Role of Butanol Solvent in Direct Liquefaction of Wood

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Wood powder was liquefied in a water/butanol (1:1 volume ratio) solution in the presence of sodium carbonate (5 wt% to wood) at 275°C under 90 atm of nitrogen. Four isomers of butanol, that is, 1-butanol, 2-butanol, i-butanol (2-methyl-1-propanol), and t-butanol (2-methyl-2-propanol) were used and their effects and roles in the liquefaction were investigated. The ratios of butanol (the ratio of the amount of butanol remaining after the reaction to the amount of butanol added initially) ranged from 0.03 to 1.0, and these depended on the species of butanol and the presence or absence of a catalyst. On the contrary, the yield of heavy oil was 45–55% in the presence of a catalyst, scarcely depending on butanol species. It was clarified that butanol did not function as a hydrogen donor solvent. Butanol acted mainly as an extraction solvent, in which undesirable reactions such as repolymerization were retarded.

1. Introduction

In recent years, serious environmental problems have occurred, such as greenhouse effect owing to the increase of concentration of carbon dioxide in the atmosphere. One of the causes for their creation is the excessive use of fossil fuels as exclusive energy sources for a long time. Now, it is hoped that diversification of energy sources and efficient utilization of unused resources would be developed. Biomass, which is only a renewable organic resource and is not responsible for carbon dioxide balance, has received increasing attention from this point.

Thermochemical conversion of biomass into a liquid product, which has been newly developed, is now gaining importance, as is biochemical conversion of biomass. Concerning thermochemical conversion, since the pioneer work by Appell et al. at the Pittsburgh Energy Research Center of the U.S. Bureau of Mines, much work has been reported. In most cases hydrogen and/or carbon monoxide were used in the presence of suitable catalysts. On the other hand, attempts have been made to liquefy biomass under milder conditions with a little or no consumption of these reducing gases. Miller and Fellows used phenol as a solvent for the production of chemicals by direct liquefaction of wood and cellulose. Yu also demonstrated that water-phenol or cyclohexanol solvent in the presence of sulfuric acid was useful for simultaneous lignin alcoholysis and cellulose hydrolysis. They intended to use organic solvents as hydrogen donors instead of hydrogen gas, and whether or not organic solvents they used are hydrogen donors, it has not been substantiated by experiments.

In the previous papers, we reported a liquid product was obtained by liquefying wood powder with a catalyst and water under pressurized atmosphere of nitrogen instead of hydrogen and/or carbon monoxide. The yield of the liquid product depended on reaction parameters, and optimum conditions were as follows: temperature 300°C, initial pressure 20–40 atm, holding time 0 min, catalyst loading 2–5 wt%.

The heating values of liquid product was 25–30 MJ/kg, and yield was 40–50%, irrespective of the variety of wood. Alkaline and alkali earth salts showed strong catalytic effects. When water alone was used as a solvent, in most cases, a liquid product was obtained in the form of a tarry lump, which often solidified on exposure to air. To obtain a fluidized product, some organic solvents were added to the reaction system. As a result, acetone, methyl ethyl ketone, 1-, and 2-propanol, 1-butanol showed marked effect on the direct formation of a fluidized product.

We also reported on the results of wood liquefaction conducted in the water/2-propanol solvent, and it was observed that 2-propanol did not function as a hydrogen donor. In this paper, four isomers of butanol [1-butanol, 2-butanol, 2-methyl-1-propanol (=i-butanol as a semi-trivial name), and 2-methyl-2-propanol (=t-butanol as a
semi-trivial names), which vary as hydrogen donors abilities, were used, and their effects and roles in the liquefaction were investigated (In this paper, for convenience, we use the semi-trivial name, butanol.).

2. Experimental

The wood (Konara, Quercus serrata Thunb.), characterized in Table 1, was chipped and ground to 80 mesh. Selection of the wood was made by Forest Development Technical Institute, (Tsukuba). Sodium carbonate and organic solvents, all of guaranteed grade, were purchased from Wako Pure Chem. Ind.

All experiments were conducted by the similar method, which is described in the preceding paper18). Oven-dried wood powder, a catalyst, water and butanol were placed in the autoclave. After sealing and flushing with nitrogen, the autoclave was pressurized to required level with nitrogen. The temperature was raised. After heating was turned off, the autoclave was cooled down to room temperature. The reaction mixture was removed for separation and analysis.

Procedure for separation to obtain a liquid product from the reaction mixture is demonstrated in Fig. 1. When 1-, 2-, or i-butanol was used, the reaction mixture after liquefaction consisted of three phases:

(i) Butanol layer; it consisted of mainly butanol including a small portion of water.
(ii) Water layer; it consisted of mainly water including a small portion of butanol.
(iii) Tar-like product; it coated the autoclave wall.

As for the two layers (i) and (ii), filtration, washing with acetone, and evaporation was conducted by using a rotary evaporator under 40 mmHg at 50°C. Heterogeneous water–tar mixtures were obtained from butanol layer (i) and water layer (ii).

Tar-like product (iii) was washed off with acetone. After filtration, acetone was evaporated using a rotary evaporator, and a heterogeneous water–tar mixture was obtained. These three portions obtained from (i), (ii), and (iii) were combined and extracted with dichloromethane. A dark brown liquid product obtained after evaporating dichloromethane using a rotary evaporator is referred to hereafter as heavy oil.

t-Butanol, which is different from 1-, 2-, and i-butanol, mixes with water freely, thus, the reaction mixture consisted of two phases: that is, aqueous layer which water and t-butanol were mixed homogeneously and tar-like product. The aqueous layer was similarly treated as (i) and (ii), and the tar-like product was treated as (iii).

<table>
<thead>
<tr>
<th>Table 1 Analysis of Wood</th>
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<tbody>
<tr>
<td></td>
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<tr>
<td>Cellulose and hemicellulose</td>
</tr>
<tr>
<td>Lignin</td>
</tr>
<tr>
<td>Alcohol and benzene soluble extracts</td>
</tr>
<tr>
<td>Ash</td>
</tr>
<tr>
<td>Elemental analysis [%]</td>
</tr>
<tr>
<td>C</td>
</tr>
<tr>
<td>H</td>
</tr>
<tr>
<td>O</td>
</tr>
<tr>
<td>N</td>
</tr>
<tr>
<td>a) The content of oxygen was determined by difference.</td>
</tr>
</tbody>
</table>

![Fig. 1 Procedure for Separation of Products](image-url)
The yield of heavy oil is defined as:

\[
\text{Heavy oil yield [%]} = \left( \frac{\text{Weight of heavy oil}}{\text{Weight of wood}} \right) \times 100 \tag{1}
\]

All calculations are made on ash and moisture free basis.

The higher heating value of heavy oil is calculated according to the Dulong’s formula:

\[
Q_h = 338.3C + 1442(H - O/8) \ [J/g] \tag{2}
\]

where C, H, and O are the weight percentage of carbon, hydrogen, and oxygen, respectively.

The elemental analysis (carbon and hydrogen) of heavy oil was made using Perkin-Elmer 2400 CHN Elemental Analyzer. The nitrogen content in original wood was very low (0.21%), and the content in heavy oil was less than 0.1%. The nitrogen in heavy oil, therefore, was neglected in this paper. The content of oxygen was calculated by difference.

The volume of overhead gas was measured by a gas meter and composition of overhead gas was analyzed with a gas chromatograph (Shimadzu GC-3BT equipped with Unibeads C column (3 mm×2 m), and Unibeads 2S column (3 mm×2 m)).

The amount of butanol in the butanol layer and the water layer (these two layers were combined and hereafter referred to as the “aqueous layer” in this paper) was analyzed with a gas chromatograph (Shimadzu GC-9A, FID detector) equipped with a glasspacked column (TSG-1, 2.6 mm×3.1 m), under the following condition: initial temperature 40°C, final temperature 180°C, heating rate 6°C/min.

3. Results and Discussion

Results of experiments, conducted under the condition of equivalent volume of butanol to water, are summarized in Table 2.

Runs 1—8 are the blank tests, in which reaction of a water/butanol mixture was conducted under a catalytic or a non-catalytic condition, in the absence of wood, to check the behavior of butanol. It is known that butanol can be converted to butene by dehydration and to carbonyl compounds by dehydrogenation, in the presence of acid catalysts. In Runs 1—8, carbonyl compounds, which correspond to products of dehydrogenation of butanol, were scarcely detected in the aqueous layer after the reaction. On the other hand, the amounts of butene evolved changed largely, depending on the isomers of butanol. 1-Butanol was very stable throughout the reaction, while t-butanol was unstable, especially, under a non-catalytic condition. In Run 8, 1.72 g of butene was evolved, which corresponded to the conversion of t-butanol to butene in 20% via dehydration. 2-Butanol and i-butanol were relatively stable, and 2—4% of these were isomerized to 1-butanol and t-butanol.

<table>
<thead>
<tr>
<th>Run</th>
<th>Wood Catalyst</th>
<th>Butanol</th>
<th>Heavy oil extracted</th>
<th>Mass balance</th>
<th>Butanol(^*)</th>
<th>(\text{(#\text{&quot;Final&quot;})})</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>-</td>
<td>-</td>
<td>12.10</td>
<td>0.02</td>
<td>0.98</td>
<td></td>
</tr>
<tr>
<td>2</td>
<td>-</td>
<td>-</td>
<td>12.13</td>
<td>0.02</td>
<td>0.98</td>
<td></td>
</tr>
<tr>
<td>3</td>
<td>-</td>
<td>2- &quot;</td>
<td>12.16</td>
<td>0.16</td>
<td>0.98</td>
<td></td>
</tr>
<tr>
<td>4</td>
<td>-</td>
<td>2- &quot;</td>
<td>12.21</td>
<td>0.27</td>
<td>0.98</td>
<td></td>
</tr>
<tr>
<td>5</td>
<td>0.25</td>
<td>i-BuOH</td>
<td>11.90</td>
<td>0.01</td>
<td>0.98</td>
<td></td>
</tr>
<tr>
<td>6</td>
<td>-</td>
<td>-</td>
<td>12.08</td>
<td>0.02</td>
<td>nil</td>
<td></td>
</tr>
<tr>
<td>7</td>
<td>0.25</td>
<td>t-BuOH</td>
<td>11.84</td>
<td>0.02</td>
<td>0.89</td>
<td></td>
</tr>
<tr>
<td>8</td>
<td>-</td>
<td>-</td>
<td>11.66</td>
<td>0.02</td>
<td>0.89</td>
<td></td>
</tr>
<tr>
<td>9</td>
<td>0.25</td>
<td>1-BuOH</td>
<td>12.17</td>
<td>0.74</td>
<td>1.02</td>
<td></td>
</tr>
<tr>
<td>10</td>
<td>0.25</td>
<td>1- &quot;</td>
<td>12.20</td>
<td>1.52</td>
<td>1.76</td>
<td></td>
</tr>
<tr>
<td>11</td>
<td>0.25</td>
<td>2-BuOH</td>
<td>12.17</td>
<td>0.22</td>
<td>0.54</td>
<td></td>
</tr>
<tr>
<td>12</td>
<td>0.25</td>
<td>2- &quot;</td>
<td>12.18</td>
<td>0.97</td>
<td>0.12</td>
<td></td>
</tr>
<tr>
<td>13</td>
<td>0.25</td>
<td>2-BuOH</td>
<td>12.05</td>
<td>2.83</td>
<td>0.06</td>
<td></td>
</tr>
<tr>
<td>14</td>
<td>0.25</td>
<td>i-BuOH</td>
<td>12.00</td>
<td>1.50</td>
<td>0.44</td>
<td></td>
</tr>
<tr>
<td>15</td>
<td>0.25</td>
<td>i-BuOH</td>
<td>11.78</td>
<td>2.25</td>
<td>0.49</td>
<td></td>
</tr>
<tr>
<td>16</td>
<td>0.25</td>
<td>t-BuOH</td>
<td>11.80</td>
<td>0.37</td>
<td>0.48</td>
<td></td>
</tr>
</tbody>
</table>

\(1\) Liquefaction condition: temperature; 275°C, pressure; 90 atm, holding time; 60 min, solvent; water(15 ml)—butanol(15 ml) [mole ratio; water: butanol=0.84:0.16].

\(\text{*}\) The ratio of “Final” to “Initial” butanol.

"Final"=the amount of butanol remaining in the aqueous layer after the reaction.

"Initial"=the amount of butanol added initially.

\(\text{**}\) In the “Final” butanol, 1-, and t-butanol which were produced from original 2-, and i-butanol via isomerization are included.
Runs 9—16 were the results of wood liquefaction. The yield of heavy oil obtained under a catalytic condition was 45—55%, scarcely depending on the isomers of butanol. On the other hand, the amounts of butanol remaining after the reaction changed drastically, the butanol (“Final”)/ (“Initial”) ratio (referred to hereafter as the butanol F/I ratio in this paper) ranged from 1.0 (1-butanol, Run 9) to 0.03 (t-butanol, Run 16).

T-butanol was converted to butene, as described earlier, and its conversion was accelerated by the presence of wood as seen in comparison between Runs 7, 8 and Runs 15, 16. Because of the presence of acids, for example acetic acid produced from wood, acid-catalyzed dehydration proceeded dominantly. The butanol F/I ratio was very low, especially under a non-catalytic condition. In Run 16, the butanol F/I ratio was 0.03 and 4.76 g of butene was produced, which indicated most t-butanol was decomposed and 55% of original t-butanol was converted to butene. In Run 16, the heavy oil yield was as low as 7%. In Run 15, in the presence of a catalyst, the butanol F/I ratio was 0.15, and 2.23 g of butene was produced, which corresponded to the conversion of t-butanol to butene in 26%. In this case, however, the oil yield was as high as 45%.

2-Butanol is generally accepted to be the most efficient hydrogen-donor among four butanols, however, the use of 2-butanol is not any more effective than that of the other three isomers in terms of the heavy oil yield.

Sodium carbonate was a good catalyst for production of heavy oil. In particular, in the case of t-butanol, the effect of the catalyst was conspicuous to give high yield of heavy oil.

In Table 2, properties of heavy oil are also shown. Heavy oil obtained under catalytic conditions had slightly higher heating value (higher carbon contents and lower oxygen contents) than that obtained under non-catalytic conditions.

Some explanations have been offered already in previous papers concerning the catalytic effect of sodium carbonate. Namely, sodium carbonate could act as a catalyst for the hydrolysis of macromolecules, such as cellulose and hemicellulose, into smaller fractions. Sodium carbonate could also function as a base to neutralize acids produced from the wood during reaction and to prevent undesirable reactions such as an acid-catalyzed dehydration of butanol. The pH of the reaction mixture was about 5 when the catalyst was used, while it was about 3.5 without a catalyst.

The role of butanol, as a solvent, is discussed here. Regarding the role of alcohol, Ross and Blessing reported their cases using propanol, butanol and tetralin as a reaction solvent in coal liquefaction. According to their report, when 2-propanol was used, a pyridine soluble product was obtained in 97% yield, while in the case t-butanol was used, its yield drastically decreased to 12%. They attributed this drastic decrease to the absence of α-hydrogen which would be a stabilizer of radicals generated during the reaction. In the liquefaction of coal, hydrogenation is a key process.

On the other hand, wood, which is mainly composed of cellulose, hemicellulose, and lignin, has a relatively high hydrogen/carbon ratio and also has a high oxygen content. To produce fuels from biomass by degradation, therefore, not hydrogenation but deoxygenation is essential.

The degradation of biomass into smaller products mainly proceeds by depolymerization and deoxygenation. During these reactions, however, some condensation and repolymerization of intermediate products also proceed. To reduce these undesirable reactions, various methods have been attempted. The use of hydrogen donors is believed to be one of the most efficient way. For example, Miller and Fellows used phenol as a hydrogen donor in the thermochemical conversion of wood.

In our experiments, however, it was demonstrated that liquefaction could proceed without hydrogen. In addition, in our earlier survey of catalysts, an experiment using Raney-Ni, which is one of the most active of hydrogenation catalysts, resulted in a poor yield of heavy oil. Then, in the series of experiments using 2-propanol, as previously reported, it was suggested that 2-propanol did not function as a hydrogen donor. In the present series of experiments using butanol, there was little difference among four butanol isomers as to the yield of heavy oil. As for the recovery of butanol, the butanol F/I ratio was 0.98 in the case using 1-butanol, which shows 1-butanol, seemingly, was not consumed during the reaction. Therefore, hydrogenolysis of wood by the hydrogen produced from butanol is not a main reaction in this liquefaction.

When hydrogen is not used, another stabilizer is needed, which prevents intermediates from further undesirable reactions. Yu proposed the scheme shown in Fig. 2 for acidic hydrolysis via trans-acetalization. He reported that intermediate phenoxyl compound (1) was detected during degradation of cellulose in phenol at 180°C. When using alcohol as a solvent instead of phenol, alkoxyl compounds (2) are formed. He, however, did not refer to the detection of alkoxyl compounds. If heating continues, phenoxyl intermediates begin...
to decompose to yield hydroxyl methyl furfural and phenol, and if prolonged heating and/or high temperature (about 300°C) prevails, hydroxyl methyl furfural is polymerized to yield high molecular weight products.

In our experiments, the reaction temperature is 275°C, which is too high for intermediates to be stable in alkoxyl or phenoxyl state. During the reaction, however, butanol reacts with intermediate carbonium ion and forms alkoxyl compound. Assuming that it incorporates with carbonium ion, butanol acts as stabilizer.

An assumption, that the reaction temperature fell in the supercritical temperature and that the water/butanol mixture performed a kind of supercritical extraction, can be ruled out by the following reasons. Firstly, although the data of critical conditions of water and butanol mixture are not available, Barr-David and Dodge measured and calculated the critical temperature of water and propanol mixture in detail20). According to the application of their method to water butanol mixture, the critical temperature of the mixture (mole fraction of butanol=0.19) is estimated to be about 350°C, which is much higher than that of the present study. Secondly, if the supercritical extraction is responsible for the high yield of heavy oil, the yield depends on the critical temperature Tc of each butanol isomer (for example Tc=290°C for 1-butanol, Tc=233°C for t-butanol). As shown in Table 2, however, the heavy oil yields are almost the same, irrespective of the butanol isomers. Thus, high yield of heavy oil in using butanol–water mixture was not caused by conducting supercritical extraction.

We conclude that hydrolysis of wood (cellulose and hemicellulose mainly) proceeds in the aqueous phase and that the breakdown products of these polymers dissolves in butanol immediately after these are formed, and butanol surrounds this unstable breakdown fragments, or incorporates with these fragments so that butanol prevents them from secondary reactions, such as repolymerization. Butanol may act mainly as an extraction solvent.

From these experiments, it was clarified that the alcohol such as 1-, and 2-butanol, was not consumed in the reaction, so that there is possibility of reuse of solvent.

4. Conclusion

The liquefaction of wood was performed using a mixture of equivalent volume of water and butanol. Four isomers of butanol(1-, 2-, t-, and t-butanol) were tested. Fluid heavy oil was obtained and its yield was 45–55% in the presence of a catalyst, scarcely depending on a kind of butanol. On the other hand, the butanol (“Final”/“Initial”) ratio ranged widely from 0.03 to 1.0, depending on the butanol isomer used and on the presence or the absence of a catalyst. It was elucidated that butanol acted not as a hydrogen donor but as an extraction solvent and a stabilizer. In particular, when using 1-butanol, the amounts of 1-butanol after the reaction was almost as the same as that before the reaction, that is to say, 1-butanol was not consumed by liquefaction. There is possibility to recycle an additional alcohol for a reaction solvent.

Acknowledgments

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References

15) Minowa, T., Yokoyama, S., Koguchi, K., Ogì, T., Kagaku
要 旨

木材の直接液化反応におけるプタノール溶媒の役割

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著者らは本質系バイオマスの直接液化に関する一連の研究を行っているが、これまでに水素や酸化触媒などの還元性ガスを用いることなく、木粉を触媒存在下、水溶液中高温（－300℃）、高圧（－100 気圧）で反応させるとアセトン可溶の重油状の液化油が得られる（Ref. 12－16）。またこの反応系にアセトンや C2、C3 の低級アルコール等を添加すると流動性に富む液化油が得られること（Ref. 17）を報告した。前回、触媒として 2-プロパノールを用いて実験を行ったところ、この液化反応で 2-プロパノールを水素供与体とする水素還元化反応でない可能性が示唆された（Ref. 18）。そこで今回、添加有機溶媒として水素供与性の異なるプタノールの異性体 4 種（1-、2-、3-、4-プタノール）を用いて液化を試み、反応に及ぼす影響及びその役割を検討した。

原料として用いたコラナ木粉の組成、元素分析値を Table 1 に示す。触媒には炭酸ナトリウムを 5 wt%（対木粉重量）用いた。実験は前報（Ref. 18）で述べたのと同じ手法で行った。反応後、反応溶液から液化油を抽出、分離する操作は Fig. 1 に示されている手順にしたがって行った。液化油の収率はジクロルメタン可溶分として定義し、Eq. (1) より求めた。


c\(_{\text{産}}\) [%] = \text{生成油の重量} \times 100
\text{原木材料の重量}

水/プタノール = 1:1 の条件下での液化の結果を Table 2 に示す。Run 1－8 は木粉の存在しない水/プタノール混合溶媒のみで反応させたプラクト・テストである。1-プタノールが反応を通じて安定であるのに対して、2-プタノールは不安定であった。特に触媒が存在しない場合は、2-プタノールの 20% が脱水反応により分解してプクタニンになるが、反応後のプタノール存在比は 0.3 であった。さらに本論文中に末尾で述べられるプタノール存在比とは、Table 2 中央 1 行を示した [BoOH ("Final") / "Initial"]（以後 2 プタノール F/I 比）を指し、反応に用いたプタノール量に対する反応終了後の反応混合溶媒中に存在するプタノールの量の比で、プタノール回収の目安となるものである。

Run 9－16 は木粉の液化の結果である。触媒存在下では液化油の収率は 45－55% で、プタノールの種類にかかわりなくほぼ一定していた。それをプタノール F/I 比は 1-プタノールで 1.0 (Run 9) と反応前のほぼ全量が残存しているのに対し、4-プタノールでは 0.03 (Run 16) とはほとんど残存しておらず、プタノール種により大きく変化した。2-プタノールは、プタノール異性体 4 種のうち水素供与体として最も活性であると考えられたが、1-プタノールを用いた場合の液化油の収率は 45% (Run 11) で、1-プタノールを用いた場合の液化油の収率とはほぼ同じであった。これらの結果や反応のマス・バランスの検討から、プタノール異性体 4 種のうち、水素供与性の違いは液化油の収率にとどまること及び、液化反応がプタノールを水素供与体とする水素還元化反応によるものではないことが判明した。

触媒（Na2CO3）の効果は顕著であるが、セルロースやヘミセルロース等の高分子の加水分解触媒として、また反応中に木材より出来てくる酸（酢酸など）を中和し、プタノールの酸触媒分解応応を阻止する塩基中和剤として作用していると考えられる。

液化反応は、木材中のセルロースやヘミセルロース高分子化合物水溶液中で加水分解され、ついて脱炭素反応又は種々の分解反応により低分子化しながら進行する。この反応の途中に生じるフラク、グメント中間体は不安定で、フラグメント同士で再結合して重合体を作りやすい。プタノールが存在する場合、反応中に生成されるカラクタラムが生じるその他プタノール層に移動し、プタノールがこの不安定なフランクトをかこむことにより、フラグメント同士の再結合などの二次反応を抑止する考えられる。すなわち、添加プタノールは抽出溶媒として作用し、安定なフラグメント中間体に対し希釈剤、安定化剤として機能する。

以上、水/プタノール（1:1）溶液中で木材の液化反応を行う。プタノール異性体 4 種につき各々の液化に及ぼす効果を検討したところ、プタノールの種によるプタノール F/I 比は、大きく変動するもかかわらず、液化油の収率は 45－55% で大きな差はみられなかった。プタノールは水素供与体として作用しているのではなく、不安定なフランクト中間体の抽出、安定剤として作用していると考えられる。

本液化反応において、添加プタノールが消費されないことが判明したが、これにより添加有機溶媒をリサイクルして液化反応を行う展望が大きく開けたと考えられる。

Keywords

Direct liquefaction, Woody biomass, Butanol

Keywords

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