Novel Design of an Integrated Pulp Mill Biorefinery for the Production of Biofuels for Transportation

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Abstract

An integrated gasification process was developed for an Ohio-based kraft pulp mill to produce liquid transportation fuels from biomass and coal. Black liquor byproduct from the pulp mill is co-gasified with coal to generate high quality syngas for further synthesis to dimethyl ether (DME) and/or Fischer-Tropsch fuels. A Texaco gasifier was chosen as the focal point for this design. Whenever possible, energy is recovered throughout to generate heat, steam, and power. Mass and energy balances were performed for individual process components and the entire design. An overall process efficiency of 49% and 53% was achieved for DME and FT-fuels, respectively.

Table of Contents

List of Figures

List of Tables

1 Introduction

The global transport sector uses approximately 70 to 90 EJ of energy per year[1]. In OECD countries, 97% of the transport sector uses petroleum-based fuels. It is estimated that the world has peaked in petroleum production, and world petroleum consumption has outpaced new-found reserves. Therefore, great efforts in research and development have been made into new vehicle technology and new fuels. A means of reducing or eliminating the dependency on petroleum is the use fuels derived from natural gas, biomass or coal. For this reason, methanol, ethanol, dimethyl ether, Fischer-Tropsch fuels, biodiesel, etc. are being researched as alternative fuels. Whatever fuel is to supplement or replace petroleum, it must address the following criteria: availability, economics, acceptability, environmental and emissions, national security, technology, and versatility[2].

This report details a gasification-based production scheme to produce dimethyl ether and Fischer-Tropsch fuels as alternative fuels that could potentially replace petroleum-based fuels in terms of the availability, environmental and emissions factors, and technology. Attention is growing in research areas where alternative fuels are produced from biomass feedstocks based on the potential for CO_2 reduction and energy security.

Fischer-Tropsch Diesel (FTD) is a promising fuel that can be produced from gasified hydrocarbons, such as coal, natural gas and biomass feed stocks. FTD is a high quality diesel fuel that can be used at 100% concentration or blended with lower quality petroleum based fuel to improve performance [3]. The main advantage of large scale production of FTD is that no changes or modifications are necessary to utilize it in current fill stations or vehicles.

With social, political and environmental demands for eco-friendly renewable transportation fuel, FTD produced from biomass should be considered. FTD does not have the logistical problems of bio-diesel. FTD does not need to be blended with regular diesel fuel. It can be run at a 100% concentration without vehicle modifications. FTD does not suffer from cold flow problems like bio-diesel[3].

Fischer-Tropsch synthesis (FTS) is a mature technology that has been commercially utilized to produce FTD by Sasol since 1955. Company such as Shell, Chevron, ExxonMobil and Rentech have been creating production facilities as FTD has become more economically feasible with the onset of high petroleum fuel costs.

Production efficiency of FTD is lost to low selectivity of hydrocarbon chains during Fischer-Tropsch synthesis. When creating FTD, middle distillates and long chained wax are desired, but regardless naphtha and light carbon chain gases are produced. Ekbom et al. created models showing Fischer-Tropsch products having a 65% biomass-to-fuel efficiency, with 43% being FTD and 22% being naphtha [4]. In a compellation of previous works, Semelsberger et al. reported FTD to have a ~59% well-to-tank efficiency, based on syngas produced by natural gas[5]. Production of FTD from coal can be assumed to have similar trends in production efficiency since FTD synthesis begins with gasification of a feed stock to create syngas.

U.S. pulp and paper mills have an opportunity to utilize biomass (as black liquor) and coal gasification technologies to improve the industry's economic and energy efficiency performance with new value-added streams including liquid transportation fuels from synthesis gas. The black liquor pulping byproduct contains cooking chemicals and calorific energy that should be optimally recovered through gasification.

Although the heating value per ton of dried black liquor solids is relatively low, the average Kraft mill represents an energy source of 250-500 MW [1,2]. Black liquor is conventionally handled in a Tomlinson recovery boiler for chemicals recovery and production of heat and power.

Although the recovery boiler has been used successfully for years, it has several disadvantages that allow for the consideration of a replacement strategy. First, the recovery boiler is capital intensive, yet it is relatively inefficient for producing electricity from black liquor [3]. In addition, gasification virtually eliminates safety concerns due to explosion hazards for the recovery boiler. Equally as important, black liquor gasification technology performs better than conventional and advanced boiler technology [1].

Chemrec AB has designed a gasification process for black liquor to produce an energy rich synthesis gas centered on a high-temperature (950-1000°C), high-pressure (32 bar) oxygen-blown gasifier. The design is similar to the Shell slagging entrained-flow gasifier for coal gasification.

The goal of this project is to design an integrated gasification process design with a U.S. pulp mill to generate high-quality syngas while also achieving a high chemical recovery yield and generating additional heat and power for the pulp mill and potential sale of electricity to the grid. Supplementing black liquor gasification with coal is a means to substantially increase the yield of fuels produced from gasification to syngas for further conversion to DME or Fischer-Tropsch fuels.

2 Background

2.1 Pulp Mill Background

2.1.1 Harvesting and Chipping

The pulping process begins at the site where trees are harvested. When all factors are taken into account, the most important idea behind cost minimization is that "optimizing forest fuel supply essentially means minimizing transport costs" [6]. Two main options are available for the transpiration of wood to the mill, one as solid logs and one as wood chips, where the wood is chipped in the forest. Chipping is advantageous because it increases the bulk volume which can be transported. The main disadvantages of chipping in the forest are the decreased length of time for which chips can be stored. After their size reduction, microbial activity in the chips increases, releasing poisonous spores, and energy is lost within the wood increasing the risk of self ignition [7].

Recently the idea of storing the wood as bundles has arisen as a viable option to improve forest-fuel logistics. Large eight cylinder machines are used to drive two compression arms which bundle the wood similar to the way a person rolls a cigarette. The figure below shows the difference between shipping loose residuals on the same size truck as a bundle [7]. This new technology reduces the impact of transporting forest-fuel matter across larger distances.

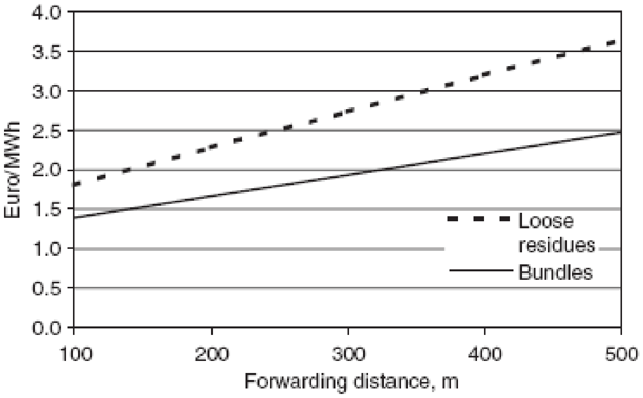


Figure 1: Price of wood as a function of transportation distance.

There are a number of available technologies for debarking wood entering the plant. Three main technologies at the head of the industry are ring style debarkers, cradle debarkers, and enzyme assisted debarking [8].

Ring style debarkers fall into two categories, wet and the more common dry debarkers. Wet debarkers remove bark by rotating logs in a pool of water and knocking the logs against the drum. Dry debarkers eliminate the use of about 7-11 tons of water per ton of wood, thus reducing water and energy use [9]. Wet debarkers need 0.04 GJ per ton of debarked logs of energy, while ring style debarkers use approx. 0.025 GJ per ton of debarked logs [10]. A Cradle Debarker has an electricity demand of 90 kWh and can debark 120 cords an hour [11]. An Enzyme assisted debarker requires a large capital investment of one million dollars for an 800 tons per day plant but requires very little energy to run, about 0.01 GJ/ton of debarked logs [10].

2.1.2 Pulping

Once the chips have been ground, the next stage is the pulping stage. Typical wood consists of about 50% fiber, 20-30% non-fibrous sugars, and 20-30% lignin [12]. There are three main processes associated with digestion. These are referred to as mechanical pulping, chemical pulping and semi-chemical. The most widely used within these processes is the Kraft process which is a chemical process [13].

2.1.2.1 Mechanical Pulping

The principle behind all mechanical pulping is to take a raw material and grind it down into individual fibers. The main advantage of the mechanical pulping process is a higher efficiency (up to 95%) than chemical pulping. Another benefit of mechanical pulping is the low energy demand ranging from 1650 to 1972 kWh/ton [10, 14]. Within mechanical pulping, three subdivisions exist: stone groundwood pulping, refiner pulping, thermomechanical pulping and chemi-thermomechanical pulping. Mechanical pulping accounts for a small percentage of paper production, around 10%. It is not very prevalent in commercial production because impurities are left in the pulp which in turn produces a weaker paper with less resistance to aging. The resulting weakening effect is compounded by the fact that the grinding action of mechanical pulping produces shorter fibers [13]. It also is the most energy intensive.

The most ancient method used to pulp is the stone groundwood pulping process. Water cooled silicon carbide teeth are used to crush the chips into pulp. It is the least energy intensive process, 1650 kWh/t pulp [10, 14], resulting in a high yield of pulp. However, expensive chemicals are required to continue processing the pulp in a paper mill because the fibers are too short.

Refiner pulping is when the wood chips are ground between two grooved discs. This process builds on the stone groundwood process by producing longer fibers which give the paper greater strength. The increased strength allows the paper to be drawn out thinner, increasing the amount of paper produced per ton. A modest 1972 kWh/ton of pulp is consumed with this process [10].

Thermomechanical pulping is used to produce the highest grade pulp of all processes which involves mechanical processes. Steam is used at the beginning of the process to soften the incoming wood chips. Next, the same process as the refiner pulping is completed to produce the pulp. Compared to the other mechanical processes, this is the most energy intensive process utilizing 2041 kWh/ton pulp as well as 0.9 GJ/ton of steam [10, 14]. Another drawback is that more lignin is left over, resulting in a darker pulp and necessitating a larger quantity of bleach for treatment.

Chemi-thermomechanical pulping is similar to thermomechanical pulping because it requires pretreatment of the wood chips before pulping. Sodium sulfite (Na_2SO_3) is added to the chips which are then heated to 130 degrees Celsius. The process advantage over the thermochemical pulping process is that it results in longer fiber stands, more flexible fibers and lower shive content. Also, a larger amount of lignin is removed requiring less bleaching in the latter stages [8]. However this process has a whopping energy demand of 26.8 GJ/ton.

2.1.2.2 Chemical Pulping

The most common practices used commercially in the United States today are chemical pulping processes. Of these, sulfate, more commonly known as kraft, pulping is known to produce the highest quality paper. Unfortunately, the losses associated with this process reduce the pulping efficiency to an approximately 50% [8]. In our plant this would mean on a day where 2500 tons of wood are processes, only 1250 ADt of pulp would be produced. The wood chips are first steamed to remove all of the excess air. Next, the dry chips are combined with a sodium hydroxide ($NaOH$) and sodium sulfide (Na_2S) solution, a solution known as white liquor. This mixture is pressurized and heated to 170 degree Celsius. Once cooked, the pulp is separated into long fibers by being moved into low pressure tanks. Approximately 4.4 GJ steam per ton 406 kWH per ton are used [10, 15, 16].

Sulfate cooking is approached in two separate manners based on the amount of pulp being processed and the time required to produce pulp. These two types are labeled batch cooking and continuous cooking.

In batch cooking, all of the chips and cooking liquor are filled into the digester where the mixture is heated under pressure and emptied. Within batch cooking, there are two different commercially available batch digesters: direct steam heating and indirect steam heating. Direct steam heating, which is popular in North America, injects steam directly into the bottom of the digester. It simplifies the digestion process and increases heat quicker. However, it dilutes the white liquor and cannot heat the digester uniformly. Liquor dilution lowers the chemical recovery and produces a lower quality pulp. Because of these side effects, indirect steam heating is used when heat economy and pulp quality are important. In this process, heat exchangers supply the white liquor with heat before it enters the digester. This eliminates the problems of white liquor dilution and digester non-uniformity [17].

Other processes have been developed for batch cooking in an attempt to match the efficiency of continuous cooking. Extended batch delignification systems have emerged such as SuperBatch and Rapid Displacement Heating. The seven basic steps to this process are: chip filling, warm liquor fill, hot liquor fill, bring-up, cooking, displacement and discharge [18].

Batch cooking is not an economically feasible approach for our solution because in order for the plant to be economically competitive, it will require an efficient manner of producing black liquor for gasification.

Continuous cooking is where the pressurized chip and liquor mixture is continuously fed through the digester. The two different kinds of continuous digesters are hydraulic and steam-liquid phase digesters. A hydraulic digester means that the digester is completely impregnated by chip and liquor solution.

The first development of this process was labeled the “modified continuous cooking process” or MCC. It is a three stage cooking system where a constant heat supply is given and within each stage the pulp is mixed with an increasingly alkaline white liquor solution. This staging process is useful because it increases the pulp quality compared to a one stage system [18]. Various research has led to the creation of the extended modified continuous cooking or EMCC. It involves the same basic principles as the MCC, except that a higher temperature white liquor washing zone is added to the end of the process. It decreases the initial hydroxide concentration and increases the amount of cooking [18]. Isothermal cooking or ITC builds on EMCC by adding a fifth white liquor washing zone. This decreases the amount of hydroxide used in the initial chip washing stage. Another advantage over MCC and EMCC is that it requires lower temperatures to run the digester, and temperatures remain constant throughout the process.

A second chemical process is called the sulfite process and operates at a lower temperature than the kraft process, produces a brighter paper, yet forms shorter fibers [8]. These shorter fibers require the resulting papers to be thicker in order to retain strength. As a result, less paper can be made per ton of wood. The sulfite process uses burnt sulfur mixed with a basic solution as the treating fluid. Black liquor is still produced, but more difficult to recover. Energy estimates for this process are 4.2 GJ/ton of pulp and 572 kWh/ton of pulp electricity. The sulfite process is only used for specialty pulp used to make very smooth paper [14].

The active alkali ingredient in most pulp mills today is sodium hydroxide (NaOH). It requires 400 kg pro ton of pulp to appropriately process the pulp. NaOH is often purchased by the plants, running a total of $165 per ton in 2001. The total energy cost of making this alkaline requires 2.85MWh/ton NaOH [19]. In the conventional, open bleaching process using a chlorine chemical for pulp bleaching, the alkaline extraction steps require 20-60 kg NaOH per ton of pulp [20]. Modern pulp mills today require 15 kg of white liquor during treatment per ton of chips coming in [21].

2.1.2.3 Semi-chemical Pulping

Semi-chemical pulping is not a very widely used process in modern day pulp mills. It is mainly used for hardwood pulping because of the short fibers it contains. These shorter strands form a more opaque, smoother and denser paper [8]. 5.3 GJ per ton and 505 kWh per ton are the energy demands for this process [13].

2.1.3 Chemical Recovery

Chemical pulping results in the formation of an energy dense byproduct called black liquor. Black liquor is used in current paper mills to create energy to fuel the entire plant. The inorganics that are contained in black liquor that cannot be used for energy are collected and reformed so that they can be used in the kraft process again.

The first stage towards recovering the chemicals given off during the digestion stage to is to remove the water. When black liquor is collected from the cooking stage, around 15 volume percent is usable black liquor solids. In order to use the black liquor solids efficiently, the solution going to the gasifier or recovery boiler must be 80 volume percent solids. Typical plants use a series of two evaporators known as multiple effect evaporators (MEE) and direct contact evaporators (DCE). MEEs uses steam to concentrate the mixture via evaporation to 50% black liquor solids. The DCEs are used following this stage by using the exhaust gasses of the recovery boiler to further reduce the mixture to the 80% solids concentration. The energy consumed by the evaporators is around 4.4 GJ/ton of pulp. [14] Canadian Office of Energy estimates 3.1 GJ/ADt and 30 kWh/ADt are used for a modern kraft pulp mill. [22]

In a recovery boiler, the organic compounds that exist in the black liquor are then oxidized in order to produce heat. The smelt from the recovery boiler is mixed with a weak white liquor solution to form green liquor. This green liquor is primarily made up of sodium carbonate (Na_2CO_3) and sodium sulfide (Na_2S). Approximately 1.1 GJ per ton of pulp and 58 kWh/per ton of pulp is required for auxiliary power for a furnace. When the black liquor is oxidized, approximately 15 GJ per ton of pulp is produced. [16]

Black liquor when it is gasified, or burned in a recovery boiler, will result in the collection of inorganic sulfur in the bottom of the reactor. During that process a mixture of sodium sulfide and sodium carbonate forms at the bottom of the typical recovery boiler. The contents of the aqueous solution are sodium carbonate, 90-100 g/L, sodium sulfide, 20-50 g/L, and sodium hydroxide, 15-25 g/L. If the white liquor rises above 35% sulfidity it is considered poisonous to the pulp, and not useful.

2.1.4 Extending the Delignification Process

Oxygen delignification, kraft pulping additives, and alternative pulping chemistry can further extend the delignification process and reduce the use of bleaching chemicals (Pulliam, 1995). The best digestion practices will only remove approximately 90 percent of the lignin in the pulp. Oxygen delignification helps reduce fading and increases strength of the paper. It is applied between the pulping and bleaching stages. It enables total chlorine free bleaching (TCF) to be possible. During delignification, the pulp is heated to around 100 degrees Celsius at 1 MPa for an hour. Fifteen kilograms of oxygen and 30 kilograms of sodium hydroxide are used in this process A one stage system will remove fifty percent of the remaining lignin, while the two stage system will remove seventy percent. [23]

Ozone bleaching is also a powerful oxidizer and is applied after the oxygen delignification process. From three to ten kilograms of ozone is required to complete ozone bleaching. The most economical way to produce ozone is through the oxygen coming out of the air separation unit. ECF or TCF sequences containing ozone offer the lowest bleaching costs. [24]

A more experimental practice introduced recently is using a pressurized peroxide stage. Increasing pressure, temperature, and perhaps a little oxygen has greatly increased the brightening power and efficiency of the peroxide stage. The pressurized peroxide stage utilized for final brightening requires 100 degrees Celsius at 0.5 MPa for 2 hours. The residence time required to reach a given brightness is also reduced to approximately 20% of that required in a conventional peroxide bleach tower. [24]

2.1.5 Bleaching

After the pulping stage, there is still a significant lignin which is closely bonded with the pulp. This requires a series of bleaching stages to remove the lignin because the lignin adds undesirable weakness and color to the paper. Before environmental controls kicked into full gear, pure chlorine (Cl_2) was used to bleach the pulp. Due to environmental concerns a whole host of chemicals including ozone, hydrogen peroxide, enzymes, and chlorine dioxide have proven to be viable substitutes.

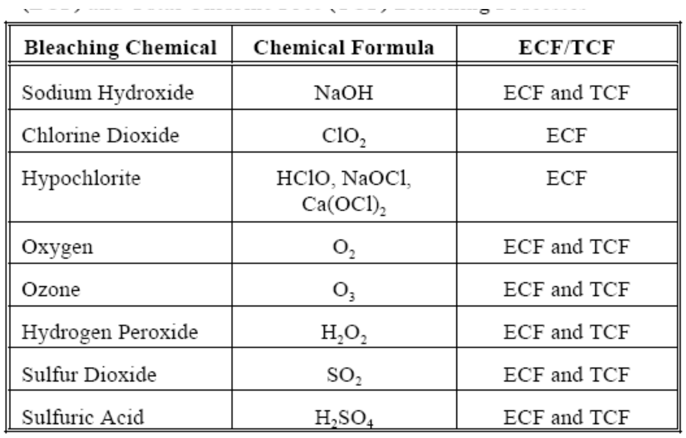
The main counter-current washing systems in kraft pulp bleaching involve three different wash water circulation systems: direct counter-current, jump-stage and/or split flow washing. Each of these stages employs alkaline or acid washes. For example, a five stage wash could look like this, (DC)(EO)DED, with the D stages using acidic solution and stages with E using an alkaline solution. Acidic solution in the past was elemental chlorine, but now used chlorine dioxide or other substitutes. Alkaline solution active chemicals are sodium hydroxide and sodium sulfide [25].

Washing systems are used to separate the white liquor from the pulp-water suspension during the bleaching phase. Free liquor exists in suspension surrounding the wood chips and is relatively simple to remove. The “fiber phase” which includes wood fibers and white liquor entrained in those fibers offers a more difficult challenge, but is required in order to make the paper efficient. Entrained liquor in the fiber phase can only be removed by diffusion or capillary force. Washing is broken up into five individual stages: dilution, mixing, dewatering, diffusion, and displacement. The water used for this process is gathered from the drying and evaporation stages.

The first stage typically uses an acidic solution which binds to the lignin. In between each bleaching stage, the chemicals are drained from the pulp and it is then washed with the aforementioned water. Only in the last acid and alkaline stages does the water have to be pure. Next, the lignin acid is removed in an E stage with sodium hydroxide. At the end of the process, the pulp is whitened by sodium hypochlorite, chlorine dioxide, or hydrogen peroxide.

Because of restrictions placed by the United States government on effluent from bleaching plants, elemental chorine free (ECF), total chlorine free (TCF) and totally effluent free (TEF) are methods that have been put into practice in order to process paper environmentally sound. Yet all of these processes require the earlier discussed oxygen delignification to be successful [26]. The best technology that exists for both TCF and ECF bleaching if used on pulp with a kappa number of less than 20 will result in the same effluent quality [27]. A comparison of chemicals used in each process is listed in the chart below:

Table 1: Bleaching chemicals for ECF and TCF bleaching processes[9].



Bleaching Chemical	Chemical Formula	ECF/TCF
Sodium Hydroxide	NaOH	ECF and TCF
Chlorine Dioxide	ClO_2	ECF
Hypochlorite	HClO, NaOCl, $Ca(OCl)_2$	ECF
Oxygen	O_2	ECF and TCF
Ozone	O_3	ECF and TCF
Hydrogen Peroxide	H_2O_2	ECF and TCF
Sulfur Dioxide	SO_2	ECF and TCF
Sulfuric Acid	H_2SO_4	ECF and TCF

In comparison, taking two pulps of the same Kappa level number, the bleaching yield in the TCF pulp will be lower than the one bleached with the ECF process [28]. In all the bleaching stages, bleaching chemicals consumption in the first-stage is directly proportional to the incoming Kappa number [27]. Bleaching costs of TCF bleaching are on par with the cost of ECF bleaching at a Kappa number of around 20 [29]. However, total operating costs are significantly higher for TCF pulps. ECF adds \$5-\$10/ton of total production cost above chlorine bleaching, while TCF adds \$40-60/ton, including capital expenditures (Pulliam, 1995). TCF pulps also are less bright and not as strong as ECF pulps. Upgrading a plant from an elemental chlorine bleach plant to an ECF plant would require a 33% increase in energy usage for the bleach plant because of the chlorine dioxide creation [8]

Recent ECF estimates approximate 2.3 GJ/ADt steam requirement and 100 kWh/ADt for bleaching [22].

2.1.6 Causticizing and Lime Kiln

Green liquor, whose main components are sodium sulfide (Na_2S) and sodium carbonate (Na_2CO_3), is a byproduct of both the gasification of black liquor process and the recovery boiler process described in the section on chemical recovery. It is formed when the smelt from the recovery boiler or gasifier is dissolved in water. In green liquor, the following concentrations exist, in grams per kilogram of water: Na_2CO_3, 163, Na_2S, 20, NaOH, 21. In order for the chemicals to be recovered for continued use in the cycle, they must go through a process called causticizing. This is where the green liquor reacts with quick lime (CaO) to form calcium carbonate and sodium hydroxide. The calcium carbonate ($CaCO_3$) is then burned in the lime kiln to regenerate it to quick lime. In the cauticizer, the two chemical reactions happen in series [30]:

$$CaO + H_2O = Ca(OH)_2$$

followed by the second stage of reactions which involves the other byproduct in green liquor that is as follows:

$$Na_2CO_3 + Ca(OH)_2 = 2\ NaOH + CaCO_3$$

The whole process is described chemically as

$$NaCO_3 + CaO + H_2O = CaCO_3 + 2NaOH$$

The calcium carbonate is returned with the sodium hydroxide as white liquor. White liquor is an aqueous solution. Its concentrations are sodium hydroxide (80-120 g/L), sodium sulfide (20-50 g/L), sodium carbonate (10-30 g/L), and sodium sulfate (5-10 g/L) (Patent).

In order that this process is continued, the lime kiln is typically run with natural gas, but other alternative are fuel oil and low level biomass to produce the required energy. Typically the energy is not recovered from the rest of the system. The lime kiln is usually fuelled by oil or gas, and requires on average 2.3 GJ/t pulp fuel and 15 kWh/t pulp electricity [10, 14, 16]. The Canadian department of the office of energy recorded a 1.2 GJ/ADt from natural gas and 50 kWh/ADt pulp for the lime kiln and causticizing stages.

2.1.7 Air Separation Unit

A crucial piece that is required for this project is an air separation unit. Air is purified as it is pulled into the unit through adsorption. The air is then compressed to 6 bar and dropped to -180 degrees Celsius. Separation occurs when the oxygen with higher boiling point drains to the bottom, while nitrogen is evaporates to the top. [31]

2.1.8 Pulp Drying

Pulp drying is not a necessary task for the paper making process. If the pulp is required to be shipped to a paper mill, however, it must be dried to 20% water. The pulp drying requires a tremendous steam and electricity demand of 4.5 GJ of steam per ton of pulp and 155 kWh/ton of pulp. [10, 14, 16] If the paper mill is located adjacent to the pulp mill, this stage can be ignored saving a large amount of energy.

2.2 Black Liquor Gasification to Syngas

Gasification of biomass is a partial oxidation reaction that converts solid biomass into product gas or synthesis gas (also called syngas)[32]. Primary syngas components are hydrogen (H2), and carbon monoxide (CO), with smaller amounts of carbon dioxide (CO2), methane (CH4), higher hydrocarbons (C2+), and nitrogen (N_2). Reactions occur between temperatures of 500-1400 °C and pressures from atmospheric to 33 bar[32].

The gasification oxidant can be air, steam, oxygen, or a mixture of these gases[32]. Air-based gasification produces a product gas with a heating value between 4 and 6 MJ/m^3 that contains high amounts of nitrogen, which is inert, while oxygen-based gasification produces a high quality product gas (heating value from 10 to 20 MJ/m^3) with relatively high amounts of hydrogen and carbon monoxide[32]. Typical components in syngas with various gasifying agents are shown in Table 2 below.

Table 2: Syngas composition from gasification with various gasifying agents [33].

Gasifying Agent	Air	Oxygen-rich	Steam	Oxygen-steam
CO	23	30	39	22
CO_2	18	26	14	35
CH_4	3	13	12	12
H_2	12	25	30	30
N_2	40	2	--	--

Syngas from biomass/black liquor gasification can be utilized in two ways: combustion for heat and power or synthesis to fuels and chemicals. Since the goal of this project is maximum production of transportation fuels from biomass, only processes that are capable to produce syngas for fuels and chemicals synthesis are considered. This requires oxygen-based gasification systems, as air-based systems have a high nitrogen content, which is inert, and lower heating value. Because of the low heating value, air-based product gas is more suitable for heat and power applications. Oxygen for gasification can be supplied either from an Air Separation Unit (ASU) or from steam for indirectly heated systems[32].

The primary input to the integrated pulp and paper mill gasification system for syngas generation is kraft black liquor at about 80% solids. Gasification of black liquor can be classified as high temperature (>700 °C) or low temperature gasification (<700 °C), depending on whether the reactions occur above or below the melting point of the inorganic alkali salt mixture formed during gasification[34]. High temperature gasification produces synthesis gas that is mainly hydrogen (H_2) and carbon monoxide (CO). Low temperature gasification produces product gas that requires tar cracking and conversion to synthesis gas via reforming [34].

There are two major designs appropriate for black liquor gasification to syngas for transportation fuels: fluidized bed black liquor steam reforming at low temperatures and high-temperature entrained-flow black liquor gasification.

2.2.1 Low-Temperature Black Liquor Gasification

Low temperature gasification occurs in indirectly heated fluidized beds at about 610°C[35]. Sodium carbonate particles comprise the fluidized bed for black liquor steam reforming at low temperatures. Steam injected at the bottom of the vessel fluidizes the bed particles and also provides a source of water needed for steam reforming[34]. Black liquor is also introduced at the bottom of the vessel through a nozzle system. In a separate refractory-lined combustion chamber, a fuel is burned in a pulse combustion mode to produce hot combustion gas. Pulsed heater bed tubes carry the hot gas to the bed, transferring heat through the tube walls to the bed material where reforming occurs. The steam reacts endothermically with the black liquor char to produce medium BTU synthesis gas with about 65% hydrogen[35]. The condensed phase material leaves the reactor as a dry solid; the sodium exits a sodium carbonate. Bed solids are continuously removed and mixed with water to form a sodium carbonate solution [35].

A gasification process that has been demonstrated for low temperature black liquor gasification has been developed by Manufacturing and Technology Conversion International (MTCI) and marketed by their ThermoChem Recovery International (TRI) subsidiary[34]. The process can be used to produce syngas either for heat and power or for fuels. Full-scale operation has been successful at two plants in North America, but these demonstration facilities treat black liquor from a pulp mill using non- kraft processes. This black liquor is much lower in sulfur than kraft black liquor, creating less severe conditions for the structural materials to endure[35].

There are some advantages to using a low-temperature gasification system. In general, lower temperature gasifiers is carried out in a less severe environment, which can help to reduce problems with materials in the gasifier. The biomass pretreatment requirements are also not as rigorous. This is more important for gasification of extra biomass than for black liquor gasification, because black liquor gasification does not require extensive pretreatment in entrained flow reactors (the alternative to low-temperature gasification). Publication materials from ThermoChem Recovery Incorporated (TRI) claim that advantages to their low-temperature system include a flexibility in the desired product, since the H_2/CO ratio can be varied from 8:1 to 2:1, and flexibility in the feedstock, since the gasifier can handle virtually any type of biomass [35]. Finally, the combustion chamber that burns fuel for indirect heating of the bed is fuel flexible; it can burn natural gas, No. 2 fuel oil, pulverized coal, recycled product gas, etc.[35].

Despite these advantages and the less harsh environment that is kept at lower temperatures, problems with materials still exist, especially for the refractory lining of the pulse combustor chamber[36]. There is a high temperature environment (1300-1500 °C) on the inside of the chamber, while on the outer surface materials interact with H_2, H_2S, steam, and movement of particles in the reactor bed, also causing stress [36]. Another disadvantage is that low temperature reactions allow tar formation, which must be destroyed with a high temperature oxygen-blown tar-cracker at ~1300°C[37]. Cracking of tars is preferred over use of a catalyst to eliminate tars because tars contain potential CO and H_2[38]. At temperatures above 1200 °C, tars are cracked with oxygen and steam (acting as a selective oxidant); no catalyst is needed [38].

2.2.2 High-Temperature Black Liquor Gasification

For fuels and chemical production, it is beneficial to conduct gasification at high temperatures for several reasons. At temperatures above 1200 °C, biomass gasification produces "little or no methane, higher hydrocarbons or tar, and H_2 and CO production is maximized without requiring a further conversion step"[32]. Gasification of black liquor is considered to be "high temperature" at ranges between 950-1000°C (as opposed to >1200°C for other biomass) due to the catalytic effect of the additional materials and chemicals in the black liquor mixture[39].

The two most common designs for high temperature gasification are fluidized beds and entrained flow gasifiers. Bubbling fluidized beds (BFB) force a gas (air or oxygen) through a bed of fine, inert sand or alumina particles to a point when the gas force equals the force weight of the solids. At this "minimum fluidization", particles appear to be in a "boiling state" [32]. Circulating Fluidized Beds (CFB) operate at gas velocities greater than the "minimum fluidization", which creates biomass particle entrainment in the exiting gas stream. As a result, particles in the gas stream must be separated from the gas with a cyclone and then channeled back to the reactor[32]. Like the BFB, high conversion and heat transfer is achieved, but the CBB heat exchange is less efficient than the BFB and high gas velocities may cause equipment damage[32].

Directly-heated bubbling fluidized bed (BFB) gasifiers are preferred over circulating fluidized bed reactors (CFB) because the BFB technology has been demonstrated more widely. A BFB provides a high heat transfer rate between biomass, inert particles, and the gas and high biomass conversion is achievable[32]. Also, CFB gasifiers have not been demonstrated using oxygen as the oxidant[32]. Both technologies are capable of producing synthesis gas from biomass at high temperatures, but further research in design and processing schemes is required.

Entrained flow gasifiers are common reactors for non-catalytic production of syngas from biomass and black liquor. Entrained flow gasification of black liquor is based on the design of a high-temperature, oxygen-blown gasifier developed by Chemrec, shown in Figure 2. The gasifier is similar to the KruggUhde/Shell slagging entrained-flow gasifier for coal gasification at higher temperatures. Direct gasification occurs at high temperatures (950-1000°C) and high-pressures (32 bar) to produce an energy-rich synthesis gas[19]. Chemrec's high-temperature, high-pressure, oxygen-blown entrained flow gasifier is at the core of a novel process called Black Liquor Gasification with Motor Fuels Production (BLGMF). This process was initiated within the EU Altener II program in 2001.

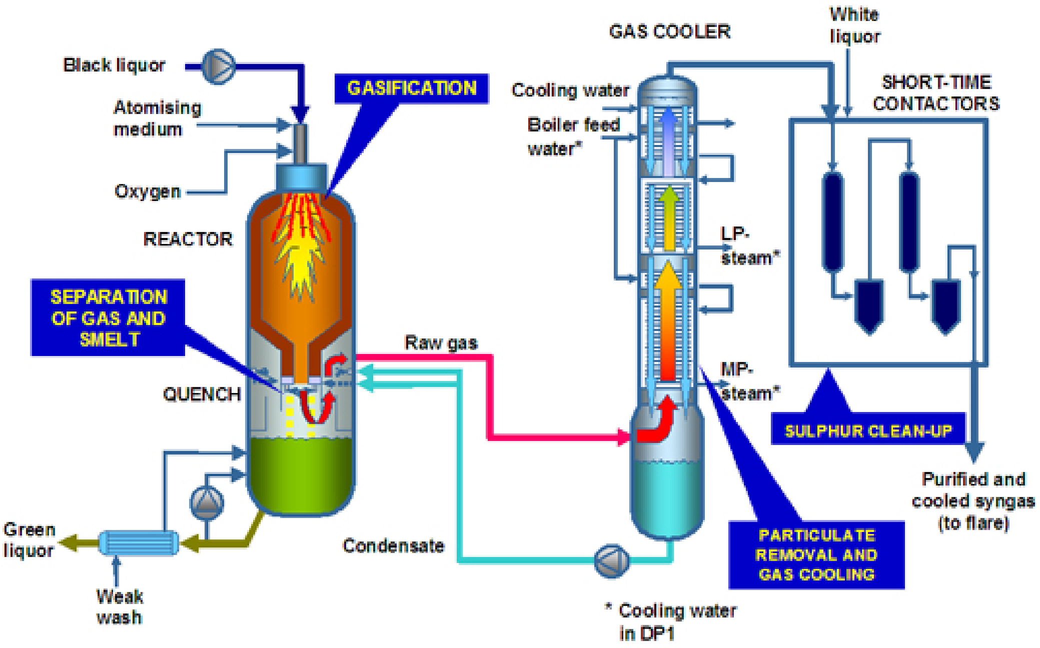


Figure 2: Chemrec gasification process [41].

The slagging, entrained flow gasifier is highly regarded for gasification of black liquor and also for coal and biomass. The technology has been proven for decades for coal gasification on a large scale. In general, the single step gasification with entrained flow gasifier is preferred over two-step fluidized bed gasification and tar cracking as high temperatures inside the reactor prevent significant formation of tar [8]. Another advantage to the entrained flow design is that the use of an oxygen-blown gasification system over air-blown requires a much smaller sized reactor, which can save money [36].

Despite these advantages, there are still drawbacks to using a high-temperature system for gasification of black liquor and biomass. Because molten inorganic alkali salt compounds create a severe environment inside the reactor, one of the most critical issues associated with high-temperature, high-pressure gasification is containment materials[34]. In order to handle this, two basic gasifier designs are considered: a refractory brick design or a cooling screen. The refractory brick design is a thick refractory lining within a metal pressure vessel[34]. The cooling screen is an alternative method which incorporates a refractory-coated helical coiled metal tube that contains pressurized cooling water[34]. This design has been used successfully in coal gasification, but has not been demonstrated to endure molten smelt from high temperature black liquor gasification[34]. Both designs are being tested at pilot plants in Pitea, Sweden.

Use of an oxygen-blown system has advantages for syngas product quality and size requirements of the gasifier, but supplying oxygen for gasification is expensive. Usually an Air Separation Unit (ASU) is required. Finally, an important barrier to the use of biomass in entrained flow reactors is the pretreatment necessary to handle the biomass. It is much more difficult to pulverize biomass particles to sizes required for entrained flow reactors than it is for coal particles. This pretreatment barrier is not a problem for the Chemrec design, as black liquor is filtered and then pressurized and pumped to the gasifier with no size reduction necessary. But if extra biomass is to gasified as well, it will be important to consider pretreatment requirements

2.2.3 Black Liquor Gasifier Recommendation

The goal of this project is to maximize the production of transportation fuels. Based on the advantages and disadvantages associated with high- and low-temperature gasification systems for black liquor and the need for high-quality syngas for fuel production, an entrained flow gasifier design should be the central focus of integrated pulp mill black liquor gasification since very little tar is produced and its similarity to coal gasification can be useful in designing an integrated process for gasification of coal and extra biomass to syngas. Finally, Oak Ridge National Laboratory has concluded that for pulp mills using the kraft process, high-temperature high-pressure systems are more efficient[42]. All of these reasons affirm that high-temperature, high-pressure oxygen-blown entrained flow gasification is the best available option for a black liquor gasification system.

An average Kraft pulp mill in the U.S. generates about 3420 tons of dry black liquor solids per day. At this scale, estimations using Chemrec's high-temperature black liquor gasification process to synthesize DME predict a fuels yield of about 824 tons/day . An economically efficient DME plant would ideally generate 1-2 million tons DME per year, which would require a 3- to 7-fold increase in capacity. Increasing the yield of chemicals and fuels and exploiting economies of scale calls for additional gasifier feedstock such as extra black liquor, woody biomass, and/or coal. In areas of the southeast U.S. where many pulp and paper mills are concentrated it may be possible to import more black liquor. In other locations, importing extra black liquor and/or biomass results in transportation costs that often reverse the economies of scale for large-scale gasification of this feedstock. Therefore, coal may be an attractive option for gasification with black liquor.

To minimize costs, gasification of coal and black liquor should occur in the same reactor. High-temperature entrained flow gasifiers with similar operating conditions have been designed separately for coal and black liquor feedstocks. It may be possible to co-gasify black liquor and coal to produce larger yields of high quality synthesis gas for further processing to Fischer-Tropsch liquids and/or DME. Several existing designs for black liquor gasification can handle other types of feedstocks, but to our knowledge, there is no current process design for the co-gasification of coal and black liquor to produce synthesis gas.

2.2.3 Coal Gasification Technology

High-temperature entrained flow gasification produces hot syngas and a molten slag of fuel mineral matter. Three existing designs are popular for entrained flow coal gasification: the Shell process, the GE/Texaco, and the Dow/Destec process. The Shell gasifier is a dry-fed gasifier, while the Texaco and Destec designs are single-stage and two-stage slurry-fed gasifiers, respectively. This project considered the popular and commercially-available technology of Shell and Texaco gasifiers for co-gasification of black liquor and syngas. Similar downstream processes can be used for the Shell and Texaco gasifier designs [43]. A Shell gasifier generates syngas with a lower moisture content and lower H_2/CO ratio than the Texaco design, as shown in Table 3. A higher amount of moisture in the Texaco gasifier syngas and a greater overall syngas volume corresponds to greater heat recovery in the downstream syngas cooler [43].

Table 3: Average syngas composition from Shell and Texaco entrained flow gasifiers.

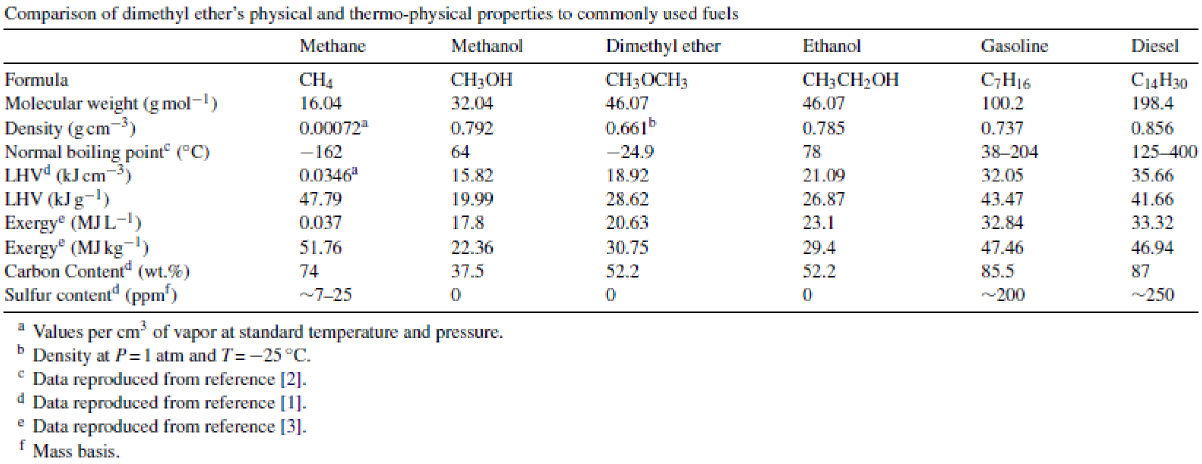
Component (mol %)	Shell	Texaco
H_2	27.6	28.6
CO	61.3	38.4
CO_2	2.2	12.6
CH_4	0.1	0.2
N_2	4.1	1.0
H_2S	1.2	1.0
H2O	2.5	17.4
Ar	0.8	0.7
H_2/CO	**0.45**	**0.74**

2.3 Background of DME Synthesis

2.3.1 Properties of DME

Dimethyl ether (DME) is the simplest ether with chemical formula: CH_3OCH_3. DME has similar properties to LPG in that it is a gas at ambient temperature and atmospheric pressure. It becomes a colorless clear liquid at 6 atmosphere at ambient temperature or at atmospheric pressure and a temperature of -25°C[44]. DME is a clean fuel that contains on sulfur or nitrogen compounds, has extremely low toxicity for humans, and has no corrosive effect on metals. Currently, the major usage of DME is as a propellant in the aerosols industry. In addition, it can be used as a clean burning fuel in diesel engines, as a household fuel (LPG alternative) for heating and cooking, as a fuel for gas turbines in power generation, as a fuel for fuel cells, and as a chemical feedstock for higher ethers and oxygenates. Its physical and thermo-physical properties of dimethyl ether compared to the other fuels are detailed in Table 2 [2].

Table 4: Comparison of dimethyl ether's physical and thermo-physical properties to commonly used fuels.



Comparison of dimethyl ether's physical and thermo-physical properties to commonly used fuels

	Methane	Methanol	Dimethyl ether	Ethanol	Gasoline	Diesel
Formula	CH_4	CH_3OH	CH_3OCH_3	CH_3CH_2OH	C_7H_{16}	$C_{14}H_{30}$
Molecular weight ($g\,mol^{-1}$)	16.04	32.04	46.07	46.07	100.2	198.4
Density ($g\,cm^{-3}$)	0.00072[a]	0.792	0.661[b]	0.785	0.737	0.856
Normal boiling point[c] (°C)	−162	64	−24.9	78	38–204	125–400
LHV[d] ($kJ\,cm^{-3}$)	0.0346[a]	15.82	18.92	21.09	32.05	35.66
LHV ($kJ\,g^{-1}$)	47.79	19.99	28.62	26.87	43.47	41.66
Exergy[e] ($MJ\,L^{-1}$)	0.037	17.8	20.63	23.1	32.84	33.32
Exergy[e] ($MJ\,kg^{-1}$)	51.76	22.36	30.75	29.4	47.46	46.94
Carbon Content[d] (wt.%)	74	37.5	52.2	52.2	85.5	87
Sulfur content[d] (ppm[f])	~7–25	0	0	0	~200	~250

[a] Values per cm^3 of vapor at standard temperature and pressure.
[b] Density at $P = 1$ atm and $T = -25$ °C.
[c] Data reproduced from reference [2].
[d] Data reproduced from reference [1].
[e] Data reproduced from reference [3].
[f] Mass basis.

2.3.2 Features of DME Synthesis Technologies

2.3.2.1 Two-stage and Single-stage dimethyl ether synthesis processes

DME can be produced from a variety of sources from coal, natural gas, biomass and municipal solid waste. Today, world's production of DME by means of methanol dehydration amounts to some 150000 ton/year[45]. It can also be manufactured directly from synthesis gas (mainly composed of CO and H_2) produced by coal/biomass gasification or natural gas reforming processes, i.e. converting syngas to methanol and then further converting the methanol to DME in the same reactor. This direct syngas to DME process (single-stage process) has more favorable in thermodynamic factors than methanol dehydration synthesis does, lower cost and very high CO conversion[46]. Some direct syngas to DME synthesis technologies have been commercialized. For example, Air Products and Chemicals, Inc. has developed the LPDME^{TM} process (Liquid Phase Dimethylether) for the production of DME from coal synthesis gases[47]. The JFE Holdings, Inc. has developed a slurry phase DME synthesis process with high syngas conversion rates and DME selectivity[48]. Topsoe's direct DME synthesis process has a very low plant investment that the largest impact to the production cost will be the cost of the natural gas feedstock.

The reactions in a single-stage syngas to DME process are as follows:

$$CO + 2H_2 \leftrightarrow CH_3OH \qquad H = -90.29 \text{ kJ/mol}$$

$$2CH_3OH \leftrightarrow CH_3OCH_3 + H_2O \qquad H = -23.41 \text{ kJ/mol}$$

$$H_2O + CO \leftrightarrow CO_2 + H_2 \qquad H = -40.96 \text{ kJ/mol}$$

The overall reaction is:

$$3CO + 3H_2 \leftrightarrow CH_3OCH_3 + CO_2 \qquad H = -244.95 \text{ kJ/mol}$$

2.3.2.2 Gas phase and liquid phase DME synthesis processes

Dimethyl ether can be synthesized both in gas phase and in liquid phase. Gas phase DME synthesis processes, in general, suffer from the drawbacks of low hydrogen and CO conversions per pass, along with low yield and selectivity of DME, coupled with a high yield of carbon dioxide. These processes are typically expensive due to high capital costs for reactors and heat exchangers, and high operating costs due to inefficient CO utilization and high recycle rates. Using an inert liquid as a heat sink for highly exothermic reactions offers a number of opportunities in syngas processing. Heat generated by the exothermic reactions is readily accommodated by the inert liquid medium. This enables the reaction to be run isothermally, minimizing catalyst deactivation commonly associated with the more adiabatic gas-phase technologies.

The liquid phase, single-stage DME synthesis process, investigated in great detail, incorporates the sequential reaction of methanol synthesis and methanol dehydration in a slurry phase reactor system[49, 50]. Combining the reversible reactions in a single-stage makes each reaction thermodynamically more favorable by utilizing its inhibiting products as reactants in the subsequent reaction. In addition to the superior heat management allowed by the liquid phase operation, the synergistic effect of these reactions occurring together yields higher quantities of

DME than that could be obtained from sequential processing. The process is based on dual-catalytic synthesis in a single reactor stage, and also based on a combination of an equilibrium limited reaction (methanol synthesis) and an equilibrium unlimited reaction (methanol dehydration).

2.3.2.3 Catalyst systems for the single-stage DME process

Typically, there are two types of catalyst systems for the single-stage DME process[51]. The first type, called the dual catalyst system, consists of a physical mixture of a methanol synthesis catalyst and a methanol dehydration catalyst. The methanol synthesis catalyst is generally a copper and/or zinc and/or aluminum and/or chromium based commercial catalyst while the methanol dehydration catalyst is generally selected from solid acid materials, including γ-alumina, silica alumina, other metal oxides and mixed oxides, crystalline aluminosilicates, crystalline zeolites, clays, phosphates, sulfates, metal halides, acidic resins, supported phosphoric acid, and heteropoly acids.

Among them, γ-Al_2O_3 has been mostly employed due to its low price, easy availability and high stability. In gas phase applications using a fixed or fluidized bed reactor, the powders of the two catalysts can be mixed followed by being formed into pellets or beads; or, separate pellets or beads can be prepared of the two catalysts. The pellets can be placed in a fixed bed reactor either in well mixed form or in a layer-by-layer arrangement. In liquid phase applications using a slurry bed reactor containing an inert liquid medium, a powder mixture of the two catalysts can be directly used.

In the second type of catalyst system for the single-stage DME process, the two functionalities are built into a single catalyst. This has been achieved either by coprecipitating methanol synthesis and dehydration components together to form one catalyst, or by precipitating methanol synthesis components onto an existing, high surface area solid acid material.

Regardless of which type of catalyst system is used and regardless of whether the process is conducted in the gas or liquid phase, maintenance of the catalyst activity is a major challenge. This is especially true when a dual catalyst system is used. Which mainly contributed to the truth that acidic component and the $Cu/ZnO/Al_2O_3$ component are totally different; the lateral interactions between the two components must be considered for the direct synthesis of DME. The currently used industrial $Cu/ZnO/Al_2O_3$ catalysts are usually operated at 220–280 ^oC. The reaction at lower temperature leads to the low reaction activity, while higher temperature results in the sintering of the catalysts. Thus, an ideal dehydration component must be operated at the temperature range for the $Cu/ZnO/Al_2O_3$ catalyst if it is used with $Cu/ZnO/Al_2O_3$ for the direct synthesis of DME. It must be highly active and stable in the temperature range from 220 to 280 ^oC.

Among the solid acids used for methanol dehydration, H-ZSM-5 and γ-Al_2O_3 are the two catalysts that have been studied intensively both for academic and commercial purposes[52]. They can be used for the direct dehydration of methanol to DME or as the dehydration components in the STD process. H-ZSM-5 was reported to be a good dehydration catalyst by several groups. For example, Ge et al. prepared some bi-functional STD catalysts using H-ZSM-5 as a dehydration component[53]. Kim et al. reported that both Na-ZSM and H-ZSM-5 zeolites could be used as effective dehydration components in STD process[54]. They pointed out that the optimized ZSM-5 composition in the admixed catalysts was determined by the acid strength of the acid component. On the other hand, some researchers reported that hydrocarbons were formed at 543K or at higher temperatures with H-ZSM-5 zeolite as a dehydration component[55-57], and the CO_x conversion decreased rapidly with time on-stream in the STD process[55]. This is due to the strong acidity of the H-ZSM-5 that catalyzes the conversion of methanol to hydrocarbons and even coke. Selective poisoning of the strong acid sites by Na^+ or NH_3 on the HZSM-5 inhibited the hydrocarbon formation and enhanced the catalyst stability. Although the DME selectivity is high for methanol dehydration on γ-Al_2O_3, the γ-Al_2O_3 exhibits much lower activity than that of H-ZSM-5[55-57]. Some researches ascribed the low activity to its Lewis acidity. Reaction mechanisms have been suggested for methanol dehydration over solid-acid catalysts. Knozinger and coworkers[56] proposed that the DME was formed via a surface reaction between an adsorbed methanol on an acidic site and an adsorbed methoxy anion on a basic site. Bandiera and Naccacheproposed that Brønsted acid–Lewis base pair sites might be responsible for DME formation in methanol dehydration over an H-mordenite[57].

There are catalyst stability problems that have to be addressed in the single-stage DME process. The reasons for the instability of catalysts include: first, it can be due to the great amount of heat released from high syngas conversion, especially in the case of fixed bed operations, because the methanol synthesis reaction is highly exothermic. When a methanol synthesis catalyst is used by itself in a once-through operation in a fixed bed, its activity normally cannot be fully utilized, because the heat released from higher syngas conversion cannot be adequately dissipated. This, in addition to the hot spots and temperature over-shooting commonly occurring in fixed bed reactors, would cause the sintering of copper in the methanol catalyst, leading to catalyst deactivation. Since the single-stage DME process provides much higher syngas conversion per pass, one would expect more severe methanol catalyst deactivation in a fixed bed operation if the potential conversion of the process is to be completely realized.

Secondly, the introduction of the acid functionality into the catalyst system also introduces additional problems. Strong acid sites will cause coke formation, leading to the deactivation of the dehydration catalyst. High temperature in a fixed bed reactor caused by high syngas conversion, hot spots, and temperature over-shooting will make this more of a problem.

The third problem is the compatibility between the methanol synthesis catalyst and the dehydration catalyst, when a dual catalyst system is used. The report by X. D. Peng et al. mentioned above shows that the rapid and simultaneous deactivation of methanol synthesis and dehydration catalysts is caused by a novel mechanism, namely, an interaction between the two catalysts. Again, the problem is related to the acidity of the dehydration catalyst--more rapid deactivation was observed when the dehydration catalyst contains acid sites of greater strength. This detrimental interaction, although not reported in the literature yet, should also occur in the gas phase operation when intimate contact between the two catalysts is provided.

In summary, there are three catalyst stability problems associated with dual catalyst systems used in current single-stage DME processes: (i) sintering of the methanol catalyst in fixed bed operation; (ii) coke formation on dehydration catalysts; and (iii) detrimental interaction between the methanol synthesis and methanol dehydration catalysts. The first problem is related to heat management, and can be circumvented by employing liquid phase reaction technologies; better heat management can be attained in a slurry phase reaction because of the presence of an inert liquid medium and better mixing. The second and the third problems are related to the acidity of the dehydration catalyst in a dual catalyst system. Therefore, a dehydration catalyst with the right acidity is crucial for the stability of a dual catalyst system.

Work on liquid phase syngas-to-DME processes and catalysts are summarized as follows:

U.S. Patent[58] and European Patent[59] to Air Products and Chemicals Inc. teach a liquid phase DME process. Syngas containing hydrogen, carbon monoxide and carbon dioxide is contacted with a powder mixture of a copper-containing commercial methanol synthesis catalyst and a methanol dehydration catalyst in an inert liquid in a three phase reactor system. The dehydration catalyst is selected from the group of alumina, silica alumina, zeolites, solid acids, solid acid ion exchange resins, and mixtures thereof.

The patent to NKK Corporation teaches a catalyst system for a slurry phase single-stage DME process. The catalyst was prepared by pulverizing a powder mixture of a copper based methanol catalyst and a pure or copper oxide doped alumina, compressing to bind said oxides, and then pulverizing again to form powders to be used in a slurry reactor[60].

In addition to dehydration catalysts used in the dual catalyst system of the single-stage DME process, the prior art also teaches catalysts which are specifically designed for methanol dehydration to DME and not necessarily for mixing with a methanol synthesis catalyst. The patents to DuPont teach improved methanol dehydration catalysts with enhanced reaction rate and reduced coking and byproduct formation, as compared to the conventional phosphoric acid-alumina catalysts[64-66]. The catalysts include aluminotitanate and aluminosilicate prepared by either coprecipitation or impregnation.

2.3.2.4 DME Synthesis Reactors

Catalytic reactions generally use fixed-bed gas phase reactors, but for exothermic reactions like methanol synthesis, methods must be devised to control temperatures in the reactor. The DME synthesis reaction has a higher equilibrium conversion rate than methanol synthesis, which produces large amounts of exothermic reaction heat. Unless one is careful to remove reaction heat and control temperatures, temperatures rise to excessive levels, which not only hurt the reaction equilibrium but also have the potential to disrupt catalyst activity. Conceptual diagrams of fixed bed reactor, fluidized bed reactor and slurry bubble column reactor are shown in Fig.3. As can be seen, in slurry bubble column reactor, fine catalyst particles are suspended in the oil solvent in the slurry. The reaction occurs as bubbles of reactant gas rise to the surface. The reaction heat is quickly absorbed by the oil solvent, which has a large heat capacity. The bubbles agitate the oil solvent, and because the oil solvent has a high heat transfer rate, temperatures inside the reactor are maintained uniform, making it easier to control temperatures. The device stands out for its simple structure and relatively few constraints in terms of catalyst form and strength compared to the fixed bed reactor.

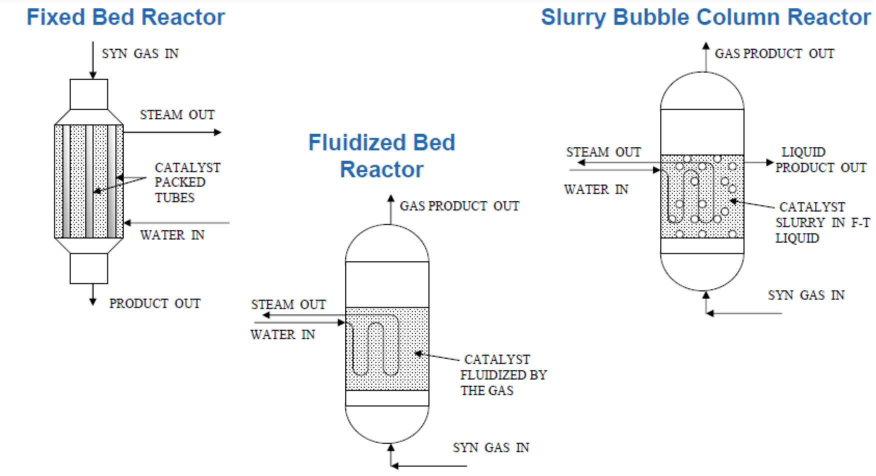


Figure 3: Conceptual diagrams of different types of reactors.

2.3.2.5 Commercial DME synthesis technologies

Haldor Topsøe designed special fixed-bed reactor to solve temperature problems in DME production. The reaction from synthesis gas to DME is a sequential reaction, involving methanol as an intermediate. The first part of the reaction from synthesis gas to methanol is quite exothermal and it is limited by equilibrium at a fairly low temperature. Therefore, the first part of the reaction takes place in a cooled reactor, where the reaction heat is continuously removed, and the equilibrium is approached at optimum conditions. The second part of the reaction from methanol to DME is much less exothermal, and the equilibrium is limited at a different temperature. Therefore, this part of the reaction takes place in a separate adiabatic fixed bed reactor. Consequently, the two-stage reactor concept permits both parts of the sequential reaction to take place at optimum conditions, while at the same time the synthesis section becomes more similar to a conventional methanol synthesis loop. With respect to technology verification at industrial scale, the only major difference between the oxygenate synthesis and the methanol synthesis is the second stage adiabatic reactor, loaded with the proprietary Topsøe dual-function catalyst. This dual-function catalyst is a unique product, developed by Topsøe in the early 1990's. Since then, this catalyst has been tested in excess of 30,000 hours in a Topsøe DME process demonstration unit. Due to the extensive catalyst testing and the simple adiabatic reactor configuration, the technology risk in the DME synthesis is minimal.

Consequently, all the process steps have been tried and approved in industrial operation. Product separation and purification – The layout of the separation and purification section depends on the specific demands for product purity. Obviously, the lower demands for product purity, the lower investment and energy consumption. In fact, substantial savings are achieved by producing fuel grade DME, i.e. DME containing minor amounts of methanol and water.

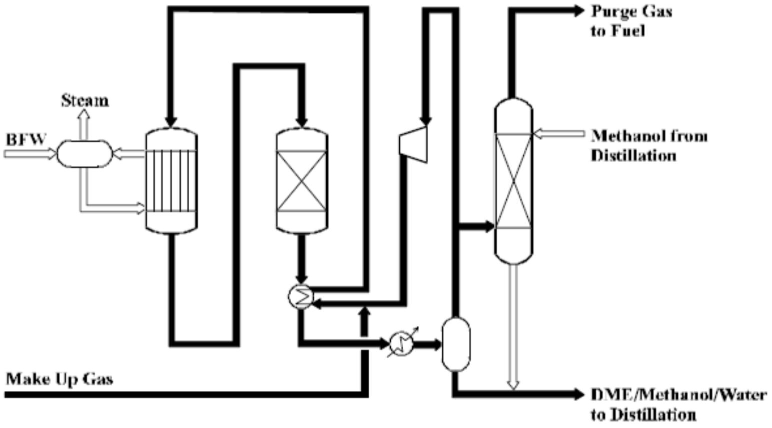


Figure 4: Topsøe gas phase technology for large scale DME production.

The process developed by the JFE Group (hereinafter referred to as the JFE Process) has reached a high degree of completion, and consists of the element technical development described below.

Because the reaction heat in the DME synthesis reaction is large, it is necessary to remove reaction heat and perform reaction temperature control properly in order to prevent a reduction of equilibrium conversion and catalyst deactivation due to temperature rise. The JFE Process uses a slurry bed reactor in which the reaction is promoted by placing the synthesis gas in contact with the catalyst in slurry in which the catalyst is suspended in a reaction medium. Because the heat capacity and thermal conductivity of the reaction medium are both large, the reaction heat is absorbed by the reaction medium and leveling of the temperature in the reactor is easy. In their demonstration plant, efficient reaction temperature control is performed by changing the pressure of steam generated by a heat exchanger installed in the reactor. With the slurry bed reactor, it is also possible to exchange the catalyst during operation when necessary. The highest equilibrium conversion rate was achieved with the composition $H_2/CO = 1.0$.

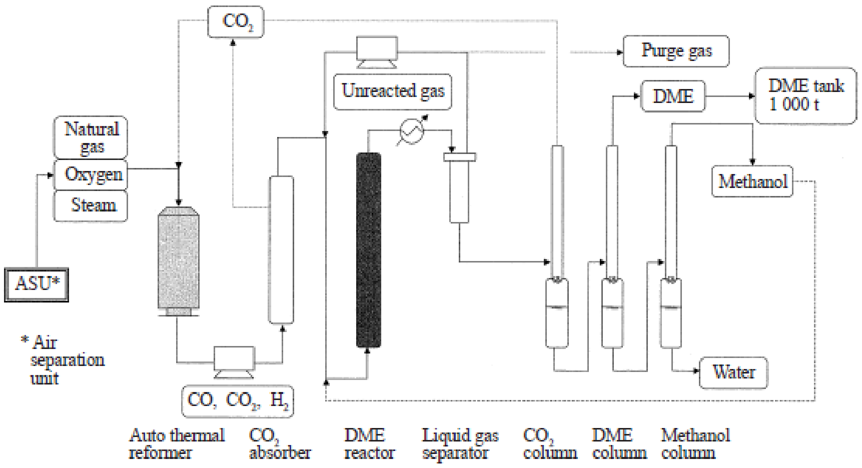


Figure 5: JFE liquid phase technology for large scale DME production.

2.3.3. DME separation and purification

Due to a chemical synergy among the three reactions in the single-stage DME synthesis process, the single pass syngas conversion in the DME reactor, or productivity is significantly greater than that in a methanol synthesis reactor. Since reactors for syngas conversion are expensive equipment for high-pressure operation at elevated temperatures, greater conversion or productivity means smaller DME reactors, associated equipment, and operation. This can reduce the cost in the syngas conversion part of the process and possibly lead to a more economic process for DME production than the traditional two-step process, namely, methanol synthesis followed by methanol dehydration in two separate reactors[61].

A number of separation schemes have been disclosed in the prior art for the one-step syngas-to-DME process. U.S. Patent 5908963 chooses to avoid the CO_2 problem by operating a fixed bed syngas-to-DME reactor in a H_2 rich regime[62]. The reactor effluent is cooled in a condenser. The condensed reaction products, methanol, water and dissolved DME, are sent to two distillation columns for DME-methanol/water separation and methanol-water separation, respectively. Part of the gaseous stream from the condenser, containing unconverted syngas, DME and a small amount of CO_2, is recycled back to the DME reactor; the rest is sent to a scrubbing column to recover DME. Methanol, from the water-methanol column, is used as the scrubbing solvent. The DME-methanol mixture from the scrubbing column is fed to a methanol dehydration reactor. Due to the high H_2:CO ratio in the reactor feed, CO_2 formation is suppressed with a small amount of CO_2 (e.g., 3 mol. %) in the reactor loop. However, the reactor is operated in a regime far away from the optimal conditions.

Methanol is also used as the scrubbing solvent in separation scheme disclosed in a paper by Bhatt et al, for a 10 tons/day one step syngas-to-DME pilot plant (referred to as Bhatt's paper hereafter)[63]. In this separation scheme, the effluent from a slurry phase syngas-to-DME reactor is first cooled to condense methanol and water out. The rest of the effluent is fed to a scrubbing column which uses methanol as a solvent. All DME, methanol and CO.sub.2 are removed from the unconverted syngas in the scrubbing column. The bottom stream from the scrubber is sent to a distillation column to regenerate methanol from DME and CO.sub.2. Due to the trial nature of the work, the DME and CO.sub.2 mixture was sent to flare without further separation.

A paper by Xie and Niuexamines different scrubbing solvents for DME separation, including methanol, water and methanol/water mixture[64]. Methanol and 50/50 methanol/water mixture exhibited similar solubility to DME; both are better than pure water.

Chinese patent application No.1085824A to Guangyu et al. describes a downstream separation scheme for a one-step syngas-to-DME process[65]. The water and methanol in the effluent from a fixed bed syngas-to-DME reactor are removed through a condenser and an absorption column, respectively. The rest of the reactor effluent enters into an extraction column. The unconverted syngas leaves the column from the top and is recycled to the DME reactor. A solvent is used in the extraction column to remove DME from the recycle stream. Water and ethanol are two solvents taught in the patent. When water is used as the extraction solvent, 5% of the CO_2 in the effluent gas is also dissolved in the water. The water solution is sent to a stripping-distillation column to recover product DME and regenerate water. When ethanol is used as the solvent, considerable amount of CO_2 (40%) is dissolved in the ethanol along with DME. The CO_2 from the bottom of the extraction column is first removed by some method (not specified). The rest is sent to a stripping-distillation column for DME-ethanol separation.

A downstream CO_2 separation scheme for a one-step syngas-to-DME process is described in a paper by Ohno, Ogawa, Shikada, Inoue, Ohyma, Yao and Kamijo, International

DME Workshop, Japan (Sept. 7, 2000), (referred to hereafter as Ohno's paper)[66]. The DME reactor effluent is chilled to remove DME, CO_2 and methanol from the unconverted syngas, which is recycled to the DME reactor. The CO_2 in the condensed liquid is removed in a CO_2 column. The rest of the liquid is separated in a second column into product DME and methanol. The scheme also includes an amine-based absorption column to remove CO_2 from the syngas generated by an autothermal reformer before the syngas is fed to the DME reactor.

U.S. Pat. No. 6,147,125 to Shikada et al. discloses a downstream separation scheme for a one-step syngas-to-DME process[67]. The methanol and water in the DME reactor effluent is condensed out first. The rest of the effluent is fed to a scrubbing column to remove DME and CO_2 from the unconverted syngas, which is recycled to the DME reactor. DME is used as the scrubbing fluid. The bottom of the scrubbing column is fed into a distillation column to separate CO_2 from DME.

In summary, there are two important cost issues associated with the scrubbing solvent. The first issue is that high solubility toward CO_2 is desirable. Better solubility translates into a smaller scrubbing column, smaller downstream distillation columns and lower refrigeration duty. The second issue is the vapor pressure of the scrubbing fluid. Lower volatility means less negative impact on the DME reactor productivity and lower operating pressure for the downstream product separation section. Therefore, the ideal scrubbing solvent should have high solubility for CO_2 and low volatility. None of the solvents in the prior art possess both of these properties. DME is good at dissolving CO_2 but has high volatility. Methanol is less volatile but its solubility for CO_2 is much to be desired. The current invention provides a means for addressing the limitations of using either DME or methanol as the scrubbing solvent.

2.3.4 DME Utilization

DME can be utilized as an energy carrier in several different areas. It is currently being used in Asia as a clean heating and cooking fuel [68]. India is planning on using DME in power generation plants [69]. However, DME's greatest potential is its use as a transportation fuel. As fuel-cell technology matures, DME can be used in steam reforming or autothermal reforming to created hydrogen at low temperatures [5]. Unfortunately, the wide spread use of fuel cell is in the future. Nonetheless, DME can be used today as a transpiration fuel in compression ignition engines.

The benefit of using DME is that it produces less polluting emissions than standard diesel fuel when used in a compression ignition engine. Figure 6 gives a comparison between diesel fuel and DME combustion [70]. DME produces less hydrocarbon CO and NOx emission. The largest emission benefit is that it produces practically no smoke. This is important since NOx and smoke are the most harmful diesel emissions.

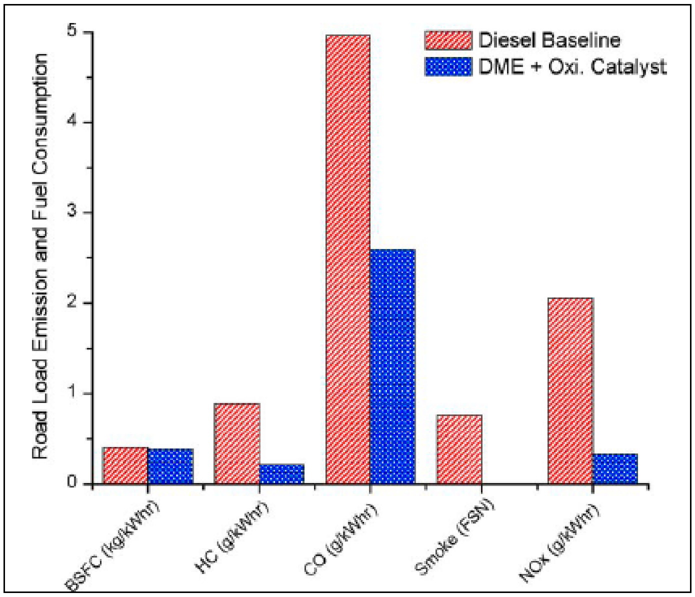


Figure 6: Road load test data comparing engine emissions using diesel and DME.

DME cannot be used in a standard compression ignition vehicle [5]. Changes must be made to account for DME physical properties. Modifications which are necessary deal with the delivery of DME to an engines combustion chamber. The viscosity of DME is ~0.13 kg/m.s @ 25°C and diesel viscosity is from 2.0 to 4.0 kg/m.s @ 25 °C. DME would leak through a standard fuel delivery system due to its lower viscosity. A fuel system with better sealing is required when using DME. Also, the fuel pump and fuel injectors of a standard compression ignition vehicle rely on the lubrication from diesel fuel to prevent wear. A lubricating additive can be added to the DME to make up for its lack of lubrication.

2.4 Fischer-Tropsch synthesis

The Fischer-Tropsch Synthesis (FTS) process has been used to create synthetic fuel since the early 1930's. The process was developed by Prof. Franz Fischer and Dr. Hans Tropsch. Fischer-Tropsch fuels were first created by Germany during World War II due to fuel embargos placed on Germany. Since then, Fischer-Tropsch process has been used to create fuel in regions where petroleum fuels are either Inexcusable, due to politics or economics. In today's society, high prices of petroleum fuel and environmental concerns have created a new interest in Fischer-Tropsch fuels [71].

The Fischer-Tropsch process can create a large array of products, including LPG, naphtha, n-paraffin, co-monomers, gasoline, diesel, ethylene, propylene, butylene, oxygenates, ethane and wax. This portion of the project is concerned with creating Fischer-Tropsch Diesel (FTD) from syngas. The syngas to FTD process starts by passing the syngas through a Fischer-Tropsch reactor where it is made into chains of hydrocarbons using a catalyst. The hydrocarbons are then separated and put through an upgrading process where FTD is made.

2.4.1. Fischer-Tropsch Reactors

The key component in the Fischer-Tropsch process is the FT reactor. These reactors are highly exothermic, on average producing 145 kJ per CH_2 formed[72]. There are two main classes of reactors that are used in producing FTD, multi-tubular fixed bed reactor (TFBR) and fluidized bed reactor [71, 73]. The fluidized bed reactor can also be subcategorized to the circulating fluidized bed (CFB) reactor, ebulating or fixed fluidized bed (FFB) reactor, and slurry-phase bubbling-bed reactor (SPR). The multi-tubular fixed bed reactor and the slurry-phase bubbling-bed reactor are of main interest since they are optimized in the creation of FTD.

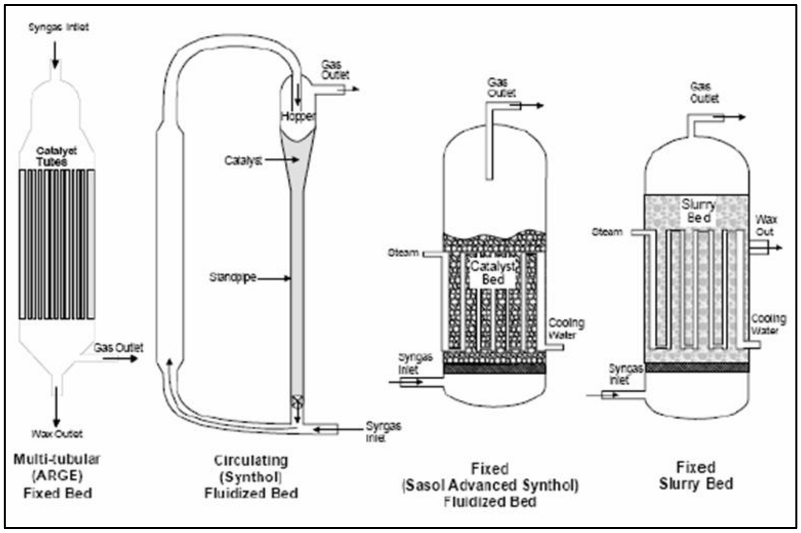


Figure 7: Multi-tubular fixed bed reactor, circulating fluidized bed reactor, ebulating or fixed fluidized bed reactor, slurry-phase bubbling-bed reactor [74].

The circulating fluidized bed reactor and fixed fluidized bed reactor are two phase reactors, of solid and gas phases. They are both High Temperature Fischer-Tropsch (HTFT) reactors operating at 320 to 350ºC. The CFB and FFB utilize only iron-based catalysts. HTFT reactors are geared to produce alkenes and straight run fuel; thus the circulating fluidized bed reactor, fixed fluidized bed reactor are of little interest when diesel production is desired [4, 72].

The multi-tubular fixed bed reactor is composed of thousands of long and narrow tubes containing the catalyst. The tube bundles are immersed in water which acts as a cooling medium. The reactor's temperature is controlled by releasing steam that is created from the water that surrounds the tubs. There is a small distance between the tube walls and catalyst, allowing for high velocities of inlet syngas. Smaller catalyst pellets cause a higher rate of conversion. Narrow tubes, small catalyst and high velocity of syngas cause large pressure differentials throughout the reactor. In order to prevent the pressure differential, narrow tubes are undesirable. However, when taking into account the activity of the catalyst, narrow tubes are preferred for more active catalysts. One of the main advantages of the multi-tubular fixed bed reactor is that no equipment is needed to separate the wax products from the catalyst since the liquid FT products leave the reactor through the bottom of the reactor, separate from the waste gas (Figure 3.1). The most important advantage of this reactor is that its performance can be easily calculated for large scale production [4, 72, 74].

The multi-tubular fixed bed reactor is a Low Temperature Fischer-Tropsch (LTFT) reactor ranging from 220-250 ºC. LTFT reactors are better suited for the creation of heavy hydrocarbons in the form of liquid wax. Later in the process, these long chain hydrocarbons are cracked to formed FTD [4, 71, 72, 74].

The multi-tubular fixed bed reactor can use either iron or cobalt catalysts. Catalyst poisoning can occur when coal or biomass is used in the creation of syngas. An advantage of the TFBR is that only the upper portion of the catalyst may be poisoned, allowing the remaining catalyst to be operational. However, to replace the catalyst in the TFBR, the reactor must be taken off line, which causes expensive downtime [72].

The slurry-phase bubbling-bed reactor (SPR) is a three phase reactor with solid, gas and liquid phases. It is also a LTFT reactor that can utilize both iron and cobalt catalyst. In the SPR small partials of catalyst are suspend in liquid while syngas bubbles propagate through the slurry. The reactor temperature is precisely controlled by steam-filled coils that snake through the slurry. The product hydrocarbons are drawn from the top of the slurry. Light hydrocarbons and un-reacted syngas exit through the top of the reactor.

The SPR reactors have only recently become a viable reactor. The SPR was tested in the 1950's and 1960's; however a viable method of separating the catalyst from the wax product was not invented until 1990 by Sasol [72]. The SPR is also a LTFT reactor which can utilize both iron and cobalt catalysts.

If a catalyst poison enters the SPR, all of the catalyst will be deactivated. Nonetheless, the key advantage of the SPR is that its catalyst can be replaced without taking the reactor offline [72].

2.4.2. Fischer-Tropsch Catalyst

Iron (Fe), Cobalt (Co), Nickel (Ni) and Ruthenium (Ru) -based catalysts are active enough to be used in FTS. However, iron and cobalt are the only catalysts utilized in Fischer-Tropsch synthesis [72] due to the various drawbacks of nickel and ruthenium. Nickel is a strong hydrogenating catalyst which forms much more methane then iron or cobalt. Nickel also converts to carbonyls, thus requiring more catalyst to be added. Ruthenium is the most active but is rare and expensive [71]. Table 5 gives the cost comparison of the four catalysts.

Table 5: Cost scale of Fischer-Tropsch catalyst in 2001 [73].

Catalyst	Cost scale
Iron (Fe)	1
Cobalt (Co)	1000
Nickel (Ni)	250
Ruthenium (Ru)	50000

When comparing iron catalysts to cobalt catalysts, iron requires a lower H_2/Co ratio from .8 to 1.7 because in the reactor, it performs a water gas shift to increase the required H_2/Co ratio [75]. Cobalt requires a water gas shift to be preformed on the syngas before it enters the reactor, to reach its H_2/Co ratio of ~2. Cobalt, however has a longer life and is more active [73]. The higher activity of cobalt is visible by looking at an example given by Dry al. et, in which the percent conversion is compared to the bed length for iron and cobalt catalyst. Dry uses the established kinetic equation for cobalt catalysts (2.4.1) [76] and for iron catalysts (2.4.2) [77] to generate Figure 8.

Cobalt $$rate = \frac{kp_{H2}p_{CO}}{(1+bp_{CO})^2} \qquad (2.4.1)$$

Iron (Fe) $$rate = \frac{mp_{H2}p_{CO}}{(p_{CO}+ap_{H2O})} \qquad (2.4.2)$$

The k and m constants were chosen so that the percent conversion of both catalysts would be equivalent at the catalyst bed entry at 3.15Mpa, thereby giving them the same intrinsic activity. Figure 8 is the plot comparing the activity of the cobalt catalyst to that of the iron catalyst, in terms of percent conversion at a given bed length. The conversion of the iron catalyst is unchanged when the pressure is increased from 3.15Mpa to 6.3Mpa. The cobalt catalyst displays a better conversion even when the intrinsic activity of iron is increased by a multiple of five [73].

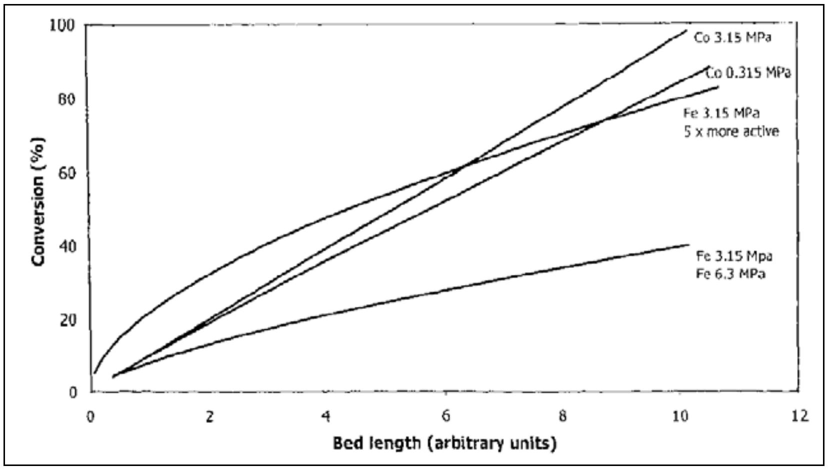
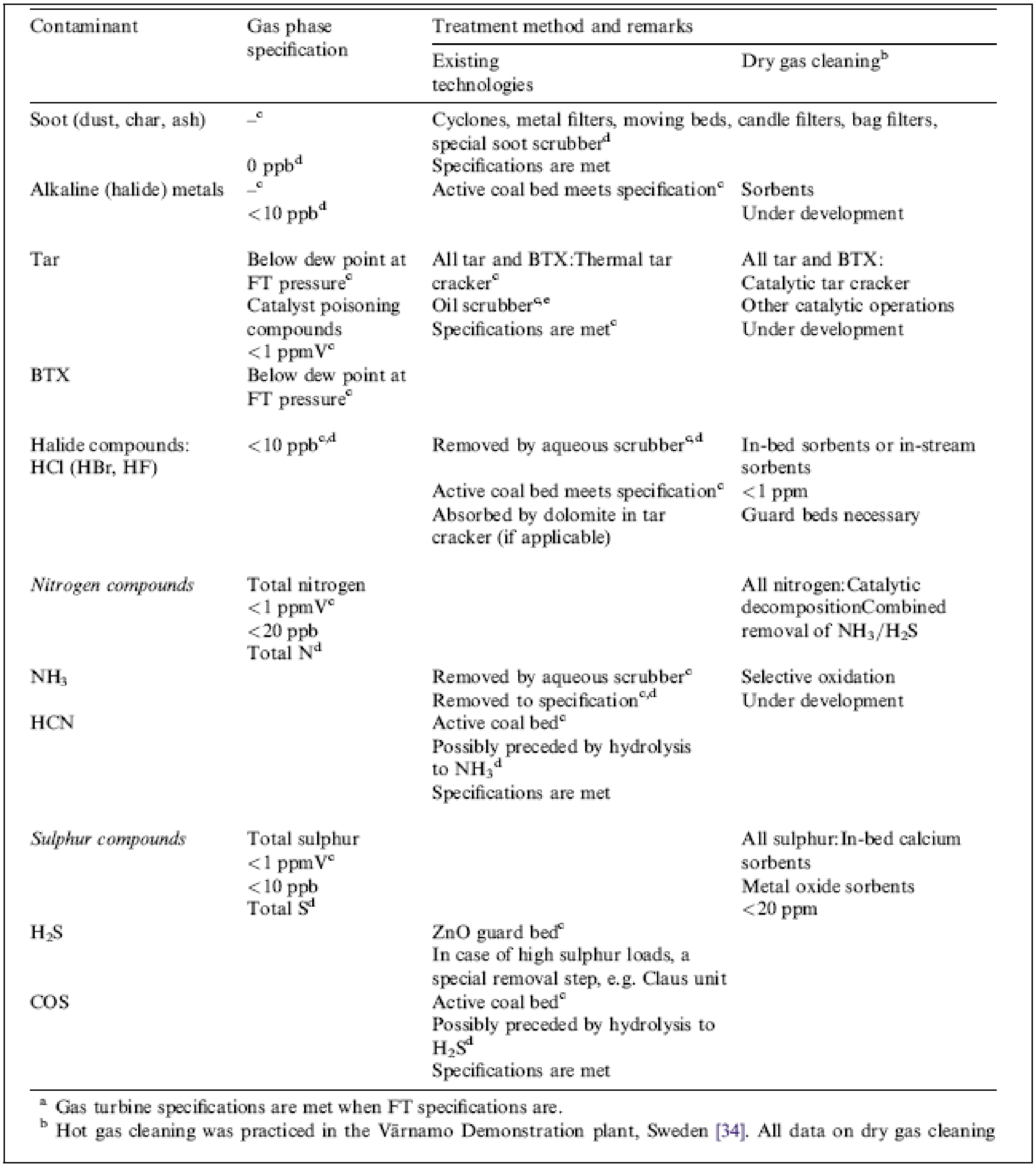


Figure 8: The calculated conversion profiles for LTFT operation with cobalt- and iron- based catalysts.

Catalysts are susceptible to poisons from contaminates. To avoid poisoning, contaminates such as tar, hydrogen sulfide, carbonyl sulfide, ammonia, hydrogen cyanide, alkali and dust particles must be removed from the syngas in a gas cleaning process[78]. The higher cost of cobalt makes it critical to prevent poisoning. Table 6 compiled by Hamlinck et al., lists specification for Fischer-Tropsch synthesis and the effectiveness of wet and dry gas cleaning methods [79].

Table 6: Contaminant specification for cobalt FT synthesis, and cleaning effectiveness of wet and dry gas cleaning [79].



Contaminant	Gas phase specification	Treatment method and remarks: Existing technologies	Treatment method and remarks: Dry gas cleaning[b]
Soot (dust, char, ash)	–[c] 0 ppb[d]	Cyclones, metal filters, moving beds, candle filters, bag filters, special soot scrubber[d] Specifications are met	
Alkaline (halide) metals	–[c] < 10 ppb[d]	Active coal bed meets specification[c]	Sorbents Under development
Tar	Below dew point at FT pressure[c] Catalyst poisoning compounds < 1 ppmV[c]	All tar and BTX: Thermal tar cracker[c] Oil scrubber[c,e] Specifications are met[c]	All tar and BTX: Catalytic tar cracker Other catalytic operations Under development
BTX	Below dew point at FT pressure[c]		
Halide compounds: HCl (HBr, HF)	< 10 ppb[c,d]	Removed by aqueous scrubber[c,d] Active coal bed meets specification[c] Absorbed by dolomite in tar cracker (if applicable)	In-bed sorbents or in-stream sorbents < 1 ppm Guard beds necessary
Nitrogen compounds	Total nitrogen < 1 ppmV[c] < 20 ppb Total N[d]		All nitrogen: Catalytic decompositionCombined removal of NH_3/H_2S
NH_3		Removed by aqueous scrubber[c] Removed to specification[c,d]	Selective oxidation Under development
HCN		Active coal bed[c] Possibly preceded by hydrolysis to NH_3[d] Specifications are met	
Sulphur compounds	Total sulphur < 1 ppmV[c] < 10 ppb Total S[d]		All sulphur: In-bed calcium sorbents Metal oxide sorbents < 20 ppm
H_2S		ZnO guard bed[c] In case of high sulphur loads, a special removal step, e.g. Claus unit	
COS		Active coal bed[c] Possibly preceded by hydrolysis to H_2S[d] Specifications are met	

[a] Gas turbine specifications are met when FT specifications are.

[b] Hot gas cleaning was practiced in the Vārnamo Demonstration plant, Sweden [34]. All data on dry gas cleaning

2.4.3. Fischer-Tropsch Mechanism

The heart of the Fischer-Tropsch reaction is present in the general form of:

$$CO+2H_2 \rightarrow \text{“-}CH_2\text{-”} + H_2O \qquad \Delta H_{298^\circ}=-165 kJ/mol \qquad (2.4.3)$$

In this reaction, syngas contain H_2 and CO come together to form long chains of -CH_2-.[75] There has been disagreement over the exact reaction and order of the reactions since the invention of Fischer-Tropsch in the early 1930's[80]. The reactions that are supposed to be occurring in the Fischer-Tropsch reactor are as follows:

$$nCO + 2nH_2 \rightarrow C_nH_{2n} + nH_2O \qquad (2.4.4)$$

$$CO + 3H2 \rightarrow CH4 + H2O \qquad \Delta H298^o = -247 kJ / mol \qquad \text{methanation} \qquad (2.4.5)$$

$$CO + H2O \rightarrow CO2 + H2 \qquad \Delta H298^o = -41 kJ / mol \qquad \text{(water gas shift)} \qquad (2.4.6)$$

$$2CO \rightarrow C + CO2 \qquad \Delta H298^o = -172 kJ / mol \qquad \text{(Boudouard reaction)} \qquad (2.4.7)$$

$$H2 + CO \rightarrow C + H2O \qquad \text{(coke deposition)} \qquad (2.4.8)$$

Reaction 2.4.4 is the production of heavy hydrocarbons of varying chain length. This is the reaction that dominates when cobalt catalyst is used. Reaction 2.4.5 creates methane gas, which is sent with the offgas to turbines for power creation. Reaction 2.4.6 demonstrates the water gas shift, which creates the H_2 to make up for an inadequate syngas ratio. The water gas shift reaction only occurs for the iron catalyst, requiring a lower temperature reaction. The Boudouard reaction creates carbon and CO_2 , both undesirable products, that required cleaning. To avoid the creation of undesirable products, product selectivity must be utilized in the Fischer-Tropsch process. Product selectivity is accomplished through the use of temperature, pressure and catalyst. Generally, creation of long chain heavy hydrocarbons is accomplished by utilizing high pressures and low temperatures [4].

2.4.4. Fischer-Tropsch Product Selection

The equation that is accepted to predict the chain growth within Fischer-Tropsch synthesis is the Anderson-Schulz-Flory (ASF) distribution [4, 72, 75, 80, 81].

$$x_{Cn} = \alpha^{n-1} (1-\alpha) \qquad (2.4.9)$$

Where X_{Cn} is the molar yield in carbon number α is the chain growth probability factor, N is the length of the hydrocarbon. The "1- α" part of the equation describes the chance that chain growth will terminate [75]. To maximize wax production and thus to maximize FTD production, α should be as high as possible [4, 79]. A plot of the chain growth is given in Figure 9.

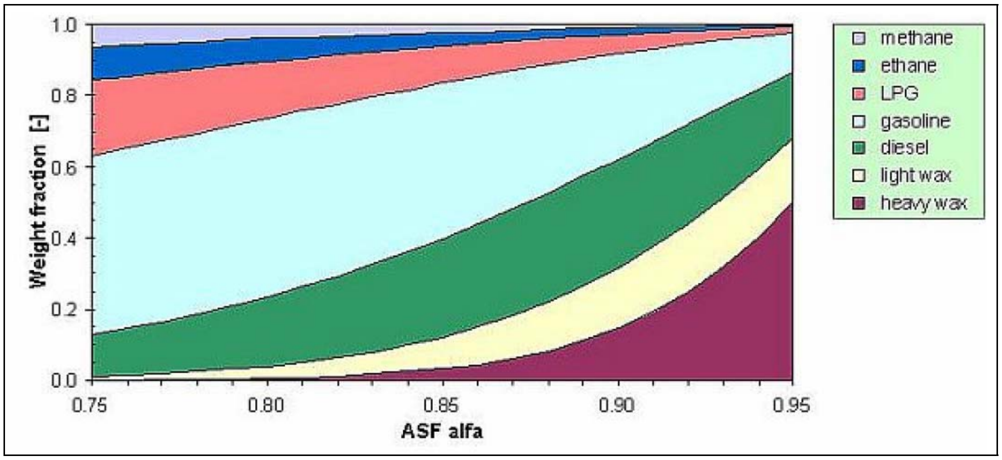


Figure 9: Product distribution for different α for the FT synthesis [82].

The exact path involved in the growth of hydrocarbons during Fischer-Tropsch synthesis is uncertain. It is generally accepted that growth occurs by a stepwise growth of polymerization of monomers [71, 72, 75]]. Figure 10 illustrates the chain growth process.

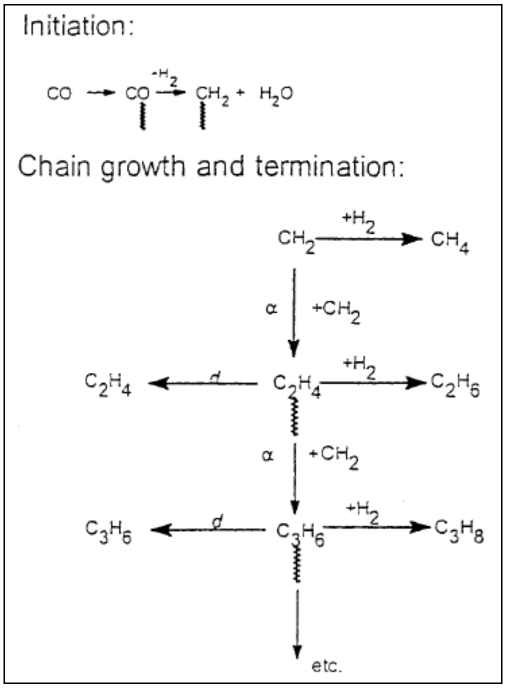
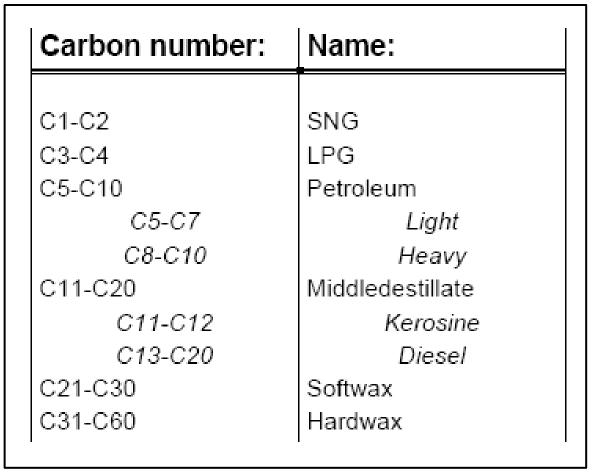


Figure 10: FT stepwise growth process.

The Figure 2.4.4 illustrates the chain growth process where monomers are absorbed by surface -CH_2- units and produce only hydrocarbons. The growth is dependent on α, the growth probability chain, where it has three possible outcomes. It may desorb an alkene, hydrogenate to desorb an alkane or continue to the chain growth process by adding another CH_2 unit [72, 73]. Fischer-Tropsch synthesis grows chains in ranging from C_1 (methane) to C_{60} (heavy waxes). Table 7 gives hydrocarbons by carbon number and their associated names.

Table 7: hydrocarbons and associated names [80].



Carbon number:	Name:
C1-C2	SNG
C3-C4	LPG
C5-C10	Petroleum
C5-C7	*Light*
C8-C10	*Heavy*
C11-C20	Middledestillate
C11-C12	*Kerosine*
C13-C20	*Diesel*
C21-C30	Softwax
C31-C60	Hardwax

As mentioned earlier, the distribution of products is dependent on choice temperature, pressure, catalyst and reactor. Figure 1.4, displays the possible distribution of products for a given probability of chain growth α. Ekbom et.al states that a high diesel production would be targeted at an α of 0.9. Using figure 11 weight percents of 32% middle distillate (C_{12}-C_{20}), 28% naphtha or gasoline (C_5-C_{11}) and 40% waxes (C_{20+}) can be estimated [4].

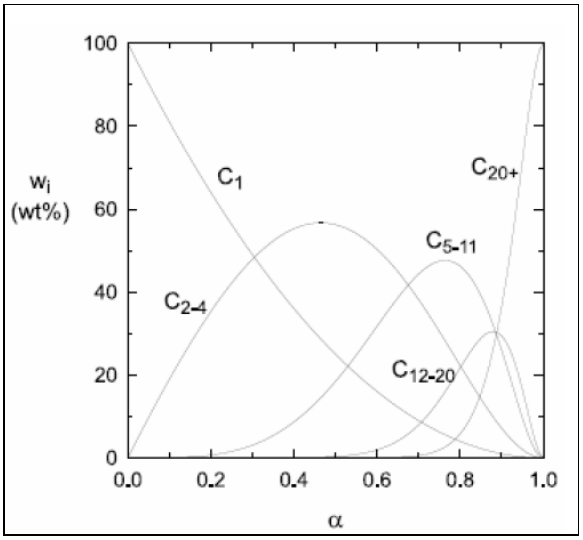


Figure 11: Anderson-Schultz-Flory distribution [80].

2.4.5. Fischer-Tropsch Product Upgrading

Fischer-Tropsch product upgrading is the process in which the hydrocarbons formed in a FT-reactor are separated according to carbon number and processed to end products. T The C_1-C_4 hydrocarbons and unconverted syngas make up what is known as offgases [83]. The offgases can be recycled back into the FT-reactor or used to create electricity in a co-firing process or create hydrogen used to crack the heavy wax to distillates [4]. The C_5-C_{11} hydrocarbons are known as naphtha, which is stove and lighter fuel. Naphtha can also be refined to gasoline. The C_{11}-C_{20} hydrocarbon products are known as the middle distillates [80]. The middle distillates are the target products of FTS geared towards diesel transportation fuel. The C_{12}-C_{20} hydrocarbons are high quality diesel transportation fuels after they have been hydrogenated [84]. The C_{20+} hydrocarbons make up the wax.

Wax is cracked into middle distillates when production is gear towards diesel fuel. The two main methods of upgrading are hydrocracking and isomerisation. Hydrocracking involves hydrogenation via a hydrogenation catalyst and cracking by an acidic catalyst. In this process, the hydrocarbon chains are broken down into to smaller chain. The hydrocracking process is over all exothermic. Hydrocracking plants are mainly configured in single-stage and two-stage configurations. The single-stage process uses hydrogenation to produce naphtha. The two-state process can produce both middle distillates and the naphtha. The process uses nitrogen and sulphur compounds to carry out hydrocracking in two separate reactors. In isomeristion, the straight chained hydrocarbons are branched, to increase octane number and cloud point. This process is done by rearranging the atoms of the hydrocarbons via a catalyst [4, 85].

2.5 Heat and Power Generation

A pulp mill producing bleached kraft pulp generates 1.7-1.8 tons (dry content) of black liquor per ton of pulp. The black liquor contains about half of the energy in the wood chips sent into the digester. Thus, black liquor represents a considerable energy source. To use this energy effectively, concentrated black liquor with 80% of black liquor solids is sent to a Tomlinson recovery boiler to recovery energy and pulping chemicals. Steam from the Tomlinson boiler provides the steam needs to run the pulp and paper mill. Before used in the process, steam is sent to a steam turbine to generate electricity to meet the mill's electricity demand.

As to meet national energy demand and to address the global warming concerns, within the next 10 to 20 years, the aged Tomlinson recovery boilers will need to be replaced. This situation provides an opportunity to introduce black liquor gasifiers as replacements for Tomlinson boilers. Gasification technology enables to convert low-grade solid fuels like biomass with low pollution into syngas, which consists mostly of hydrogen (H_2) and carbon monoxide (CO). Syngas can be passed over catalysts to synthesize cleaned transportation fuel. Or syngas can be burned efficiently in a gas turbine to generate electricity. The BLGMF (Black Liquor Gasification to Motor Fuels) project designs to convert black liquor to high-quality transportation fuel such as DME. Black liquor gasification benefits the inorganic chemicals recovery, steam production, and syngas production. In United States and Sweden commercial black liquor gasification technology are ongoing in development.

Our project designs to use the newest gasification technology to convert black liquor (from a reference pulp and paper mill) and coal into transportation fuels DME and F-T diesel. A reference pulp and paper mill producing 2000 tons (ADt) per day of paper pulp would consume 61.3 kg/s LP (4.5 bar), 37.5 kg/s MP (12 bar) of steam and 58MWe electric power. In our project, the steam and power source – the Tomlinson recovery boiler will be replaced with a high pressure entrained slurry black liquor gasifier. In the heat and power generation part we would design to recovery heat from raw syngas cooling, and to generate power from unconverted syngas in a combined gas turbine system.

3 Process Design

3.1 Pulp Mill

3.1.1 Reference Plant

While there was an insufficient amount of data available on the reference plant in Ohio, energy usage data was obtained through the pulp mill presented by STFI in Sweden. The current reference mill in Ohio produced an average of 2000 metric tons of air-dried pulp per day. However, for the purposes of this project, data was gathered from the Swedish Energy Agency's black liquor gasification for motor fuels project.

The KAM pulp mill was developed by Swedish research program KAM (Kretslopps Anpassad Massafabrik). The goal of the program was to develop a series of papers from 1996 to 2003 which detailed the highest efficiency pulp mill by using the most advanced technologies available to the authors at that time. Design specifications were geared toward high utilization of renewable resources and reduction of carbon dioxide emissions. In order to further reduce CO_2 emissions, biofuels were used where there was an excess energy demand. Biofuels are assumed to be CO_2 neutral. For all calculations, "The Eco-Cyclic Pulp Mill" or KAM2, part of the MISTRA Research Program, is used. This pulp mill relies on kraft pulping technology, which is the most common pulping technology used by paper mills today. The bleaching is done through a process called Elemental Chlorine Free (ECF) bleaching.

A pulp mill produces pulp that is 50 percent moisture. This moisture must be removed from the pulp if it is to be transported to a paper mill where it is manufactured into paper. If the paper mill is adjacent to the pulp mill, no drying is required. However, if the pulp has to be transported further to a paper mill, there is a large steam and electricity demand at the pulp mill. To simplify calculations, we decided to use only a pulp mill rather than an integrated pulp and paper mill. As a result, the pulp mill will require a steam demand listed in the tables below.

The pulp mill found in the papers does not exist because the pulp mill plant cannot economically upgrade their plant with the most advanced hardware. This reference pulp mill consumes 10 GJ/ADt (air dried tonne of pulp) compared to an average of 15.4 GJ/ADt for the Swedish Pulp industry today [4]. According to an independent study by the Canadian Office of Energy, the average pulp mill consumes 12.2 GJ/ADt [22]. This number is close to the reference mill steam consumption and the data was most readily available for the KAM2 pulp mill. As a result, the KAM2 mill will be used as the baseline. The attached calculations cannot currently be precisely duplicated and are for reference purposes only. For purpose of comparisons, the data calculated from the KAM2 mill will be compared with the data from the mill in Ohio.

The pulping process begins in the woodyard, where logs are imported using truck and rail to be debarked and chipped. The KAM2 reference pulp mill consumes 4148 metric tons of wood available to be pulped per day. The resulting pulp produced is 2000 ADt per day. The debarking of that wood produces an additional 362.5 metric tons of bark per day. The bark is used to fire the lime kiln and generate steam to feed back into the pulping cycle. The type of wood will change the energy going into the system. The LHV of wood varies from 16 MJ/kg to 20 MJ/kg . This gives an energy flow from 760 to 960 MW into the system. The amount of energy available from the bark is 67.13 MW based on a LHV of 16.0 MJ/kg [86].

3.1.1.1 Chemical Processing

The woodchips are then impregnated with white liquor and cooked at a high temperature for several hours. The four prime components of the white liquor solution are: NaOH, Na_2CO_3, Na_2S, and Na_2SO_4. For the calculations, the following concentrations are used below [87].

Table 8: White liquor composition.

Compound	White Liquor Composition (kg/ADt)	White Liquor Usage (kg/day)	White Liquor Usage (kg/s)
NaOH	293	586000	6.78
Na_2CO_3	85	170000	1.97
Na_2S	156	312000	3.61
Na_2SO_4	31	62000	0.72

The pulp is then washed in order to separate the pulp from the cooking liquors. This removes a large amount of the lignin in the wood. The resulting byproduct, cooking liquor, is called black liquor due to its color. Pulp is sent to an oxygen delignification system where more lignin is removed before it is bleached in a bleach plant. The bleaching occurs by cycling the pulp through a series of acid and alkaline stages. This stage reduces the amount of lignin in the pulp so that the pulp is an acceptable brightness for consumers. Finally the pulp is dried and sent to a paper mill to be manufactured into paper.

Black liquor is the combination of the lignin residue with water and the chemicals used for the extraction. When the black liquor is extracted from the system, it is taken as a "weak wash". Around 13% – 17% of the weak wash is the energy dense black liquor solids. In order to recover the active sodium from the black liquor, the water must be removed from the system. This is done in a six stage process through a series of evaporators, and the demand of the steam is a function of liquors being processed. A pulp plant will use the recovery boiler to oxidize the black liquor in order to produce steam and electricity for the entire plant. The smelt created by the oxidation of the black liquor is quenched in water and recovered. The resultant solution is called green liquor and injected into a chemical recovery system. For purposes of calculations, green liquor will contain the following amounts in the pulp mill KAM2 pulp mill [87]:

Table 9: Green liquor composition.

Compound	Green Liquor Composition (kg/ADt)	Green Liquor Produced (kg/day)	Green Liquor Produced (kg/s)
NaOH	10	20000	0.23
Na_2CO_3	477	954000	11.04
Na_2S	161	322000	3.73
Na_2SO_4	32	64000	0.74

The green liquor is then causticized where the Na_2CO_3 reacts with quicklime (CaO) and water (H_2O) to form sodium hydroxide (NaOH) and calcium carbonate ($CaCO_3$). The calcium carbonate is fired in a lime kiln to reduce it to quicklime to be reused, and the sodium hydroxide is used in the pulping process.

Consumption of chemicals can vary from mill to mill and is regarded as confidential. Approximately 10-20 kg of NaOH and 5-10 kg of CaO per metric ton of pulp are consumed during the recovery process. Using data found for the reference mill, the following amount of chemicals are required to be added to the system in the KAM2 mill [87].

Table 10: Chemical compound addition.

Chemical Addition Compound	Requirement (kg/ADt)	Addition (kg/day)	Addition (kg/s)
NaOH	14	28000	0.32
CaO	16	32000	0.37

3.1.1.2 Energy Demand

When the KAM2 mill does not include a gasifier, there is a sufficient amount of electricity produced in the recovery boiler as well as an excess amount of bark which can be sold.

A schematic of what the KAM2 Eco-Cyclic Pulp Mill process includes is found below with each stage's respective heat and electricity demand. Energy and electricity demand data is published as a function of the amount of air dried tonnes of pulp (ADt) processed. In the KAM2 mill, 2000 ADt/day is removed from the washer to be processed into paper. Using the available values, 58.42 MW of electricity and 300.24 tonnes of steam per day are required.

Table 11: Steam Demand Pulp Mill.

	Medium Pressure Steam (GJ/Adt)	Low Pressure Steam (GJ/Adt)	Daily Steam Consumption of 2000 ADt	
Woodyard			0	
Digester	1.39	0.29	3360	
Brown Stock Washing			0	
Oxygen Delignification	0.38		760	
Bleach Plant	1.43	0.27	3400	
Final Screening			0	
Pulp Dryer		2.21	4420	
Black Liquor Evaporation	0.95	2.71	7320	
Recausticising			0	
Cooling Towers			0	
Raw Water Treatment			0	
Wastewater Treatment			0	
Bleaching Chemicals			0	
Other (including losses)	0.15	0.2	700	
Sum	**4.3**	**5.68**		
	Total Mill Steam use per day		19960	GJ/day
			300.24	t/h

Using an ECF process of bleaching, 1.71 tonnes of black liquor is recovered per tonne of pulp [88]. As a result, the reference mill produces 3420 tonnes dry solids per day. The recovery boiler typically produced 15.7 GJ/ADt of pulp, steam and 655 kWh/ADt of pulp, electricity [22].

For our plant that produced 2000 air dried tones of pulp per day, the boiler production is given in the chart below.

Table 12: Energy produced by KAM2 boiler.

KAM2	Steam (tonne/hr)	Electricity (MWe)
Supplied by Boiler	463	54.6

Black liquor combustion in the recovery boiler provides electricity and steam to power the KAM2 pulp mill. While this is ordinarily a sufficient process to meet the plant's energy demand, the removal of the black liquor from the system requires energy input from external sources. The chart below displays the calculated values of electricity and steam that are produced through the recovery boiler and the associated back pressure steam turbines.

Table 13: Energy produced by KAM2 boiler.

	Steam (tonne/hr)	Electricity (MWe)
Supplied by boiler	336	39.42

From the calculations derived in Appendix A, the energy demand for the modified pulping section of the plant is 56 MW of electricity and 267 tonnes per day of steam. The demand for the steam in the plant is met by the recovery boiler alone, but there is a significant amount of electricity which must be generated through the off gasses in the fuel process.

All pulping and integrated mills have a second, smaller recovery boiler that is used to burn fuel oil, bark or natural gas to help meet auxiliary energy demands within the mill. In the KAM2 mill, high pressure steam generated in the boilers is fed into back-pressure steam turbines which generates electric power, and the heat demand is met using a steam of medium pressure (10-12 bar) and low pressure (3-4 bar).

3.1.2 Group Design Modifications

3.1.2.1 Energy

Because of the design shift from a basic recovery boiler, there is an opportunity to save energy due to a reduced load on the chemical recycle process. However, more chemicals will need to be purchased which will offset the energy gains.

Weak black liquor is removed to contribute towards the gasification process, and 6333 tonnes per day of the weak wash is distributed to the gasifier. Because it is a weak mixture, only 950 tonnes of black liquor dry solids are present in this solution. This means that 2470 tonnes, or 72.2% of black liquor solids will go through the normal recovery cycle.

As a result, there will be a reduced steam and electricity load on the evaporators. However, the plant will lose valuable chemicals that will need to be supplemented in order to effectively pulp the next process.

The energy savings per day can be found in the chart below.

Because the energy and electricity values are based on air dried tonnes of pulp, the assumption to determine energy saved is that there is a linear correlation between black liquor lost and the pulp that provides that determination. Therefore, to perform these calculations, a pulp content of 1444.4 ADt/day is used for all calculations after the washer. Energy is saved through the reduced load in causticizing, and in black liquor evaporation. This reduces the energy consumption of the plant to 56.33 MW of electricity and 269.7 tonnes of steam per hour.

Table 14: Daily electricity demand.

Energy Consumption (Berglin,2003)				
	Electricity Consumption (kWh/ADt)	Daily Electricity Consumption of 2000 ADt	Plant Modified Energy Consumption	
Woodyard	45	90000	90000	
Digester	44	88000	88000	
Brown Stock Washing	60	120000	120000	
Oxygen Delignification	60	120000	120000	
Bleach Plant	80	160000	160000	
Final Screening	45	90000	90000	
Pulp Dryer	120	240000	240000	
Black Liquor Evaporation	30	60000	43332	
Recausticising	60	120000	120000	
Cooling Towers	20	40000	40000	
Raw Water Treatment	20	40000	40000	
Wastewater Treatment	30	60000	60000	
Bleaching Chemicals	57	114000	114000	
Other (including losses)	30	60000	60000	
Sum	**701**			
Total Mill Electricity use per Day		1402000	1385332	kWh/d
		58.42	57.72	MWe

Table 15: Daily steam demand.

	Modified Medium Pressure Steam (GJ/Adt)	Modified Low Pressure Steam (GJ/Adt)	Modified Daily Steam Consumption (GJ/day)	
Woodyard			0	
Digester	1.39	0.29	3360	
Brown Stock Washing			0	
Oxygen Delignification	0.38		760	
Bleach Plant	1.43	0.27	3400	
Final Screening			0	
Pulp Dryer		2.21	4420	
Black Liquor Evaporation	0.69	1.96	5285	
Recausticising			0	
Cooling Towers			0	
Raw Water Treatment			0	
Wastewater Treatment			0	
Bleaching Chemicals			0	
Other (including losses)	0.15	0.2	700	
Sum	**4.04**	**4.93**		
	Total Mill Steam use per day		17925.04	GJ/day
			269.7	t/h

3.1.2.2 Chemical Recovery

A huge problem for this process will be the sodium loss that occurs in the plant. A removal of some of the black liquor will remove a significant amount of active chemicals in the pulping process. Once the black liquor is oxidized, the products which aren't burned are quenched and form a solution called green liquor. There will be a smaller amount of green liquor present because of less burned black liquor. While the KAM2 mill has a green liquor flow of 15.74 kg/s, when the black liquor is removed, 11.37 kg/s of green liquor flows into the causticization process if no supplements are added to the black liquor.

Na_2CO_3 is the chemical that leaves the recovery boiler which will be recausticized to form NaOH. Na_2SO_4 is active in the smelt, reacting with carbon atoms to form Na_2S, the primary active chemical in sodium carbonate formation. The following formula describes the main reaction that drives the formation of Na_2CO_3:

$$Na_2S + CO_2 + H_2O \rightarrow Na_2CO_3 + 2H_2S$$

For the sake of simplicity, it is assumed that all of the Na_2SO_4 is converted to Na_2S which is then fully converted into Na_2CO_3. Back calculations performed on the KAM2 mill [87] found that 82.2% of Na_2CO_3 is converted into NaOH. Calculations show that 17,534 tonnes of sodium sulfide must be added to continue the pulping process at a rate that sustains pulp production.

3.1.2.3 Pulp Mull Effluent

There is a high cost to producing pulp to the environment. It has the potential to generate significant quantities of wastewater. The average pulp mill will produce 60 cubic meters of wastewater per metric tonne of pulp produced. For the model purposes this would be the equivalent of 120 cubic meters per day or about 45,000 cubic meters of wastewater per year.

For the current pulp mill, the treatment of the effluent will be through a three stage process: primary clarification, secondary treatment and tertiary treatment. Current standards that regulate current pulp mills require just two stages of effluent treatment. However, it is anticipated that future legislation will require pulp mills to require further treatment.

The large, suspended solids are removed through dissolved air flotation which removes 80% of the impurities [89]. Simple chemical treatment of the remaining sludge will be the aerobic process that uses chlorine and hydrogen peroxide to fill the filamentous bacteria in the wastewater[90]. While it is an old technology, it is the most convenient because these chemicals are the same ones which are being used in the bleaching process of the pulp downstream from the energy flow.

The final stage is experimental because most mills do not have tertiary treatment in their infrastructure since two stages meet the current federal regulations. In order to prepare for the future, this already top-of-the-line pulp mill will again make further use of the ozone created for the bleaching process to react with the pretreated wastewater to give final impurity of less than 100g/L [91]. This is an acceptable amount to dump into a waterway.

3.2 Black Liquor and Coal Gasification to Syngas

The general design of the coal-black liquor gasifier is based on a GE/Texaco design. The Texaco gasifier design was chosen for black liquor-coal gasification because the technology is "simpler and more reliable" than dry-fed units, generates a higher H_2/CO ratio, and also "allows for more flexibility in feedstock selection" [92]. Furthermore, if the feedstock blend is altered, hardly any changes to the gasification design are necessary [92]. Because the Texaco gasifier requires a slurry feed, and weak black liquor is an aqueous solution of about 15-17 % solids, the significant energy requirement for evaporation of black liquor to 80% solids for dry-feed gasification is avoided. The general operating conditions for a Texaco gasifier are summarized in Table 16. The slurry should contain approximately 50-60 % solids [92, 93].

Table 16: General operating parameters for Texaco gasifier [93, 94].

Gasifier Operating Conditions Range			
Temperature	1200-1500	C	
Pressure	20-40	bar	*for power generation*
	60-80	bar	*fuels synthesis*
Oxygen	0.8-0.9	kg/kg fuel	

The normal operating temperature range for a Texaco gasifier is 1250-1450°C [95]. Gasification of biomass and coal should occur at relatively high temperatures because little or no methane and tars are produced. Also, high temperatures maximize production of desired products, H_2 and CO [32].

Texaco gasifier operating pressures are normally within a range of 20-40 bar, but can be as high as 60-80 bar for fuels synthesis [93] . Gasifier pressures should exceed pressure requirements for downstream synthesis reactors to avoid the cost of intermediate gas compression steps [32]. Increasing the pressure has little affect on the product distribution, especially above oxygen-to-fuel ratios of 0.8 [94] . The pressure requirement for DME synthesis is 50 bar so this operating pressure was chosen for the design.

The gasifier control system is crucial to the operation and performance of the gasifier. The control system maintains the ratio of oxygen to fuel and controls the amount of carbon fed to the gasifier to achieve desired target ratios for synthesis gas with a high H_2/CO ratio [92]. This allows for more flexibility in selecting and blending fuel sources, which is advantageous to this design that utilizes at least two feedstocks in potentially varying amounts (e.g., coal, black liquor, and extra biomass).

The oxygen-to-fuel ratio affects carbon conversion in the gasifier and usually ranges from 0.8 to 0.9. There are no added benefits in syngas composition and quality for oxygen-to-fuel ratios exceeding 0.9 [94]. Compressed oxygen should be supplied to the gasifier at pressure greater than the reactor gasification pressure by a factor of 1.2 [96]. Therefore, the Air Separation Unit will supply 95% pure oxygen to the gasifier at a flow rate of 59.3 kg/s and a pressure of 60 bar [94, 97]. The electricity requirement for the ASU is .261 kW_e/kgO_2, for a total of 55.7 MW_e for the design [97].

3.2.1 Gasifier Scale and Fuel Yield

For economic production of DME fuel, about 1-2 million tons of DME per year is desired. To determine the scale of the coal-black liquor design, an existing coal-biomass gasification plant was evaluated. The large-scale European IGCC gasification plant, NUON Power Buggenum, produces about 250 MW_e and 4.0 Mm^3/day syngas from a coal-biomass feedstock blend using the Shell Gasification Process [98],[99] . A fuel input of 2000 tons per day of coal produces this yield.

The synthetic fuel yield goal is based on the availability of black liquor at an average kraft pulp mill, the economic requirement of 1-2 MTPY DME, and the average coal feed to a current IGCC facility. For a first approximation, it was assumed that the average pulp and paper mill would gasify all of the black liquor solids plus an additional 2000 tons of coal per day. Using efficiency and yield results from Chemrec's BLGMF process, the original design for this project, this input corresponds to 0.8 million tons DME per year. From this point on, the gasification process was designed to achieve 0.8 million tons per year DME.

3.2.2 Gasifier Fuel Source

Black liquor: A kraft pulp mill produces about 3420 tons of black liquor solids per day. The properties of black liquor are shown in Table 17. After pulping, the solids content of weak black liquor exiting the digester is 16-18% solids. In order to be burned in a conventional Tomlinson recovery boiler, weak black liquor is evaporated to about 80% solids. Since a Texaco gasifier requires coal-water slurry, the black liquor does not need to be evaporated before it is mixed with coal.

Table 17: Properties and composition of kraft black liquor.

Component	% Wt (Dry)
Carbon	35.7%
Hydrogen	3.7%
Nitrogen	0.1%
Sulfur	4.4%
Oxygen	35.8%
Sodium	19.0%
Potassium	1.1%
Chlorine	0.3%
LHV (MJ/kg)	12.0
Percent solids (%)	17.0
Temp (°C)	95.0

Coal: The pulp mill location assumed for this report is Chillicothe, Ohio. Large-scale coal mines near this location produce Pittsburgh No. 8 bituminous coals. A whole seam channel analysis from Western Pennsylvania Pittsburgh No. 8 bituminous coals was obtained from the Penn State Coal Database by Dr. Gareth Mitchell. The coal and ash analysis is presented in Table 18 and Table 19, respectively.

Table 18: Coal analysis of Pittsburgh No. 8 bituminous coal sample from Washington County, Pennsylvania.

Pitts No. 8 Coal	***PSOC 1561***
Component	% Wt (Dry)
Ash	9.4%
Volatile Matter	39.4%
Fixed Carbon	51.1%
Carbon	74.2%
Hydrogen	5.1%
Nitrogen	1.4%
Total Sulfur	3.9%
Oxygen (by diff)	6.0%
Calorific Value (d,mmf) Btu/lb	14959
Calorific Value (d,mmf) MJ/kg	34.79

Table 19: Ash analysis of Pittsburgh No. 8 bituminous coal sample from Washington County, Pennsylvania.

Ash Component	% of Ash
SiO_2	36.3%
Al_2O_3	17.6%
TiO_2	0.76%
Fe_2O_3	36.7%
MgO	0.6%
CaO	3.0%
Na_2O	0.3%
K_2O	1.4%
P_2OS	0.6%
SO_3	1.7%

The combination of black liquor and coal feed to the gasifier was based on the solids requirement for the gasifier considering that weak black liquor is about 17% solids. The gasifier slurry requires approximately 55% solids. For every 100 kg of weak black liquor there are 17 kg of solids and 83 kg of water. In order to make a slurry with 55% solids, an additional 84 kg of coal are needed. The mass balance for the resulting coal-black liquor blend (including ash) is shown in Table 20. More detailed calculations are included in Appendix B. The heating value for the composite fuel blend is 30.97 MJ/kg.

Table 20: Mass balance for coal-black liquor gasifier feed.

	From Black Liquor (kg)	From Coal (kg)	Total (kg)	Wt. Percent
Carbon	6.1	62.7	68.7	67.8%
Hydrogen	0.6	4.3	4.9	4.9%
Nitrogen	0.0	1.1	1.2	1.1%
Sulfur	0.7	3.3	4.0	4.0%
Oxygen	6.1	5.1	11.2	11.0%
Sodium	3.2	0	3.2	3.2%
Potassium	0.2	0	0.2	0.2%
Chlorine	0.1	0	0.1	0.05%
SiO_2	0	2.9	2.894	2.9%
Al_2O_3	0	1.4	1.403	1.4%
TiO_2	0	0.1	0.061	0.1%
Fe_2O_3	0	2.9	2.926	2.9%
MgO	0	0.0	0.048	0.0%
CaO	0	0.2	0.242	0.2%
Na_2O	0	0.0	0.026	0.0%
K_2O	0	0.1	0.112	0.1%
P_2O5	0	0.0	0.005	0.0%
SO_3	0	0.1	0.136	0.1%
Total (kg)	***17.0***	***84.3***	***101.3***	

The project goal for DME synthesis was 0.8 million tons per year. Assuming a cold gas efficiency of 51% and a syngas heating value of 11.7 MJ/kg, the DME synthesis reactor requires

124,228 GJ/day (1,990 MW) of syngas energy, or a syngas mass flow rate of 123 kg/s. In order to determine the amount of gasifier input fuel required to produce 123 kg/s of syngas, actual syngas yields from a coal-fed Texaco gasifier were found for gasifier oxygen-to-fuel ratios similar to the parameters for this design project. For oxygen-fuel ratios near 0.9, the average fuel to synthesis gas ratio was 0.535. Detailed calculations are included in Appendix D.

The performance of the coal-black liquor gasification system is summarized in Table 21. Black liquor and coal are gasified at an efficiency of about 70%.

Table 21: Performance of coal-black liquor gasification.

Component	Mass Flow (T/d)	Mass Flow (kg/s)	Energy (MW)
Total Fuel Feed	5691.8	65.9	2040.5
Coal	4738.0	54.8	1908.1
Black Liquor Solids	953.8	11.0	132.5
Oxygen Feed	5122.7	59.3	
Steam (water) Feed	2276.7	26.4	
Syngas	10629.3	123.0	1437.8
Efficiency			70.5%

3.2.3 Gasifier Synthesis Gas Composition

Modeling of the actual synthesis gas composition exiting the gasifier was beyond the scope of this project but the syngas composition from the gasifier could be estimated based on results of similar gasification processes and conditions. In general, the syngas composition from high temperature, high-pressure gasification processes will be relatively insensitive to the coal type in the feed [92, 100]. Differences in syngas composition should also be negligible for gasification of biomass and coal [100].

The amount of black liquor in the gasifier is about 17 wt. %, with coal making up 83% of the feed on a weight basis and 94% of the feed on an energy basis. Therefore, it is possible to estimate the syngas composition from a Texaco gasification process using existing syngas composition data found in the literature. Three experimental Texaco gasification synthesis gas compositions from various coal feedstocks were used to generate a model syngas composition for the black-liquor/coal gasification process. The composition and distribution of three actual syngas streams and an average syngas stream is shown in Table 22. Assuming a syngas model composition as a close approximation to an actual syngas stream from the Texaco gasification process, the average composition from three feedstocks was calculated and used in processes downstream of the gasifier. From the average syngas composition and individual calorific values, the overall syngas calorific value was calculated, as shown in Table 23.

Table 22: Experimental syngas composition and estimated syngas stream.

Raw Syngas	Feed 1	Feed 2	Feed 3	Average
H_2	38.7	37.9	34.4	37.0
CO	46.6	45.2	45.3	45.7
CO_2	11.5	13.2	15.8	13.5
CH_4	0.7	0.9	1.9	1.2
N_2	2	1.7	1.9	1.9
H_2S	0.7	0.6	-	0.7
H_2/CO Ratio	0.830	0.838	0.759	0.809
Feed 1: Pittsburgh high volatile bituminous coal. CV 35.540 MJ/kg, 7.2% ash [93]				
Feed 2: Japanese lignite, high-vol C bituminous. CV 22.840 MJ/kg, 13% ash [93]				
Feed 3: Bituminous coal, 1.9% sulfur, CV 24.5 MJ/kg [100]				

Table 23: Syngas calorific value.

Component	Mole %	MW	Wt. %	HV (MJ/kg)
H_2	37.0	2.02	3.7%	120.1
CO	45.7	28.01	62.7%	10.9
CO_2	13.5	44.01	29.1%	0
CH_4	1.2	16.04	0.9%	50.1
N_2	1.9	28.01	2.6%	0
H_2S	0.7	34.08	1.1%	0
Syngas				**11.69**

3.2.4 Slag Properties and Chemical Recovery

Molten slag from the gasifier is quenched in a water bath, forming a glassy solid (which is "virtually non-leachable"), which then falls into a lock hopper for removal [43]. For coal gasification, this waste product can improve the economics of gasification processes as these materials can be sold and utilized safely in industries such as cement manufacturing and construction. The cost for disposal is also avoided.

When black liquor is added to coal, complications may arise in how the waste material is handled, utilized, and disposed. Inorganic black liquor chemicals will fuse with coal ash compounds as glassy solids from the quench bath. The recovery of valuable cooking chemicals required for the pulping processes will be prevented if the inorganic black liquor chemicals (e.g., sodium) cannot be isolated from the solid product using low-cost chemical or physical processes. Sodium from black liquor is typically recovered from the recovery boiler and recycled to the digester, improving the economics of the pulping process.

The effects of adding black liquor to a slurry-fed coal gasifier were modeled with a thermochemical modeling software package, FactSage. Individual compounds and phases were identified under current gasifier design reactor conditions in a reducing environment (1420 °C, 50 bar, 0.9 oxygen-fuel ratio). All products were assumed to achieve equilibrium within the reactor. The simulation at these conditions predicted both solid and liquid phases in the product. The chemical compositions of the products are summarized in Table 24.

The simulation indicates that 30% of the inorganic products will exist as a solid phase when exiting the gasifier. This may reveal that these products will remain within the syngas and need to be removed by separation. The results also show that 100% of the sodium (coming from black liquor) exists as a liquid, which will form the molten slag that is quenched into a solid, glass-like product. Sodium is of interest because this desired compound is usually recovered and recycled in black liquor combustion and gasification processes. FactSage modeling confirms that all of the sodium will exit as a molten slag. Sodium recovery will not be possible if the fused solid product is non-leaching. These results may be useful for further study on the behavior of black liquor and coal mixtures in entrained flow reactors, the chemical behavior of the solid product, and the implications for industrial uses of these solid waste materials.

Table 24: Solid and liquid phases predicted by FactSage modeling package for reactor conditions: 1420^{o}C, 50 bar, 0.9 oxygen-to-fuel ratio.

Compound	Phase	Wt.	Wt.%	Mole
Na	liq	13.48	26.76%	0.5865
$Na_6Si_2O_7$	liq	19.48	38.67%	0.0636
Na_2S	liq	0.55	1.08%	0.0700
NaCl	liq	0.60	1.18%	0.0102
Na_4TiO_4	liq	0.53	1.05%	0.0260
Fe_3P	liq	0.04	0.08%	0.0002
$MgAl_2O_4$	solid	0.58	1.16%	0.0041
$KAlO_2$	solid	4.09	8.12%	0.0042
$CaAl_2O_4$	solid	1.19	2.35%	0.0075
$CaAl_4O_7$	solid	1.87	3.72%	0.0072
Fe	solid	4.88	9.70%	0.0875
FeSi	solid	3.08	6.12%	0.0367
Total		50.37		

	Liquid Phase	34.67	68.83%	
	Solid Phase	15.70	31.17%	

3.2.5 Process Options and Flexibility

Because there is “no noticeable change in syngas composition or quality” when the feedstock blend to the Texaco gasifier is altered, the process can be adapted to meet a variety of demands based on supply of biomass, coal, and black liquor near the integrated pulp mill [92]. Based on the existing coal-black liquor gasification design to produce 0.8 Million tons of DME per year, it is not necessary to gasify all the black liquor produced from an average pulp mill if the black liquor is not evaporated before feeding to the gasifier. Based on the current design, the feed requirements for black liquor and coal to the gasifier are shown in Table 25. The extra 2500 tons of black liquor solids represent a significant unexploited energy source.

Table 25: Fuel mass requirements for gasification feed.

Component	Mass Flow (T/d)	Mass %
Total Fuel Feed	5691.8	
Coal Requirement	4738.0	83.2%
Black Liquor Solids Requirement	953.8	16.8%
Average Black Liquor Solids Production	3420	
Unused Black Liquor Solids	2466	

Several potential options exist to exploit the extra black liquor:

- The existing conventional Tomlinson recovery boiler could be used to combust the black liquor for heat and power. Despite low efficiencies in the recovery boiler, this may be advantageous for the pulp mill since cooking chemicals can be recovered and recycled to the digester. The safety hazard associated with the Tomlinson recovery boiler still exists.
- A separate dedicated black liquor gasification process similar to the Chemrec design could be incorporated. This would boost overall process efficiency (greater than for Tomlinson recovery boiler) and also enable the recovery of cooking chemicals, which is not guaranteed when black liquor is co-fed into a coal gasifier. Adding an additional gasifier would significantly increase capital costs for the integrated pulp mill gasification design.
- The coal-black liquor gasification design could be enhanced to handle a much larger feed of black liquor and coal.
- The black liquor could be partially evaporated and the ratio of black liquor to coal in the gasifier could be increased.

3.3 Dimethyl Ether Synthesis

3.3.1 Syngas Clean-up

The major components of the syngas at the outlet of an entrained flow slagging gasifier are CO, H_2, and CO_2. Some N_2, CH_4 and small amounts of H_2S are present. Some amount of char (unconverted carbon) and ash are also contained in the exit flow of the gasifier. Table 26 provides the composition of the raw syngas.

Table 26: The composition and components of the raw syngas.

Components	Mole percentage	Mass percentage
CO	45.7	0.62683
H_2	37.0	0.03659
CH_4	1.2	0.00916
CO_2	13.5	0.29094
N_2	1.9	0.02560
H_2S	0.7	0.01084

Syngas quenching

The quench ensures that the char and ash particles will be non-sticky to prevent fouling issues. After capture in a filter, these particles will be recycled to the gasifier to increase the carbon conversion efficiency. Among the four main alternatives for quenching, a water quench will be used in the gas cleaning system which uses sensible heat from the syngas to vaporize water. The hot syngas will be totally quenched with water to about 300°C.

Particle removal

Wet solids removal systems use water scrubbers operating at a temperature lower than the dewpoint of the gas so that the smallest solid particles can act as nuclei for condensation and ensure efficient operation. Dry solids removal systems use candle filters that can remove all solids from the gas at temperatures between 300 and 500°C. Above 500°C, alkali compounds may pass the filters in significant amounts. Below 300°C, the filters may be blinded of deposits of ammonium chloride (NH_4Cl) [10] (C. Higman and M. van der Burgt, "Gasification", Elsevier, 2003).

Sulfur compounds

The major part (>90 %) of the sulfur components in the feed are hydrogen sulfide (H_2S). Up to 99.8 % of the coal sulfur can be removed in the acid gas removal process. Since the syngas will be used to produce DME, deep sulfur removal will be required to protect the catalyst downstream. Usually, Rectisol physical solvent (methanol as solvent) AGR (acid gas removal) process will be applied. But the relatively low temperature (40°C) in the AGE process will result in great heat loss in the gas cleaning process. Herein, zinc oxide will be used as sorbent for H2S removal. In this case, remarkably higher desulfurization temperatures of ca. 400°C will be obtained[101].

Nitrogen compounds

Nitrogen from the gasifier can be molecular nitrogen and fuel bound nitrogen, such as hydrogen cyanide (HCN) and ammonia (NH_3), which have very high solubilities in water, and may therefore be removed in water scrubbing[102]. Since the main component in the raw is molecular nitrogen not fuel bound nitrogen, we do need to use water scrubbing to remove them. And molecular nitrogen in the raw syngas flow will not be removed.

3.3.2 DME synthesis

3.3.2.1 Characteristics of DME synthesis reactions

In the introduction part, we have reviewed the existing commercial technologies of DME production. Herein, due to the syngas H_2/CO ratio (~0.81), we are going to employ a single-step reaction to synthesize DME from syngas based on JFE and Air Products & Chemicals technologies[48, 58]. The reactions are shown below:

The overall reaction:

$$3CO + 3H_2 \leftrightarrow CH_3OCH_3 + CO_2 \qquad H = -244.95 \text{ kJ/mol} \qquad (1)$$

In practice, the reactions shown in the formulae (2), (3), and (4) below occur simultaneously:

$$CO + 2H_2 \leftrightarrow CH_3OH \qquad H = -90.29 \text{ kJ/mol} \qquad (2)$$
$$2CH_3OH \leftrightarrow CH_3OCH_3 + H_2O \qquad H = -23.41 \text{ kJ/mol} \qquad (3)$$
$$H_2O+CO \leftrightarrow CO_2 + H_2 \qquad H = -40.96 \text{ kJ/mol} \qquad (4)$$

The two molecules of methanol synthesized from CO and H_2 in formula (2) are dehydrated in formula (3) to produce DME. The water produced in formula (3) is recycled as hydrogen in formula (4). In the overall reaction, the H_2/CO ratio is 1:1.

When H_2/CO is not 1:1, the reaction formulas concerning DME synthesis are as follows:

$$2CO + 4H_2 \leftrightarrow CH_3OCH_3 + H_2O \qquad (5)$$
$$2CO + 4H_2 \leftrightarrow 2CH_3OCH_3 \qquad H = -244.95 \text{ kJ/mol} \qquad (6)$$

Figure 12 shows equilibrium conversion (ideal) of synthesis gas (CO conversion plus H_2 conversion) for the three DME synthesis reactions, formula (1), (5) and (6). In each reaction, the equilibrium conversion has its maximum peak where the H_2/CO ration corresponds to the stoichiometric value. The maximum equilibrium conversion for formula (1) is much higher than those for formula (5) and (6)[48].

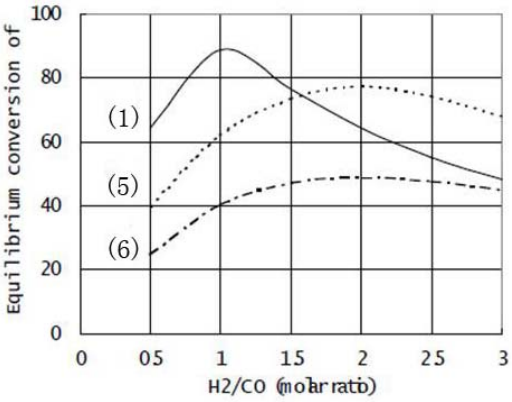


Figure 12: Equilibrium conversion of synthesis gas.

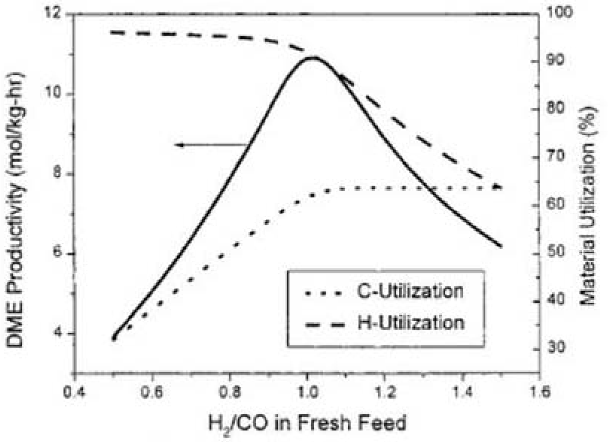


Figure 13: The effect of the H2/CO ratio on DME productivity and materials utilization.

Air Products and Chemicals also drew the same conclusion[103]. A very strong dependence of the DME productivity on the H_2/CO ratio in the fresh feed gas is observed. The maximum productivity occurs at a H_2/CO ratio of 1.0. The productivity drops by about 65% and 44% when the ratio changes to 0.5 and 1.5. Since our syngas H_2/CO ratio is about 0.8 which is close to 1, we will directly use the cleaned syngas.

3.3.2.2 Catalyst system for the single-stage DME synthesis

The single-step DME synthesis catalysts are powdered catalysts contains between about 75 and about 90 wt % copper-containing methanol synthesis catalyst and the remainder of said powdered catalyst consists essentially of methanol dehydration catalyst[104]. The methanol synthesis catalyst is $Cu/ZnO/Al_2O_3$ and methanol dehydration catalyst is alumina. To main the catalyst activity, stability and reaction activity, 270^{o}C and 50 bar are chosen as the operation conditions.

3.3.2.3 Reactors

A single-step gas phase process would generally require less equipment than multi-step gas processes. However, a single-step gas-phase process would still suffer from a large reactor exotherm due to the high net heat of reaction. Hence, it is necessary to remove reaction heat and perform reaction temperature control properly in order to prevent a reduction of equilibrium conversion and catalyst deactivation due to temperature rise. A slurry phase reactor is going to be used in which the reaction is promoted by placing the synthesis gas in contact with the catalyst in slurry in which the catalyst is suspended in a reaction medium. Because the heat capacity and thermal conductivity of the reaction medium are both large, the reaction heat is absorbed by the reaction medium and leveling of the temperature in the reactor is easy.

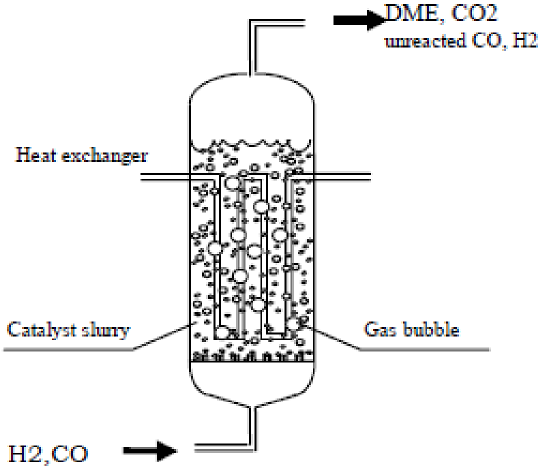


Figure 14: Concept of slurry phase rector (JFE Holdings, Inc).

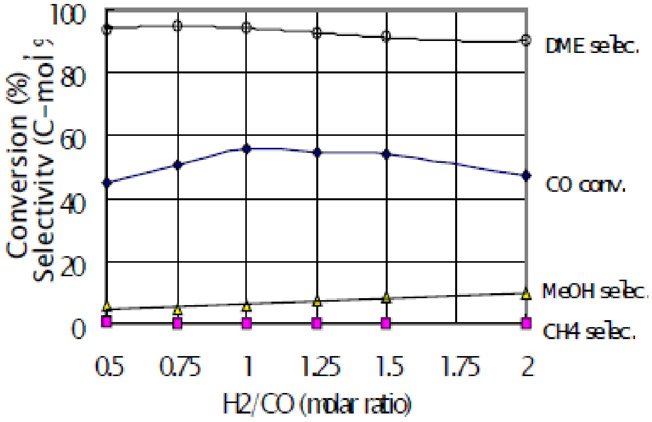


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Figure 15: Conversion and selectivity as a function of H2/CO.

3.3.2.4 CO conversion and efficiency

Fig. 15. shows the effect of H_2/CO ratio on syngas conversion and product selectivity. The dependence of one-through conversion on the reaction pressure and temperature are shown in Fig.6[48]. From Fig.3.3.4, when H_2/CO ratio is 0.8, the DME selectivity is more than 95% and syngas conversion is more than 50%. From Fig.16., at 270°C and 50 bar, the CO conversion is about 60%. Therefore, we suppose our CO conversion is 60%, and hence the syngas to DME efficiency is about 51%.

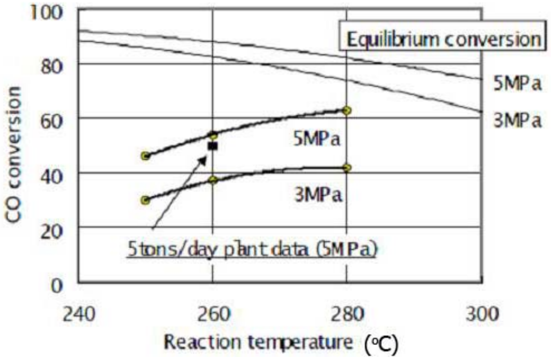

Figure 16: CO conversion as a function of temperature and pressure.

3.3.3 Product separation and purification

The separation scheme design is based on the invention of Peng. et al[105]. The DME reactor effluent, which is a mixture of DME, methanol, CO_2 and water and unconverted syngas will be cooled and fed to a high-pressure flash column. The high-pressure flash column will separate the polar molecules and non-polar molecules. The vapor phase containing DME, CO_2 and unconverted syngas (non-polar molecules) will pass through a scrubbing column. DME is used as the scrubbing solvent to remove DME and CO_2 and methanol from the unconverted syngas. The mixture of DME and CO_2 from the bottom of the scrubbing column is fed to a DME-CO_2 distillation column to separate CO_2 from the product DME.

3.4 Fischer-Tropsch synthesis

This section will describe and elaborate on a design for the production FTD, based on black liquor and coal feed stocks. Company such as Sasol and Texaco, which produce large amount of FTD, do not share the specifics of there plant designs. For this reason, scraps of information that are found in literature must be pieced together with assumptions to create a design.

Figure 28 list all of the major parameters of the FTD production design. LTFT was used because it produces a greater yield of FTD then HTFT. A slurry-phase bubbling-bed reactor was chosen because of its higher efficiency compared to a fixed bed reactor. Slurry-phase bubbling-bed reactors also have responsive temperature control and low down time in the case of catalyst poisoning. An iron based catalyst was chosen because of its low H_2/CO ratio requirement, so that an external water gas shift was not necessary. An α of 0.94 was used to maximize wax production and minimize light hydrocarbon production.

Table 27: FT-diesel fuel synthesis parameters used in FT-diesel production design.

Synthesis Parameters	
FT synthesis	Low Temperature Fischer-Tropsch
FT reactor	Once through Slurry-phase bubbling-bed reactor
FT reactor temperature	260°C
FT reactor pressure	30.7 bar
Catalyst	Iron based
α	0.94

Figure 17 is the mass and energy flow diagram of this project's FTD design. This design, from the point of clean syngas to reactor products, is base and scaled up from a case study and design found in Larson et al.[81]. A distribution of FT-products product from wax hydrocracking was taken from Rytter et al.[106]. Details of the development of this design are found in Appendix D.

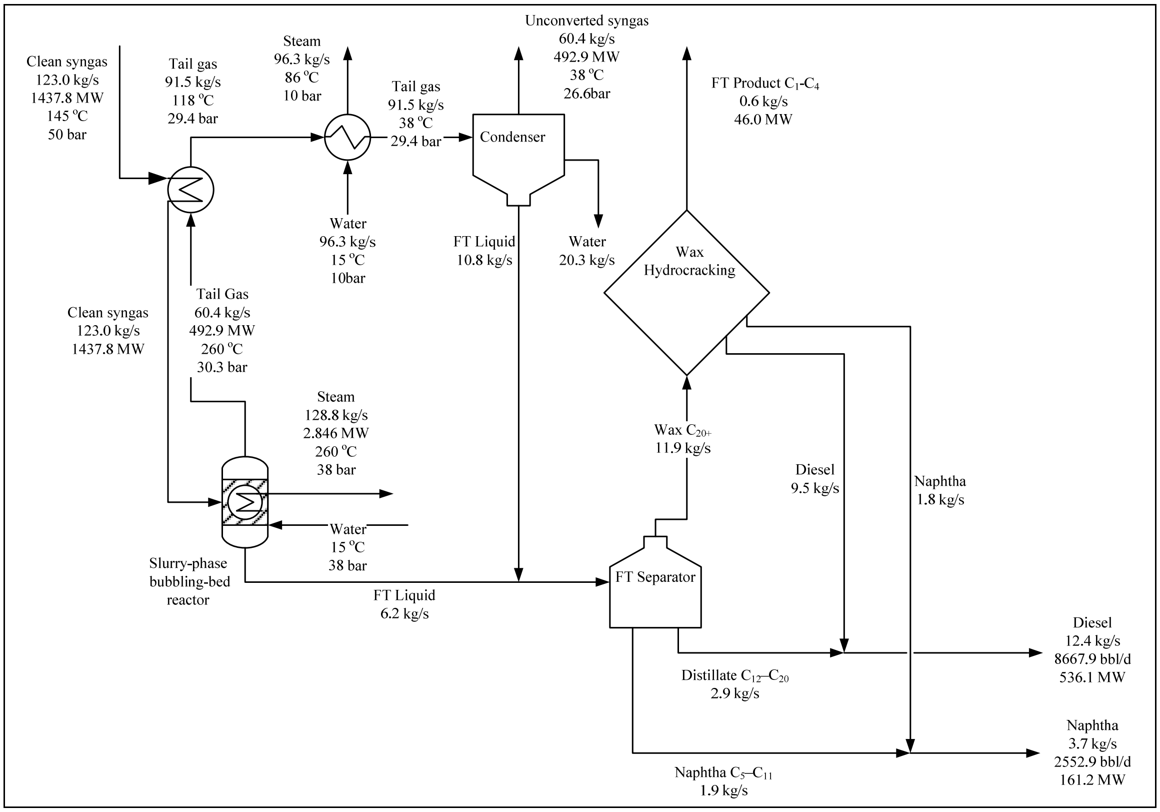

Figure 17: FTD production from clean syngas.

3.5 *Heat and Power Generation Process Design*

3.5.1 Heat Recovery System Design

The hot raw syngas from the gasifier contains chemical energy and sensible heat. The syngas can be water quenched to recovery chemicals or flow through a heat exchanger to recovery sensible heat to produce steam for the steam turbine. The syngas cooler is more efficient than that with a water quench (Maurstad, 2005). But it will add capital costs. There are two classes of syngas coolers: fire tube boilers and water tube boilers. In the fire tube boiler design, the hot raw syngas flows inside the tubes and high pressure steam is generated on the outside. Water tube boilers can handle higher steam pressure.

Our heat recovery system design was shown in Figure 18. Hot raw syngas (1400°C, 50 bar) was sent to a water tube syngas cooler. It would generate high pressure steam (117 bar) for steam turbine and process steams (MP 13 bar and LP 4.5 bar) for the pulp and paper mill. The cooled high pressure syngas (50 bar) would be sent to the syngas cleaner. The water before sending to the syngas cooler would be preheated with recovered heat from HRSG exhaust gas. The tubes of the syngas cooler are subjected to high pressure.

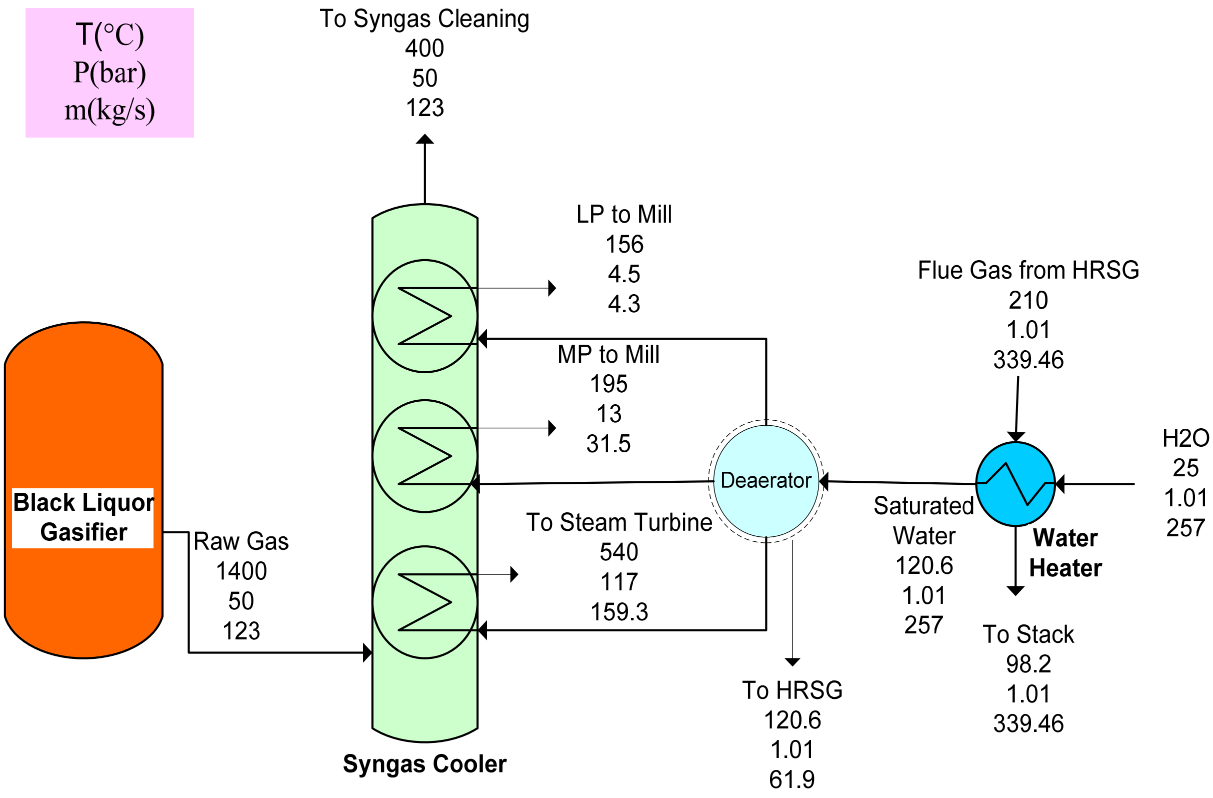

Figure 18: The block of heat recovery process design.

3.5.2 Power Generation Process Design

There are different ways to generate power in the pulp and paper mill. The following describes the most common ways.

1) Tomlinson Recovery Boiler

Present kraft pulp and paper mills use black liquor as an energy resource to generate power and heat in the Tomlinson recovery boiler/steam turbine systems. While the Tomlinson recovery boiler with Rankine steam cycle has low thermal efficiency, low power-to-heat ratio, high capital cost, corrosion and smelt drawbacks.

2) BLGCC

Pressurized black liquor gasification combine cycle (BLGCC) has been recognized by the American Forest & Paper Association through Agenda 2020 as one of the key technologies in a sustainable perspective to improve energy and capital efficiency in the pulp and paper industry. Chemrec BLGCC system has the capability to split the sulfur and into separate process steams, which improves chemicals recovery. Also, BLGCC improve pulp mill energy yields. Larson [107] and Stigsson [108] introduced combined biomass and black liquor gasifier/gas turbine cogeneration (Figure 19) at pulp and paper mills. The BLGCC systems improve chemicals recovery and maximize the electricity production while providing all of mill's process steam needs.

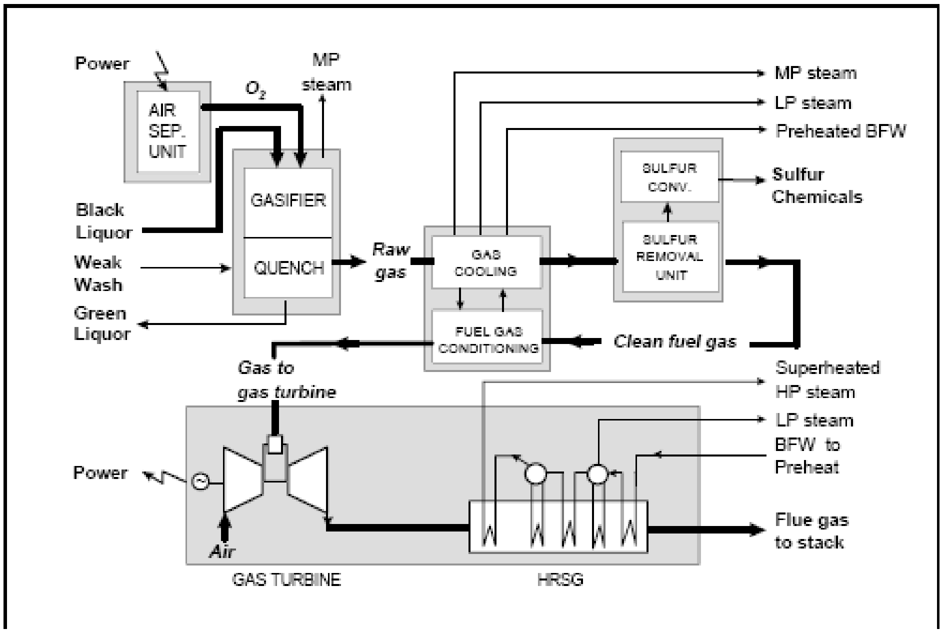

Figure 19:Chemrec BLGCC recovery island (Refer to Stigsson etc. 1999).

3) Biorefinery Process

There are several ways to design a biorefinery process to gasify black liquor to generate DME (or F-T liquid). Referring to Larson [109] the following designs were introduced:

a. Biorefinery process to generate DME with a Rankine power system.

In the design of biorefinery process with a Rankine power system, all of the synthesis gas from the black liquor gasifier is sent to a liquid-phase DEM synthesis reactor. Uncovered syngas is separated from DME and 97% of it is recycled to the reactor. The 3% purge gas is sent to the hog fuel boiler and burned with an amount of wood residues to generate sufficient steam to meet all of the mill's process steam needs. Heat recovered from the black liquor gasification and syngas processing are integrated into the boiler to increase steam production and minimize the need of woody residues. The generated steam is expanded through a back-pressure turbine to generate some electricity for the mill's process electricity needs. To note that to fully meet the mill's electricity need, some electricity must be imported from the grid.

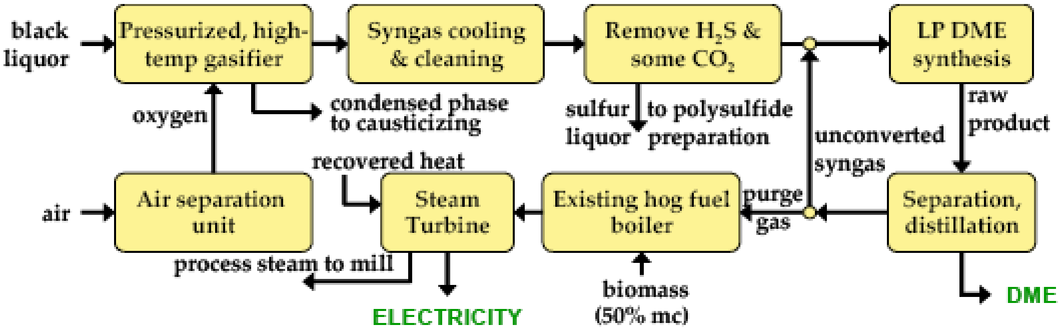

Figure 20: Schematic of biorefinery DME with a Rankine power system (Larson, 2006).

b. Biorefinery process to generate DME with a combined biomass gasifier and gas turbine cycle.

In order to increase electricity generation, the biorefinery process was adjusted to increase the efficiency with which electricity is being generated. The adjusted process is shown in Figure 21. In this process, woody biomass is gasified and used a fuel for a gas turbine-steam turbine combined cycle (GTCC). In the GTCC, the electricity to steam production ratio is higher than that of the boiler/steam turbine system. To deliver the same amount of process steam more biomass is needed. But electricity production is considerable greater than biorefinery process with a boiler/steam turbine system.

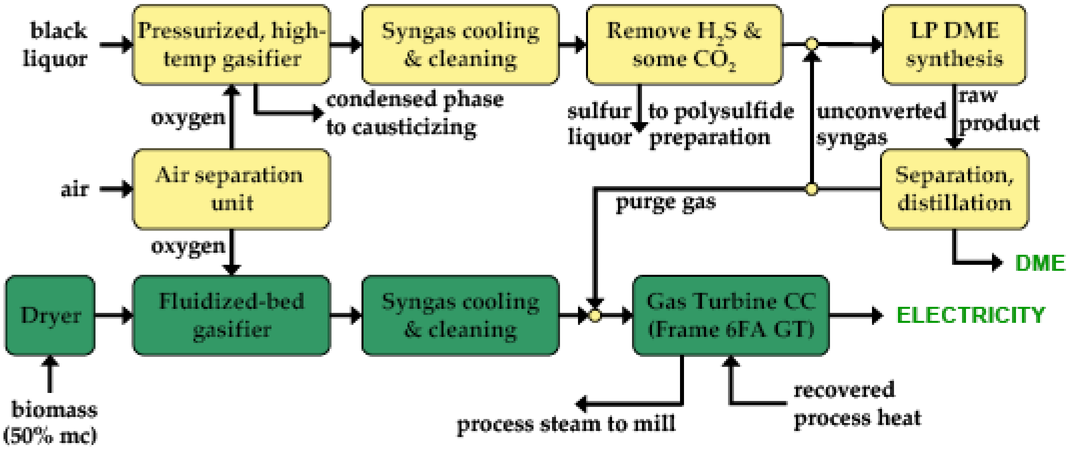

Figure 21: Schematic of biorefinery for DME with a combined biomass gasifier and gas turbine cycle (which is presented by darker shadings) (Larson, 2006).

c. Biorefinery process to generate DME with a once-through synthesis design.

Another approach to increasing electricity production is to decrease the level of syngas recycle to the synthesis reactor. Thus, more uncovered gas is available for power generation. The biorefinery process is similar to the process b (Figure 21). The syngas recycle loop is eliminated and syngas only passes once through the reactor. The DME production is much lower than in the process b but the required amount biomass is relatively low. The schematic of the process is shown in Figure 22.

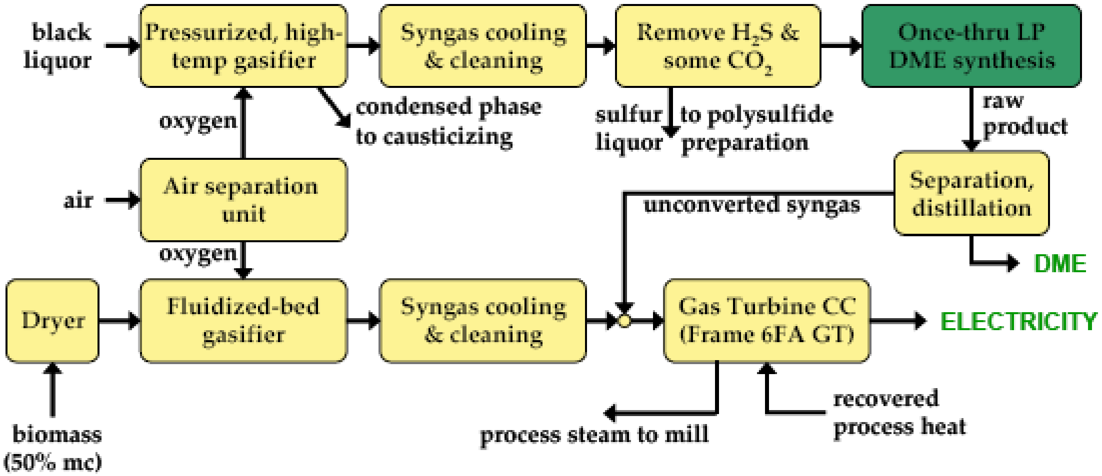

Figure 22: Schematic of biorefinery for DME with a once-pass synthesis design (Larson, 2006).

Considering large part of unconverted energy was out of biofuel synthesis, we designed to use this energy to generate electricity in a gas turbine. The high temperature exhaust gas from gas turbine was sent to a heat recovery steam generator (HRSG) to superheat steam for a steam turbine to generate more electricity. Our aim of process design is to maximize steam and power generation to meet the pulp/paper mill's demand with the bio-fuel generation. The diagram of process design was shown in Figures 23 and 24.

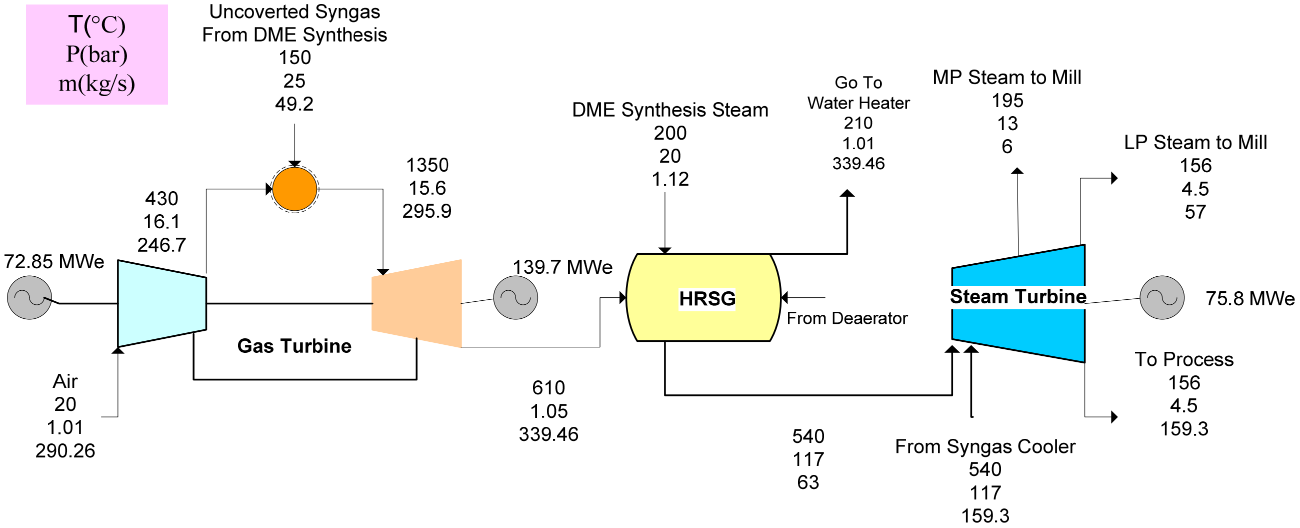

Figure 23: Power generation with unconverted syngas from DME synthesis.

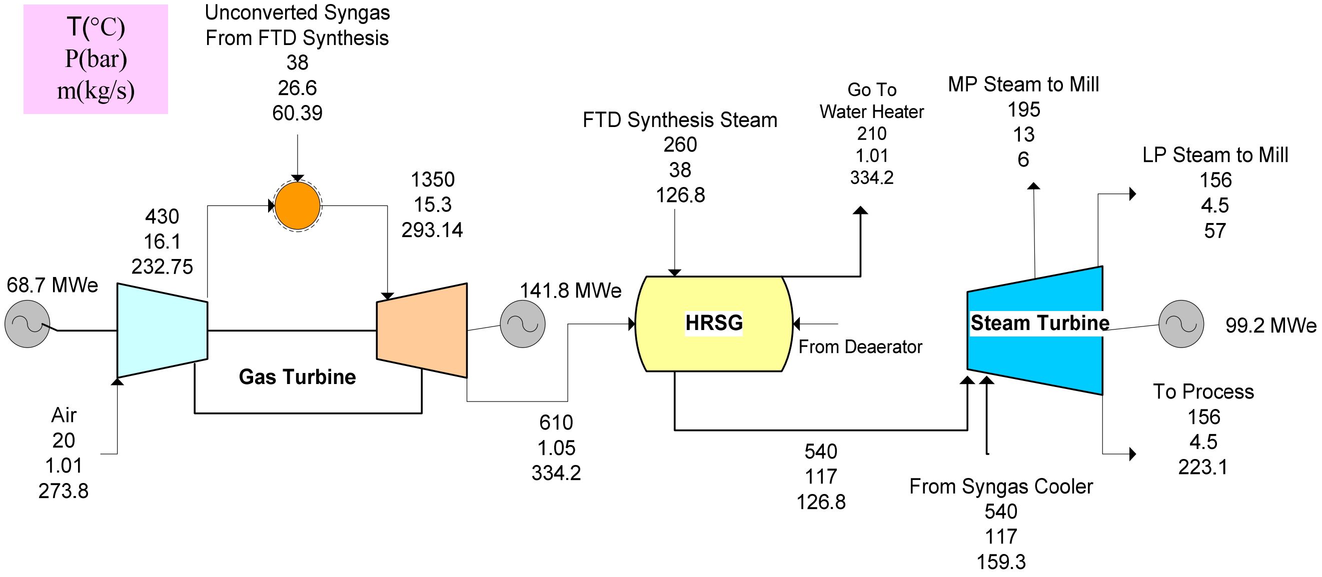

Figure 24: Power generation with unconverted syngas from FTD synthesis.

3.5.3 Design Considerations

1. Gas Turbine

A gas turbine is also called a combustion turbine. It is a rotary engine that extracts energy from a flow of hot gas produced by combustion of gas or fuel oil in a steam of compressed air. Gas turbines are used in industrial plants to drive equipments such as compressors, pumps, and generators, and in electrical utilities to produce power. The compressed air (typically 10 to 25 bar) reacts with the fuel in the combustor. Hot pressurized flue gases expand in the turbine, driving the compressor and the generator [110]. The exiting gases from a gas turbine can be recovered to produce steam. This steam can be injected into the steam injected gas turbine (SIGT) or into a separate steam turbine (steam and gas turbine, STEG).

The overall efficiency of the STEG system (up to 60%) is higher than that of STIG due to the higher efficiency of steam expansion in the steam turbine than in the gas turbine. The heat exchanger used to produce steam from gas turbines flue gases is the heat recovery steam generator (HRSG). The HRSG consists of the steam superheater sections (the flue-gas path containing finned pipe modules), the evaporation section, and the economizer section (for feedwater preheating). A condensing/extraction steam turbine is used in a combined heat and power system as the steam can be extracted for use as process steam or expanded completely to the condenser and fully utilized for power generation. Gas turbines increase the efficiency of a combined heat and power system with increased the turbine rotor inlet temperature (TRIT). The new generation of ‘G’ and ‘H’ gas turbines give greater than 60% efficiency by achieving TRIT above 1400°C.

When choosing a gas turbine the compressor and expander operating conditions are met. That is to meet inlet temperature with sufficient mass flow with the certain outputs. With the designed output of 100MW, “F” GE gas turbine was chosen.

In our refinery design, a gas turbine-steam turbine combined cycle (GTCC) was used. The gas turbine used uncovered syngas and recovered process heat to generate electricity. A heat recovery steam generator (HRSG) operated the gas turbine exhaust heat to generate steam for the biorefinery process steam and a steam turbine generator. Also, the steam from the synthesis reactor was superheated in the HRSG. The HRSG makeup water could be preheated using extracted heat from syngas.

Because of the low heating value of syngas, more mass flow of gas was needed to achieve the turbine inlet temperature. Thus, more power output was achieved. But there was a high fraction of water vapor (24.9 wt%) in the gas turbine exhaust, which would put more stain on materials and decrease material life.

2. Gas cleaning

Quaak [110] introduced basic knowledge on gasification systems. Before the producer gas can be used in a gas turbine, it must be cleaned of tars, alkali metals, and dust. Alkali metals, dust, and tars cause corrosion and erosion of cylinder walls and pistons. The quality requirements for gas turbine flue gas are listed in Table 28. The ceramic filter operating at high temperature could be an option for hot clean-up, which is more efficient than low-temperature quench and wet scrubbing technologies. Alkali compounds in the biomass are vaporized during gasification. When the product gas is cooled below 500°C the vapors condense and deposit on entrained solids. So, alkali compounds can be removed with particulate removal below 500°C. In our process, raw syngas is first cooled in a syngas cooler to about 450°C, and then filtered.

Table 28: Quality requirements for gas turbine fuel gas.

Gas characteristic	Unit of measure	Level
Minimum LHV	MJ/Nm^3	3–11
Particles	ppm	< 2-30
Alkali metals	ppm	< 0.2-1.0

3. Combustion stability in Gas Turbine

Stigsson [108] and Larson [109] noted that from the experience accumulated in Integrated Gasification Combined Cycles (IGCC) and experimental work, combustion stability is not a major issue when the fuel calorific value is above 4-6 MJ/m^3_n (at normal conditions of 1 atm, 0°C). Syngas produced with pure oxygen gasification has a heating value of 8-20 MJ/m^3_n. In our design considered, no particular flame stability problems are envisaged.

4. Steam Turbine:

There are two basic steam turbine designs: back pressure and condensing. We chose back pressure steam turbine and let the steam leaving the turbine go into the steam distribution system to meet the steam requirement from pulp/paper process demand.

3.5.4 Design Main Issues

1. Recovery Heat from Syngas Cooling

In our design, we used a syngas cooler to recovery heat to generate electricity other than to use a water quench to recovery chemicals. From Table 29 we can see a large part of energy (54.4 MWe) was recovered from raw syngas.

Table 29: Power from Syngas cooled steam.

Flow Rate of steam	kg/s	159.3
Power	MWe	54.37

2. Recovery Energy from Biofuel Synthesis Waist Steam

In F-T diesel synthesis process, a large flow rate of waist steam was generated. We recovered this part of energy by sending the steam to HRSG to be superheated and then sending it to the steam turbine to generate electricity. This steam could generate 22 MWe electricity.

Table 30: Power from F-T diesel synthesis waist steam.

Flow Rate of steam	kg/s	126.8
Power	MWe	21.77

3. Recovery Heat from HRSG Exhaust Gas

Exhaust gas from HRSG still was in high temperature (210°C). We designed to recover this heat to saturate water in a water heat exchanger. The saturated water then was sent to the syngas cooler to generate steams. This part of heat recovery increased the system efficiency.

Figure 25showed the detailed energy and mass flow in the water heater. The recovered energy from HRSG exhaust gas was shown in Table 31.

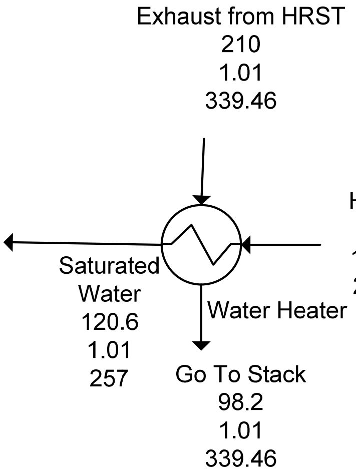

Figure 25: Energy and mass flow in the water heater.

Table 31: The recovered energy of from HRSG exhaust gas to saturate H2O in the Water Heater.

Temperature	°C	120.6
Pressure	bar	1.01
Flow Rate	kg/s	257.02
c_p^a	kJ/kgK	1.901
Energy H_2O absorbed	MW	**46.71**

4. Recovery Energy from HRSG

A HRSG was designed to recover heat from gas turbine exhaust gas. High temperature (610°C) exhaust gas superheated steam from biofuel synthesis or from the deaerator for steam turbine to increase power generation. From Table 32 we can see, 21 MWe power can be recovered from HRSG.

Table 32: Power generated in the steam turbine with energy recovered from HRSG.

Power from MP Steam		
Flow Rate	kg/s	6
Power	MWe	1.94
Power from LP Steam		
Flow Rate	kg/s	57
Power	MWe	19.45
Power from HRSG recovered heat	MWe	21.4

3.5.5 Power and Heat Generation Conclusion

The main operation parameters of power and heat generation were listed in Table 33. The output of heat and power was listed in Table 34. Our design generated enough steam to meet the paper/pulp process needs, and generated sufficient electricity to meet all of the mill's internal electricity needs. There was also additional electricity generated for selling.

Table 33: Main operating parameters of power and heat generation.

Gas Turbine		HRSG		Steam Turbine	
Air mass flow	290 kg/s	Evaporation pressure	130 bar	HP steam conditions	540°C/110bar
Air inlet pressure	1.01 bar	Superheater Dp/p	10%	MP steam conditions	195°C/13bar
Pressure ratio	17	Superheater temperature	540 °C	LP steam conditions	156°C/4.5bar
Compressor polytropic efficiency	0.89	Heat loss	0.70%	Turbine efficiency	0.485
Turbine inlet temperature	1350 °C	Steam pressure out of HRSG	117 bar		
Turbine efficiency	0.6	HRSG outlet gas temperature	210 °C		
Compressor pressure drop	0.5 bar				
Exhaust temperature	610 °C				

Table 34: Heat and power generation in the design.

Heat

Pulp and Paper Mill Steam Requirement

		MP	LP
Pressure	bar	13	4.5
Flow Rate	kg/s	37.5	61.3

Steam Generated in the Design

		MP Steam for Mill		LP Steam for Mill		Superheated Steam for ST	
		ST	Syngas Cooling	ST	Syngas Cooling	HRSG	Syngas Cooling
Temperature	°C	195	195	156	156	540	540
Pressure	bar	13	13	4.5	4.5	117	117
Flow Rate	kg/s	6	31.5	57	4.3	63	159.3

Power

Pulp and Paper Mill Power Requirement (MWe)	56.3

Power Generation	Gas Turbine		Steam Turbine		
	DME Purge Gas	FTD Purge Gas	LP Steam	MP Steam	Steam from Syngas Cooler
MWe	139.70	141.8	19.45	1.94	54.37
Efficiency	0.6		0.485		
Total MWe	215.46	217.56			

4. Design Summary

The DME design and FTD design were designed based on equivalent feeds of coal and black liquor. The coal and black liquor were gasified to syngas at efficiency of 70.5%. The syngas is sent to the DME design and the FTD design individually.

In the DME design the clean syngas is converted to DME product at an efficiency of 51.1%. The entire system efficiency for the DME design was calculated to be 48.6%. The efficiency of clean syngas to FTD and naphtha was 48.5% The overall system efficiency of the FTD design from feed stock to FTD liquids was 52.6%

The main efficiency loses from the coal and black liquor gasification was due to ASU. The air separation unit, which creates oxygen for paper bleaching and syngas processing, had an energy loss of 55.7 MWe. Utility energy losses for the DME design and FTD design were included in the individual process efficiency. Table 35 gives the energy flow going in and out of the DME design and the FTD design.

Table 35: Energy and efficiency summary of DME design and FTD design.

	DME Design	FTD Design
Coal feed [MW]	1908.1	1908.1
Black liquor [MW]	132.5	132.5
Energy flow in [MW]	2040.6	2040.6
Loss ASU [MW]	167.1	167.1
DME [MW]	735.2	n/a
Diesel [MW]	n/a	536.1
Naphtha [MW]	n/a	161.2
Gas turbine [MW]	225.9	229.8
Steam turbine [MW]	199.9	313.8
Energy flow out [MW]	993.9	1073.8
Design plant efficiency [%]	48.7	52.6

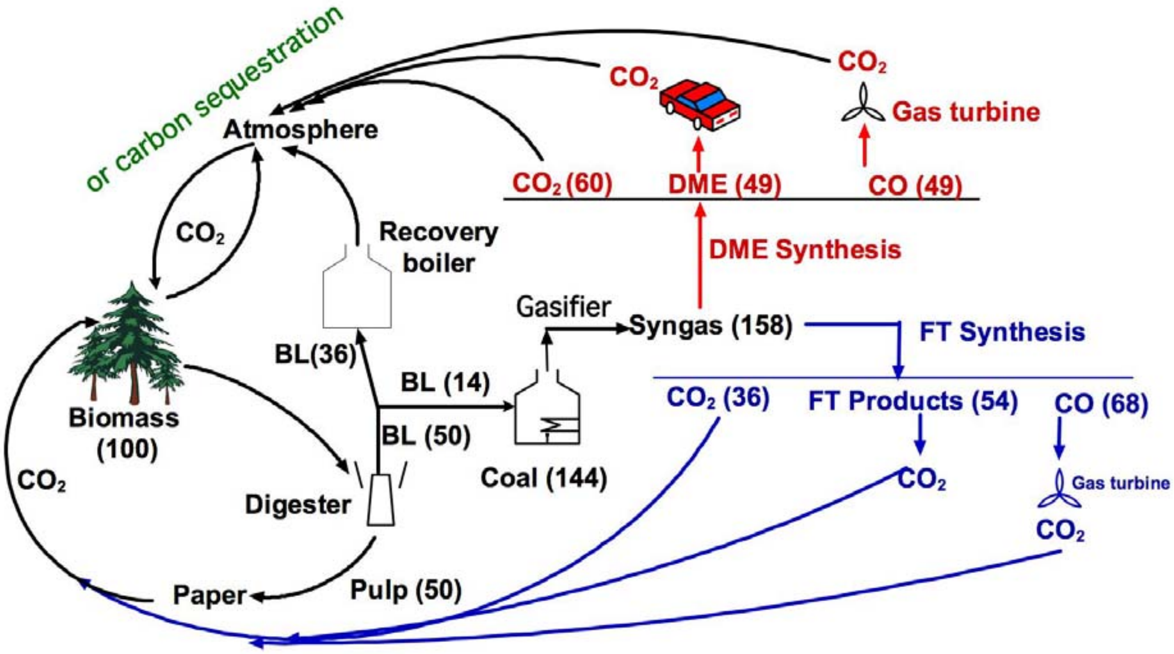

Figure 26: Carbon cycle analysis of DME and FTD designs.

Fig. 26 shows the carbon cycle analysis of the overall process. If we assume 100 carbons in the biomass feed, we will get 50 carbons in black liquor and 50 carbons in the pulp from the digester. Part of black liquor will be sent to the recovery boiler which has 36 carbons in it and the rest of 14 carbons will be sent to the gasifier with coal. According to the black liquor and coal ratio we used, there are 144 carbons in the coal. Therefore, 158 carbons are in the product syngas due to the mass balance. If DME is produced, 49 carbons will go to DME, 60 carbons go to carbons dioxide and 49 carbons will go to carbons monoxide. After combustion of DME and CO, all carbons in DME and CO will convert to carbons dioxide finally. Alternatively, 54, 36, 68 carbons in the syngas will go to FT products, CO_2 and CO, respectively. CO_2 produced will be released to the atmosphere or conserved by carbons sequestration. Part of CO_2 will be absorbed by biomass and converted to O_2 by photosynthesis. So far, one carbon cycle is completed.

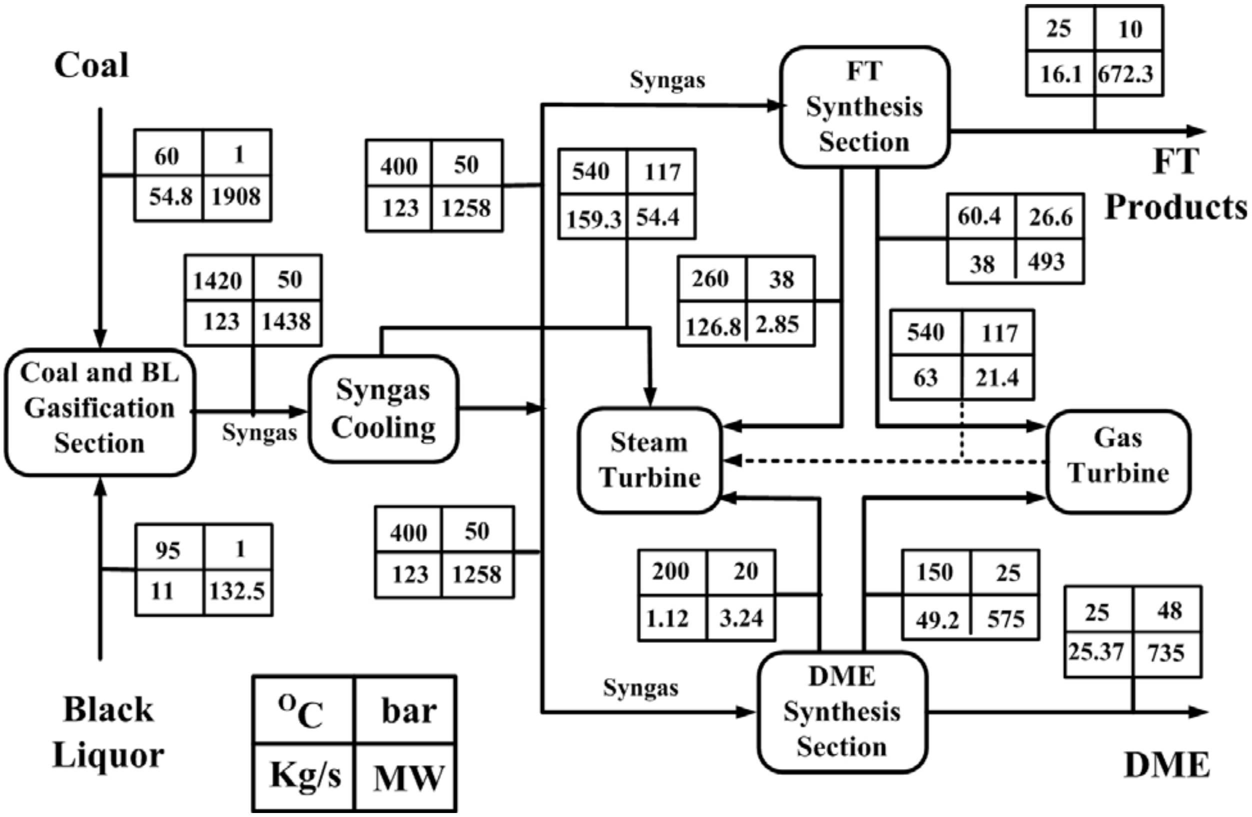

Figure 27: Mass and energy flow of DME design and FTD design.

Fig. 27 shows the energy and mass flow in the coal/black liquor to fuel process for both the DME design and FTD design. The DME design and FTD design, from the point of clean syngas to fuel products, used different assumption in the configuring of the designs. The designs were scaled from designs found in literature and reflect the liquid product efficiency from the designs. The majority of the assumption made for the DME design and the FTD design were for the heat and steam recovery. It is difficult to account for the heat requirement of a fuel production plant by scaling alone. Each and every component of the plant consuming and producing heat must be accounted for. This is a source of error in either design. The DME design and the FTD design were conservatively calculated. Literature reports both plants to have efficiency in the 60% to 70% range. The next step in the design of these plants would be to verify the outputs with computer modeling.

5. Conclusion

The results of this project should be confirmed with computer modeling and a complete economic evaluation as the next phase of the design process. For black liquor and coal gasification to synthesis gas and further processing to Fischer-Tropsch diesel and DME, a higher efficiency was achieved for Fischer-Tropsch fuels. Fischer-Tropsch fuels can also be easily integrated into existing fuel distribution infrastructure and used in engines without any modifications. Based on these factors, a current plant design recommendation for this project would include a reactor for Fischer-Tropsch fuels. If a niche for DME is developed in the future or a fleet of vehicles can be modified for DME, it may be beneficial to also include a module for DME synthesis in order to produce both fuels from gasification of coal and black liquor.

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Appendix

Appendix A

MP Steam Demand

Steam tables show the specific enthalpy of MP steam at 11 bar and 200 degrees Celsius to be 2.822 GJ/tonne.

$$4.3\frac{GJ}{ADt}*2000\frac{ADt}{day}*\frac{1}{24}\frac{day}{hr}*\frac{1}{2.822}\frac{tonneMPsteam}{GJ}=126.98\frac{tonne}{hr}$$

LP Steam Demand

Steam tables show the specific enthalpy of LP steam at 3.5 bar to be 2.732 GJ/tonne.

$$5.68\frac{GJ}{ADt}*2000\frac{ADt}{day}*\frac{1}{24}\frac{day}{hr}*\frac{1}{2.732}\frac{tonneMPsteam}{GJ}=173.26\frac{tonne}{hr}$$

Total Steam Demand

$$173.26\frac{tonne}{hr}+126.98\frac{tonne}{hr}=300.24\frac{tonne}{hr}$$

Power required to run mill

$$701\frac{kWh}{ADt}*2000\frac{ADt}{day}*\frac{1}{24}\frac{day}{hr}*\frac{1}{1000}\frac{MWe}{kW}=58.42MWe$$

Energy into System

$$4148\frac{tonnewood}{day}*1000\frac{kg}{tonne}*\frac{1}{86400}\frac{day}{s}*16\frac{MJ}{kg}=768.15MW$$

$$4148\frac{tonnewood}{day}*1000\frac{kg}{tonne}*\frac{1}{86400}\frac{day}{s}*20\frac{MJ}{kg}=960.19MW$$

Bark Energy Flow

$$362.5\frac{tonnebark}{day}*1000\frac{kg}{tonne}*\frac{1}{86400}\frac{day}{s}*16.0\frac{MJ}{kg}=67.13MW$$

Black Liquor Used

$$950\frac{tonnes}{day}*1000\frac{kg}{tonne}*12.1\frac{MJ}{kg}*\frac{1}{86400}\frac{day}{\sec onds}=133.04MW$$

Modified Steam Demand

Modified MP Steam Demand

Steam tables show the specific enthalpy of MP steam at 11 bar and 200 degrees Celsius to be 2.822 GJ/tonne.

$$4.3\frac{GJ}{ADt}*2000\frac{ADt}{day}*\frac{1}{24}\frac{day}{hr}*\frac{1}{2.822}\frac{tonneMPsteam}{GJ}=119.3\frac{tonne}{hr}$$

Modified LP Steam Demand

Steam tables show the specific enthalpy of LP steam at 3.5 bar to be 2.732 GJ/tonne.

$$5.68\frac{GJ}{ADt}*2000\frac{ADt}{day}*\frac{1}{24}\frac{day}{hr}*\frac{1}{2.732}\frac{tonneMPsteam}{GJ}=150.4\frac{tonne}{hr}$$

Total Steam Demand

$$150.4\frac{tonne}{hr}+119.3\frac{tonne}{hr}=269.7\frac{tonne}{hr}$$

Na_2SO_4 required

$$144130\frac{tonneNaOH}{day}*\frac{1}{.822}\frac{tonneNa_2SO_4}{tonneNaOH}=17534\frac{tonneNa_2SO_4}{day}$$

Appendix B:

Composite Fuel Blend to Texaco Gasifier

Solids requirement: 55 wt. % solids
Black liquor solids content: 0.17 kg solid/kg weak black liquor

Assuming 100 kg of black liquor feed:
83 kg water
17 kg black liquor solids

To achieve 55 wt% solids:

$$\frac{(17+x)}{(17+83+x)} = 0.55$$

Coal requirement = x = 84.4 kg

Based on the solids distribution 84.4 kg coal/17 kg black liquor and the composition of coal and black liquor, the composite fuel blend composition was calculated using Excel.

	From BL (kg)	From Coal (kg)	Total (kg)	Wt. Percent
Carbon	6.1	62.7	68.7	67.8%
Hydrogen	0.6	4.3	4.9	4.9%
Nitrogen	0.0	1.1	1.2	1.1%
Sulfur	0.7	3.3	4.0	4.0%
Oxygen	6.1	5.1	11.2	11.0%
Sodium	3.2	0	3.2	3.2%
Potassium	0.2	0	0.2	0.2%
Chlorine	0.1	0	0.1	0.05%
SiO_2	0	2.9	2.894	2.9%
Al_2O_3	0	1.4	1.403	1.4%
TiO_2	0	0.1	0.061	0.1%
Fe_2O_3	0	2.9	2.926	2.9%
MgO	0	0.0	0.048	0.0%
CaO	0	0.2	0.242	0.2%
Na_2O	0	0.0	0.026	0.0%
K_2O	0	0.1	0.112	0.1%
P_2O5	0	0.0	0.005	0.0%
SO_3	0	0.1	0.136	0.1%
Total (kg)	***17.0***	***84.3***	***101.3***	

Coal Requirement from Experimental Syngas Yield

The coal-black liquor gasification process was designed to achieve an annual DME yield of 0.8 million tons per year DME.

Experimental results were found in the literature to determine an average syngas composition. The calorific value of syngas was calculated from the average syngas composition and lower heating values of individual syngas components.

Table B.1: Average syngas composition

Raw Syngas	**Feed 1**	**Feed 2**	**Feed 3**	**Average**
H_2	38.7	37.9	34.4	37.0
CO	46.6	45.2	45.3	45.7
CO_2	11.5	13.2	15.8	13.5
CH_4	0.7	0.9	1.9	1.2
N_2	2	1.7	1.9	1.9
H_2S	0.7	0.6	-	0.7
H_2/CO Ratio	0.830	0.838	0.759	0.809

Feed 1: Pittsburgh high volatile bituminous coal. CV 35.540 MJ/kg, 7.2% ash. H.D. Schilling, B Bonn, U Krauss. Coal Gasification. 1981, Graham & Trotman.

Feed 2: Japanese lignite, high-vol C bituminous. CV 22.840 MJ/kg, 13% ash. *H.D. Schilling, B Bonn, U Krauss. Coal Gasification. 1981, Graham & Trotman.*

Feed 3: Bituminous coal, 1.9% sulfur, CV 24.5 MJ/kg. From Chmielniak, T. and Sciazko, M. *Co-gasification of Biomass and Coal for Methanol Synthesis. Applied Energy 74 (2003) 393-403.*

Table B.2: Average syngas composition

Components	**Mole %**	**MW**	**Wt. %**	**HV (MJ/kg)**
H_2	37.0	2.02	3.7%	120.1
CO	45.7	28.01	62.7%	10.9
CO_2	13.5	44.01	29.1%	0
CH_4	1.2	16.04	0.9%	50.1
N_2	1.9	28.01	2.6%	0
H_2S	0.7	34.08	1.1%	0
H_2/CO Ratio	**0.8**			
HV (MJ/kg)	**11.69**			**11.69**

0.8 Million tons of DME per year = 2191.78 tons per day

DME

Density = 0.67 kg/L (at 20 °C)
Calorific value = 28.98 MJ/kg

1 barrel = 42 gallons = 159 liter
1 J/s = 10^{-6} MW_t

$$\left(\frac{2198.78 tons}{day}\right)\left(\frac{1000 kg}{ton}\right)\left(\frac{28.98 x 10^6 J}{day}\right) = 63517.8\frac{GJ}{day}$$

Assuming a cold gas efficiency of DME production is 51.1%, the syngas energy required:

$$\frac{\left(63517.8\frac{GJ}{day}\right)}{0.51} = 124228\frac{GJ}{day}$$

The syngas mass requirement:

$$\left(\frac{124228 GJ}{day}\right)\left(\frac{1000 MJ}{GJ}\right)\left(\frac{1 kg}{11.6 MJ}\right)\left(\frac{ton}{1000 kg}\right) = 10629\frac{ton}{day} = 123\frac{kg}{s}$$

The syngas yield is known, but the amount of fuel required to generate a mass of syngas is unknown.

Experimental results from a source that included mass flow rates of coal input, oxygen flow rates, and mass flow rates of syngas components from a Texaco gasifier were used to determine how much coal/black liquor fuel feed is required to generate 123 kg/s syngas.

Only sample runs with oxygen-to-fuel ratios similar to the current project design (O_2/fuel=0.9) were used to determine the mass of fuel needed to generate a mass of syngas. The source fuel is coal residues from Illinois No. 6 bituminous coal, which differs from this design project's black liquor and Pittsburgh No. 8, but the value is assumed to be reasonable if the assumption remains constant that changing the gasifier feedstock causes insignificant changes to syngas composition and yield.

The average fuel/syngas mass ratio is 0.534.

Table B.3: Fuel input and syngas component mass flow rates[94].

Fuel In (kg/s)	**O_2/Fuel**	**CO**	**H_2**	**CO_2**	**CH_4**	**H_2S**	**N_2**	**Syngas Mass (kg/s)**	**kg Fuel per kg Syngas**
76.66	0.866	123.80	6.00	9.99	0.15	0.13	0.53	140.60	0.55
56.26	0.832	81.85	4.53	20.61	0.04	0.80	0.07	107.91	0.52
132.79	0.848	204.16	10.57	29.96	0.19	0.68	0.42	245.98	0.54
									0.535

Chemrec Gasification Process

Table B.4: Fuel input and syngas component mass flow rates.

Temp	975	C
Pressure	32	bar
Oxygen	1172	ton/day
Gasifier Feed	140	ton/hr
Black Liquor	3420	dry tons/day
DME yield	824	tons/day

Table B.5: Fuel input and syngas component mass flow rates[94].

Syngas	mole%
H_2	30.55
CO	29.70
CO_2	14.93
CH_4	1.05
N_2	0.19
H20	22.09
H_2S	1.44
COS	0.05
H_2/CO	**1.03**

Air Separation Unit Requirements

Based on the design by D. Cocco for an IGCC power plant for DME synthesis, the oxygen pressure should be compressed to 1.2 times the gasifier pressure.

Assuming gasifier pressure of 50 bar

Oxygen pressure = (1.2)*(50) = **60 bar**

The mass flow rate of oxygen from the ASU to the gasifier was determined by the oxygen-fuel requirement the gasifier.

Oxygen-to-fuel requirement = 0.9 kg oxygen/kg fuel

Oxygen mass flow rate = (0.9)*(65.9) = **60.3 kg/s**

The air flow rate required to the ASU was determined by calculating the air to oxygen mass flow rate ratios for the D. Cocco IGCC design and relating them to our design.

Similarly, the energy contained in the oxygen from the ASU to the gasifier was calculated using the ratio approach.

	D. Cocco	**Our Design**
Oxygen (kg/s)	68.1	60.3
Air (kg/s)	278.6	X
Oxygen (MW)	68.1	X

Oxygen mass flow rate = X = [(60.3)*(278.6)]/68.1 = **242.6 kg/s**

Oxygen energy content = X = [(60.3)*(113)]/68.1 = **98.4 MW**

Appendix C: Dimethyl Ether Synthesis

In order to enjoy the scale merit of production, the size of a single DME plant should be at least 1 to 2 million tons per year capacity. In addition, based on the availability of the feed (black liquor and coal), our goal for DME production is 0.8 million tons per year, that is 2191.78 tons per day.

Parameters[93]:
1J/s= 10^{-6} MWt
1 barrel = 42 gallons = 158.99 Liter
DME Density: 0.67 kg/L (20 ^{o}C, 5×10^{5}Pa)
DME molecular weight: 46.07
DME Calorific value: 28.98 MJ/kg

DME:
Mass:
2191.78 t/d= 2191.78*1000/0.67/158.99 = 20575.59 bbl/d
Mass flow rate:
25.37kg/s
Energy:
2191.78 t/d*28.98 = 63517.78 GJ/d= 735.16MWt

Syngas:

Table C.1: The composition of Syngas([43])

components	Mole percentage	Mass percentage	Molecular weight	LHV (MJ/kg)
CO	45.7	0.62683	2.02	10.9
H2	37.0	0.03659	28.01	120.1
CH4	1.2	0.00916	44.01	50.1
CO2	13.5	0.29094	16.04	
N2	1.9	0.02560	28.01	
H2S	0.7	0.01084	34.08	

Syngas average molecular weight:
(45.7*2.02 + 37.0*28.01 + 1.2*44.01 + 13.5*16.04 + 1.9*28.01 + 0.7*34.08) = 20.42
Syngas heating value:
(0.62683*10.9 + 0.03659*120.1 + 1.2*50.1) = 11.69 MJ/kg
At 270 ^{o}C and 50 bar, CO conversion is 60%.
Efficiency:
(1/3*0.6*46.07*28.98)/(1/45.7*20.42*11.687) = 0.51
Energy of syngas needed per day:
63517.78/0.51= 124228.17 GJ/d =1437.83 MWt
Mass of syngas needed per day:
124228.17/11.69 = 10629.33 t/d
Mass flow rate:
123.02 kg/s

Purge gas:
CO conversion is 60%, 40% unconverted syngas is sent to gas turbine:
Energy:
124228.17*0.4 = 49691.27 GJ/d = 575.13 MWt
Mass:
49691.27/11.69 = 4251.73 t/d
Mass flow:
49.21 kg/s

Steam:
Steam calculation is based on reactions 1) $2CO + 4H_2 = 2CH_3OCH_3$; 2) $2CH_3OH = CH_3OCH_3 + H_2O$; 3) $H_2O + CO = H_2 + CO_2$. The equilibrium conversion of reaction 3) is 88.7%, therefore if 1 g DME is produced, 0.044 g H_2O is produced.
Mass:
2191.78*0.044 = 96.44 t/d
Mass flow:
1.12 kg/s
Energy:
Energy per mole steam (from 20 bar 200°C to 1 bar 25°C): 280.2073251 GJ/d
$\Delta H_{vap}H_2O + (200-100)*Cp(H_2O(g)) + (100-25)*Cp(H_2O(l)) + RT*\ln(20bar/1bar)$
= 40.6 kJ/mol + 100*33.58 J/mol + 75* 75.3 J/mol + 8.314*373.5*ln20 J/mol
= 40.6 kJ/mol + 3358 J/mol + 5647.5 J/mol + 9302.6 J/mol
= 58.9 kJ/mol
96.44*1000/18* 58.9= 280.21 GJ/d = 3.24 MWt

Summary:

Table C.2: DME properties

Parameters	
DME density/(kg/L)	0.67
DME molecular weight	46.07
DME calorific value/(MJ/kg)	28.98

Table C.3: Overall reaction conversion and efficiency

$3CO+3H_2 = CH_3OCH_3 + CO_2$	
CO one through conversion	0.6
STD Effeciency	0.511299382
STD cold gas effeciency(paper)	0.71
STD ideal effeciency (paper)	0.826
STD ideal effeciency (calc)	0.852165637

Table C.4: Energy and mass flow

	DME	**Syngas**	**Purge gas**	**Steam**
Energy/(GJ/d)	63517.78	124228.17	49691.27	280.20
Energy/(MWt)	735.16	1437.83	575.13	3.24
Mass/(t/d)	2191.78	10629.33	4251.73	96.44
Mass flow (kg/s)	25.37	123.02	49.21	1.12
P/bar	48	50	25	20
T/oC	25	1420	150	200

Appendix D: FTD Synthesis

Two different LTFT designs where considered for the FTD production design; a case study based on a Salso design from Steynberg et al. and a case study modeled in Aspen Plus by Larson et al [72, 81]. Both case studies used slurry-phase bubbling reactors utilizing iron based catalyst.

The Steynberg et al. case study was initially examined. The Steynberg et al. case study provided a mass and energy balance for Fischer-Tropsch synthesis from the point of gasifying coal to pre-upgraded Fischer-Tropsch production. This case study is given in Figure D.1 and Table D.1.

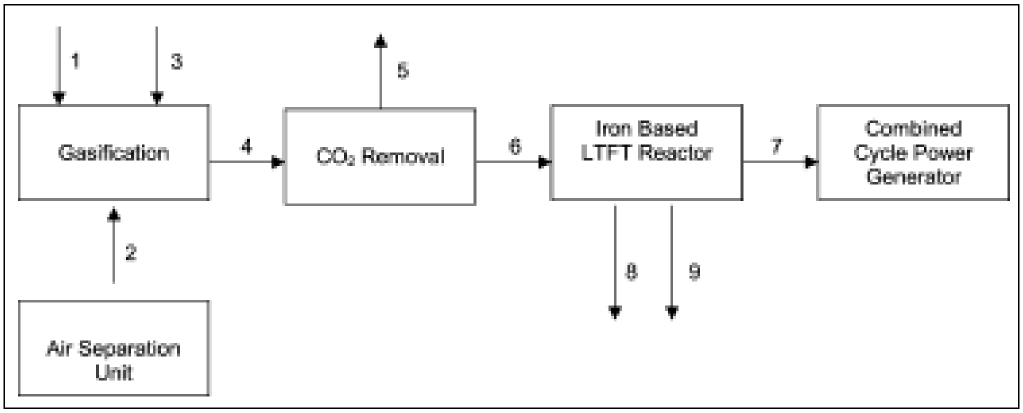
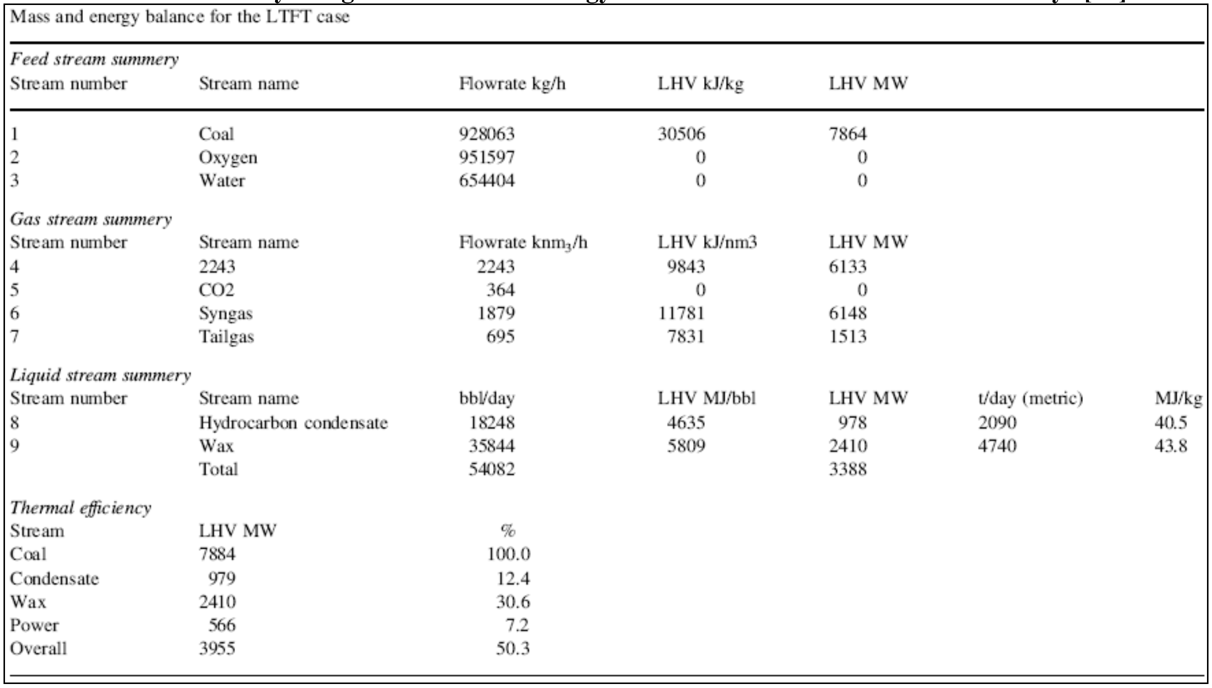


Figure D.1: Steynberg et al. mass and energy flow diagram for LTFT with iron catalyst [72].

Table D.1: Steynberg et al. mass and energy flow balance for LTFT with iron catalys [72]t.



Mass and energy balance for the LTFT case

Feed stream summery					
Stream number	Stream name	Flowrate kg/h	LHV kJ/kg	LHV MW	
1	Coal	928063	30506	7864	
2	Oxygen	951597	0	0	
3	Water	654404	0	0	
Gas stream summery					
Stream number	Stream name	Flowrate knm$_3$/h	LHV kJ/nm3	LHV MW	
4	2243	2243	9843	6133	
5	CO2	364	0	0	
6	Syngas	1879	11781	6148	
7	Tailgas	695	7831	1513	
Liquid stream summery					
Stream number	Stream name	bbl/day	LHV MJ/bbl	LHV MW	t/day (metric)	MJ/kg
8	Hydrocarbon condensate	18248	4635	978	2090	40.5
9	Wax	35844	5809	2410	4740	43.8
	Total	54082		3388		
Thermal efficiency					
Stream	LHV MW	%			
Coal	7884	100.0			
Condensate	979	12.4			
Wax	2410	30.6			
Power	566	7.2			
Overall	3955	50.3			

The clean syngas to Fischer-Tropsch productions portion of the Steinberg's case study was scaled down to provide mass flow rates for the FTD design. Though Steynberg et al. case study provides a mass and energy balance, assumptions and back calculations were necessary to provide adequate data to scale down the design. The syngas gas used in the Steynberg et al. case study is given in Table D.2. Using the mole % data giving in Table D.2, and the volumetric flow rate of clean syngas from Table D.1, the mass flow rate of syngas from the Steynberg et al. case study was calculated to be 395.5 kg/s.

Table D.2: Syngas gas used in the Steynberg et al. case study [72].

Species	mole %
H_2	29.26
CO	37.36
CO_2	13.3
CH_4	0.16
H_2O	19.43
Inert	0.49

Table D.1 shows the Steynberg et al. design produce 18248 bbl/day of hydrocarbon condensate and 35844 bbl/day of wax. The hydrocarbon condensate is assumed to be hydrocarbon chains from C_5 to C_{20} and the wax is assumed to be C_{20+} hydrocarbon chains. The hydrocarbon condensate would make up 30.6 % of the FT products and wax would make up 69.4%. These product percentages correspond to an α of 0.94 on a Anderson-Schultz-Flory distribution, given in Figure D.2. The hydrocarbon chain product produced from an α of 0.94 are given in Table D.3. Though Steynberg et al. did not account for C_1 to C_4 products; they are produced and are part of the tailgas. Using an α of 0.94 assumes that approximately 2% of the FT-products will be C_1 to C_4. Thus, it was assumed that the Steynberg et al. design used α of 0.94 and this product distribution was then used for the FTD design of this project.

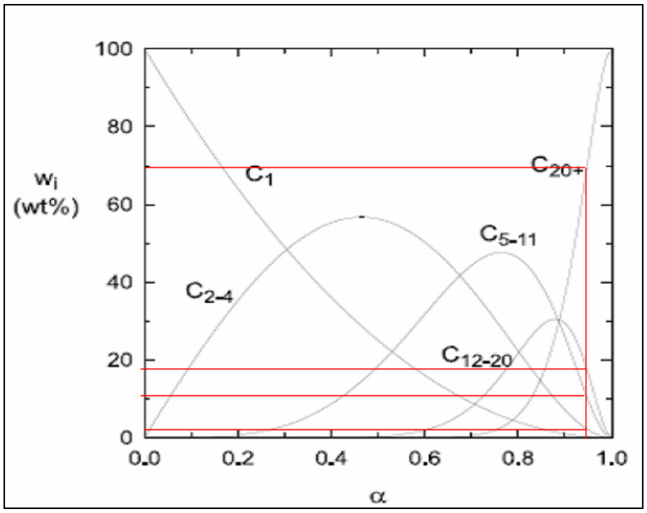


Figure D.2: Anderson-Schultz-Flory distribution, with plots of calculated selectivities (% carbon atom basis) of carbon number product cuts as a function of the probability of chain growth. The red lines indicate products for an α of 0.94

Table D.3: The hydrocarbon product extrapolated to be produced from Steynberg et al. case study, in percent weight.

α = 0.94	
C_{20+}	70
C_{12}-C_{20}	17
C_5-C_{11}	11
C_1-C_4	2
total	100

FT-product upgrading via hydrocracking of wax is achieved at ~400 °C with the addition of a small amount of hydrogen. However, Steynberg et al. stated that "product upgrading units have a negligible impact on the utility systems[72]." Thus, product upgrading was assumed to be a "black box" with an input of wax going in and a distribution of upgraded products coming out with no effect on the efficiency of the system.

Rytter et al. reported hydrocracking of wax to yelled 80% diesel, 15% Naphtha and 5% C_1-C_4 gases [106]. These values were used to calculating the FT-production distribution for the FTD design.

The efficiency from clean syngas to FT-product in Steynberg et al. case study is 55%. However, the syngas used by Steynberg et al. was more energetic than that for this design, having a LHV of 15.5 MJ/kg compared to 11.7 MJ/kg. To account for this, the FT-reactor for this project's design yields a lower mass flow rate even at the scaled down rate, so that the design would have an efficiency of 55% while using a syngas LHV of 11.7 MJ/kg.

The Steynberg et al. case study was based on 395.5 kg/s of clean syngas using two sets of first stage reactors followed by second stage reactors with all four reactors running at maximum output. The Steynberg et al. case study uses the minimum feasible scale of this reactor combination. This project's FTD design is based on 123 kg/s of clean syngas. Thus, the Steynberg et al. reactors will provide a system's efficiency that is not realist for a system scaled down to utilize 123 kg/s of clean syngas. So the efficiency of the Steynberg et al. case study is greater than that of any possible efficiency for a 123 kg/s of clean syngas design, but will provide insight to the true efficiency.

Table D.4 Figure D.3 are the mass and energy balance of Steynberg et al. case study and a possible FTD design for this project. The FTD design is scaled down from the Steynberd et al. case study at a factor 0.21. The scale is based on the energy flow of the Steynberg et al. case study's syngas to that of this project's syngas.

Table D.4 Mass and energy balance of the Steynberg et al case study FTD design both with estimated final produce from upgrading.

	Steynberg et al.	*FTD design*
Coal feed mass flow [kg/s]	**257.8**	**54.8**
Coal feed energy flow [MW]	**7864.0**	**1908.1**
Black liquor mass flow [kg/s]		**11.0**
Black liquor energy [MW]		**132.5**
Total fuel feed mass flow [kg/s]	**257.8**	**65.9**
Total fuel feed energy [MW]	**7864.0**	**2040.5**
Clean syngas [kg/s]	**395.5**	**123.0**
Clean syngas LHV [MJ/kg]	**15.5**	**11.7**
Clean syngas [MW]	**6149.0**	**1437.8**
Hydrocarbon condensate [kg/s]	**24.2**	
Wax [kg/s]	**54.9**	
Total products [kg/s]	**79.1**	**18.5**
scale	**0.23**	**0.23**
FT-product C_{20+} [kg/s]	**55.3**	**12.9**
FT-product C_{12}-C_{20} [kg/s]	**13.4**	**3.1**
FT-product C_5-C_{11} [kg/s]	**8.7**	**2.0**
Tailgas flow [kg/s]	**316.5**	**104.5**
Tailgas LHV [MJ/kg]	**4.8**	**3.4**
Tailgas [MW]	**1513.0**	**353.8**
C_1-C_4 in tail gas [kg/s]	**1.6**	**0.4**
C_1-C_4 LHV approximant [MJ/kg]	**46.0**	**46.0**
C_1-C4 Energy [MW]	**72.7**	**17.0**
waste gas in tailgas [kg/s]	**314.9**	**104.2**
waste gas in tailgas [MW]	**1440.3**	**336.8**
Wax cracking product - diesel [kg/s]	**44.3**	**10.4**
Wax cracking product - naphtha [kg/s]	**8.3**	**1.9**
Wax cracking product - C_1-C_4 [kg/s]	**2.8**	**0.6**
Diesel [kg/s]	**57.7**	**13.5**
Diesel [bbl/day]	**40214.1**	**9403.2**
Diesel LHV [MJ/kg]	**43.1**	**43.1**
Diesel energy [MW]	**2487.2**	**581.6**
Naphtha [kg/s]	**17.0**	**4.0**
Naphtha [bbl/day]	**11843.9**	**2769.4**
Naptha LHV [MJ/kg]	**44**	**44**
Naphtha energy [MW]	**747.8**	**174.9**
C_1-C_4 [kg/s]	**8.7**	**0.6**
C_1-C_4 LHV approximant [MJ/kg]	**46.0**	**46.0**
C_1-C_4 Energy [MW]	**434.8**	**32.3**
Energy sum MW	**3235.0**	**756.4**
Syngas to FT-product efficiency	**52.6**	**52.6**
Feed to FT-product energy efficiency	**41.1**	**37.1**

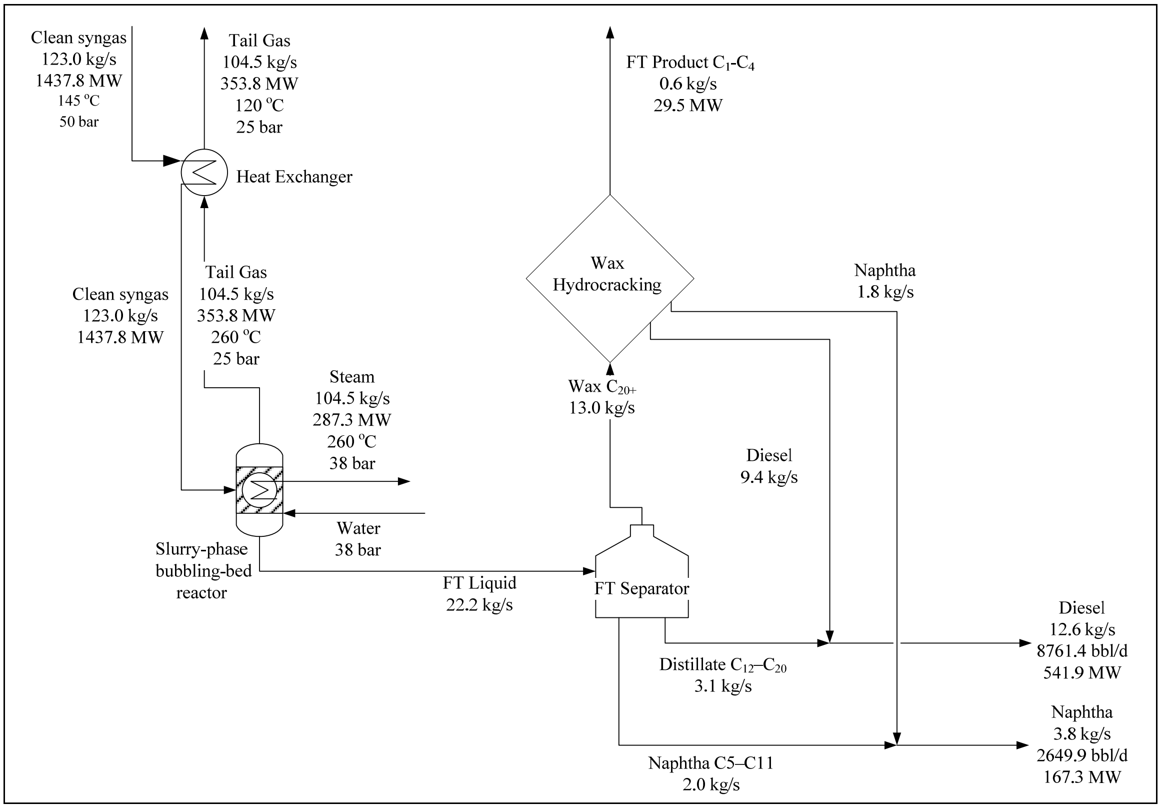


Figure D.3 Mass and energy balance of the Steynberg et al. case study FTD design both with estimated final produce from upgrading.

The tailgas and C_1 to C_4 products are not included in the syngas to FT-product efficiency or the feed to FT-product efficiency. The tailgas and C_1 to C_4 products are sent to turbines for power generation, which is included in overall system efficiency.

As mentioned previously, the Steynberg et al. case study design is not feasible at a lower scale. For this reason the Larson et al. case study was examined. The Larson et al. case study design utilizes a once through slurry-phase bubbling reactors utilizing iron based catalyst, given in Figure D.4.

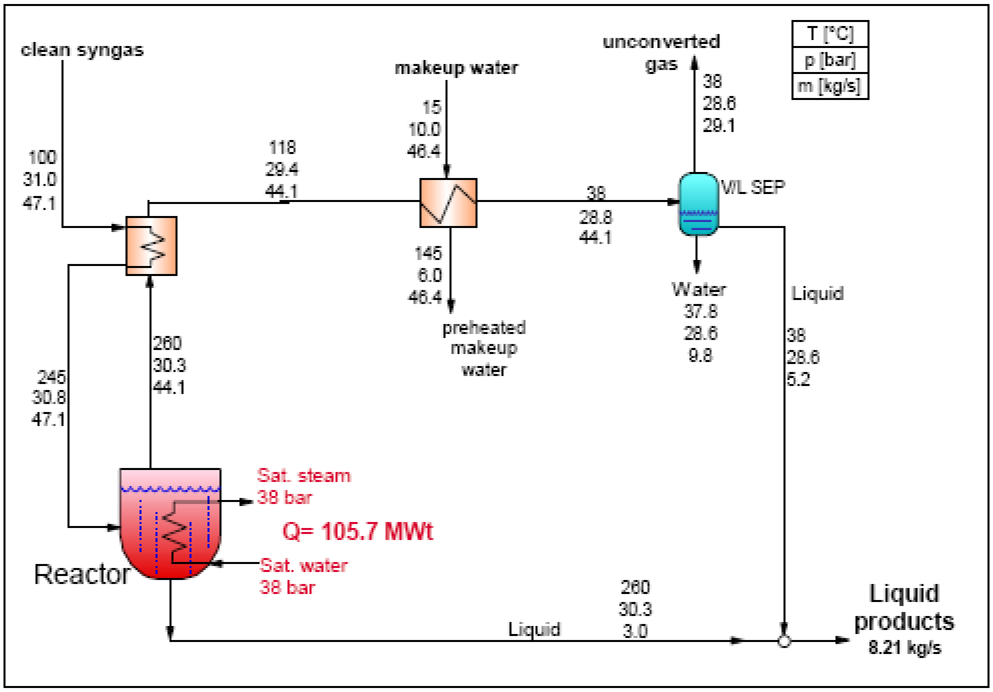


Figure D.4: Energy and mass balance of Larson et al. case study

The Larson et al. case study is based on 47.1 kg/s of clean syngas, which is a low flow rate than that of this project's FTD design. Larson et al. gave no information on product selectivity of its FT-products. An assumption can be made that a LTFT reactor will target high wax production to achieve the largest amount of FTD possible. An α to target FTD production will be no less than 0.9. Thus, an α of 0.94 was assumed as in the previous case.

The Larson et al. case study did not provide a composition of the syngas used, however it did give a H_2/CO ratio of 1.11. This mean that the syngas used in the Larson et al. case study is more energetic than the syngas produced and used in this project design. Table D.4 and Figure D.5 give the mass and energy balance of the Larson et al. and the FTD design used for this project. The final design is scaled up from Larson et al. at a factor 2.1. Table D.4 and Figure D.5 were scaled and developed using the same method and assumptions used to create Figure D.3 and table D.4

Table D.3 Mass and energy balance of the Larson et al. case study FTD design both with estimated final produce from upgrading.

	Larson et al.	*FTD design*
Coal feed mass flow [kg/s]		54.8
Coal feed energy [MW]		1908.1
Black liquor mass flow [kg/s]		11.0
Black liquor energy [MW]		132.5
Total fuel feed mass flow [kg/s]		65.9
Total fuel feed energy [MW]		2040.5
Clean syngas [kg/s]	47.1	123.0
Clean syngas LHV [MJ/kg]	14.7	11.7
Clean syngas [MW]	692.8	1437.8
Hydrocarbon condensate [kg/s]		
Wax [kg/s]		
Total products [kg/s]	8.2	17.0
scale	2.1	2.1
FT-product C_{20+} [kg/s]	5.7	11.9
FT-product C_{12}-C_{20} [kg/s]	1.4	2.9
FT-product C_5-C_{11} [kg/s]	0.9	1.9
Tailgas flow [kg/s]	29.1	60.4
Tailgas LHV [MJ/kg]	8.2	8.2
Tailgas [MW]	237.5	492.9
C_1-C_4 in tail gas [kg/s]	0.2	0.3
C_1-C_4 LHV approximant [MJ/kg]	46.0	46.0
C_1-C4 Energy [MW]	7.6	15.7
waste gas in tailgas [kg/s]	28.9	60.1
waste gas in tailgas [MW]	229.9	477.2
Wax cracking product - diesel [kg/s]	4.6	9.5
Wax cracking product - naphtha [kg/s]	0.9	1.8
Wax cracking product - C_1-C_4 [kg/s]	0.3	0.6
Diesel [kg/s]	6.0	12.4
Diesel [bbl/day]	4176.5	8667.9
Diesel LHV [MJ/kg]	43.1	43.1
Diesel energy [MW]	258.3	536.1
Naphtha [kg/s]	1.8	3.7
Naphtha [bbl/day]	1230.1	2552.9
Naptha LHV [MJ/kg]	44	44
Naphtha energy [MW]	77.7	161.2
C_1-C_4 [kg/s]	0.9	0.6
C_1-C_4 LHV approximant [MJ/kg]	46.0	46.0
C_1-C_4 Energy [MW]	45.2	29.8
Energy sum MW	336.0	697.3
Syngas to FT-product efficiency [%]	48.5	48.5
Feed to FT-product efficiency [%]		0.34

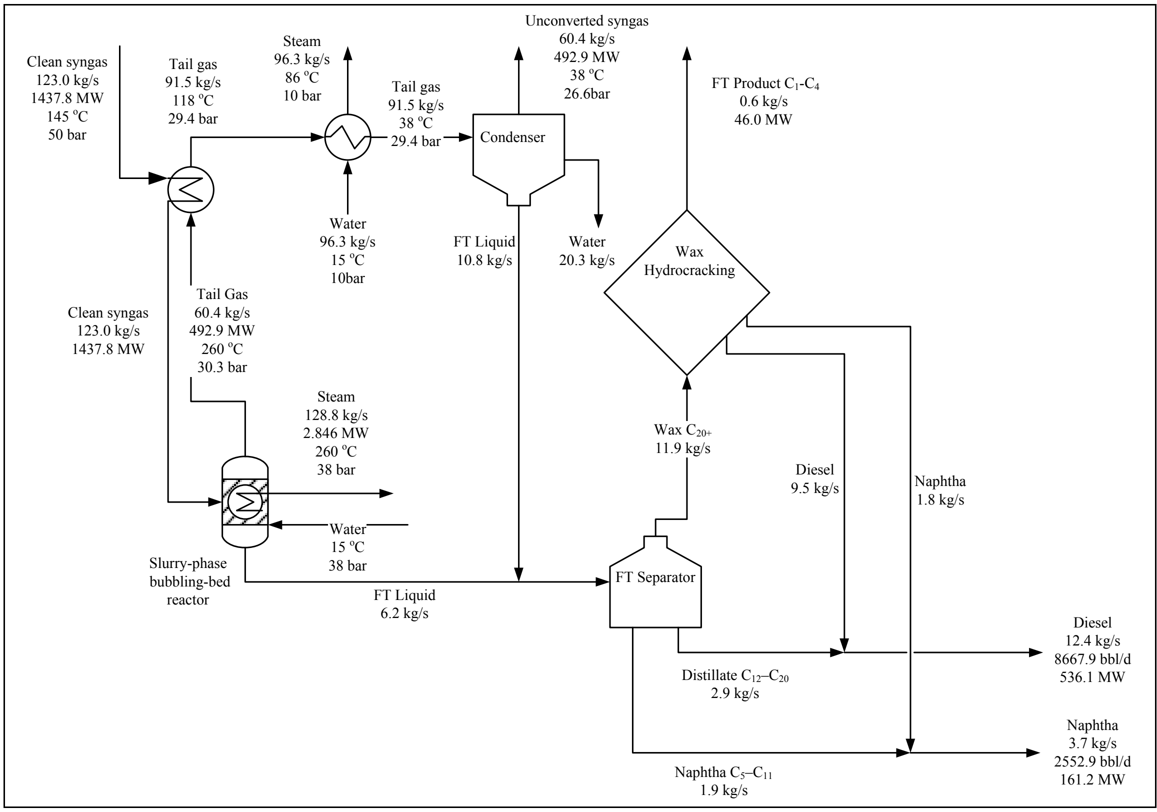


Figure D.5: Mass and energy balance of the Larson et al case study FTD design both with estimated final produce from upgrading.

The syngas to FT-product efficiency of the FTD project design based on Larson et al. is 48.5 %, where the design based on the Steynberg et al. case study is 52.6 %. The FTD design based on the Larson et al. case study was used for this project, because its scale is closer to that of the case study it was based on, thus providing a more likely efficiency.

Diesel conversion:

$$1\frac{bbl}{day} = 0.001435\frac{kg}{s} \qquad 4.3\frac{kg}{s} = 2996.516\frac{bbl}{day}$$

$$1\frac{ton}{hour} = 0.277778\frac{kg}{s} \qquad 1\frac{kg}{s} = 3.599997\frac{ton}{hour}$$

Well to tank report		
	LHV	
Diesel	43.1	MJ/kg
Naptha	44	MJ/kg
Methane	50	MJ/kg

Well-to-Wheels analysis of future automotive fuels and powertrains in the European context
WELL-TO-TANK Report Version 2c, March 2007

Appendix E: Heat and Power Generation

1. Heat Recovery Calculation

Property of raw syngas:

Temperature	°C	1400
Pressure	bar	50
Flow Rate	kg/s	123
Energy	MWt	1437.8
CO:H_2		0.8096
H_2 mole percent	%	37
H_2 mass percent	%	3.66
H_2 c_p[a]	kJ/kgK	16.39
CO mole percent	%	45.7
CO mass percent	%	62.68
CO cp[b]	kJ/kgK	1.273

a. http://www.engineeringtoolbox.com/hydrogen-d_976.html

b. http://www.engineeringtoolbox.com/carbon-monoxide-d_975.html

Property of cooled syngas:

Temperature	°C	400
Pressure	bar	50
Flow Rate	kg/s	123
H_2 c_p	kJ/kgK	14.58
CO cp	kJ/kgK	1.106
Energy supplied from cooler	MW	179.81
Energy to generate steam for ST	MW	173.05

Heat Exchange:

Saturated Water

Temperature	°C	120.6
Pressure	bar	1.01
c_p[a]	kJ/kgK	1.901

a. http://www.engineeringtoolbox.com/water-vapor-d_979.html

MP Steam Heat Exchanger

MP Steam

Temperature	°C	195
Pressure	bar	13
Flow Rate	kg/s	31.5
c_p	kJ/kgK	2.733

Enthalpy	MJ/kg	2.7895
Energy of MP Steam used	MW	6.41

LP Steam Heat Exchanger		
LP Steam		
Temperature	°C	156
Pressure	bar	4.5
Flow Rate	kg/s	4.3
c_p	kJ/kgK	2.339
Enthalpy	MJ/kg	2.753
Energy of LP Steam used	MW	0.36

Mass flow rate of steam for ST:

Available Energy	MW	173.05
Steam Property		
Temperature	°C	540
Pressure	bar	117
c_p	kJ/kgK	2.5895
So, mass flow rate	kg/s	159.34

Heat exchange calculation in Water Heater:

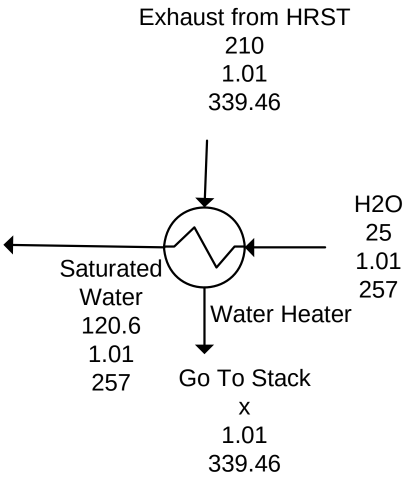


Figure E.1: Mass and energy flow of Water Heater.

Saturated H_2O		
Temperature	°C	120.6
Pressure	bar	1.01
Flow Rate	kg/s	257.02
c_p^a	kJ/kgK	1.901

Energy H_2O absorbed	MW	46.71

Using energy balance to calculate the temperature of flue gas to stack.

Flue gas from HRST

Mass flow rate	kg/s	339.46
CO_2 mass percent:		0.7512
Temperature	°C	210
Pressure	bar	1.01
c_p	kJ/kgK	0.996
H_2O mass percent:		0.2488
c_p	kJ/kgK	1.94
Cp of flue gas	kJ/kgK	1.231

So,

The temperature of flue gas to stack	°C	98.2

HRSG Calculation

Evaporation pressure	bar	130
Superheater Dp/p	%	10
Superheater temperature	°C	540
Heat loss	%	0.7
Steam pressure out of HRSG	bar	117

2. Power Generation from DME Purge Gas

Gas Turbine Calculation

Pressure ratio		17
Compressor polytropic efficiency		0.89
Turbine inlet temperature	°C	1350
Compressor pressure drop	bar	0.5
Turbine efficiency[a]		0.6
Air inlet pressure	bar	1.01
Exhaust temperature	°C	610
Compressed air pressure	bar	16.14
Pressure in turbine	bar	15.64
Compressed air flow rate	kg/s	246.72
Air mass flow	kg/s	290.26
Purge gas from DME Fuel Synthesis	kg/s	49.2

Exhaust mass flow	kg/s	339.46
Flue gas mass flow rate	kg/s	295.92
CO_2 generated	kg/s	222.29

a. http://en.wikipedia.org/wiki/Gas_turbine

Property of Purge Gas from DME Synthesis

Syngas		
Syngas flow rate	kg/s	123
$CO:H_2$		0.8096
Energy	MW	1437.8
Reactor Efficiency	%	60
H_2 mole percent	%	37
CO mole percent	%	45.7
Purge Gas		
Energy	MW	575.12
Temperature	°C	150
Pressure	bar	25
Flow rate	kg/s	49.20

Reaction in Gas Turbine:

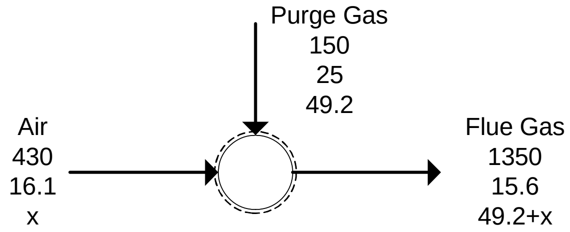


Figure E.2: Mass and energy flow diagram for gas turbine combustor with DME purge gas.

Combustion		
$2CO+O_2 \rightarrow 2CO_2$ + 566 kJ/mol		
CO mole percent:	%	45.7
CO_2 mass percent:		0.7512
Combustion Heat	kJ	258.66
$2H_2(g) + O_2(g) \rightarrow 2H_2O(g)$ + 653.4kJ/mol		
H_2 mole percent:	%	37
H_2O mass percent:		0.2488
Combustion Heat	kJ	241.76

Flue Gas		
H_2O vapor Cp[a]	kJ/kgK	2.663
Energy	kW	(49.2+x)*0.2488*2.663*(1623-298)
CO_2 Cp[b]	kJ/kgK	1.314
Energy	kW	(49.2+x)*0.7512*1.314*(1623-298)

a.http://www.engineeringtoolbox.com/water-vapor-d_979.html

b. http://www.engineeringtoolbox.com/carbon-dioxide-d_974.html

Air		
Cp	kJ/kgK	1.075
Energy	kW	(x)*1.075*(703-298)

Purge Gas		
CO Cp[a]	kJ/kgK	1.051
CO mass percent		0.6268
Energy	kW	4051.42
H_2 Cp[b]	kJ/kgK	14.49
H2 mass percent		0.0366
Energy	kW	49.2

a. http://www.engineeringtoolbox.com/carbon-monoxide-d_975.html

b. http://www.engineeringtoolbox.com/hydrogen-d_976.html

Energy from Purge Gas	MW	575.12

Energy Balance:

$E_{air} + E_{combus} + E_{purgegas} = E_{fluegas}$

From energy balance we got:

x= 246.72 kg/s

Gas Turbine Generate Electricity

Flue Gas

Mass flow rate	kg/s	295.92

H_2O Vapor

mass percent	%	0.2488
Temperature	°C	1350
Pressure	bar	15.6
Enthalpy	MJ/kg	5.406
Specific Heat (c_p)	kJ/kgK	2.521

H_2O Steam

mass percent	%	0.2488
Temperature	°C	610
Pressure	bar	1.05
Enthalpy	MJ/kg	3.7264
Specific Heat of Steam (c_p)	kJ/kgK	2.212

CO_2

mass percent	%	0.7512
Temperature	°C	1350
Pressure	bar	15.6
Enthalpy	MJ/kg	1.9209
Specific Heat (c_p)	kJ/kgK	1.314
Temperature	°C	610
Pressure	bar	1.05
Enthalpy	MJ/kg	0.8836
Specific Heat (c_p)	kJ/kgK	1.203
Turbine Efficiency		0.6
Power Generated by Flue Gas	MWe	212.55

Power needed to compress air

Mass flow rate of air	kg/s	290.26
Compressor Efficiency		0.6
Assume it is dry air, below 100C, c_p[a]	kJ/kgC	1.06
Temperature	°C	20
Pressure	bar	1.01
Enthalpy	MJ/kg	0.0212
Temperature	°C	430
Pressure	bar	16.1

Specific Heat (c_p)[b]	kJ/kgK	1.072
Enthalpy	MJ/kg	0.43952
Power needed to compress air	MWe	72.85

a. http://www.engineeringtoolbox.com/enthalpy-moist-air-d_683.html

b. http://www.engineeringtoolbox.com/air-properties-d_156.html

Power from Gas Turbine	MWe	139.70

3. Power Generation from FT Purge Gas

Gas Turbine Calculation

Turbine polytropic efficiency		0.6
Compressed air flow rate	kg/s	232.75
Air mass flow	kg/s	273.82
Purge gas from DME Fuel Synthesis	kg/s	60.39
Exhaust mass flow	kg/s	334.21
Flue gas mass flow rate	kg/s	293.14
CO_2 generated	kg/s	220.21

Property of Purge Gas from FT Synthesis

Syngas		
Syngas flow rate	kg/s	123
$CO:H_2$		0.8096
Energy	MW	1437.8
Reactor Efficiency	%	50.5
H_2 mole percent	%	37
CO mole percent	%	45.7
Energy	MW	492.90
Temperature	°C	38
Pressure	bar	26.6
Flow rate	kg/s	60.39
C1-C4		
Energy	MW	46.00
Temperature	°C	38.00
Pressure	bar	38.00
Flow rate	kg/s	0.60
Purge Steam		
Energy	MW	360.9

Temperature	°C	260
Pressure	bar	38
Flow rate	kg/s	126.8

Reaction in Gas Turbine:

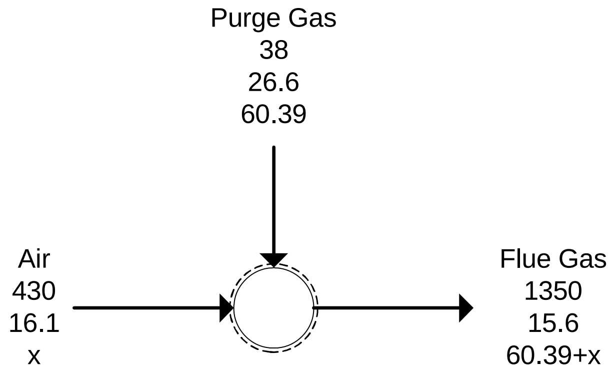


Figure E.3: Mass and energy flow diagram for gas turbine combustor with FTD purge gas.

Energy from Purge Gas 538.90 MWe

From energy balance we got:

x= 232.75 kg/s

Gas Turbine Generate Electricity

Flue Gas

Mass flow rate	kg/s	293.14

H_2O Vapor

mass percent	%	0.2488
Temperature	°C	1350
Pressure	bar	15.6
Enthalpy	MJ/kg	5.406
Specific Heat (c_p)	kJ/kgK	2.521

H_2O Steam

mass percent	%	0.2488
Temperature	°C	610
Pressure	bar	1.05
Enthalpy	MJ/kg	3.7264

Specific Heat of Steam (c_p)	kJ/kgK	2.212

CO_2

mass percent	%	0.7512
Temperature	°C	1350
Pressure	bar	15.6
Enthalpy	MJ/kg	1.9209
Specific Heat (c_p)	kJ/kgK	1.314

Temperature	°C	610
Pressure	bar	1.05
Enthalpy	MJ/kg	0.8836
Specific Heat (c_p)	kJ/kgK	1.203

Turbine Efficiency		0.6
Power Generated by Flue Gas	MWe	210.55

Power needed to compress air

Mass flow rate of air	kg/s	273.82
Compressor Efficiency		0.89
Assume it is dry air, below 100C, c_p[a]	kJ/kgC	1.06

Temperature	°C	20
Pressure	bar	1.01
Enthalpy	MJ/kg	0.0212

Temperature	°C	430
Pressure	bar	16.1
Specific Heat (c_p)[b]	kJ/kgK	1.072
Enthalpy	MJ/kg	0.43952

Power needed to compress air	MWe	68.73

a. http://www.engineeringtoolbox.com/enthalpy-moist-air-d_683.html
b. http://www.engineeringtoolbox.com/air-properties-d_156.html

Power from Gas Turbine	MWe	141.82

4. Power Generation from Steam Turbine

Property of MP Steam[a]

Pressure	bar	13
Temperature	°C	195
Enthalpy	MJ/kg	2.7895

Specific Heat of Steam (c_p)	kJ/kgK	2.733
Turbine Efficiency		0.9

Property of LP Steam

Pressure	bar	4.5
Temperature	°C	156
Enthalpy	MJ/kg	2.753
Specific Heat of Steam (c_p)	kJ/kgK	2.339
Turbine Efficiency		0.485

Property of Superheated Steam

Pressure	bar	117
Temperature	°C	540
Enthalpy	MJ/kg	3.4567
Specific Heat of Steam (c_p)	kJ/kgK	2.5895

a. http://www.spiraxsarco.com/esc/SSW_Properties.aspx

Steam Turbine Generate Electricity

Required Electricity	MWe	56.3

Power from MP Steam

Flow Rate	kg/s	6
Power	MWe	1.94

Power from LP Steam

Flow Rate	kg/s	57
Power	MWe	19.45

Power from Syngas cooled steam

Flow Rate	kg/s	159.3
Power	MWe	54.37

Generated power in ST with DME purge gas	MWe	75.76

Power from FTD Synthesis Steam

Flow Rate	kg/s	126.8
Power	MWe	21.77

Generated power in ST with FTD purge gas	MWe	99.2

Steam Distribution

Required MP Steam	kg/s	37.5
Required LP Steam	kg/s	61.3
MP Steam from Syngas heated	kg/s	31.5
LP Steam from Syngas heated	kg/s	4.3

Appendix F: Concept Map