[Review Paper]

Liquid Fuel Production from Woody Biomass by Direct Liquefaction

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Taking into consideration creation of alternative energy and environmental preservation, we have attempted to produce a liquid fuel by direct liquefaction of woody biomass, which is the only renewable organic resource, and which fixes carbon dioxide in the atmosphere. Wood was made to react in an aqueous solution of potassium carbonate under pressurized atmosphere of nitrogen without using reducing gases such as hydrogen and/or carbon monoxide. Heavy oil-like liquid products, having heating values of 25—30 MJ/kg, were obtained at yields of 45—50%, under the following optimum reaction conditions: Temperature: 300°C, Initial pressure: 20—40 atm, Holding time: 0—30 min. Potassium carbonate loading: 2—5 wt%. Carbonate and hydrogencarbonate of potassium, sodium and calcium showed strong catalytic effects. Species of the wood did not significantly effect the liquid product yield.

The liquid product obtained by this method was viscous, which caused troubles in handling. In order to improve this property, some organic solvents, such as 1-, 2-propanol, 1-butyl alcohol, were added to the reaction system. As a result, liquid products with low viscosity were obtained at yield in the range of 50—70%, at 275°C. It was found that the added alcohol did not function as a hydrogen donor but as a stabilizer of unstable products from wood, and that it was not consumed during liquefaction. Since this indicated the possibility of recycling the added alcohol, experiments were conducted in which a water/2-propanol mixture was used repeatedly as a solvent. As a result, it was found that liquid product yields were almost the same, even when recycled solvents were used.

This liquefaction method can be applied not only to woody biomass but also to various organic wastes such as sewage sludge.

1. Introduction

1.1 Biomass as Energy

Recently, we are all aware of the serious environmental problems, on a global scale, such as acid rain caused by NO_x and SO_x and the greenhouse effect attributed to increasing concentration of CO_2 in the atmosphere. One of the causes for these phenomena rests largely with the excessive consumption of fossil fuels, such as oil and coal, which has been going on for a long time. Now, in consideration of environmental problems and the depletion of resources, it is strongly desired to develop technologies useful for diversifying energy sources and utilization of hitherto unused resources. In these circumstances, biomass has been attracting much attention as a source of energy.

“Biomass” is a generic term for all animate organic matter, excluding fossil fuels, in which not only crops, wood and marine products but also organic wastes, such as municipal solid waste,

sewage sludge and pulp derived black liquor, are widely included. Biomass, as an energy source, has two striking characteristics. Firstly, biomass is the only renewable organic resource and also one of the most abundant resources. It is reported that annual production of forestry biomass alone amounts to about seven to eight times the annual energy consumption of the world¹⁾. Secondly, biomass fixes carbon dioxide in the atmosphere by photosynthesis. It is reported that, if the amount of grown biomass is equal to that of burned biomass, there would be no net build-up of carbon dioxide in the atmosphere, because the amount released in combustion would be compensated for by the amount absorbed by the biomass during photosynthesis²⁾.

Among various kinds of biomass, woody biomass has been used traditionally, as an energy, for a long time and even to this day, in the form of firewood or charcoal. It is, however, next to impossible to use firewood or charcoal as an alternative fuel for commercial equipment and industrial processes where fossil fuels, in particular oil, are used at present. It is necessary to

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develop technologies, which make possible conversion of biomass to a more suitable form, such as liquid or gas.

Woody biomass is a complex substance which is compounded of three major macro-molecule components, which are cellulose, hemicellulose and lignin. Owing to their high contents of oxygen, woody biomass has heating values much lower than those of fossil hydrocarbons. The efficient removal of oxygen, therefore, is essential to produce a fuel which is competitive with fossil fuels.

1.2 Classification of Biomass Conversion Technology

Biomass conversion technology is roughly classified into two categories, which are biochemical conversion and thermochemical conversion. Biochemical conversion, which is represented by ethanol fermentation, has a long history, and has been studied to a great extent to date. Thermochemical conversion can be further subdivided into gasification, pyrolysis and direct liquefaction. The last two processes are sometimes confused with each other, and a simplified comparison of the two follows. Both are thermochemical processes in which feedstock organic compounds are converted into liquid products. In the case of liquefaction, feedstock macro-molecule compounds are decomposed into fragments of light molecules in the presence of a suitable catalyst. At the same time, these fragments, which are unstable and reactive, repolymerize into oily compounds having appropriate molecular weights. With pyrolysis, on the other hand, a catalyst is usually unnecessary, and the light decomposed fragments are converted to oily compounds through homogeneous reaction in the gas phase. The differences in operating conditions for liquefaction and pyrolysis are shown in **Table 1**. For liquefaction, the working pressure is extremely high as compared with that of pyrolysis. Considering the design of reaction apparatus, pyrolysis is more favorable. However, in case moisture content of feedstock is high, a drying process becomes necessary, making pyrolysis unfavorable in terms of total energy required. Biomass generally has high moisture contents in the range of 50–95%. Consequently, liquefaction is considered to be more suitable for converting biomass.

Table 1 Comparison of Liquefaction and Pyrolysis

Process	Temperature [°C]	Pressure [atm]	Drying
Liquefaction	250–300	50–200	unnecessary
Pyrolysis	400–500	1–5	necessary

1.3 Summary of Biomass Liquefaction Research^{3)–5)}

Concerning the liquefaction of woody biomass, it is already more than half a century since Fierz-David reported the production of a liquid product by reacting cellulose with hydrogen under high pressure and in the presence of an alkali salt⁶⁾. Subsequently, there has been successive reports to date. These researches, however, were concentrated mainly on the pulping of wood and related studies. Research on the production of liquid fuels was first undertaken, at Pittsburgh Energy Research Center (PERC) of the U. S. Bureau of Mines by Appell *et al.* in the 1960's. Appell *et al.* reacted wood chips, municipal solid wastes and others, in an aqueous solution of sodium carbonate with carbon monoxide pressurized to about 280 atm at 350–400°C, and obtained a liquid product at an yield of 40–50%⁷⁾. This process, which is called the PERC process, was initially developed at Pittsburgh, and later the work was transferred to a pilot plant scale research being conducted in Albany, Oregon. Elliott *et al.* of the Battell Pacific Northwest Laboratory studied the process in the Albany plant and attempted to upgrade and characterize the liquid products obtained from the PERC process^{8)–10)}. In the meanwhile, in the 1970's, at the Lawrence Berkely Laboratory of the University of California, the other process, known as the LBL process, was developed, in which wood was pretreated by hydrolysis with sulfuric acid, and the resulting slurry was liquefied under the same conditions as the PERC process^{11)–13)}. Since then, based on the Biomass Liquefaction Project under IEA, (International Energy Agency), many works, on laboratory scale, have been reported till the mid-1980's, by Boocock *et al.* of University of Toronto^{14)–17)}, by Eager *et al.* of University of Saskatchewan^{18)–20)}, by Chornet *et al.* of University of Sherbrooke²¹⁾, and till the end of 1980's on small plant scale, by White *et al.* of University of Arizona²²⁾, and by Meier *et al.* of Institute of Wood Chemistry²³⁾. In most cases, carbon monoxide and/or hydrogen were used in the presence of suitable catalysts. Upgrading of liquid products obtained by these processes, also, has been attempted^{24)–26)}. On the other hand, processes using a little or no carbon monoxide or hydrogen, also, were investigated on laboratory scale, such as the methods of Miller *et al.*, who used phenol as hydrogen donor solvent instead of hydrogen gas²⁷⁾, of Schuchardt *et al.*, who used formate/inert gas instead of carbon monoxide gas²⁸⁾.

In our laboratory, also, we have studied thermochemical conversion of woody biomass, under the Sunshine Project sponsored by the Ministry of

International Trade and Industry (MITI)^{29)~35)}. Wood was reacted in an aqueous solution in the presence of alkali catalysts without using reducing gases, which yielded a liquid product. We hereby report the procedure of our research and present the newly obtained results.

2. Liquefaction Conducted in Water

2.1 Procedure of Liquefaction

The feedstock used in experiments was Konara, which is characterized in **Table 2**. The wood was chipped, ground to 80 mesh and dried prior to liquefaction. All experiments were performed in a stainless steel autoclave of 100 ml capacity. The wood powder, potassium carbonate and water were added to the autoclave. The autoclave was flushed, then pressurized with nitrogen. The temperature was raised and maintained at a required level for a definite time. After heating was terminated, the autoclave was cooled, and then opened. A reaction product, which consisted of a tar-like material and an aqueous layer, was removed. From this mixture, a dark brown viscous product was obtained by filtration, evaporation and extraction, and the separation procedure is shown in **Fig. 1**. This viscous product is referred to as “heavy oil”, hereafter, and its yield is defined as follows:

$$\text{Heavy oil yield [\%]} = \frac{\text{Weight of heavy oil [g]}}{\text{Weight of wood [g]}}$$

The heating value of heavy oil, Qh , was calculated, using the Dulong's formula:

$$Qh = 338.3C + 1,442(H - O/8)$$

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

Table 2 Analysis of Wood

Composition [wt%]			
Cellulose and hemicellulose	Lignin	Alcohol and benzene soluble extracts	Ash
77.89	21.27	2.08	0.38
Elemental analysis [wt%]			
<i>C</i>	<i>H</i>	<i>O</i>	<i>N</i>
46.65	5.83	47.31 ^{a)}	0.21

a) The content of oxygen was determined by difference.

Fig. 1 Separation Process of Products

2.2 Effects of Reaction Parameter

In order to determine the optimum reaction condition, systematic studies were carried out with reaction parameters, and typical results are summarized in **Table 3**. The yields of heavy oils strongly depended on the reaction parameters, that is, pressure, temperature, holding time and wood/potassium carbonate (catalyst) ratio.

The pressure in **Table 3** denotes initial pressure of nitrogen charged with autoclave. With rise in temperature, the vapor pressure of water increased and the total pressure also increased. When the initial pressure was 20 atm, for instance, the final

Table 3 Effects of Reaction Parameters

Initial pres. [atm]	Reaction temp. [°C]	Holding time [min]	Wood/catalyst ratio [g/g]	Heavy oil extracted	
				Yield [%]	Heating value [MJ/kg]
5	350	30	5/1	5.9	35.5
20	350	30	5/1	16.4	33.8
100	350	30	5/1	19.6	31.6
20	250	30	5/1	20.3	17.4
20	300	30	5/1	28.4	29.1
20	375	30	5/1	23.3	32.7
20	400	30	5/1	15.0	35.5
20	350	0	5/1	24.6	30.3
20	350	180	5/1	14.7	35.8
20	350	30	5/0	5.0	28.9
20	350	30	5/0.1	21.4	30.4
20	350	30	5/0.5	26.2	32.0
20	350	30	5/2	24.6	33.4
20	300	0	5/0.2	47.6	24.4
20	300	0	5/0.5	43.8	25.6

Catalyst: K₂CO₃, Water 30 ml.

pressure attained was 172 atm at 350°C. With respect to pressure, 20–40 atm of initial pressure (170–180 atm of final pressure) was recommended. Heavy oils obtained at above 40 atm tended to solidify on exposure to air, and heavy oil obtained at above 80 atm formed emulsion with dichloromethane.

With respect to temperature, yield of heavy oil was the highest at 300°C. Above 300°C, with rise in temperature, yields of heavy oil and contents of oxygen in the heavy oil both diminished. At 400°C, a large amount of gas (40% yields) evolved. In most cases, heavy oils obtained were viscous and tended to partially solidify when allowed to stand in air, while the heavy oil obtained at 375°C had fluidity and did not harden. This phenomenon seems to be related to the critical condition of water used for the solvent. The critical temperature of water is 374°C and the liquefaction proceeded under near critical condition, where water is known to be a strong solvent.

The holding time denotes the period during which the required temperature is maintained and does not include periods of preheating and cooling. We compared the yields of heavy oil, solid residue and gas and the contents of carbon, hydrogen and oxygen, respectively, in these products. As a result, the following were found: the highest yield was obtained when holding time was 0 and the yields decreased with time. As the holding time was prolonged, oxygen contents in heavy oil decreased, as the removal of oxygen proceeded rapidly during the first 30 minutes, and heavy oil, once produced, repolymerized and formed solid residue. These results suggested that liquefaction proceeded in a quite short period at an early stage.

Potassium carbonate was used as a catalyst and its effect was conspicuous. The heavy oil yield was quite low unless potassium carbonate was added. No significant difference was observed, however, on heavy oil yield within the range of potassium carbonate loading of 2–20%. Molton *et al.* suggested that high alkali concentration favored undesirable side reactions, such as aldol condensation, and decreased heavy oil yield³⁶⁾. Present results indicate that a level of 4–5% potassium carbonate is preferable.

From the results described thus far, it was clarified that liquefaction proceeded in an aqueous layer, without reducing gases, at initial pressure of 20 atm and at temperature of 300°C, for periods of 0–30 minutes in the presence of 4–5% of potassium carbonate. Heavy oil yield of about 45% was attained under these maximum conditions, which are shown in two runs at the bottom of **Table 3**.

Table 4 Effects of Variety of Catalyst

Catalyst [g]	Heavy oil extracted					
	Yield [%]	CHR [%]	Elemental analysis [%]			
			C	H	O	
None	—	22.2	31.4	67.39	6.94	25.67
CaCO ₃	0.290	39.6	52.8	63.39	6.45	30.16
Ca(OH) ₂	0.215	48.5	64.1	62.36	6.69	30.95
Na ₂ CO ₃	0.154	50.8	71.1	66.54	6.92	26.54
NaOH	0.119	50.7	70.1	65.82	7.14	27.04
HCOONa	0.198	50.4	66.7	62.93	6.20	30.87
NaCl	0.169	15.9	21.7	64.29	7.03	28.68
K ₂ CO ₃	0.200	47.6	62.0	62.06	6.33	31.61
KOH	0.161	51.0	70.0	64.90	7.34	27.76
HCOOK	0.244	52.1	70.7	64.26	7.07	28.67

Heavy oils obtained in these experiments had heating value in the range of 25–30 MJ/kg, which was slightly lower than that of 31–35 MJ/kg of oils obtained by PERC and other processes using hydrogen and/or carbon monoxide.

2.3 Effect of Variety of Catalyst

The effects of different species of alkali and alkaline earth salts catalysts are shown in **Table 4**. The effect of catalysts was conspicuous and the yields of heavy oil obtained in the presence of catalysts were about twice that in their absence. Among potassium and sodium salts, no significant difference was observed on the yields or the heating values of heavy oils, except for sodium chloride. In the case of sodium chloride, the yield of heavy oil was lower than that in the absence of a catalyst and separation after the reaction was found to be difficult because of heterogeneity of the heavy oil. As shown in **Table 4**, it was found that alkali and alkaline earth salts, except for the chloride, gave high yields of heavy oils.

Some explanations are offered here, concerning catalytic effects and the roles of alkali salts. Alkali salts, such as sodium carbonate and potassium carbonate, can act as catalysts for hydrolysis of macromolecule, such as cellulose and hemicellulose, into smaller fragments³⁾. The micellar-like broken-down fragments produced by hydrolysis are then degraded to smaller compounds by dehydration, dehydrogenation, deoxygenation and decarboxylation. These compounds once produced, rearrange through condensation, cyclization and polymerization leading to new compounds³⁾. Russell *et al.* recognized formation of aromatic compounds when cellulose was thermochemically converted in an alkali solution³⁷⁾. They suggested that these aromatic compounds were formed by condensation or cyclization of unstable intermediate fragments, which were generated by degradation of cellulose.

Alkali salts, such as sodium carbonate and potassium carbonate, can also function as a base.

The pH of an aqueous layer after the reaction was about 5.5 when such a catalyst was added, while it was about 3.5 without a catalyst. Experiments conducted on water-organic solvent mixture, which are described later, revealed that in a strongly acidic solution, yield of heavy oil was low and yield of solid residue was high, instead. Alkali salts, as a base, neutralized acids generated from the wood during reaction and prevented occurrence of undesirable reactions, such as polymerization.

Appell *et al.* proposed the following mechanism for sodium carbonate-catalyzed liquefaction of wood in the presence of carbon monoxide³⁸⁾.

(1) Generation of sodium formate:

(2) Dehydration of vicinal hydroxyl groups in a carbohydrate:

(3) Reduction of newly formed carbonyl group with formate ion:

(4) Regeneration of formate ion:

According to this scheme, deoxygenation occurs

through decarboxylation from ester formed by hydroxyl group and formate ion derived from carbonate. Based on Appell's scheme Schuchardt reacted sugar cane bagasse with formate under inert gas instead of using sodium carbonate and carbon monoxide gas, and obtained oil²⁸⁾. In our experiments, carbon monoxide, which was neither initially charged, evolved during the reaction. It is thus considered that actual liquefaction conditions are similar to those in which CO is present and the above-mentioned reactions may also proceed.

2.4 Effects of Variety of Woody Biomass

Eleven varieties of woods, three varieties of barks, and sugar cane bagasse were liquefied, and the results are shown in Table 5. The yields of heavy oil were 50±5%, except for Japanese larch and Japanese red pine and, therefore, only small differences were observed among the yields. As for barks, their yields of heavy oil ranged from 20 to 27%, which were much lower than those of woods, while for sugar cane bagasse, its yield was similar to those of woods.

In Fig. 2 is shown the relationship between heavy oil yield and lignin content. It can be seen that two groups exist, that is, the wood group including sugar cane bagasse, and the bark group, though no clear-cut relationship can be observed in each group. Some reasons, for lower yields of the heavy oil from barks than those from woods, are discussed here. In Fig. 3 is shown the amounts of gas and solid residue derived from individual feedstocks. The amount of evolved gas, which consisted mainly of CO₂, hardly depended on the lignin contents of the feedstocks. On the other hand, it is obvious that the amount of solid residue

Table 5 Relationship between Feedstock Material and Heavy Oil

Material	Analysis of feedstock materials Chemical composition ^{a)} [wt%]				Heavy oil extracted		Remarks ^{b)}
	C&H	L	A&B	Ash	Yield [%]	Heating value [MJ/kg]	
WOOD							
Japanese oak (<i>konara</i>)	76.36	23.81	0.80	0.44	47.60	24.4	1)
Japanese cottonwood (<i>doronoki</i>)	80.99	22.34	1.80	0.53	52.26	23.9	2)
Japanese beech (<i>buna</i>)	83.18	23.77	1.20	0.61	53.62	21.7	3)
Japanese cedar (<i>sugi</i>)	77.14	32.22	1.37	0.31	43.84	26.7	4)
Japanese hemlock (<i>tsuga</i>)	72.21	32.43	3.13	0.28	50.40	24.4	5)
Spruce (<i>tohi</i>)	73.93	27.54	1.67	0.33	47.66	25.0	6)
Japanese larch (<i>karamatsu</i>)	72.67	28.40	1.26	0.25	37.30	28.2	7)
Japanese red pine (<i>akamatsu</i>)	66.21	28.09	2.69	0.30	39.26	23.9	8)
Red lauan (<i>nanyo-zai</i>)	61.89	33.67	1.42	0.21	47.48	26.0	9)
Kapur (<i>nanyo-zai</i>)	72.81	35.30	1.16	0.78	52.88	22.7	10)
Kamerere (<i>nanyo-zai</i>)	75.61	33.38	1.50	0.84	54.50	24.1	11)
BARK							
Japanese larch (<i>karamatsu</i>)	56.70	47.51	7.72	4.46	21.76	28.4	12)
Japanese red pine (<i>akamatsu</i>)	46.55	44.94	9.00	2.16	19.50	26.1	13)
Yezo spruce (<i>ezomatsu</i>)	54.38	39.47	8.60	3.84	27.10	28.3	14)
BAGASSE							
Sugar cane bagasse	73.61	23.80	1.90	2.54	49.16	27.7	15)

a) C&H: Cellulose and hemicellulose, L: Lignin, A&B: Alcohol and benzene extracts.
b) Number in parentheses corresponds to that in Fig. 2 and Fig. 3.

Fig. 2 Relationship between Lignin Content and Heavy Oil Yield

Fig. 3 Relationship between Lignin Content and Solid Residue and Gas

increased in proportion to the lignin content. Lignin is a macromolecule, which consists of alkylphenols and has a complex three-dimensional structure. It is generally accepted that free phenoxyl radicals are formed by thermal decomposition of lignin at above 250°C and that the radicals have a random tendency to form solid residue through condensation or repolymerization. As reported in the previous section, the yield of heavy oil decreased as the holding time was prolonged, owing to the formation of solid residue by repolymerization of heavy oils once produced. In the case of barks containing larger amounts of lignin than woods, yields of heavy oil could be lower, attributed to repolymerization of the primary heavy oils. Boocock *et al.* proposed flash aqueous pyrolysis of wood for production of liquid fuels because rapid heating and quenching can give better yields than ordinary aqueous phase liquefaction^{39,40}.

3. Liquefaction in the Presence of Organic Solvent

3.1 Effects of Addition of Organic Solvent

Wood was converted to heavy oil by the above-mentioned liquefaction process. Heavy oil obtained, however, was a viscous tarry lump, which sometimes caused troubles in handling. If this method is applied to a continuous reactor, it is highly desirable that the viscosity of heavy oil could be reduced to produce heavy oil which is easily separable from an aqueous layer. For this purpose, some organic solvents were added to the reaction system to improve these points.

The effects of eight organic solvents are shown in Table 6. Runs without addition of organic solvent and/or catalyst are also shown, for comparison. In Run 2, where no organic solvent was added, organic compounds such as methanol, ethanol, 1-, and 2-propanol, 1-butanol, acetone,

Table 6 Effects of Addition of Organic Solvent

Run	Wood [g]	Catalyst K ₂ CO ₃ [g]	Water [ml]	Organic solvent	[ml]	Heavy oil extracted				
						Yield [%]	Elemental analysis			Properties of primary products
							<i>C</i>	<i>H</i>	<i>O</i>	
1	5.0	0	30	—	0	5.0	70.90	6.97	22.13	tarry lump
2	5.0	0.2	30	—	0	47.6	62.06	6.33	31.61	tarry lump
3	5.0	0.5	0	acetone	30	57.8	77.10	8.50	14.40	tarry lump
4	5.0	0.5	15	acetone	15	33.0	59.08	6.69	34.23	fluid
5	5.0	0	15	acetone	15	59.8	63.22	6.46	30.32	fluid
6	5.0	0.5	25	MEK	5	39.8	66.66	6.52	26.82	fluid
7	5.0	0	25	MEK	5	26.4	63.77	6.74	29.49	powdery
8	5.0	0.5	25	ethyl acetate	5	68.4	64.18	6.66	29.16	fluid
9	5.0	0	25	ethyl acetate	5	30.2	64.29	6.41	29.30	powdery
10	5.0	0.5	25	methanol	5	33.2	60.24	6.52	33.24	tarry lump
11	5.0	0.5	25	ethanol	5	36.8	67.15	6.78	26.07	tarry lump
12	5.0	0.5	25	1-propanol	5	50.1	66.39	6.48	27.13	fluid
13	5.0	0.5	25	2-propanol	5	51.6	65.68	6.45	27.87	fluid
14	5.0	0.5	25	1-butanol	5	33.0	62.55	6.32	31.13	fluid
15	5.0	0	25	1-butanol	5	40.6	62.98	6.49	30.53	powdery

This Run was performed at 350°C for 30 min.

methyl ethyl ketone, acetic acid were chromatographically identified in an aqueous layer after the reaction.

When only acetone was used as a reaction solvent, the yield of heavy oil was quite high and the yield of solid residue was also very high. The sum of both yields exceeded 100%, which means that acetone itself had reacted. In addition, the heavy oil obtained in this run was a solid-like tarry lump which was difficult to manipulate. On the other hand, the addition of equivalent volume of acetone to water (Run 4 and 5) led to the formation of heavy oil having low viscosity, both in the presence, and absence, of a catalyst.

When the ratio of organic solvent (acetone) to water was about one, the effect of a catalyst was obscure, and when the ratio of organic solvent to water diminished to below 20 vol%, the effect of a catalyst became conspicuous, on the formation of heavy oil with low viscosity. In the cases of water/organic solvent=5/1 ratio, and when methyl ethyl ketone, ethyl acetate, propanol and butanol were added in the presence of a catalyst, heavy oils having low viscosity were obtained. Especially, when adding 1-, and 2-propanol, the primary product separated from an aqueous layer so easily after the reaction that it could be decanted. Unless a catalyst was added, heavy oil obtained was a powdery tarry lump which was difficult to separate. Unlike the cases of propanol and butanol, the addition of methanol and ethanol was ineffective, resulting in low yield and the formation of a tarry lump, even in the presence of a catalyst.

Liquefaction was also examined in the case of addition of acetic acid (not shown in **Table 6**). Here, however, yield of a large amount of solid residue resulted and a complete separation of heavy oil and solid residue from an aqueous layer was not attained. Liquefaction did not proceed favorably under an acidic condition.

Among organic solvents tested, propanol, butanol, acetone, methyl ethyl ketone and ethyl acetate were found to be effective on the formation of heavy oil having low viscosity. All these solvents except ethyl acetate may be reproduced from wood during liquefaction. This suggests that the solvent can be recovered for reuse. The behavior of an organic solvent added is an important factor in its recovery. The effects of 2-propanol, one of the most effective solvents, therefore, were investigated.

3.2 Effects of Addition of 2-Propanol

Results of experiments conducted under the condition of equivalent volume of 2-propanol to water are shown in **Table 7**. For comparison, the

run conducted in water alone is also shown. Dichloromethane was used, instead of acetone, as extraction solvent of heavy oil in these experiments, since it was necessary to measure the amount of acetone which was generated via degradation of wood and conversion of 2-propanol in an aqueous layer. The heavy oil, therefore, shall hereafter be defined as "dichloromethane soluble compounds".

Yields of heavy oil exceeded 50% in most cases, while those conducted under the condition in which water alone was used were 37% at 275°C. Especially, at 275°C, a yield of 70% was attained. In these cases, however, the sum of yields of heavy oil, solid residue and gas exceeded 100%. This suggests that 2-propanol itself reacted, and this phenomenon was observed when acetone was added as described in the previous section.

Yields of solid residue significantly decreased to below 6%, as compared to the yields of 14–20% when water alone was used as a solvent.

Yields of gas ranged from 19 to 32%. Components of the gas were mainly carbon dioxide and propylene, and the sum of these yields amounted to 98 vol% of gas evolved. The volume ratio of carbon dioxide to propylene ($\text{CO}_2/\text{C}_3\text{H}_6$) was about 2 in the presence of a catalyst, while it was about 0.7 in its absence. The effect of the catalyst was obvious to remove oxygen efficiently in the form of CO_2 and to retard conversion of 2-propanol into propylene.

Properties of heavy oils obtained are shown in **Table 8**. It was found that viscosity of heavy oil decreased largely with the addition of 2-propanol. In Runs 1–6, sodium carbonate, as a catalyst, slightly affected yield of heavy oil, while the heavy oils were upgraded by the addition of the catalyst. Heavy oils obtained in the presence of a catalyst had higher heating values, lower viscosities and lower average molecular weights as compared to those obtained in the absence of a catalyst.

The effects of ratio of water to 2-propanol are shown in **Table 9**. Under the condition of

Table 7 Effects of Addition of 2-Propanol

Run	Temp. [°C]	Pres. [atm]	Catalyst [wt%]	Yield [wt%]		
				Heavy oil	Solid residue	Gas
1	250	70	0	52.8	1.3	20.3
2	250	70	5.0	56.7	0.6	18.5
3	275	90	0	75.7	5.9	23.7
4	275	90	5.0	70.3	0.3	25.8
5	300	120	0	51.1	5.9	32.0
6	300	120	5.0	46.3	4.2	22.3
7 ^{a)}	275	90	5.0	37.0	14.1	23.2

Reaction solvent: Water (15 ml)/2-Propanol (15 ml), Wood; 5.0 g, Catalyst; Na_2CO_3 , Holding time: 60 min.

a) Solvent: Water 30 ml alone, without 2-propanol.

Table 8 Properties of Obtained Heavy Oil

Run	Heavy oil yield [%]	Elemental analysis			Heating value [MJ/kg]	Average molecular weight	Viscosity [Pa·s]
		C [%]	H [%]	O [%]			
1	52.8	62.25	6.20	31.55	24.3	367	1.1
2	56.7	64.06	6.48	29.46	25.7	309	0.6
3	75.7	58.32	7.23	34.45	23.9	448	0.6
4	70.3	66.50	6.80	26.70	27.5	393	0.2
5	51.1	64.70	6.90	28.40	26.7	320	1.4
6	46.3	67.76	6.72	25.52	28.0	257	0.9
7	37.0	65.64	6.20	28.16	26.1	385	7—8

Table 9 Effects of the Ratio of Water/2-Propanol

H ₂ O/2-PrOH [ml] [ml]		Holding time [min]	Catalyst Na ₂ CO ₃ [wt%]	Yield [wt%]		
				Heavy oil	Solid residue	Gas
15	/ 15	60	0	75.7	5.9	23.7
15	/ 15	60	5.0	70.9	0.3	25.8
20	/ 10	60	5.0	50.9	11.3	24.8
25	/ 5	60	0	23.8	32.5	36.2
25	/ 5	60	5.0	46.0	6.4	32.6
28	/ 2	60	5.0	46.1	11.3	25.9
30	/ 0	60	5.0	37.0	14.1	23.2

Reaction condition: Pressure 90 atm, Temperature 275°C, Holding time 60 min.

Table 10 Mass Balance of 2-Propanol

Run	Catalyst Na ₂ CO ₃ [wt%]	Initial 2-propanol [g]	Final			PrOH (F/I) ^{d)}
			2-Propanol [g]	Propylene [g]	Acetone [g]	
1 ^{a)}	0	11.54	11.93	0.77	0.07	1.03
2	5.0	11.44	11.71	0.38	0.02	1.02
3	0	11.66	10.53	1.08	0.12	0.90
4	5.0	11.68	10.42	0.63	0.04	0.89
5	0	11.63	9.93	0.82	0.53	0.85
6	5.0	11.44	8.49	0.06	0.23	0.75
7 ^{a)}	5.0	0	0.3	0.09	trace	—
8 ^{b)}	0	11.64	1.25	6.97	trace	0.11
9 ^{b)}	5.0	11.67	8.4	2.87	trace	0.72

Reaction conditions

a) No 2-PrOH, Solvent: Water 30 ml, Wood: 5.0 g, Temperature: 275°C, Pressure: 90 atm, Holding time: 60 min.

b) No wood, solvent: Water (15 ml)/2-PrOH (15 ml), Temperature: 275°C, Pressure: 90 atm, Holding time: 60 min.

c) See Table 7.

d) I="Initial" 2-propanol=the amount of 2-propanol added initially.

F="Final" 2-propanol=the amount of 2-propanol remaining in the aqueous layer after the reaction.

equivalent volume of 2-propanol to water, the aqueous layer contained more than 90% of heavy oil. It is highly desirable to enrich the heavy oil into a tar-like product fraction (see **Fig. 1**) for easy separation of heavy oil. When the water : 2-propanol ratio was 25:5, in the presence of a catalyst, a tar-like product floated on the aqueous layer and separated easily by decanting. When water : 2-propanol ratio was 20:10 and 28:2, though a tar-like product partially separated, further extraction was needed to recover the heavy oil completely. The optimum ratio of water to 2-propanol was around 25 to 5.

3.3 Recovery of 2-Propanol

The recovery of 2-propanol, added initially in the reaction, must be conducted for its reuse. It is well known that 2-propanol is converted mainly to propylene by dehydration and to acetone by

dehydrogenation. Thus, the amounts of 2-propanol, propylene and acetone were measured and compared before and after the reaction. The results are shown in **Table 10**, in which "Initial" 2-propanol denotes the amount of 2-propanol added initially, "Final" 2-propanol, propylene and acetone denote the amounts of these detected in an aqueous layer after the reaction, and 2-PrOH(F/I) denotes the ratio of "Final" 2-propanol to "Initial" 2-propanol.

To check the behavior of 2-propanol, two blank tests were conducted with and without a catalyst in the absence of wood powder. About 60% of 2-propanol was converted to propylene in the absence of a catalyst, while only 15% of 2-propanol was converted in its presence. Not only in Runs 8 and 9, but also throughout Runs 1—6, amounts of propylene evolved in the presence of a catalyst were

less than those in its absence. The effect of a catalyst was conspicuous to prevent undesirable degradation of 2-propanol.

In Runs 1 and 2, at 250°C, the F/I ratio was about 1.0. Thus, 2-propanol did not seem to be consumed during the reaction. The F/I ratio decreased and the amounts of acetone inversely increased with the rise in temperature.

A role of 2-propanol, as a reaction solvent, is discussed here. In the field of coal liquefaction, organic solvents such as tetralin is widely used as a hydrogen donor solvent. Ross and Blessing used 2-propanol as a reaction solvent to liquefy coal and obtained a pyridine soluble product in higher yield than that using tetralin⁴¹⁾. Based on their results, Vasilakos and Austgen performed liquefaction of pure cellulose using tetralin or 2-propanol, and found that solid conversion of 90% or more could be attained by both solvents⁴¹⁾. On the other hand, Miller and Fellows reacted cellulose or wood in phenol and obtained oils²⁷⁾. In these experiments, the effective liquefaction was attributed to the high performance of 2-propanol or phenol as a hydrogen donor. Ross and Blessing proposed a mechanism of reduction by hydrogen of 2-propanol⁴¹⁾. This is as follows:

According to this scheme, when one mole of 2-propanol is consumed, one mole of acetone is produced.

In our experiments, at 250°C, the yield of heavy oil was 56% and the (F/I) ratio was 1.0, which suggests that despite the fact that 2-propanol was

seemingly not consumed, liquefaction proceeded. The (F/I) ratio decreased and the amounts of acetone increased at 275°C and 300°C. The amount of acetone produced, however, was only 3% of 2-propanol consumed. We could safely say, therefore, that hydrogenolysis with 2-propanol is not a main reaction in this liquefaction.

As it was suggested that 2-propanol could not function as a hydrogen donor, liquefaction using four isomers of butanol were tried. These were 1-butanol, 2-butanol, *i*-butanol and *t*-butanol, which vary in their effectiveness as hydrogen donors, and their effects and roles in liquefaction were investigated. (Concerning nomenclature “butanol”, we used the semi-trivial name for convenience’s sake in this paper.)

3.4 Effectiveness of Butanol as Hydrogen Donor on Liquefaction

The results of experiments conducted under the condition of equivalent volume of butanol to water are shown in Table 11.

Runs 1—8 are the blank tests, in which a water/butanol mixture alone was reacted under a catalytic or non-catalytic condition in the absence of wood, in order to check the behavior of butanol. Butanol can be converted to butene by dehydration and to carbonyl (or aldehyde) compounds by dehydration in the presence of an acidic catalyst. In Runs 1—8, compounds which correspond to products of dehydrogenation of butanol, were scarcely detected in an 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 stable throughout the reaction, while *t*-butanol was unstable. Especially, in the absence of a catalyst,

Table 11 Effects of Addition of Butanol

Run	Wood [g]	Catalyst Na ₂ CO ₃ [g]	Butanol	[g]	Heavy oil yield [wt%]	Mass balance				BuOH (<i>F/I</i>) ^{a)}
						Gas [g]			Solid residue [g]	
						Total [g]	CO ₂ [g]	C ₄ H ₈ [g]		
1	—	0.25	1-BuOH	12.10	—	0.02	0.02	trace	nil	0.98
2	—	—	1-BuOH	12.13	—	0.02	0.02	trace	nil	0.98
3	—	0.25	2-BuOH	12.16	—	0.16	0.13	trace	nil	0.81
4	—	—	2-BuOH	12.21	—	0.27	0.16	0.07	nil	0.82
5	—	0.25	<i>i</i> -BuOH	11.90	—	0.01	0.01	trace	nil	0.90
6	—	—	<i>i</i> -BuOH	12.08	—	0.02	0.02	trace	nil	0.86
7	—	0.25	<i>t</i> -BuOH	11.84	—	0.02	0.01	0.01	nil	0.81
8	—	—	<i>t</i> -BuOH	11.66	—	1.74	0.01	1.72	0.02	0.30
9	5	0.25	1-BuOH	12.17	54.8	0.78	0.69	trace	0.24	~1.0
10	5	—	1-BuOH	12.20	30.4	0.57	0.53	trace	1.17	0.81
11	5	0.25	2-BuOH	12.17	45.6	0.54	0.40	0.12	0.58	~0.8
12	5	—	2-BuOH	12.18	27.4	1.00	0.88	0.02	1.25	~0.7
13	5	0.25	<i>i</i> -BuOH	12.05	56.5	0.75	0.65	trace	0.16	0.86
14	5	—	<i>i</i> -BuOH	12.00	30.0	0.44	0.41	trace	1.40	0.86
15	5	0.25	<i>t</i> -BuOH	11.78	44.5	3.49	1.10	2.23	0.53	0.15
16	5	—	<i>t</i> -BuOH	11.80	7.4	5.47	0.68	4.76	2.50	0.03

Reaction condition: Pressure 90 atm, Temperature 275°C, Holding time 60 min.

a) I =the amount of butanol added initially.

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

20% of *t*-butanol was converted to butene.

Runs 9–16 show the results of wood liquefaction. The yield of heavy oil obtained in the presence of a catalyst was 45–55%, scarcely depending on the isomers of butanol. On the other hand, the BuOH(*F/I*) ratio changed drastically and ranged from 1.0 to 0.03. The BuOH(*F/I*) ratio was about 1 when 1-butanol was used, which shows 1-propanol was seemingly not consumed during the reaction. Nevertheless, heavy oil was obtained in 55% yield. 2-Butanol is generally accepted to be the most efficient hydrogen donor among four butanols. However, the yield of heavy oil using 2-propanol was 45%, which was almost the same as that using *t*-butanol, which is hardly expected to function as a hydrogen donor. Based on these results, we can safely conclude that hydrogenolysis of wood by hydrogen released from butanol is not a main reaction in this liquefaction.

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 do proceed. To prevent these undesirable reactions of intermediates, various methods have been attempted. The use of hydrogen is believed to be one of the highly effective methods. When hydrogen is not used, another stabilizer is needed. Yu conducted solvolysis of cellulose and reported that there existed intermediates of phenoxyl compounds (conducted in phenol) and alkoxyl compounds (conducted in alcohol) at 180°C⁴³. The scheme he proposed is shown in Fig. 4. If heating continues, the 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 may react with intermediate carbonium ion and form alkoxyl compounds. Assuming that it incorporates with

Fig. 4 Scheme of Hydrolysis *via* Transacetalization

carbonium ion, butanol acts as stabilizer. We speculate that hydrolysis of wood (cellulose and hemicellulose mainly) proceeds in an aqueous layer and that butanol surrounds this unstable breakdown fragments, or incorporates with these fragments so that butanol prevents them from secondary reactions, such as repolymerization.

Since it was clarified that the propanol or butanol was not consumed as a hydrogen donor in the liquefaction, there shows the possibility of repeated use of additional organic solvents. As a further step, extended batch experiments, in which a reaction solvent was recycled, were tried and its latest results are reported in 3.5.

3.5 Liquefaction Using Recycled Solvent

Experiments consisted of a series of five sequential runs. In each run, the experiment was conducted using the same apparatus and by a similar method described thus far: wood powder was liquefied in a reaction solvent in the presence of sodium carbonate at 275°C at 90 atm for 30 min. A water/2-propanol mixture was used as a reaction solvent in the first run, and the aqueous layer that remained in the previous run was used, supplemented with a prescribed water, for the second to the fifth runs.

The results are shown in Table 12. Since heavy oil was obtained from a tar-like product fraction alone (see Fig. 1) in this series of experiments, heavy oil was obtained, thus far, in lower yield than that extracted from both a tar-like fraction and an aqueous layer. Among the five runs, there was scarcely significant difference on yield of heavy oil, though it decreased at the fifth run. Heavy oils obtained had almost the same elemental composition, heating value and property. The aqueous layer after the reaction was effective when used repeatedly as a reaction solvent.

4. Conclusion

Wood was converted to a heavy oil-like liquid

Table 12 Effects of Solvent Recycling

Series	Heavy oil obtained				
	Yield [%]	Elemental analysis			Heating value [MJ/kg]
		C [%]	H [%]	O [%]	
Run					
1	37.4	68.5	8.2	23.3	30.6
2	36.3	68.6	8.2	23.2	30.7
3	31.3	68.2	7.7	24.1	30.1
4	35.0	68.9	8.0	23.1	30.6
5	29.6	68.3	8.3	23.4	30.7

Reaction conditions

Wood: 20 g, Catalyst: Na₂CO₃ 1 g.

Solvent: Water (100 ml)+2-propanol (20 ml) at the 1st run.

Recovered aqueous layer (90 ml)+Water (30 ml) at the 2nd–5th runs.

Temperature: 275°C, Pressure: 90 atm. Holding time: 30 min.

product in an aqueous solution of alkali carbonate catalyst without using reducing gases such as hydrogen and/or carbon monoxide. The addition of some organic solvents, such as propanol, to the reaction system led to the formation of heavy oil, having low viscosity, at high yields. The additional alcohol was not consumed as a hydrogen donor and could be used repeatedly as a reaction solvent.

5. Future Scope

The liquefaction process described thus far has been developed for woody biomass. Nevertheless, this process can be applied not only to woody biomass but also to various organic wastes, such as pulp sludge, sewage sludge, or alcohol fermentation stillage^{44,45}. If these organic wastes would be treated by this liquefaction method to give heavy oil, which would be used as a source of energy for operation of liquefaction of wastes, then, wastes treatment cost would be economized.

The liquefaction technology may be evaluated as one of the highly promising biomass conversion technologies, although some technical problems need to be solved. If a total system is built, in which biomass is planted and grown and then the biomass is used as fuel and/or chemicals, self-sufficient and carbon-neutral energy can be supplied. For the promotion of this system, further development of technologies are needed not only for conversion itself but also for others, for example, plantation, afforestation and irrigation.

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要 旨

直接液化法による木質系バイオマスからの燃料油の製造

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唯一の再生可能な有機資源であるバイオマスを直接液化し、液体燃料を製造することを試みた。

コナラ木粉を、水素や一酸化炭素などの還元性ガスを用いることなく、水溶液中触媒存在下、高温高压で反応させ、重油状の液化油を得ることができた。初圧 20 気圧（終圧 100 気圧）、温度 300°C、保持時間 0～30 分、触媒添加率 4～5 wt% の最適条件下で、発熱量 25～30 MJ/kg の液化油が 45～50% の収率で得られた。触媒については、炭酸ナトリウムなどのアルカリ金属塩が顕著な添加効果を示した。原料にコナラ以外の木材、樹皮などを用いた場合、液化油の収率は、木材に関しては約 50% で、樹種による違いはほとんど認められなかったが、リグニン含有量の高い樹皮の場合では 20～27% と低くなった。

上記の方法で木材から得られた液化油は粘性が高いので、これを改善するために反応系に有機溶媒を添加して液化を試みたところ、アセトンやプロパノール、ブタノールを添加すると、流動性に富む液化油が収率よく得られることがわかった。水

/2-プロパノール＝1：1、温度 275°C、圧力 90 気圧、保持時間 60 分の時、液化油の収率は 70% に達した。また、水/2-プロパノール＝5：1 の時に反応後の処理操作が極めて容易な液化油が収率よく得られた。本液化反応において、2-プロパノールは反応中に水素供与体として働いていないことが示唆されたので、水素供与性の異なるブタノールの異性体 4 種を用いて液化を試みたところ、液化油の収率は 45～55% で、ブタノール種に関わりなくほぼ一定していた。これらの反応のマスバランスの検討から、液化反応が添加低級アルコールを水素供与体とする水素化反応によるものではないことが判明した。添加低級アルコールが反応中に消費されないことが判明したので、反応溶液をリサイクルして液化を試みたところ、リサイクル溶媒を用いても流動性のよい液化油が十分な収率で得られることがわかった。

本液化法は木粉のみならず、アルコール発酵残さや下水汚泥などの他のバイオマスにも広く応用でき、廃棄物処理方法としても有用であることが示唆された。

Keywords

Woody biomass, Direct liquefaction, Alternative fuel production