Liquid Fuel Production by Co-liquefaction of Eucalyptus Wood and Brown Coal

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Abstract. The development of efficient technologies for the conversion of woody biomass to liquid fuels is an important research area. Authors paid attention to the solvent recycle type direct liquefaction of the woody biomass because reaction condition is mild. However, when only the woody biomass is liquefied, the polarity of the product is high. As a result, the following two problems are caused. Because when the product oil is mixed with diesel oil of the petroleum origin, the phase separation is caused, and as a result, it cannot be used as a composite fuel. Because the solid is generated by the condensation of the hydroxyl compounds with the high polarity, the amount of the recycling solvent cannot be secured. Then, the authors tried co-liquefaction of the woody biomass and the brown coal. Because the polarities of the brown coal are lower than the woody biomasses, it is expected that the polarity of the product oil lowers. Moreover, abundant hydrogens of the woody biomass are expected to promote the cracking of the brown coal. The followings are found as a result of the present study. The cracking of the high-boiling fraction is promoted when the woody biomass and the brown coal are co-liquefied and diesel oil fraction yield increases.

Keywords: woody biomass, brown coal, co-liquefaction, pyrolysis

1. Introduction

The international community has a responsibility to reduce emissions of carbon dioxide, the most contributing greenhouse gas associated with the conversion of fossil resources to energy. In Kyoto Protocol, overseas afforestation under the Clean Development Mechanism was introduced. In a similar way, the use of internationally transferred mitigation outcomes was accepted in Paris Agreement. The selection condition of partner country of overseas afforestation includes a natural condition, the problem of uncertainness of the dominion directum, the tax system, etc. Because Australia fills the terms and conditions above to some degree, afforestation in Australia has started [1].

The carbon is stocked on the ground if land without vegetation becomes a forest and the equivalent amount of CO2 in the atmosphere decreases. However, after growing up, the tree might emit more CO2 by respiration, the fallen leaf and withering than photosynthesis. Therefore, it is necessary to harvest the tree regularly and to use it effectively in the afforestation to CO2 reduction [2].

Meanwhile, the development of alternatives to fossil fuels is currently of significant practical importance because fossil-based resources, such as petroleum, may well be exhausted in the near future. Then, authors thought about the alternatives to fossil fuels as effective use of the afforestation tree. Wood-based biomass is an alternative to fossil fuels that has attracted attention because it is renewable by photosynthesis in a relatively short time frame and its use as an energy source is carbon neutral.

The handling of woody biomass is, however, labor intensive and so the collection and transport of this material can be costly. For this reason, it is preferable to convert woody biomass to an alternative fuel, such as diesel oil or heavy oil, at locations near the forested site where the biomass is produced.
A direct liquefaction process incorporating a circulating solvent system has been investigated for this purpose [3]. This liquefaction process has a number of benefits, including high efficiency, because constant replenishing of the solvent is not required. In addition, the part of the liquefaction oil produced in the system is itself employed as the circulating solvent, which allows the use of mild reaction conditions, including low pressures.

Unfortunately, studies concerning this process have also identified that the biomass liquefaction oil used as the process solvent forms much amount of solid residue, leading to the deficiency of the circulation solvent, because the biomass liquefaction products contain a lot of hydroxy group which causes high polarity and undesirable condensation reactions between the liquefaction products [4]. As a result of these problems, it may be difficult to secure the quantity of solvent required to operate the system with solvent circulation.

Moreover, when only the woody biomass is liquefied, the polarity of the product is high. As a result, the phase separation is caused when the product oil is mixed with diesel oil of the petroleum origin, and hence, it cannot be used as a composite fuel.

A potential means of addressing this issue is the co-liquefaction of coal with the cellulosic biomass, because the polarity of the coal is lower than that of the woody biomass and it is expected that the polarity of the product oil lowers. Moreover, abundant hydrogen from the woody biomass is expected to promote the cracking of the coal. Process flow scheme is shown in Fig. 1.

![Fig. 1: The proposed process flow scheme of co-liquefaction of Eucalyptus wood and brown coal](image)

In the work presented herein, the co-liquefaction of wood-based biomass (Eucalyptus Camaldulensis, named as Eucalyptus wood) with the brown coal (LoyYang coal) was investigated with regard to product yields and other factors. Eucalyptus wood is suitable for afforestation in Australia, because it is an Australian native, is strong under dry circumstances and grows fast. LoyYang coal is used because it is cheap and produced a lot in Australia. However, it spontaneously combusts when it is dried though a lot of moisture is contained [5].

2. Experimental

2.1. Materials

<table>
<thead>
<tr>
<th></th>
<th>Proximate analysis [wt%-dry basis]</th>
<th>Ultimate analysis [wt%-dry basis]</th>
<th>Moisture [wt%]</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Ash</td>
<td>Volatile Matter</td>
<td>Fixed Carbon</td>
</tr>
<tr>
<td>Eucalyptus Camaldulensis</td>
<td>2.58</td>
<td>78.92</td>
<td>18.50</td>
</tr>
<tr>
<td>LoyYang Coal</td>
<td>1.03</td>
<td>50.27</td>
<td>48.70</td>
</tr>
</tbody>
</table>

Eucalyptus wood (provided by Forest Research and Management Organization) and LoyYang coal (provided by Research and Education Center of Carbon Resources, Kyushu Univ.) were ground in air using a planetary mill (PM100, Verder Scientific Co.) to get particle diameter less than 150 and 75 µm, respectively. The resulting ground material was dried at 110°C for 180 min under vacuum condition prior to use. Tetralin
(boiling point 207°C; hydrogen donor solvent), 1-methylnaphthalene (boiling point 245°C; non-hydrogen donor solvent), anthracene (mock cool; hydrogen acceptor) and sulfur powder (promoter) were purchased from Wako Pure Chemical Industries. Limonite slurry (30 wt% slurry in light oil fraction of brown coal liquefaction oil; catalyst) was provided by Kobe Steel. The analysis values of Eucalyptus wood and Loy Yang coal used for this experiment are shown in Table 1.

2.2. Co-liquefaction Trials

10 g of the 1:1 mixture of Eucalyptus wood and Loy Yang coal was charged together with tetralin or 1-methylnaphthalene of 20 g, limonite slurry of 0.8 g (Fe 1.5 wt% on the sample basis) and sulfur powder of 0.12 g (200 mol% on the limonite-Fe basis), into a 100 ml autoclave equipped with an electromagnetic induction-type stirrer. After the autoclave was sealed, the air inside was replaced with hydrogen gas at a pressure of 4.5 MPa and the autoclave was heated to 450°C by an external electric furnace with stirring at 500 rpm. After allowing 60 min retention at 450°C for the liquefaction reaction, the autoclave was air-cooled and the internal headspace gas was collected.

The chemical composition of this product gas mixture was determined by gas chromatographs with thermal conductivity detector (GC-TCD) and hydrogen flame ionization detector (GC-FID). The liquid slurry from the autoclave was also collected and separated into fractions on the basis of boiling point using simple distillation; initial boiling point to 250°C (light fraction), 250 to 350 °C (diesel fraction) and 350°C or more (tank bottom fraction). The light fraction was subsequently further separated into two fractions by phase separation: water phase (water fraction) and oil phase (solvent fraction). Moreover, the tank bottom fraction was subsequently further separated into two fractions: toluene-soluble (heavy fraction) and toluene-insoluble (residue). Yield of solvent fraction is shown by the negative value if solvent fraction is fewer than the fed solvent. In addition, structural analyses of the heavy fraction were carried out using proton nuclear magnetic resonance apparatus (¹H-NMR). And, structural analyses of the residue were carried out using Fourier transform infrared spectroscopy (FT-IR). Finally, ultimate analysis of the all fractions was carried out using CHN Analyzer. The amount of hydrogen consumed was calculated as the sum of hydrogen in the gaseous compounds (except hydrogen molecule) from the result of gas composition, and increased amount of hydrogen in liquid and solid from their ultimate analyses. The hydrogen consumption is then given by dividing this by the initial amount of hydrogen in the initially packed solid. Namely the hydrogen consumption shows how much vapor phase hydrogen was consumed based on the hydrogen of the wood and coal samples.

![Co-liquefaction Trials Graph](image)

Fig. 2: Product yields of liquefaction and co-liquefaction of Eucalyptus wood and Loy Yang coal with tetralin as hydrogen donor solvent

2.3. Hydrogen-donating Properties

In order to assess the capacity of the woody biomass liquefacts for hydrogen donation, a combination of Eucalyptus wood and anthracene was also subjected to co-liquefaction in the same manner as described above. In this regard, 1-methylnaphthalene was used as non-hydrogen donor solvent. The resulting slurry was collected and separated into hexane-insoluble and hexane-soluble fractions. The hexane-soluble fraction was subsequently analyzed by GC-FID.
3. Results and Discussion

3.1. Synergy Effect under Hydrogen Donation Solvent Coexistence

The product yields obtained from the liquefaction and co-liquefaction of Eucalyptus wood and Loy Yang coal with tetralin as hydrogen donor solvent are shown in Fig. 2 and the hydrogen consumptions are shown in Fig. 3. For the purpose of comparison, a calculated product yield and calculated hydrogen consumption for the co-liquefaction are also included. The calculated values were produced by taking the arithmetic average of the results for the individual pure Eucalyptus wood and Loy Yang coal liquefactions and thus can be considered the theoretical or expected values. Products promote the decomposition of the heavy fraction derived from Loy Yang coal by increasing the hydrogen consumption.

![Fig. 3: Hydrogen consumptions in liquefaction and co-liquefaction of Eucalyptus wood and Loy Yang coal with tetralin as hydrogen donor solvent](image)

The FT-IR spectra of the resulting residues are shown in Fig. 4 and structural parameters obtained from Brown-Ladner method of the heavy fraction [6] are shown in Table I. Calculation values are also obtained by weighted also obtained by weighted arithmetic average of the results for the individual pure Eucalyptus wood and Loy Yang coal liquefactions.

From Fig. 4, it can be noted that distinguishing peaks of the residue derived from brown coal (1200 cm$^{-1}$, phenol: 1300 cm$^{-1}$, aromatic aldehyde and ester: 1600 cm$^{-1}$, aromatic ring) are smaller than calculated average values in the actual measured IR spectrum of the co-liquefaction residue. The results suggest that
though the residue yield of the measurement value is close to calculation value, the woody biomass liquefaction products promote the decomposition of the residue derived from brown coal too.

From Table I, the measured co-liquefaction structural parameters of the heavy fraction appear closer to the structural parameters resulting from the calculated value. Because average structure of heavy fraction doesn't change by co-liquefaction, it is thought that the heavy fraction derived from the woody biomass became a residue in donated hydrogen to the brown coal liquefaction products.

From the above results, we can arrive at some conclusions regarding the nature of the interaction between Eucalyptus wood and Loy Yang coal during the co-liquefaction process. Brown coal liquefaction products that becomes residue or heavy fraction by re-polymerization in isolated reaction is stabilized by accepting hydrogen from the heavy fraction derived from the woody biomass and becomes diesel fraction. On the other hand, the heavy fraction derived from the woody biomass that donates hydrogen re-polymerizes and becomes a residue. As a result, heavy fraction yield decreases, diesel fraction yield increases and hence the residue yield was not apparently affected.

Table 2: structural parameters obtained from brown-ladner method [6] of the heavy fraction resulting from liquefaction and co-liquefaction of eucalyptus wood and loy yang coal

<table>
<thead>
<tr>
<th></th>
<th>Co-liquefaction (measured)</th>
<th>Co-liquefaction (calculated)</th>
<th>Eucalyptus</th>
<th>Brown coal</th>
</tr>
</thead>
<tbody>
<tr>
<td>fa</td>
<td>0.83</td>
<td>0.83</td>
<td>0.82</td>
<td>0.83</td>
</tr>
<tr>
<td>Haus/Caus</td>
<td>0.87</td>
<td>0.89</td>
<td>1.10</td>
<td>0.81</td>
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<tr>
<td>n</td>
<td>1.24</td>
<td>1.25</td>
<td>1.18</td>
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<tr>
<td>σ</td>
<td>0.39</td>
<td>0.40</td>
<td>0.56</td>
<td>0.33</td>
</tr>
</tbody>
</table>

fa: Fraction of aromatic carbon
Haus/Caus: Atomic hydrogen to carbon ratio of hypothetical unsubstituted aromatic material
n: Average number of carbon atoms in aliphatic carbon chains to aromatic rings
σ: Average degree of substitution of aromatic ring

3.2. Synergy Effect under Non-hydrogen Donation Solvent Coexistence

The hydrogen donation capacity of the woody biomass liquefaction products for hydrogen donation is shown in Fig. 5. The capacity was measured by amount of generated 9, 10-dihydroanthracene by reaction of anthracene and ground Eucalyptus wood under the non-hydrogen donation solvent existence.

![Graph](image-url)

Fig. 5 The hydrogen donation capacity of the Eucalyptus woody biomass liquefaction products
From Fig. 5, it can be seen that the amount of generation of 9, 10-dihydroanthracene doesn't change even if Eucalyptus wood is added. Therefore, the hydrogen donation of Eucalyptus wood is not admitted under the non-hydrogen donation solvent coexistence.

The product yields obtained by the liquefaction and co-liquefaction of Eucalyptus wood and Loy Yang coal with tetralin as hydrogen donor solvent are shown in Fig. 6. Because solvent fraction is fewer than the fed solvent, yield of solvent fraction is shown by the negative value. The calculated value obtained as above was also given in Fig. 6.

From Fig. 6, it can be seen that the actual measured co-liquefaction yields of residue was lower than the calculated average values and that the measured fractions other than residue and solvent yield were higher than the corresponding calculated values. In addition, the largest negative value in the measured co-liquefaction data indicates the larger amount of decomposed solvent than simple expectation from the sum of the single liquefactions. And, the amount of next cycle solvent cannot be secured under any conditions so far examined.

![Product yield graph](image)

Fig. 6 Product yields of liquefaction and co-liquefaction of Eucalyptus wood and Loy Yang coal with 1-methylnaphtarene as non-hydrogen donor solvent

The results suggest that the decomposition of the brown coal and the initial solvent is promoted by co-liquefaction, and yields of other fractions are increased in Fig. 6 under the non-hydrogen donation solvent coexistence. On the other hand, because the conversion of the sample is high under the hydrogen donation solvent coexistence, it is thought that the amount of next cycle solvent was able to be secured in Fig. 2.

3.3. Comprehensive Discussion

The synergy effect of co-liquefaction of the woody biomass and the brown coal was thought not as decomposition promotion by hydrogen donation from woody biomass to brown coal but as decomposition promotion of brown coal by catalyst-like action of woody biomass liquefaction products. This looks like the synergy effect of co-liquefaction of the woody biomass and the polypropylene in [7]. Because the brown coal decomposition radicals accept hydrogen under the hydrogen donation solvent existence, it is thought that the hydrogen consumption seemed to be increased by co-liquefaction.

It will be necessary to examine the hydrogen donation capability of solvent fraction for next cycle, in the future.

4. Conclusion

The effects of the co-liquefaction of the woody biomass (Eucalyptus wood) with the brown coal (Loy Yang coal) have been investigated and the following results were obtained.

1) The synergy effect of co-liquefaction of the woody biomass and the brown coal is the decomposition promotion of brown coal by catalyst-like action of woody biomass liquefaction products.
2) It was confirmed that securing the amount of next cycle solvent is possible under the hydrogen donation solvent coexistence.

3) It will be necessary to examine the hydrogen donation capability of solvent fraction for next cycle.

5. Acknowledgment

The authors wish to thank Prof. J. Hayashi at Kyushu University who kindly supplied sample LoyYang coal, and Mr. Fuzimoto and Mr. Hoshino who kindly helped us during our experiments.

6. References


