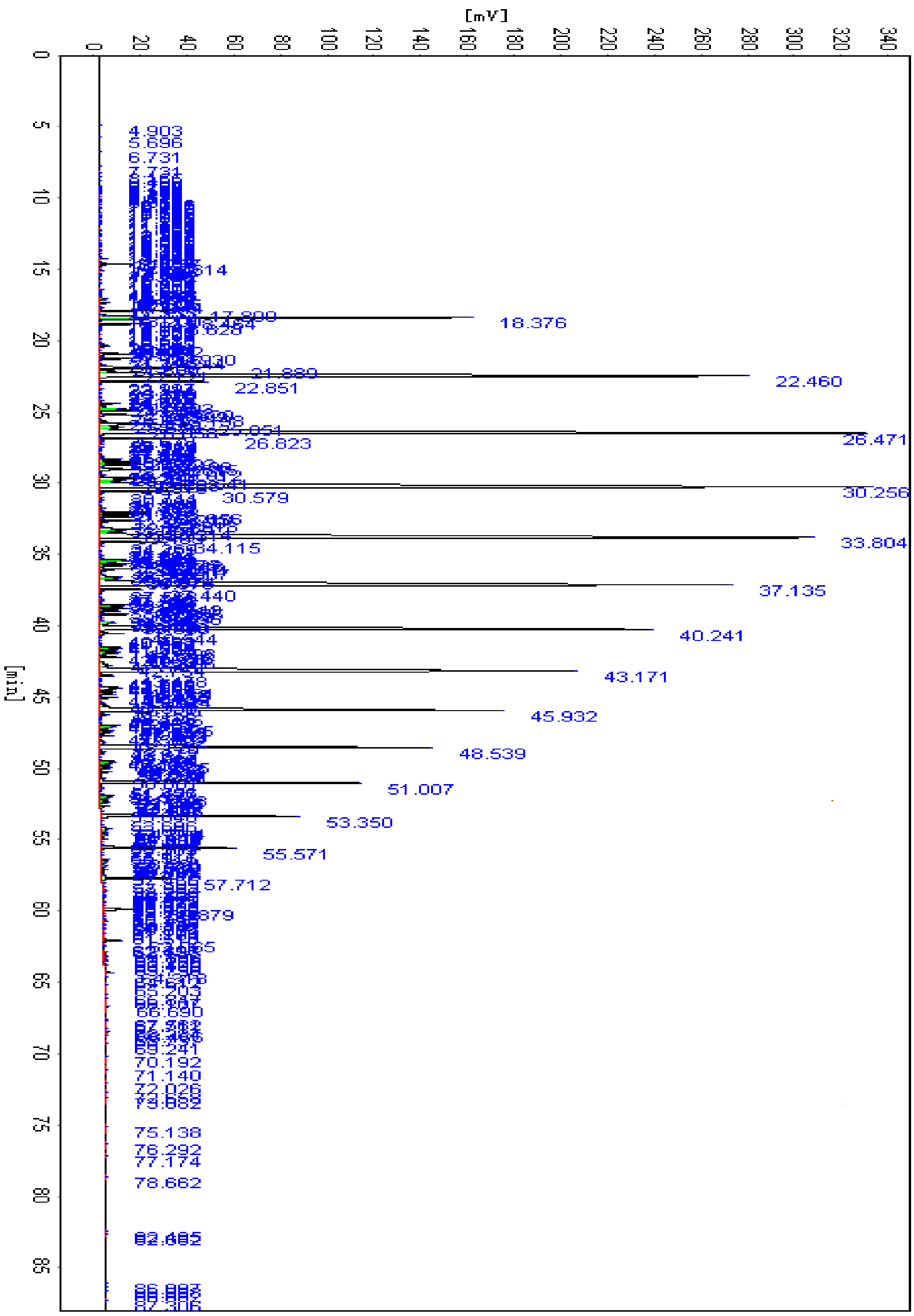
NL/hr and the temperature of the reaction was 230 ºC.

The operation of the equipment (used in this research project under the conditions set) was successful, in that the FTS yielded the desired products. These have FT hydrocarbon characteristics (such as normal straight chain and paraffin-based), a wide carbon number distribution, and normal proportions of the different components. It was also established that a high CO_2 and CH_4 content had no adverse effect on the FT reaction under the chosen operating conditions.

The BTL process used in the project is estimated to produce 2.2 kg of liquid products and wax per every 50 kg of raw biomass material. The main factor that restricted the yield of production was the efficiency of the biomass gasification process.

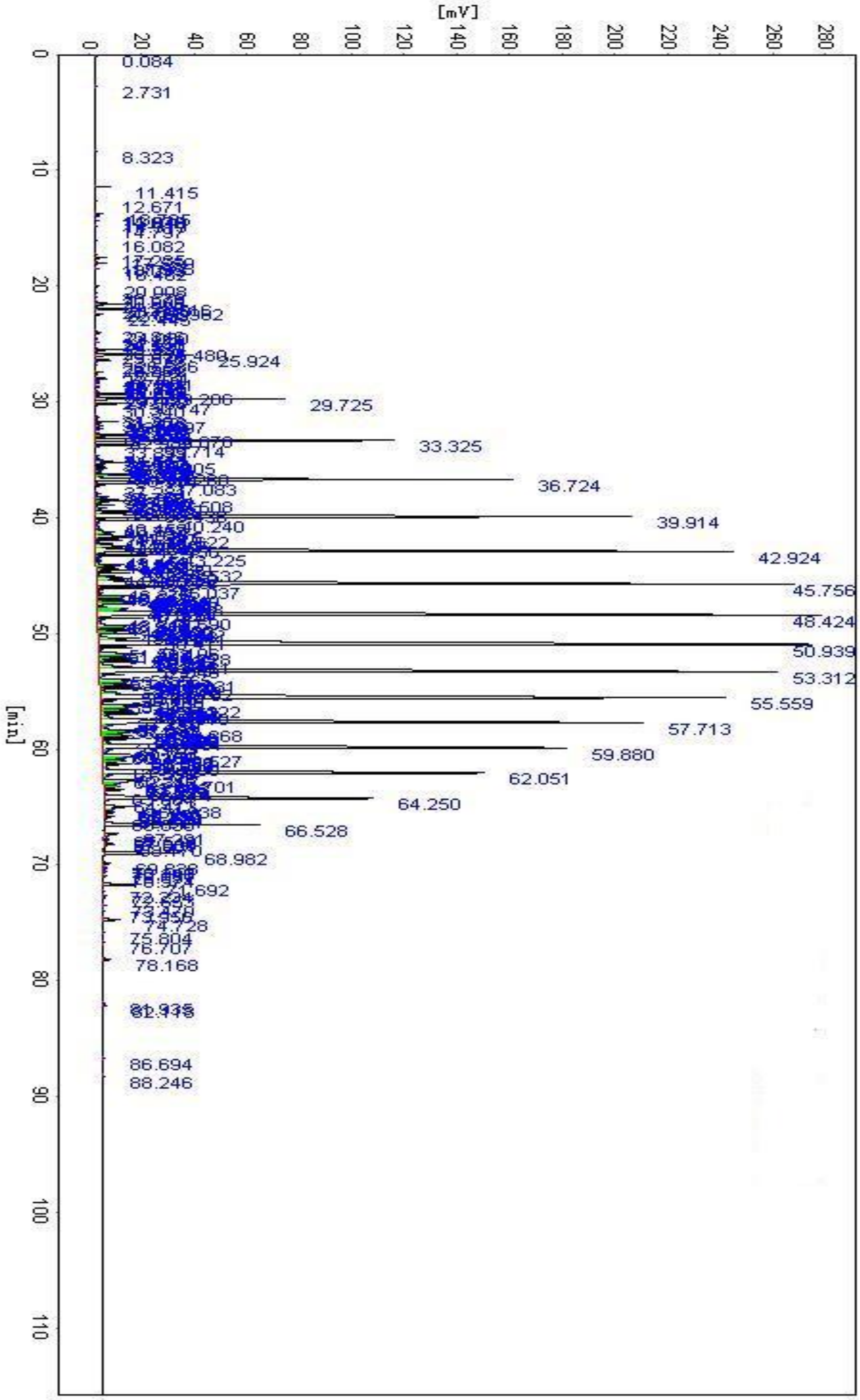
Appendix A

The chromatogram of light oil


[mV]
[min]
18.376
22.460
26.471
30.256
33.804
37.135
40.241
43.171
45.932
48.539
51.007
53.350
55.571
57.712

Appendix B

The chromatogram of heavy oil


[mV]
[min]
0.084
2.731
8.323
11.415
12.671
16.082
25.924
29.725
33.325
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39.914
42.924
45.756
48.424
50.939
53.312
55.559
57.713
59.880
62.051
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68.982
74.728
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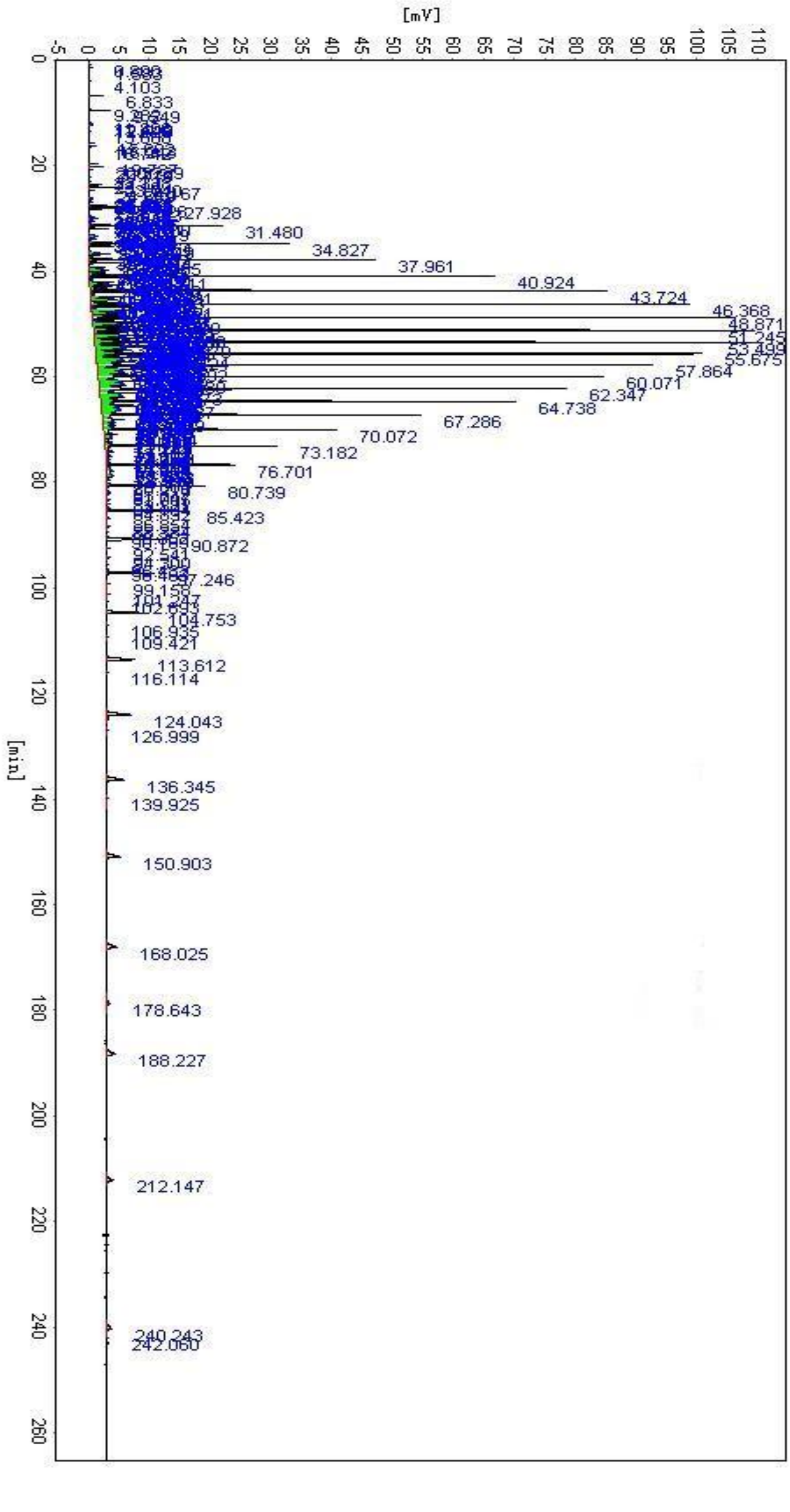
78.168
86.694
88.246

Appendix C

The chromatogram of wax


[mV]
[min]
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6.833
27.928
31.480
34.827
37.961
40.924
43.724
46.368
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55.675
57.864
60.071
62.347
64.738
67.286
70.072
73.182
76.701
80.739
85.423
90.872
99.158
104.753
109.421
113.612
116.114
124.043
126.999
136.345
139.925
150.903
168.025
178.643
188.227
212.147
240.243
242.060