Evaluation of CO$_2$ Mitigation by BTL Biofuels from Woody Biomass through Simulated Case Studies

S. Fujimoto*, T. Yanagida*, M. Ogata*, and T. Minowa*1

Abstract – In order to optimize the yield of biofuels and CO$_2$ mitigation, process design and simulation for our BTL (Biomass to Liquids) process were performed, and a case study was carried out. The process consisted of steam gasification of woody biomass, gas cleaning, compression, FT (Fischer-Tropsch) synthesis reaction, hydrogenolysis, and distillation. It was found that 21.3 kL/d of liquid hydrocarbons could be produced from 100 t/d of collected biomass by this process, and 34.1 t/d CO$_2$ mitigation was achieved. It was observed that the process that uses only biomass might not effectively achieve CO$_2$ mitigation. If the CO$_2$ emission factor of an external electricity source is lower and it is more efficient as compared to biomass-fired power generation, an external electricity source is recommended. The recycling of the offgas discharged from the FT reactor into the gasifier could increase the yield of liquid hydrocarbons. However, it could not improve the total extent of CO$_2$ mitigation because of the increase in the energy consumption of the process. In addition, recycling might make the process and/or the operation complex. In biofuel production, although the increase in the yield of liquid hydrocarbons is important, the actual degree of CO$_2$ mitigation achieved should be considered, and an effective process and operation should be developed accordingly.

Keywords – Biomass, BTL (Biomass to Liquids), CO$_2$ mitigation, environmental evaluation, Fischer-Tropsch (FT) synthesis.

1. INTRODUCTION

Environmental issues are becoming serious year by year. This is due to the environmental imbalance caused by our lifestyle that largely depends on fossil fuels. In particular, global warming is one of the most serious issues threatening the environment. The methods of mitigation of global warming are being explored on an international scale. The promotion of the utilization of renewable resources has been proposed. Since biomass is the only renewable resource that contains organic carbon, it has attracted considerable attention as an effective means of providing a solution to this problem. Biomass can be converted into energy-generating materials—such as charcoal, syngas, and liquid fuels—that have low environmental impact.

A large amount of CO$_2$ is emitted from vehicles used for transportation. Since the liquid fuel produced from biomass can be substituted for the fuels currently used in vehicles, such as gasoline and light oil, remarkable CO$_2$ mitigation might be achieved.

In this situation, the use of bioliquid fuels, such as bioethanol, ETBE (ethyl tertiary-butyl ether), BDF (biodiesel fuel), and BTL (biomass to liquids) diesel oil, which are produced from biomass, is an attractive option. In Japan, ETBE mixed with gasoline is being sold since end of April 2007 [1].

Biofuels can be produced by biochemical process such as fermentation process or thermochemical process such as BTL process. BTL process mainly consists of gasification of biomass and synthesis of liquid fuels from syngas. A limitation on feedstock in BTL process is smaller than that in biochemical process. From BTL process, methanol [2]–[4], DME [5], liquid hydrocarbons [6] can be produced. In these products, hydrocarbons are obtained by Fischer-Tropsch synthesis reaction. Since the hydrocarbons can be directly used in diesel engines, it may be spread easily. The hydrocarbons are one of the most promising biofuels.

Since the feedstock of biofuel is costly, the economics becomes important issue. Hamelinck et al. estimated the economics of BTL process that contained FT synthesis reaction [7]. The economic evaluation of the process in which ETBE production process and BTL process were combined was also performed [8]. Consequently, possibility of realization of this process could be indicated.

On the other hand, CO$_2$ might be emitted during the production of biofuels, for example, during cultivation, harvest, transportation, and conversion. Therefore, it is important that the amount of CO$_2$ emitted during the production of biofuel be estimated.

From these situations, in order to evaluate CO$_2$ mitigation by biofuels obtained in BTL process, this study developed a process design and performed process simulation. The basic amount of biofuels was estimated by process simulation using assumption based on literatures. Energy demand was also calculated by the process simulation. From the relationship between the amount of biofuels and energy demand, the CO$_2$ mitigation achieved was investigated by a case study. That is, the effect of diversion of a part of biomass collected as feedstock of biofuels for energy supply to the process on CO$_2$ mitigation achieved was investigated. Further, the effect of the effect of the recycle of offgas generated from the process was examined.
Fig. 1. Schematic representation of the BTL process

Table 1. Composition of woody biomass. Source: [9]

<table>
<thead>
<tr>
<th>Name of the element</th>
<th>cellulose</th>
<th>hemicellulose</th>
<th>lignin</th>
<th>woody biomass</th>
</tr>
</thead>
<tbody>
<tr>
<td>Composition</td>
<td>0.5</td>
<td>0.2</td>
<td>0.27</td>
<td>3.8</td>
</tr>
<tr>
<td>C</td>
<td>6</td>
<td>5</td>
<td>20</td>
<td>3.8</td>
</tr>
<tr>
<td>H</td>
<td>10</td>
<td>8</td>
<td>24</td>
<td>5.3</td>
</tr>
<tr>
<td>O</td>
<td>5</td>
<td>4</td>
<td>8</td>
<td>2.2</td>
</tr>
<tr>
<td>Unit molecular weight</td>
<td>162</td>
<td>132</td>
<td>392</td>
<td>86.2</td>
</tr>
</tbody>
</table>

2. PROCESS DESIGN AND ASSUMPTIONS

Figure 1 shows a schematic representation of the intended process for this study. This process consists of steam gasification of woody biomass, gas cleaning, compression, FT synthesis reaction, hydrogenolysis, and distillation.

Properties of Woody Biomass

Table 1 shows the properties of woody biomass. Those of cellulose, hemicellulose and lignin were referred to literature [9]. Woody biomass was estimated based on that of Japanese cedar, and the content of lignin, cellulose, hemicellulose, and ash in the woody biomass was fixed at 27 wt%, 50 wt%, 20 wt%, and 3 wt%, respectively [8], [9]. The average molecular structure of woody biomass for simulation was assumed to be C_{3.8}H_{5.3}O_{2.2}. In this study, the quantity of collected biomass, including 20 wt% of moisture, was fixed at 100 t/d.

Gasifier

The woody biomass and steam were supplied to a gasifier. Steam was generated via heat exchange between water and syngas at the outlet of the gasifier. In the gasifier, the steam gasification progressed as shown in Equations 1 to 5.

\[ C_6H_{10}O_5(s) + H_2O(g) \rightarrow 6H_2(g) + 6CO(g) \]  

\[ C_5H_8O_4(s) + H_2O(g) \rightarrow 5H_2(g) + 5CO(g) \]  

\[ C_{20}H_{20}O_8(s) + 12H_2O(g) \rightarrow 24H_2(g) + 20CO(g) \]  

\[ CO(g) + H_2O(g) \rightleftharpoons H_2(g) + CO_2(g) \]  

\[ 3H_2(g)+CO(g) \rightleftharpoons CH_4(g) + CO_2(g) \]

It was assumed that the temperature in the gasifier was 900°C and the pressure is equal to atmospheric pressure. Chaudhari et al. [10] indicated that the conversion into gas was enhanced significantly beyond 700°C in steam gasification of char derived from biomass. That is, the conversion was increased from 34 to 89% for a change in temperature from 700°C to 800°C. From this result, it can be considered that the conversion reaches approximately 95% at 900 °C. In this study, the conversion was assumed to reach 95%. From the result indicated by [10], it is found that increasing temperature decreased CH_4 beyond 700°C. Hanaoka et al. [11] showed that the amount of CH_4 was negligible in air-steam gasification of 900°C by the thermodynamic equilibrium calculation. They also observed that 5 to 10% CH_4 in syngas is obtained in the experiment. From these results, it was assumed that CH_4 of 5% was contained in syngas. The concentrations of the gases excluding CH_4 were calculated as 80% at the chemical equilibrium composition.

In the FT synthesis reaction, H_2/CO ratio of 2.1 is theoretically desired when H_2 and CO are completely consumed. However, the optimum H_2/CO ratio changes with the conversion of FT synthesis reaction. In previous study [12], it was indicated that H_2/CO ratio of 1.74 was optimum for FT synthesis reaction with the conversion of CO into hydrocarbons of 80% by process simulation though an effect of H_2/CO ratio on the conversion of CO in FT synthesis reaction was not taken account of. Therefore, in this study, the amount of steam generated was controlled in order to obtain an H_2/CO ratio of 1.74.

In the experiment, the carbon that does not convert into gas is assumed to convert into char and tar and/or is lost. It might be error in measurement or analysis. In this study, it was assumed that 2.5% each of char (charcoal) and tar was generated though they were uncertain. This
distribution of char and tar would not affect on simulation results because the yield of liquid hydrocarbon is invariable irrespectively of the distribution. Char was removed from the bottom of the gasifier.

Gas Cleaning
Syngas was cleaned by a scrubber and was separated from tar. The temperature of the syngas was decreased via heat exchange with water in order to supply it into the gasifier.

Compression
The syngas was compressed using three compressors. The efficiency of the compressors were assumed at 85%. The compression induced heating of the syngas. Two heat exchangers were set between the compressors in order to cool the syngas to 65°C. Tijmensen et al. mentioned that FT synthesis reaction operated at pressures ranging from 2 to 4 MPa. On the other hand, reduction of partial pressures for CO and CO2 by more inert gas decreases yield of liquid hydrocarbon [6]. In this study, since CO2 generated in the gasifier was contained in the syngas as inert gas, it was assumed that the syngas pressure finally reached 5 MPa. The outlet pressures of the first and second compressors were controlled to minimize the electricity consumption of the three compressors.

FT Synthesis Reaction
In the FT synthesis reactor, the chains of hydrocarbons were lengthened by the FT reaction as shown in Equations 6 and 7.

\[
\text{nCO(g) + (2n+1)H}_2\text{(g) \rightarrow C}_n\text{H}_{2n+2}(g, l, s) + n\text{H}_2\text{O(g)} \quad (6)
\]

\[
\text{nCO(g) + 2nH}_2\text{(g) \rightarrow C}_n\text{H}_{2n}(g, l, s) + n\text{H}_2\text{O(g)} \quad (7)
\]

Olefin and paraffin both were generated in the actual reaction. However, Pellegrini et al. [13] mentioned that small percentage of olefins is produced by using cobalt-based catalyst. In experiments that were carried out by [14] paraffin was main product when cobalt-based catalyst was used. Therefore, it was assumed in this study that only paraffin was generated. It was assumed that the conversion of CO into hydrocarbons was 80% and that the hydrocarbons were generated based on a Schulz-Flory distribution. The value of the Schulz-Flory distribution function, \( \alpha \), changes by \( \text{H}_2/\text{CO} \) ratio, temperature, pressure etc. Tijmensen et al. [6] showed product distribution for different \( \alpha \). The yield of wax increases with increasing \( \alpha \).

In the authors’ research center (Biomass Technology Research Center, National Institute of Advanced Industrial Science and Technology (AIST), Japan), it is an aim that \( \alpha \) exceeds 0.9 by end of 2008 FY. It is promising and will be accomplished, as stated in [15]. Therefore, \( \alpha \) was assumed to 0.9 in this study. In this simulation, the maximum carbon number of the paraffin was 36.

### Distillation and Hydrogenolysis
Liquid hydrocarbons were separated from offgas and water by gas-liquid phase separation and two-liquid-phase separation, respectively. The separated liquid hydrocarbons were heated to 350°C and were then fed to a first distillation column. In the first column, the hydrocarbons with a carbon number more than 21 were discharged from the bottom of the column. The heavy hydrocarbons were supplied to the hydrogenolysis reactor and were cracked by hydrogen in the offgas. In this simulation, hydrogenolysis was assumed to progress randomly. The cracked hydrocarbons were returned to the first distillation column again.

The hydrocarbons with a carbon number less than 20 were discharged from the top of the first distillation column. The light hydrocarbons were fed to a second distillation column. The hydrocarbons with a carbon number between six and nine were discharged from the top of the second distillation column, while those with a carbon number between 10 and 20 were discharged from the bottom.

### Offgas
The offgas discharged from the FT reactor was used for hydrogenolysis, and it was then combusted, thus acting as a heat source for the gasifier and for the distillation process. A part of the offgas could be returned to the gasifier to increase the amount of liquid hydrocarbons.

### Simulation
A steady-state process simulator (PRO/II; Invensys Systems Japan Inc.) was used for the process design simulation. The energy balance and the material balance could be obtained from the simulation results, including the degree of heat and electricity required for the process. In this study, the amount of collected biomass, i.e., feedstock biomass, was fixed at 100 t/d. The case studies were performed under the conditions shown in Table 2.

In the first case study, three cases were examined for the effect of energy utilization on the amounts of liquid hydrocarbons produced and the CO2 mitigation achieved. In case I, which was the base case, all the collected biomass was used for hydrocarbon production. In case II, a part of the biomass was used as a heat source in the gasifier and the distillation column. In case III, the electricity consumed in the plant was generated by an on-site biomass-fired power-generation system using a part of the collected biomass.

### Table 2. Conditions for case studies I and II

<table>
<thead>
<tr>
<th>Case study I</th>
<th>Case study II</th>
</tr>
</thead>
<tbody>
<tr>
<td>Case I</td>
<td>Case II</td>
</tr>
<tr>
<td>Off-gas</td>
<td>Combustion</td>
</tr>
<tr>
<td>Duty of heat</td>
<td>Heavy oil</td>
</tr>
<tr>
<td>Electricity</td>
<td>External</td>
</tr>
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<td></td>
<td></td>
</tr>
</tbody>
</table>
In all cases, irrespective of the plant capacity, the heat loss was 10%, and the electrical efficiency of the on-site power-generation system was also 10%. In cases II and III, since a lesser amount of biomass was used as feedstock for producing liquid hydrocarbons, the amount of hydrocarbons produced was also lesser.

In the second case study, offgas was recycled and the effect of offgas utilization on the amount of liquid hydrocarbons produced and the CO$_2$ mitigation achieved was investigated. In order to avoid the accumulation of inert gases such as CO$_2$ in the offgas recycling process, the flow rate of the offgas supplied to the gasifier was maintained at the rate at which the offgas was discharged in the first case study. The surplus offgas was used as a heat source for the gasifier and the distillation column.

3. RESULTS AND DISCUSSION

Base Case

The mass balance and the carbon balance of case I, which was the base case, are shown in Table 3. In case I, 5.2 t/d of liquid hydrocarbons having carbon number between six and nine, and 11.7 t/d of liquid hydrocarbons having carbon number between 10 and 20 were obtained from 100 t/d of biomass and 42 t/d of water. In addition, 56.5 t/d of offgas and 35.1 t/d of water were discharged as byproducts.

<table>
<thead>
<tr>
<th>In</th>
<th>Mass (t/d)</th>
<th>Carbon (t/d)</th>
<th>Carbon (%)</th>
<th>Out</th>
<th>Mass (t/d)</th>
<th>Carbon (t/d)</th>
<th>Carbon (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Biomass</td>
<td>100</td>
<td>38.3</td>
<td>100.0</td>
<td>C$_{5-9}$</td>
<td>5.2</td>
<td>4.3</td>
<td>11.3</td>
</tr>
<tr>
<td>Water</td>
<td>42</td>
<td>0</td>
<td>0</td>
<td>C$_{10-20}$</td>
<td>11.7</td>
<td>9.8</td>
<td>25.7</td>
</tr>
<tr>
<td>Offgas</td>
<td>56.5</td>
<td>21.8</td>
<td>57.1</td>
<td>Water</td>
<td>61.8</td>
<td>0.4</td>
<td>1.0</td>
</tr>
<tr>
<td>Tar</td>
<td>3.4</td>
<td>1.0</td>
<td>2.5</td>
<td>Char</td>
<td>3.4</td>
<td>1.0</td>
<td>2.5</td>
</tr>
<tr>
<td>Total</td>
<td>142</td>
<td>38.3</td>
<td>100.0</td>
<td>Total</td>
<td>142</td>
<td>38.3</td>
<td>100.0</td>
</tr>
</tbody>
</table>

From the carbon balance, 37.2% of the carbon that was fed as feedstock, was converted to liquid hydrocarbons. Around 57.1% was converted to offgas. The source of 44.4% of the carbon in the offgas was CO$_2$. Furthermore, char and tar had 2.51% of the carbon respectively.

Figure 2 shows the energy demands of the main equipment. The gasifier required 465 GJ/d of heat, while 32.4 GJ/d of heat was required for distillation. The three compressors consumed 27.2 MWh/d (96.2 GJ/d) of electricity.

The discharged offgas yielded a considerable amount of combustion heat, i.e., 397 GJ/d. Hence, it could be used as the heat source for the gasifier and for distillation. However, because it was found to be insufficient, heavy oil or biomass were used additionally to compensate for the insufficiency in the case studies.

Case Study I

In the base case, although the offgas yielded a considerable amount of combustion heat, it was found to be unable to satisfy the entire energy demand. An alternative energy supply system to overcome the insufficient supply was therefore considered.

![Fig. 2. Energy demands of the main equipment](image-url)
Figure 3 shows the yield of liquid hydrocarbons in case study I. In cases II and III, the yield of liquid hydrocarbons decreased because a part of the total collected biomass was used for fulfilling the energy demand. The yield in case II decreased by 7.3%, while that in case III reduced by 35.9%.

Figure 4 shows the energy supply and energy demand in the process. In this figure, the negative sign indicates energy demand. Since heavy oil and external electricity were generated from fossil fuel, CO$_2$ is emitted by use of them. Due to the low efficiency of electricity, a large amount of biomass was used up by the biomass-fired power-generation system in case III. This was a significant cause of the remarkable reduction in the amount of hydrocarbons yielded.

Figure 5 shows the CO$_2$ mitigation achieved in case study I, and the CO$_2$ emission factors, which were listed in a literature [16], are shown in Table 4. Since the liquid hydrocarbons generated from the biomass can be used as an alternative to fossil fuels, it can decrease the CO$_2$ emission due to the fossil fuels. In case I, 10.9 t/d and 10.2 t/d of CO$_2$ were emitted from heavy oil and from the external source of electricity, respectively. On the other hand, since the yield of liquid hydrocarbons from the biomass was 55.2 t/d, the total CO$_2$ mitigation achieved was 34.1 t/d, which is indicated by the gray bar in this figure. In case II, the yield of liquid hydrocarbons decreased due to the combustion of a part of the biomass that acted as a heat source. However, since heavy oil was not used, the extent of CO$_2$ mitigation increased. In case III, although the process was carried out without using a fossil fuel, the extent of CO$_2$ mitigation decreased as compared to that in case II. The degree of CO$_2$ mitigation achieved in this case was the same as that in case I in which a fossil fuel was used.

From these results, it is evident that if the process is carried out using only biomass, it might not effectively achieve CO$_2$ mitigation.
**Table 4. CO₂ emission factors. Source: [16]**

<table>
<thead>
<tr>
<th></th>
<th>kg-CO₂/L</th>
</tr>
</thead>
<tbody>
<tr>
<td>Heavy oil</td>
<td>2.939</td>
</tr>
<tr>
<td>Electricity</td>
<td>0.3821</td>
</tr>
<tr>
<td>Gasoline</td>
<td>2.529</td>
</tr>
<tr>
<td>Light oil</td>
<td>2.644</td>
</tr>
</tbody>
</table>

**Case Study II**

The recycling of offgas was considered in order to improve the yield of liquid hydrocarbons and the degree of CO₂ mitigation achieved. In this study, the offgas from the FT reactor was returned to the gasifier. However, in order to avoid the accumulation of inert gases, the flow rate of the offgas to the gasifier was maintained at the same rate at which it was discharged in the first case study.

Figure 6 shows the yield of liquid hydrocarbons. Case IV was considered as the base case in the offgas recycling process. By offgas recycling, the yield of liquid hydrocarbons increased by 6.23 t/d as compared to that in case I. Even in case V, in which a part of the biomass was used as the heat source, the yield of liquid hydrocarbons was almost the same as that obtained in case I.

Figure 7 shows the energy supply and demand. It was observed that the recycling of offgas increased the heat demand in the gasifier. Therefore, the consumption of heavy oil or biomass of the gasifier increased. In particular, in case IV, the consumption of heavy oil drastically increased. In addition, since the flow rate of syngas generated in the gasifier increased, the electricity consumption of the compressors also increased.

Figure 8 shows the extent of CO₂ mitigation. In case IV, although the yield of liquid hydrocarbons increased, the total extent of CO₂ mitigation remarkably reduced because of the increased fossil fuel consumption. In case VI in which no fossil fuel was used, although the yield of liquid hydrocarbons was small, the relative degree of CO₂ mitigation increased. However, the absolute degree of CO₂ mitigation could not reach that in cases II and V.
Table 5 shows the summary of the yield of liquid hydrocarbons, the absolute degree of CO\(_2\) mitigation, and the unit amount of liquid CO\(_2\) mitigation in the entire process. As mentioned above, in cases III and VI in which no fossil fuel was used, the relative degree of CO\(_2\) mitigation increased, although the yield of liquid hydrocarbons decreased. The unit amount of liquid CO\(_2\) mitigation was 2.58 and 2.45 in cases III and VI, respectively. However, the absolute degree of CO\(_2\) mitigation achieved was not the best possible. Thus, even if the unit amount of liquid CO\(_2\) mitigation achieved was the greatest, it does not imply that the process can actually maximize CO\(_2\) mitigation. If the yield of liquid hydrocarbons is relatively low, the degree of CO\(_2\) mitigation might reduce. Therefore, the on-site biomass-fired power-generation system was unable to achieve enough CO\(_2\) mitigation in our study. Here, the CO\(_2\) emission factor in Japan, which is lower, was used in this study. The on-site biomass-fired power-generation system might be acceptable in other countries.

The recycling of offgas could increase the yield of liquid hydrocarbons. However, it could not improve the degree of CO\(_2\) mitigation because of the increased energy consumption of the process. In addition, recycling might make the process and/or the operation complex.

In biofuel production, although the increase in the yield of liquid hydrocarbons is important, the actual degree of CO\(_2\) mitigation achieved should be considered, and an effective process and operation should be developed accordingly.

### REFERENCES


