Development of An Integrated System Model for Production of Fischer-Tropsch Liquid Fuels from Biomass

Nargess Puladian¹, Jingge Li and Shusheng Pang
Chemical and Process Engineering Department
University of Canterbury, Christchurch, New Zealand
¹Email: nargess.puladian @pg.canterbury.ac.nz

Abstract— An integrated system model for conversion of woody biomass to liquid fuels through gasification and FT synthesis was developed in the UniSim Design simulation environment. The model consists of biomass drying, biomass gasification, gas cleaning and conditioning, Fischer-Tropsch (FT) liquid fuel synthesis, FT crude hydro-treating and power generation. The model is based on mass and energy balances, and chemical reactions involved in each operation unit. For modelling of the gasification process, a three stage quasi equilibrium model including pyrolysis, char-gas reactions and steam-gas reactions was developed. Correction factors were also introduced to fine-tune the introduced parameters employed in the model. Also, user defined models were developed for drying and hydro-treating sections. The simulator’s built-in unit operations were used to model the gas cleaning, gas conditioning, FT synthesis and power generation.

The model predicted that the maximum chemical efficiency of 50% and overall energy efficiency of 61% were achieved for a plant of 100 MWth (input) which are comparable with values reported in literature. A sensitivity analysis was conducted to study the effect of gasification condition (steam to biomass ratio and temperature), gas conditioning and FT synthesis reactor’s condition (pressure and temperature) on the plant efficiency. The system model developed in UniSim Design can be applied for optimization of the process of FT liquid fuels production from biomass.

Keywords-component; system modeling; Fischer-Tropsch synthesis; biomass gasification, UniSim Design

I. INTRODUCTION

Biomass as a carbon-neutral resource is getting more and more attention for generation of bioenergy and transport fuels. Technologies of combustion, gasification, pyrolysis, fermentation and extraction have been developed for conversion of biomass to heat, electricity, methanol, ethanol and bio-diesel[1]. An alternative way we interested at the University of Canterbury (UoC) is Fischer-Tropsch (FT) liquid fuels from biomass via gasification. FT crude can be refined in a conventional refinery and the FT gasoline and diesel can be directly used in the current transport infrastructure[2]. More importantly, FT fuels generates less environmental pollution than conventional fossil fuels [3, 4]. FT synthesis process has three main steps: gasification of biomass to synthesis gas (syngas), FT synthesis of the syngas to crude and refining of the crude. In addition, the off-gas from the FT synthesis reactor and the heat recovered in a FT plant can be used for electricity and steam generation.

A pilot scale 100 kWth dual fluidized bed (DFB) gasifier has been constructed at the UoC for biomass gasification following the pioneer work at the Vienna University of Technology [5-7]. The DFB gasifier consists of a bubbling fluidized bed (BFB) gasification reactor fluidized with steam as the gasification agent and a fast fluidized bed (FFB) combustion reactor fluidized with air for char combustion and flue gas. This process produces a hydrogen-rich producer gas with higher calorific value of approximately 13 MJ/Nm³ compared with that from air gasification, which is approximately 5 MJ/Nm³ [5]. It is also able to produce a syngas with the desired ratio of H₂/CO suitable for FT synthesis of transport fuels [8].

The design and operation of a FT plant need to be optimized for maximum conversion efficiency and minimum operation costs. Mathematical simulation has been proven to be a powerful tool to fulfill such task. This paper is to establish an integrated system model and to analyze the effect of operation condition on conversion efficiency of production of FT liquid fuels from woody biomass.

The energy efficiency of FT liquid fuel synthesis from woody biomass resources has been reported in literature [9-11]. The energy efficiencies of a plant with direct air blown pressurized gasifier was reported to be 37.7% and that of a plant with indirect air-blown atmospheric gasifier was reported to be 49.8% [9]. In these two cases a once-through FT reactor was used with 80% CO conversion. In a separate study, the maximum energy efficiency of 61.8 % was reported for BTFL plant with indirect heating entrained flow (EF) gasifier while the efficiency of a plant with conventional EF gasifier was 51.3%[10]. The energy efficiency of FT liquid fuel production was found to be 59% using fast internally circulating fluidized bed (FICFB)
gasifier with subsequent steam reforming step for gas conditioning in a once-through FT reactor.

It should be considered CO₂ effect and CO conversion efficiency in the system modeling. CO₂ in the syngas acts as inert gas in the FT synthesis to reduce the partial pressure of reactants of CO and H₂ and thus reduce the selectivity of FT catalysts toward liquid hydrocarbons. Therefore, CO₂ removal will help with increasing the catalysts selectivity and the liquid fuel production.

It was shown that at CO conversion efficiency over 85%, the selectivity to liquid fuels in the FT reactor decreased significantly which led to lower liquid yields [12]. In addition, higher CO conversion results in lower FT reaction rates thus the FT reactor volume is substantially increased and capital investment increased.

The objective of this work is to develop an integrated system model including biomass drying, DFB gasification, gas cleaning and conditioning, FT liquid fuel synthesis, FT crude hydro-treating and exhaust gas utilization from the FT reactor. The system is modeled using a combination of user-defined and built-in unit operations within UniSim Design environment. The effect on the system performance is studied of biomass gasification conditions such as temperature and steam to biomass ratio, gas conditioning, FT synthesis conditions including pressure and CO conversion. This study particularly optimizes the effect of the DFB gasification on the overall efficiency of the integrated FT system. Firstly, the operation conditions of the DFB gasifier are identified to produce a hydrogen rich syngas for FT synthesis. Secondly, energy recovery and reuse is optimized to make the gasification and biomass drying energy self-sufficient[13].

II. MODEL ESTABLISHMENT

A. Material and Process

A simplified process diagram of the integrated plant is shown in Figure 1. For efficient gasification of biomass in a fluidized bed, the biomass feedstock are in the form of pellets or chips with particle size of 2–30 mm and has moisture content of less than 20% on oven dry basis [6, 14]. However, the woody biomass from forest harvesting and wood processing commonly has a moisture content of 50 to 150% (oven dry basis) thus needs drying before the gasification.

The proximate and ultimate analyses of radiata pine are given in TABLE I.

<table>
<thead>
<tr>
<th>TABLE I</th>
<th>Proximate and ultimate analysis of radiata pine[15].</th>
</tr>
</thead>
<tbody>
<tr>
<td>Proximate Analysis wt% (od)</td>
<td>Ultimate Analysis, wt% (od)</td>
</tr>
<tr>
<td>H₂O</td>
<td>0</td>
</tr>
<tr>
<td>Volatile</td>
<td>84</td>
</tr>
<tr>
<td>Fixed carbon</td>
<td>15.6</td>
</tr>
<tr>
<td>Ash</td>
<td>0.4</td>
</tr>
<tr>
<td>S</td>
<td>0.02</td>
</tr>
</tbody>
</table>

In the simulation, a 100 MW plant was used which is likely the feasible scale in the area where abundant biomass is available from forest harvesting and wood processing plants such as in Central North Island, New Zealand. The wood chips are assumed to be the feedstock which firstly enters the rotary dryer to be dried from green to around 17% (od). The dried biomass then goes to the DFB gasifier where the temperature of the BFB gasification reactor is controlled between 750°C to 850°C while the FFB combustion reactor is controlled at around 100 °C higher. As the flue gas from the FFB reactor is from combustion of char, it is very clean and its heat can be efficiently extracted. The hot flue gas is firstly used for air preheating and then for steam generation, both of which are used in the DFB gasification system. Finally the exhaust flue gas is used for biomass drying. For FT liquid fuel synthesis application, the producer gas has to be cooled form initial temperature of 700-800 °C to around 340˚C for the following gas cleaning section [16]. The heat from producer gas cooling is recovered for steam generation as well.

The producer gas from DFB gasifier contains tar, ammonia, hydrogen sulfide and hydrogen chloride as the major impurities. The concentration of tar compounds needs to be less than dew point at corresponding pressure of the FT synthesis reactor in order to prevent fouling problems of hydrocarbon condensation [16]. The concentration of ammonia and hydrogen sulfide has to be reduced to 1ppm and hydrogen chloride to less than 10 ppb.

For the tar removal section, after cyclones which removed the particles, an absorber/stripper system operating with rape seed methyl ester (RME) as the tar absorbent is applied.
Ammonia and hydrogen chloride are removed in a wet scrubber after tar removal. For hydrogen sulfide removal, a ZnO fixed bed reactor is used for which the syngas is firstly reheated to 350°C which is the operating temperature of ZnO reactor [17]. It is followed by a gas conditioning step for adjusting the H₂/CO ratio to be 2 in the syngas except that this ratio is achieved directly in the DFB gasification. The gas conditioning step can be either a high temperature water-gas shift converter or a steam reformer. The water-gas shift reaction is exothermic and operates at temperatures between 300°C to 400°C while stream reforming operates at much higher temperature of around 850°C. In the steam reformer, a proportion of the syngas has to be burnt to provide the heat requirement of the reaction which is highly endothermic.

The FT liquid fuel synthesis reactor operates at elevated pressure of 26 to 50 bar therefore a compression step is included in the process. The gas is compressed in two steps. First step is to increase the pressure to 6 bar to increase the wet scrubber efficiency while the absorption efficiency of ammonia and hydrogen chloride increases with pressure. After gas conditioning, this gas is pressurized to the target level.

FT synthesis can be operated either at high temperature FT synthesis (HTFS) or at low temperature (LTFS). In HTFS, temperature is between 300–330°C targeting product of naphtha and olefins. However, more paraffinic and waxy products suitable for diesel production can be obtained in LTFS operating between 200–230°C. In this work a slurry type reactor with LTFT is adopted and the temperature is controlled by cooling water which boils to generate steam as supplementary stream of energy.

The wax-rich products from the LTFT reactor go to hydro-treating section operating at 400°C and elevated pressure (50 bar). The hydrogen required for hydro-treating is obtained from the synthesis gas after gas conditioning by applying pressure swing adsorption (PSA) technology for hydrogen separation. During hydro-treating, some light hydrocarbon is generated which is recycled to FT synthesis reactor. The final fuel products of the system are a mixture of diesel and naphtha.

The off-gas from FT synthesis reactor is used for power generation via gas turbine. Power is also generated using steam generated from the process. However, if the biomass feedstock is too wet and the flue gas heat from FFB reactor is not sufficient, the flue gas from power generation can be used for biomass drying as well.

### B. Rotary Dryer and DFB Gasifier

In the UniSim Design software simulating, the biomass is first dried in a rotary dryer to achieve the target moisture content of 17%. The input parameters to the drying operation are: i). mass flow rate and temperature of the flue gas as drying medium and ii). mass flow rate of wood chips as feedstock.

For establishing the model for the DFB gasifier system in UniSim Design, the whole process is divided into four steps including three steps in the BFB gasification reactor (initial pyrolysis, char-gas reactions and steam-gas shift reaction) and one step in FFB combustion reactor (combustion of char and supplementary fuel (RME & tar)). The three steps in the BFB gasification reactor are modeled by a quasi-three stage equilibrium model. For the pyrolysis step, a macro code in visual basic language is written in a user defined unit operation converting the woody biomass to pyrolysis gas and char at the operation temperature. For char-gas reactions, a Gibbs reactor is designed to calculate the equilibrium of char-gas reactions with limited amount of steam. The limited steam-gas shift equilibrium reaction also occurs in the designed equilibrium reactor. The un-reacted char flows into the FFB reactor where the char and supplementary fuel (RME & tar) are burnt which process is modeled as a conversion reactor. The proposed modeling of biomass drying and gasification has been validated using experimental data and the details can be found in [13].

### C. Gas cleaning

For the tar removal, a system of RME scrubber in integration with a stripper, similar to the OLGA system is used which the process is illustrated in Figure 2 [18]. The tar in the system from biomass gasification is absorbed by the RME in the scrubber and the tar-loaded RME is then heated and circulated in the stripper where the tar is released and carried away by a stream of hot air. The hot air is used in the FFB combustion reactor for recovery of the tar energy. The Soave-Redlich-Kwong (SRK) equation and no-random two-liquid (NRTL) model for activity coefficient model were employed for system equilibrium calculation in UniSim Design. The RME composition was taken from[19]. A water scrubber system is used for ammonia and hydrogen chloride removal with SRK equation and NRTL activity model. A simple component splitter is used for hydrogen sulfide removal by ZnO fixed bed.

### D. Gas Conditioning

A plug flow reactor is modeled in the UniSim Design for high temperature water-gas shift reaction. The reaction rate constant including diffusion resistances is used[20]. The effective reaction rate (mol CO reacted/m³.hr) is determined by:

![Figure 2. A schematic diagram of tar removal system.](image-url)
\[ r_s = k \cdot \psi \cdot (172 \times \rho_{\text{bed}}) \times (Y_{\text{CO}} \cdot Y_{\text{H}_2} \cdot Y_{\text{CO}_2} / \rho_{\text{eq}}) \] (1)

Where \( \rho_{\text{bed}} \) is the bed density of reactor in kg/m\(^3\), \( Y_i \) is the mole fraction of each component, \( i \), \( K_{\text{eq}} \) is the equilibrium constant of water-gas shift reaction.

\[ k = \exp(15.95 - 4900/T) \quad (T \text{ in K}) \]
\[ \psi = 0.816 + 0.184 \times P \quad P < 11.8 \text{ bar} \]

**E. FT Synthesis**

Anderson-Schulz-Flory (ASF) theory is used for modeling of the FT synthesis reaction and product distribution as described in (2) [16].

\[ \log W_n / n = n \cdot \log \alpha + \log(1 - \alpha^2) / \alpha \] (2)

Where \( W_n \) is the weight fraction of a product with \( n \) carbon atoms, \( \alpha \) is the chain growth probability factor which is the characteristics of the FT synthesis catalyst and is a function of catalyst selectivity towards liquid hydrocarbons (S\(_{C5+}\)) as defined by (3)[21].

\[ \alpha = 0.75 - 0.373 \sqrt{-\log(S_{C5+}) + 0.25 \times S_{C5+}} \] (3)

In the FT reactor, a high selectivity of liquid products as well as a high conversion of syngas is required. The selectivity towards liquid products depends on several factors including operation temperature, operation pressure, the reactant composition, and the FT reactor configuration. Water and carbon dioxide act as inert in the FT reactor and have a negative influence on the liquid products’ selectivity. The following formula was used for calculating the selectivity of cobalt catalyst [21].

\[ S_{C5+} = 1.7 - 0.0024 \times T - 0.088 \times Y_{\text{H}_2} / Y_{\text{CO}} + 0.18 \times (Y_{\text{H}_2} + Y_{\text{CO}}) + 0.0078 \times P \] (4)

In which, \( Y_i \) is the mole fraction of component \( i \), \( T \) is reactor temperature (K) and \( P \) is the operation pressure (bar).

By using the cobalt catalysts, the reaction kinetics indicated by the CO consumption rate (mol/s.kg\(_{\text{cat}}\)) can be determined by (5) which was proposed by Yates and Satterfield (cited in[21]).

\[ r_{FT} = a \cdot P_{\text{CO}} \cdot P_{\text{H}_2} / (1 + b \cdot P_{\text{CO}})^2 \] (5)

In which, \( P_{\text{CO}} \) and \( P_{\text{H}_2} \) are partial pressure of carbon monoxide and hydrogen respectively, (bar), and \( a \) and \( b \) are kinetic parameters as listed in **TABLE II**.

<table>
<thead>
<tr>
<th>FT synthesis kinetic parameters [21]</th>
</tr>
</thead>
<tbody>
<tr>
<td>a</td>
</tr>
<tr>
<td>b</td>
</tr>
<tr>
<td>R</td>
</tr>
<tr>
<td>T</td>
</tr>
<tr>
<td>-E_a</td>
</tr>
<tr>
<td>H_{\text{ads}}</td>
</tr>
<tr>
<td>k_0</td>
</tr>
<tr>
<td>Catlyst Density</td>
</tr>
</tbody>
</table>

**F. Hydro-treating**

Catalytic hydro-cracking which converts the high hydrocarbon chain compounds such as paraffin to lighter hydrocarbons is commonly used for the treatment of FT liquid fuel from LTFT process. In a single stage hydro-cracking, the feed (FT wax) is heated to the desired temperature and fed to the hydrocracker. The effluent from hydro-cracking reactor enters a high pressure separator where hydrogen rich gases are separated and recycled to the reactor inlet while the condensed liquid is sent to a flash drum where the additional light gases are removed. The condensed liquid is sent to the fractionation column and the desired products are recovered and sent to the storages[22]. The kinetic of hydro-treating reactions is comprised of complicated cracking and isomerization reactions. A user defined model for hydro-treating of FT liquid fuel has been developed in UniSim Design based on methodology used in [23].

**G. Power Generation**

A combined cycle including gas turbine and steam turbine is assumed for power generation to achieve high efficiency[24]. The heat of the gas turbine exhaust gas was recovered to produce medium pressure steam which is fed to the steam turbine to generate additional electricity.
A pinch analysis has been conducted on the integrated system to maximize the heat recovery and minimize the hot and cold utilities. The surplus of the high and medium pressure steam generated from the heat recovery in the system (gasification section and FT synthesis reactor) is fed to the steam turbine as well.

H. Energy Efficiency

The energy efficiency of the system can be represented by three terms: 1). Chemical efficiency $\eta_{ch}$, 2). Steam efficiency, $\eta_s$, and 3). Power efficiency, $\eta_p$ as determined by the following equations:

$$\eta_{ch} = \frac{(M_a \cdot LHV_n + M_d \cdot LHV_d + M_{fg} \cdot LHV_{fg})}{(M_b \cdot LHV_b + M_{RME} \cdot LHV_{RME})}$$  

(6)

$$\eta_s = \frac{M_s \cdot (H_{LPS} - H_{cond})}{(M_b \cdot LHV_b + M_{RME} \cdot LHV_{RME})}$$  

(7)

$$\eta_p = \frac{Power_{net} \cdot (M_b \cdot LHV_b + M_{RME} \cdot LHV_{RME})}{(M_b \cdot LHV_b + M_{RME} \cdot LHV_{RME})}$$  

(8)

In which, $M_a$, $M_d$, $M_{fg}$, $M_b$, $M_s$ and $M_{RME}$ are the mass flowrates of respectively naphtha, diesel, fuel gas, biomass, steam and RME respectively (kg/s). $LHV_n$, $LHV_d$, $LHV_{fg}$, $LHV_b$, and $LHV_{RME}$ are the corresponding low heating values of naphtha, diesel, fuel gas, biomass and RME (MJ/s). $H_{LPS}$ and $H_{cond}$ are the enthalpy values of low pressure steam and condensate (MJ/kg), and $Power_{net}$ is the net power generated in the system excluding that consumed within the system.

III. RESULTS AND DISCUSSIONS

The system model was solved in the UniSim Design simulation environment and the results were compared with literature data. The model has been employed for sensitivity analysis on the various parameters including the DFB gasification operation conditions (temperature and steam to biomass ratio), gas conditioning, the operation condition in the FT reactor. The results are presented in the following sections.

A. The effect of gasifier operation condition

The model predicted the effect of gasification temperature is shown in Figure 3, from which it can be seen that the system chemical efficiency increases significantly with the gasification temperature. With the gasification temperatures increasing from 750°C to 850°C, the chemical efficiency increases from 26% to 34%. At higher temperatures, the gas yield from the gasification is higher resulting in higher liquid fuel yield from the FT synthesis.

However, the power generation efficiency decreases with the gasification temperature as the methane content of the syngas decreases.
The steam generation efficiency decreases by increasing the gasification temperature from 750°C to 800°C while it increases by further increasing the temperature to 850°C. At the temperature interval between 750°C and 800°C, the char generated in the gasification system satisfies the gasification energy requirement by increasing the preheated air temperature. As a result, the less heat of flue gas is recovered for steam generation as more heat is recovered for air preheating. For the gasification temperature interval between 800°C and 850°C, the char generated in the system is not sufficient for the gasification system therefore some supplementary fuel is required to be burnt in FFB reactor as well. By keeping the air preheating temperature constant, more steam is generated as the flue gas temperature from FFB reactor is higher.

The model predicted the effect of steam to biomass ratio is shown in Figure 4 for S/B ratio increasing from 0.61 to 1.2. From the results, it was found that increasing the S/B ratio has negative impact with the chemical efficiency decreasing as the excess fuel demand of the system increases dramatically. The same pattern has been observed for power and steam efficiencies.

B. The effect of gas conditioning

In this study both the gas conditioning and methane steam reforming have been simulated to investigate the consequences if the water-gas shift converter is replaced by the methane steam reformer. As the producer gas from biomass gasification contains around 10% methane, the methane can be converted to H₂ and CO if the methane steam reformer is used. The simulation results are presented in Figure 5 from which it has been observed that using methane steam reformer, the chemical efficiency increase dramatically from 34% to 50%. This is the compensation of the power generation loss which is not enough for power self-supply. Steam efficiency of the system also decreases slightly in steam reforming scenario.

C. The effect of CO conversion and operation pressure in the FT synthesis

The model predicted that with increasing the CO conversion from 85% to 90%, the chemical efficiency increases considerably while power and steam efficiencies decreases remarkably as shown in Figure 6. With higher CO conversion, more fuel products are produced and less off-gas is exhausted from the FT reactor for power and subsequent steam generation.

The model has revealed that with increasing the FT operation pressure, the catalyst selectivity and chain growth probability increase as shown in Figure 7. Therefore, higher pressure results in higher chemical efficiency while at lower pressure due to the higher off-gas heating value, the power and steam efficiency are higher as illustrated in Figure 8.

CONCLUSIONS

An integrated system model was developed for conversion of woody biomass to liquid fuel via biomass drying, biomass steam gasification in a dual fluidized bed (DFB) gasifier, gas cleaning and conditioning, Fischer Tropsch (FT) synthesis, hydrotreating and power generation. A combination of user defined and built-in unit operation was employed to model each operation unit. Pinch analysis was conducted on the system to maximize the heat recovery and steam generation. The system model developed in the present study has been employed to investigate the effect of various operation parameters on the system chemical efficiency, power generation efficiency and steam generation efficiency. These parameters included gasification temperature, steam to biomass ratio in the gasification, gas conditioning, CO conversion and pressure in the FT synthesis.

It has been found that biomass temperature was more
increasing steam to biomass ratio had negative impact on the system efficiencies. Replacing shift converter with steam methane reforming increased the chemical efficiency to 50% and overall efficiency to 61% although a proportion of the gas was used to provide energy for steam reforming reaction. Increasing CO conversion from 85% to 90% was also very effective in increasing the chemical efficiency. Chemical efficiency was increased dramatically by replacing shift converter with efficiency decreased resulting in slight decrease in total efficiency.

REFERENCES


