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Catalytic Liquefaction of Wood with Carbon Monoxide and Synthesis Gas*

By

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一酸化炭素および合成ガスによる木材の接触液化*

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1. Introduction

Although the coal liquefaction is one of the most promising processes for new oil production as a substitute for petroleum, wood resources are also important for alternative liquid fuel, because wood is a renewable biomass, and large amount of the wastes are produced from wood industry. There are three processes for pro-

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duction of liquid oil from lignocellulosic materials : The first is production of alcohol from sugars which are obtained by hydrolysis of wood. The second is an indirect process in which wood is subjected to gasification, giving CO and H_2 from which methanol or hydrocarbons can be synthesized. The third is direct liquefaction of wood with CO or H_2 gas.

The Bureau of Mines U. S. A. has developed a process for converting solid organic wastes to a sulfur-free oil potentially suitable for use by powerplants or for conversion of gasoline and diesel fuels.[1] Another report described a method of converting organic urban refuse, waste paper, and sewage to oil by treating these materials with carbon monoxide and water.[2]

Present paper describes the results of works in which wood was subjected to the reaction under the presence of carbon monoxide or synthesis gas to obtain liquid fuels.

2. Experimental

2.1 Substrates

As a cellulose substrate, Toyoroshi (filter paper) No. 2 was used, and as wood substrates, *Fraxinus mandshurica* var. *japonica* (Klason lignin 21.1%, 60–100 mesh) and *Larix kaempferi* (Klason lignin 28.4%, 40–60 mesh) grown both in the Tomakomai Experiment Forest, Hokkaido University were used.

2.2 Procedure

Twenty grams of substrate were suspended in water or organic solvents and reacted over catalyst (about 1% of substrate) under various pressure of carbon monoxide or synthesis gas in a 500 mℓ autoclave with magnetic stirrer. One series of the experiment was carried out by an experimental planning method using L9 (3^4) orthogonal table. Selected factor and level of factor are as follows.

Reaction temperature	250°, 300°, 350°C
CO initial pressure	20, 30, 40 kg/cm^2
Catalyst	Na_2CO_3, K_2CO_3, NH_4OH

After reaction, water was separated, and reaction mixture was extracted with benzene and acetone, respectively, to obtain water-, benzene- and acetone-soluble fractions. In other series of experiment, the reaction was carried out in organic solvent such as cyclohexanol, turpentine oil, ethanol and toluene over the catalysts, $Fe(CO)_5$, Fe_2O_3 and $Fe_2O_3 \cdot SO^-_3$, under the pressure of synthesis gas.

2.3 Analysis of the products

After measuring of the gas volume, a sample of the residual gas was analyzed by means of gaschromatography. The reaction products were characterized by elementary analysis, IR and NMR spectra and gaschromatography.

3. Results and discussion

3.1 Liquefaction of cellulose and wood under carbon monoxide

The results obtained from cellulose and wood are shown in Tables 1 and 2, respectively. The tendency of reaction for wood is almost the same as that of cellulose. Reaction temperature was significant at 1% significance level for the yield of benzene soluble fraction. The results are shown in Fig. 1. It was assumed that benzene soluble fraction corresponds to oil. Cellulose gave practically no benzene soluble fraction at the temperature 250°C, but gave 20–25% this fraction at 300–350°C. On the other hand, wood gave benzene soluble fraction only at 350°C, in higher yield (32.3+2.8%) than cellulose. The fact may be explained that wood contains lignin with less oxygen functions. According to analysis of variance for conversion, catalyst was significant at 1% significance level, and temperature and carbon monoxide pressure were significant at 5% significance level. Sodium and potassium carbonates are found to be very effective catalysts, especially the former, but ammonium hydroxide seems to be less effective. Carbon monoxide pressure

Table 1. Liquefaction of cellulose by carbon monoxide

Catalyst	Temp. (°C)	CO Initial pressure (kg/cm²)	Maximum pressure (kg/cm²)	Final pressure (kg/cm²)	Conversion (%)	Benzene soluble (%)	Acetone soluble (%)	Water soluble (%)
	250	20	102	28	95.8	0	28.1	16.2
Na_2CO_3	300	30	205	49	94.8	23.0	0	9.4
	350	40	251	62	98.6	28.3	0.6	4.9
	300	20	170	33	95.0	21.2	7.0	9.4
K_2CO_3	350	30	300	55	96.7	27.7	0.5	8.0
	250	40	140	48	94.5	0	27.2	18.0
	350	20	250	32	87.1	18.7	1.5	5.9
NH_2OH	250	30	113	31	82.6	0.4	13.7	18.2
	300	40	210	47	94.1	12.3	10.0	20.2

Table 2. Liquefaction of wood by carbon monoxide

Catalyst	Temp. (°C)	CO Initial pressure (kg/cm²)	Maximum pressure (kg/cm²)	Final pressure (kg/cm²)	Conversion (%)	Benzene soluble (%)	Acetone soluble (%)	Water soluble (%)
	250	20	100	25	98.7	0	43.7	13.3
Na_2CO_3	300	30	201	45	97.1	0	33.8	13.7
	350	40	251	61	98.3	35.7	0.6	9.3
	300	20	165	30	96.2	0.5	33.2	10.3
K_2CO_3	350	30	291	55	96.7	32.1	0.8	4.1
	250	40	136	45	92.0	0.1	40.3	13.4
	350	20	250	30	93.3	29.0	2.2	9.1
NH_4OH	250	30	110	31	85.3	0.1	13.7	17.9
	300	40	210	48	85.4	2.2	19.7	18.2

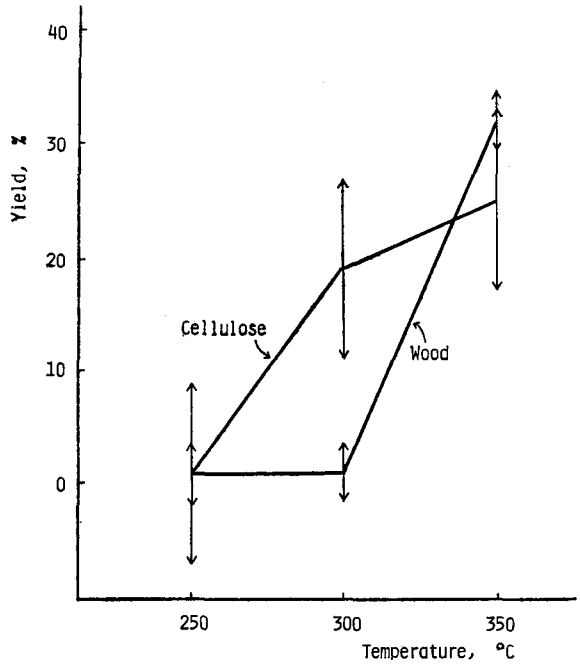


Fig. 1. Effect of temperature on the yield of benzene soluble oil.

may not affect the conversion, but higher initial carbon monoxide pressure and higher temperature seems to contribute to produce more light oil with lower oxygen content.

3.2 Off-gas analysis

The results of analysis for off-gas are shown in Table 3. Carbon dioxide can be formed not only by the reaction of carbon monoxide and carbohydrates but also from water shift reaction:

$$CO+H_2O \rightleftarrows CO_2+H_2$$

This reaction occurs evidently at higher temperature, and cannot be avoided during the liquefaction reaction, but it must be minimized. One of the advantages of low

Table 3. Analysis of off-gas

Ex. No.	Material	Catalyst	Temp. (°C)	Initial pressure (kg/cm²)	Total gas (liter)	H_2	Air	CO	CH_4	CO_2	Reacted gas (liter)
						(liter)					
1	Cellulose	NH_4OH	300	40	27.7	tr.	2.7	12.6	tr.	7.4	5.0
2	"	Na_2CO_3	350	40	38.9	9.8	1.4	11.8	tr.	15.9	6.1
3	Wood	Na_2CO_3	350	40	33.5	9.7	1.6	8.1	0.06	14.0	4.3
4	"	NH_4OH	350	20	14.2	2.0	2.0	2.0	0.09	8.1	6.1
5	"	"	250	30	16.8	tr.	1.7	12.6	0	2.5	2.5
6	"	"	300	40	31.3	3.2	0.9	13.6	tr.	13.6	10.4

temperature (250°C) is very little carbon monoxide consumption by the water-gas shift reaction. As the temperature is raised, the liquefaction reaction proceeds well, but the water-gas shift reaction begins to consume carbon monoxide. The amount of carbon dioxide changed from carbon monoxide after reaction with carbohydrates can be estimated by substraction of hydrogen volume from total carbon dioxide volume. The reacted carbon monoxide volume amounted to 5–6 ℓ (mean values), corresponding to deoxygenation of 2–3 oxygen atoms from a glucose anhydrate. The fact indicates some retaining oxygen functions in the product oils.

3.3 Characterization of benzene soluble oil

3.3.1 IR spectra

Infrared absorption spectra of benzene soluble fractions from cellulose and wood are shown in Fig. 2. It is surprising that the absorption bands originated from aromatic rings can also be observed in the spectrum of benzene soluble fraction from cellulose. Further the absorption bands at 1600 and 1500 cm^{-1} which may be caused by skeletal vibrations of aromatic ring are observed not only in the product from wood, but also in that from cellulose. And the both spectra have almost the same absorption bands. Absorption bands at 850 and 810 cm^{-1} of fingerprint region assumed to be those originated by C–H out-of-plane deformation of aromatic ring are also observed in both spectra. The fact indicates that cellulose molecule may likely be converted to aromatic compounds during the reaction, after deoxygenation and dehydration.

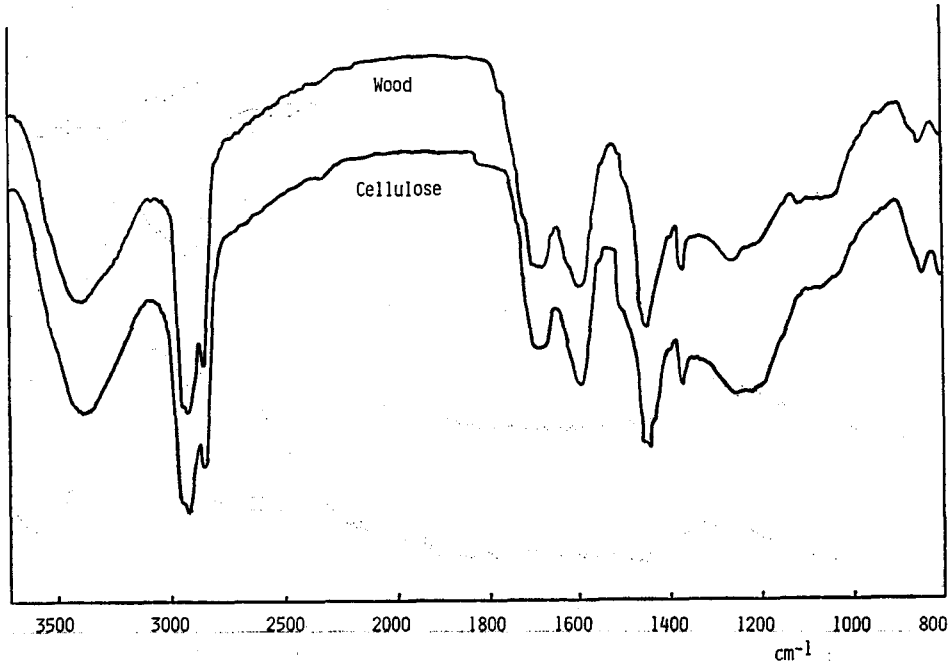


Fig. 2. IR spectra of benzene soluble fraction from degradation products of cellulose and wood by CO.

3.3.2 ^{1}H-NMR spectra

^{1}H-NMR spectra of benzene soluble fractions are shown in Fig. 3. There is an intense peak group at δ 0.5-1.8, corresponding to methylene and end methyl ($-CH_2-CH_3$) protons in the product oils of both cellulose and wood, suggesting that

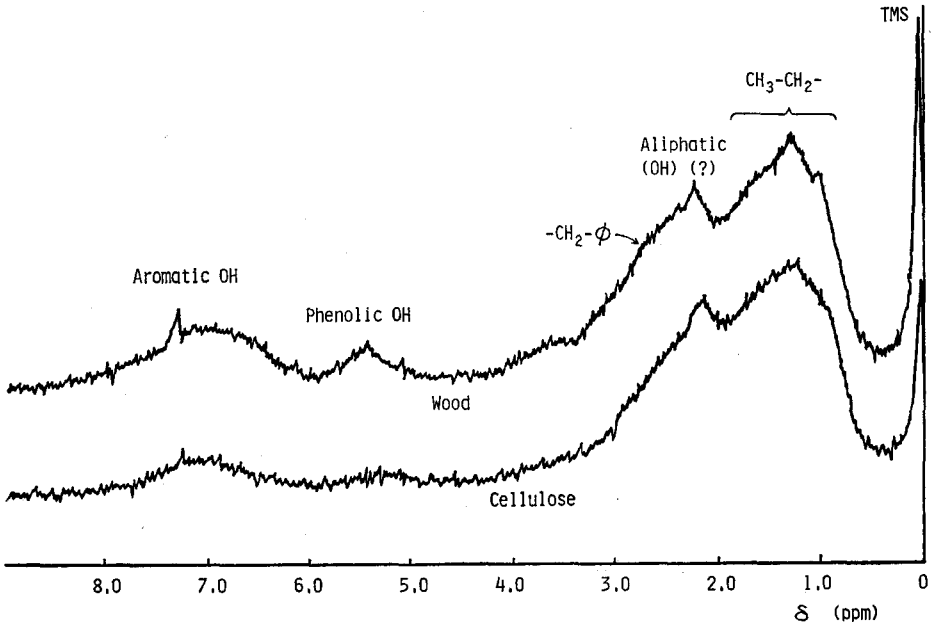


Fig. 3. ^{1}H-NMR spectra of benzene soluble fraction.

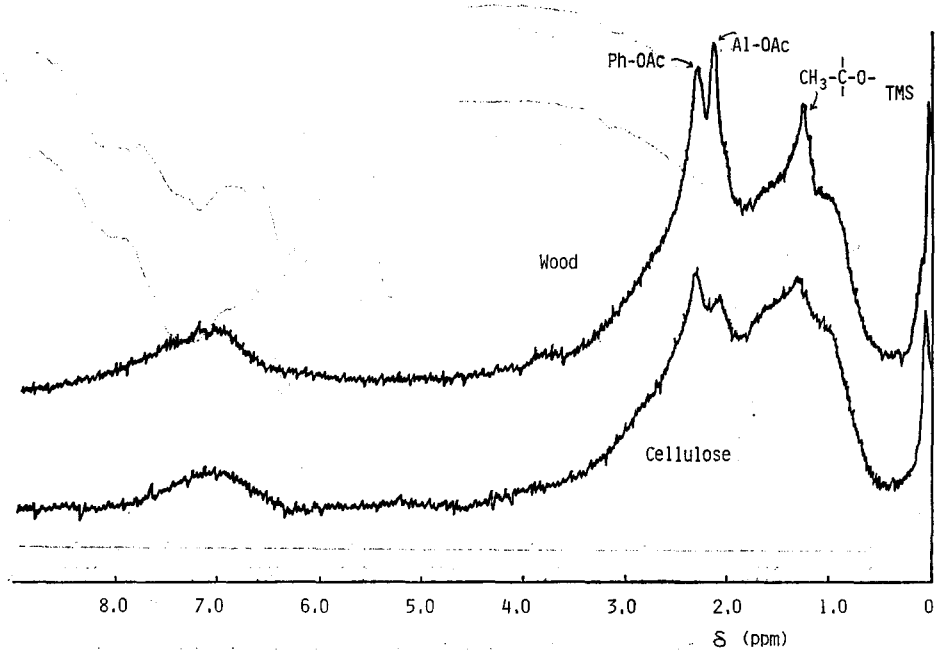


Fig. 4. ^{1}H-NMR spectra of acetylated benzene soluble fraction.

the products are composed of almost reduced compounds. The second prominent peak group at δ 1.8-2.4 can be attributed to the protons of $-CH_3$, $-CO-CH_3$ or $>C=CH_2-$. A broad peak at δ 6.2-7.5 assigned to aromatic protons is observed also in the product oils of cellulose, indicating again a possibility of aromatization of polysaccharides. A broad absorption peak at δ 4.7-6.0 can be assigned to protons of phenolic hydroxyl groups. A sharp signal at δ 2.2 may likely be originated from alcoholic hydroxyl protons. A peak reagion at δ 3.2 seems to be assigned to protons of $-CH_2OH$ or $-CH_2OR$. Fig. 4 shows ^1H-NMR spectra of acetylated benzene soluble fraction from cellulose and wood. In these spectra, the peaks at δ 2.2 assigned to alcoholic hydroxyl protons and that at δ 4.7-6.0 assigned to phenolic hydroxyl protons are disappeared, and instead of them, two new sharp peaks at δ 2.0 and 2.4 appeared. They correspond to protons of aliphatic acetoxyls and those of aromatic acetoxyls. These results obtained from IR and NMR spectra indicate that product oils are almost reduced by carbon monoxide, and a part of carbohydrate skeletons may undergo aromatization during the reaction.

3.3.3 Reaction mechanism of deoxygenation by carbon monoxide

YOUNGQUIST et al.[3] proposed probable mechanism deoxygenation by carbon monoxide as follows:

Scheme

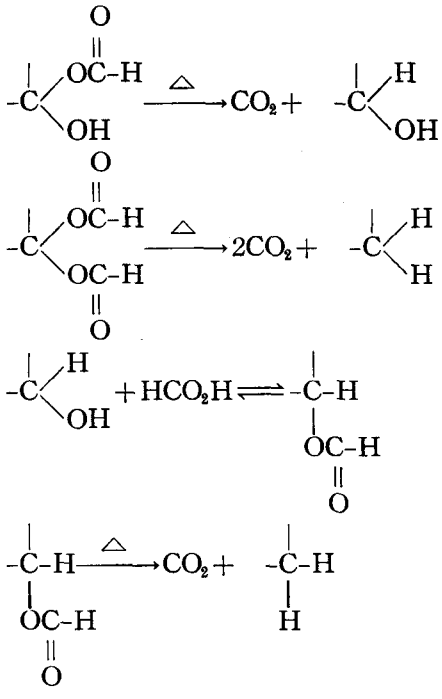
1. $CO+H_2O \rightleftharpoons HCO_2H$
2. $CO+OH^{\ominus} \rightleftharpoons HCO_2^{\ominus}$
3. $HCO_2^{\ominus}+H_2O \rightleftharpoons HCO_2H+OH^{\ominus}$
4. $-\overset{|}{C}OH+HCO_2H \rightleftharpoons -\overset{|}{C}-OCH+H_2O$ (O)

$$-\overset{|}{C}-O-\overset{|}{C}-H \xrightarrow{\triangle} CO_2+ -\overset{|}{C}-H$$ (O)

5. $-\overset{|}{C}=O+H_2O \rightleftharpoons -\overset{|}{C}(OH)(OH)$

$$-\overset{|}{C}(OH)(OH)+HCO_2H \rightleftharpoons -\overset{|}{C}(OC-H)(OH)+H_2O$$ (O)

$$-\overset{|}{C}(OCH)(OH)+HCO_2H \rightleftharpoons -\overset{|}{C}(OC-H)(OC-H)+H_2O$$ (O, O)



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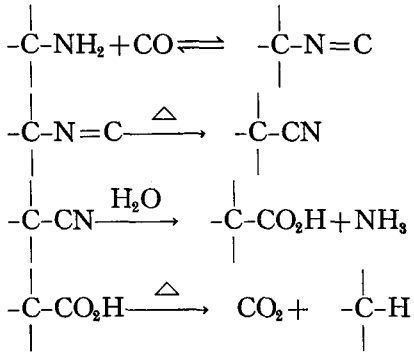

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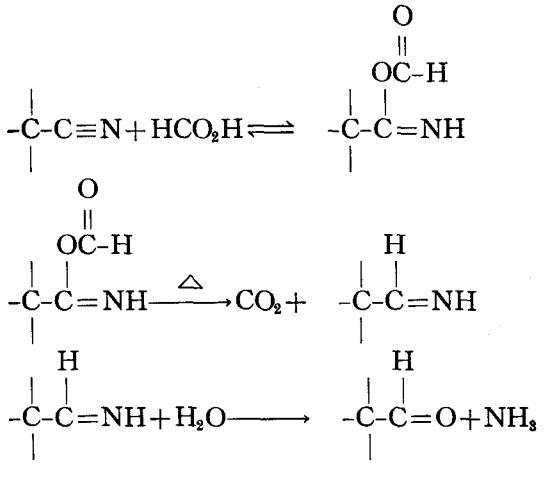

Carbon moboxide can be converted to sodium formate in 50–100% yields when pressurized in basic aqueous solutions in a batch reactor. Formation of sodium formate and its hydrolysis (Scheme 3) are well known. Formic acid is only an organic acid which can directly esterize hydroxyl groups in normal form. YOUNGQUIST et al.[9] observed that polyvinyl alcohol is changed to formate ester by treating with carbon monoxide and water in the reactor, like Scheme 4 and 5. Also, when benzophenone or pivaldehyde are subjected to the oil forming reaction conditions, diphenylcarbinol and neopentyl alcohol are produced.

The decarboxylation steps in Scheme 4 and 5 which produce reduction appear to be operative because formate esters of polyvinyl alcohol produce hydrocarbons when heated in the reactor under reaction conditions identical to those used for oil formation except that only water is present in addition to the ester. Further, the reduction of benzophenone and pivaldehyde to diphenylcarbinol, diphenylmethane is produced in the reduction of benzophenone.

This mechanism indicates that formate ion and/or formic acid is the reactive intermediate that allow oxygen to be stripped from organic wastes to produce oil by this process. In case of cellulose, the stoichiometry of the reaction may be written empirically as :

$$(C_6H_{10}O_5)_x + 5H\text{-}C(=O)OH \longrightarrow (C_6H_{10})_x + 5CO_2 + 5H_2O$$

cellulose formic acid oil

Oxygen from cellulose, after reaction, appears in the product mixture as carbon dioxide. Since cellulose has approximately 50% oxygen by weight, the maximum theoretical oil yield (assuming complete oxygen removal and retention of carbon and hydrogen) is 50% by weight. Pressurizing the reactor with carbon monoxide (which generates formate ion and/or formic acid in weakly acidic or alkaline aqueous solutions) or charging sodium formate along with the wastes are equally effective and carbon dioxide is a major constituent of the by-product gases.

However, wood contains 20–30% lignin which is aromatic in nature, and its oxygen content is much lower than that of wood polysaccarides, and easily reacts with hydrogen over catalyst. The fact suggests that in case of wood, water-gas shift reaction may not be disadvantageous, or synthesis gas could be applied to wood liquefaction.

3.4 Liquefaction in organic solvents

We described above the liquefaction of wood and cellulose by using carbon monoxide in basic aqueous solution. But this process has some demerits in practical point of view.

1) Energy consumption is much higher to heat large amount of water than organic solvents.
2) Reaction temperature must be kept under 375°C (critical point of water), because above 375°C, all the water is in vapor phase, giving very high pressure.

3) Price of carbon monoxide is higher than that of hydrogen or synthesis gas. These problems relate to economics of the process. Since both carbon monoxide and hydrogen are usually made from synthesis gas, it would be much advantageous to use the cheaper synthesis gas directly. And it is reasonable to use heavy oil of liquified product as solvent.

3.4.1 Liquefaction of hardwood (*Fraxinus mandshurica* var. *japonica*)

As in the present work, enough amount of the heavy oil was not available, some organic solvents were used as models. Results of preliminary experiments of liquefaction of cellulose and wood in organic solvents under the initial pressure of 40 kg/cm^2 of synthesis gas ($CO : H_2$ 1 : 1) over the catalyst $Fe(CO)_5$(1%) are shown in Table 4. $Fe(CO)_5$ which is soluble in organic solvents and intimate to carbon monoxide may be advantageous as a catalyst. In the table, only per cent conversion is noted, because exact oil yield could not be determined in cyclohexanol or turpentine oil. In the present experiment, benzene insoluble fraction is assumed to be unreacted residues that makes conversion to lower values in general. Nevertheless, 99.9% of cellulose at reaction temperature 320°C, and 98.7% of wood at 300°C were converted to benzene soluble products in cyclohexanol. Turpentine oil is also good solvent, although it gave somewhat lower conversion than cyclohexanol. However, ethanol does not seem to be good solvent. These results indicate that synthesis gas and organic solvent are effective for liquefaction of wood. It is expected that heavy oil from the product oils may be an excellent solvent for liquefaction of wood, because it should be very intimate to the degradation products of wood.

In this reaction, it is presumed that reduction of polysaccharides by carbon monoxide and hydrogenolysis of lignin by hydrogen would proceed parallel.

Table 4. Liquefaction of cellulose and wood by CO and H_2 in organic solvents

Ex. No.	Material	Solvent	Reaction temp. (°C)	Maximum pressure (kg/cm^2)	Final pressure (kg/cm^2)	Conversion (%)
11	Cellulose	Cyclohexanol	250	100	40	58.1
12	〃	〃	320	165	45	99.7
13	〃	Ethanol	300	155	40	56.4
14	〃	Turpentine oil	300	130	42	96.8
15	Wood	Cyclohexanol	300	132	43	98.1
16	〃	Turpentine oil	300	120	—	88.6

3.4.2 Liquefaction of softwood (*Larix kaempferi*)

Larch wood was used as a sample of softwood for liquefaction in cyclohexanol and toluene under the pressure of synthesis gas over catalysts Fe_2O_3 and $Fe_2O_3 \cdot SO_3^-$. The results are shown in Table 5. With the catalyst Fe_2O_3 at 300° and 350°C, wood was completely dissolved into cyclohexanol, giving conversion of 100%.

Table 5. Results of liquefaction of larch (*Larix kaempferi*) with CO and H_2 under catalysts

Ex. No.	Reaction temp. (°C)	Reaction time (hour)	CO : H_2 (30 kg/cm²)	Solvent	Catalyst	Conversion (%)	Viscosity (c. p.)	Off-gas (lit.)
21	300	2	2 : 1	Cyclohexanol	Fe_2O_3	98.4	11.8	10.5
22	300	2	1 : 1	»	»	98.6	40.8	12.9
23	300	2	1 : 2	»	»	99.0	44.6	14.3
24	350	2	2 : 1	»	»	100	14.0	17.2
25	350	2	1 : 1	»	»	100	12.8	16.5
26	350	2	1 : 2	»	»	100	12.9	16.9
27	350	2	1 : 2	»	$Fe_2O_3 \cdot SO_3^-$	99.2	20.0	9.5
28	350	1	1 : 1	»	»	97.4	13.4	12.4
29	300	2	1 : 1	Toluene	»	48.6	1.4	11.8
30	350	2	1 : 1	»	»	67.3	1.4	11.1

Table 6. Analysis of off-gas

Ex. No.	Off-gas (liter)	H_2	Air	CO	CH_4	CO_2
21	10.5	2.1	1.1	6.1	0.2	1.1
22	12.5	5.5	0.5	6.1	trace	0.8
23	14.3	6.3	2.3	4.9	trace	0.9
24	17.2	8.4	1.4	5.5	0.3	1.5
25	16.5	6.6	1.2	6.9	0.2	1.7
26	16.9	6.4	1.7	7.4	0.2	1.2
27	9.5	2.9	2.4	4.1	0.1	0.1
28	12.4	4.1	1.0	5.0	0.1	1.4
29	11.8	4.2	1.1	5.4	trace	1.0
30	11.1	4.4	1.0	2.3	0.3	3.0

Table 7. Distillation results of product oils

Ex. No.	Distillate (b. p. 230°C/5 mm Hg) % of wood	Residual oil (% of wood)	Total oil (% of wood)
21	30.0	29.0	59.0
22	19.0	36.5	55.5
23	32.0	46.0	78.0
24	32.5	39.5	72.0
25	25.0	40.4	65.0
26	28.0	41.5	69.5
27	29.5	42.5	72.0
28	24.5	35.5	60.0
29	4.5	6.5	11.0
30	5.5	8.5	14.0

But the values of viscosity of reaction mixture (solvent and product oils) obtained at 350°C are much lower than those obtained at 300°C, indicating promotion of degradation at higher temperature.

The super acidic catalyst $Fe_2O_3 \cdot SO_3^-$ is known to show excellent effect on hydrogenolysis of coal, but the results of ex. no. 27 and 28 show higher viscosity, suggesting insufficient degradation. It is presumed that highly acidic catalyst promotes dehydration of carbohydrates and lignin, resulting polymerization or condensation which competes with degradation reaction. When toluene was used as a solvent, much unreacted residues in carbonized state were formed. The fact indicates that toluene is not suitable as a solvent.

The results of analysis of off-gass by gaschromatography are shown in Table 6. Carbon dioxide seems to be formed during the reduction of the substrate to form oil, but may formed also via the water-gas shift reaction from small amounts of water in the wood or that produced during the reaction, as described before. And the water-gas shift reaction occurs at higher temperature as the amounts of carbon dioxide in ex. no. 24–26 (at 350°C) are suggestive.

The results of distillation of products oils are shown in Table 7. The highest distillable oils of 32 and 32.5% can be obtained from ex. no. 23 and 24 which were carried out in cyclohexanol with synthesis gas ($CO : H_2$ 1 : 2), over Fe_2O_3 at 300°C, and with gas ($CO : H_2$ 2 : 1) at 350°C, respectively. Ex. no. 27 liquefied over $Fe_2O_3 \cdot SO_3^-$ shows also good yield distillable oil inspite of high viscosity of the

Table 8. Acidic and neutral oils from product oils (b. p. 230°C/5 mm Hg)

Ex. No.	Acidic oil (%)	Neutral oil (%)
21	18.3	81.7
22	16.4	83.6
23	11.9	88.1
24	8.8	91.2
25	10.7	89.3
26	15.7	84.3

Table 9. Phenols and carboxylic acids of acidic oils

Ex. No.	Phenols (%)	Carboxylic acids (%)
21	29.9	44.8
22	29.9	48.4
23	37.3	58.1
24	29.7	49.6
25	30.9	47.1
26	33.5	67.3

reaction mixture. When the constituent of carbon monoxide increases, yield of distillable seems to increase, as seen in ex. no. 21.

Table 8 shows acidic and neutral fractions in the distillable oils (b. p. 230°C/5 mm Hg). Eighty to ninety one % of the oils are composed of neutral oil, and acidic oil is minor. The constituents of acidic acids are shown in Table 9. The phenols may be mainly formed from lignin, and carboxylic acids may be derived from carbohydrates.

3.4.3 Characterization of product oils

i) Elementary analysis

The results of elementary analysis of distillable and residual oils are shown in Tables 10 and 11. A formula obtained by Bechtel National Inc.[4] as the results of elementary analysis is added for reference. The distillable oils involve much more hydrogen and less oxygen contents, comparing to the formula. However, the residual oils involve lower hydrogen and oxygen contents than the Bechtel's formula.

From these results, it is clear that distillable oils are reduced and degraded sufficient to form oils, but the reduction of residual oils are insufficient and composed of high molecular materials.

Table 10. Elementary analysis and formula of product oils (230°C/5 mmHg)

Ex. No.	$CO:H_2$	C (%)	H (%)	O (%)	Formula
21	2 : 1	74.41	9.96	15.63	$C_6H_{9.63}O_{0.95}$
22	1 : 1	70.79	9.85	19.36	$C_6H_{10.01}O_{1.23}$
23	1 : 2	71.29	10.53	18.18	$C_6H_{10.64}O_{1.15}$
24	2 : 1	75.41	10.08	14.51	$C_6H_{9.63}O_{0.87}$
25	1 : 1	74.90	9.80	15.30	$C_6H_{9.42}O_{0.92}$
26	1 : 2	75.06	10.01	14.93	$C_6H_{9.59}O_{0.89}$

$C_6H_{7.56}O_{3.19}+1.69CO=C_6H_{7.56}O_{1.5}+1.69CO$
Wood Oil

Table 11. Elementary analysis and formula of residual oil

Ex. No.	$CO:H_2$	C (%)	H (%)	O (%)	Formula
21	2 : 1	74.23	6.57	19.20	$C_6H_{6.37}O_{1.16}$
22	1 : 1	74.81	6.58	18.61	$C_6H_{6.34}O_{1.12}$
23	1 : 2	75.30	6.70	18.00	$C_6H_{6.40}O_{1.08}$
24	2 : 1	81.42	6.91	11.67	$C_6H_{6.11}O_{0.65}$
25	1 : 1	74.31	6.23	19.46	$C_6H_{6.04}O_{1.18}$
26	1 : 2	80.52	7.12	12.36	$C_6H_{6.37}O_{0.69}$

ii) IR spectra

Fig. 5 shows IR spectra of the residual oils from ex. no. 21 and 23. Large absorption bands at 3400 cm^{-1} indicates that considerable hydroxyl groups still remain in the oils. Absorption bands of unconjugated carbonyls are seen in 1700 cm^{-1}.

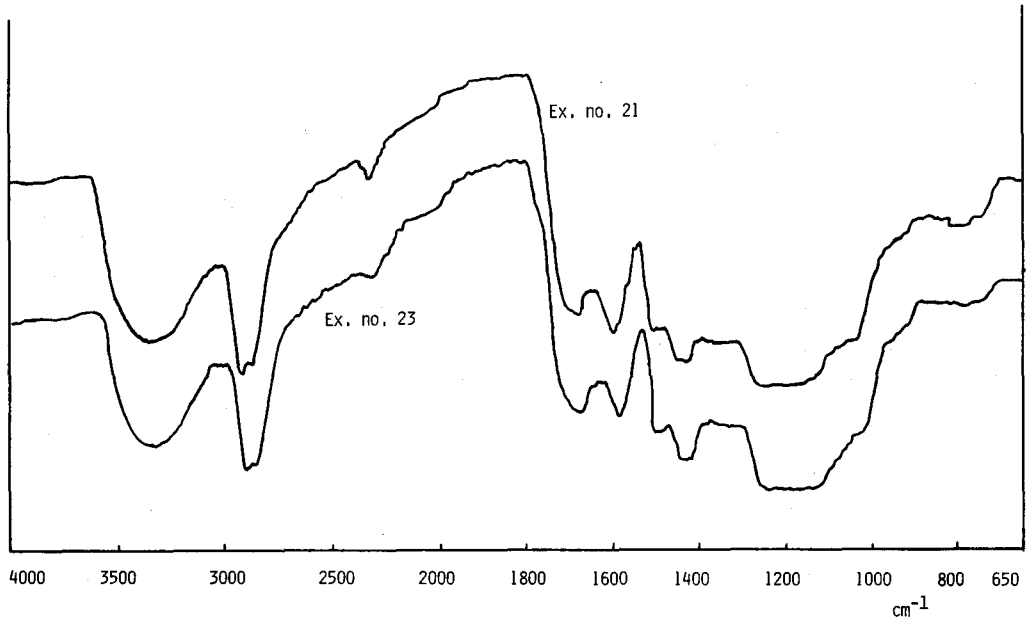

Fig. 5. IR spectra of product oils from Ex. no. 21 and 23.

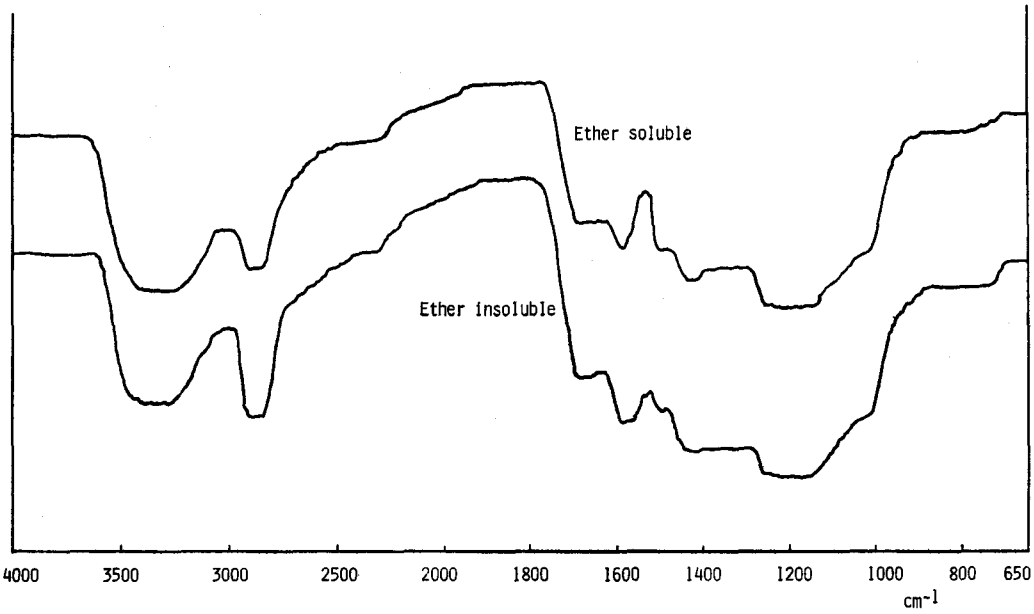

Fig. 6. IR spectra of product oils from Ex. no. 23.

Fig. 6 shows IR spectra of ether soluble and insoluble fractions of residual oils of ex, no. 23. The absorption pattern is almost the same as each other.

iii) ^{1}H-NMR spectra

^{1}H-NMR spectra of the product oils from ex. no. 23 ($CO : H_2$ 1 : 2, at 300°C) and 24 ($CO : H_2$ 2 : 1, at 350°C) are shown in Fig. 7. In the spectrum of ex. no. 23, a large peak at δ 6.5 is characteristic and assigned to protons of -CH=CH-ϕ

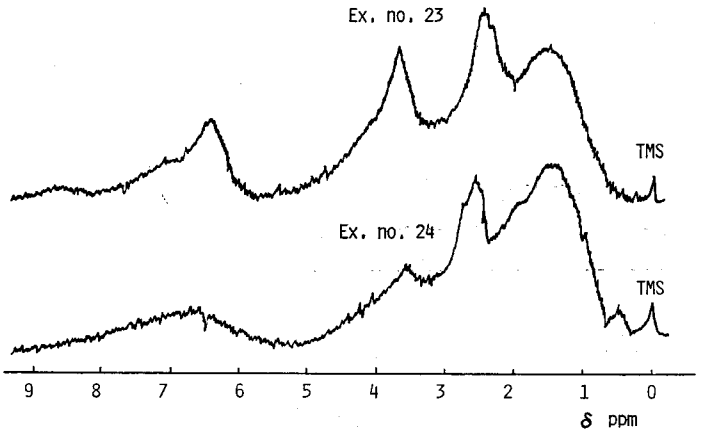

Fig. 7. ^{1}H-NMR spectra of residual oils of Ex. no. 23 and 24.

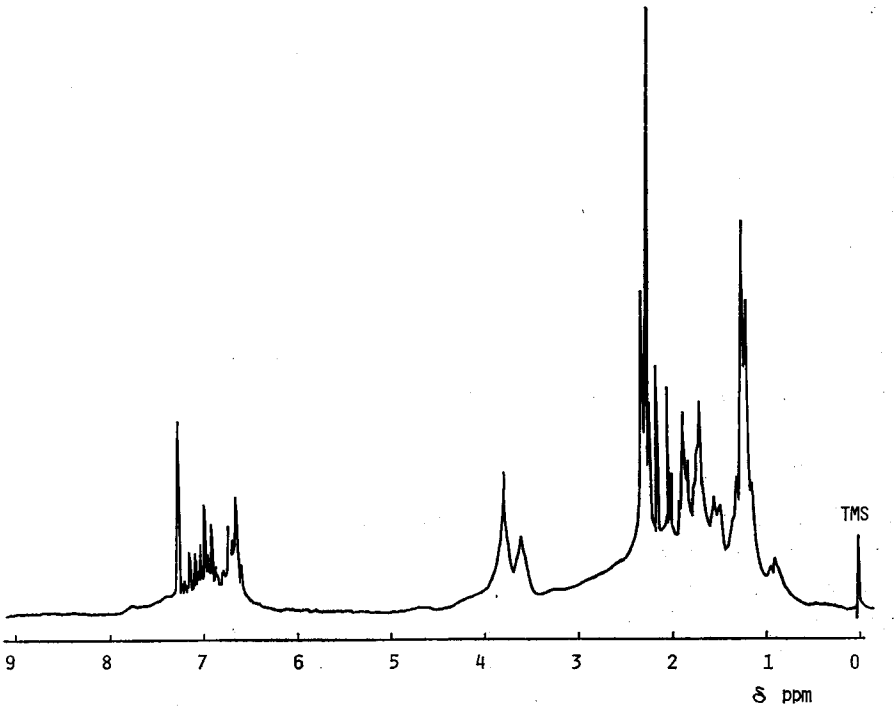

Fig. 8. ^{1}H-NMR spectra of acetylated ether soluble residual oils of Ex. no. 21.

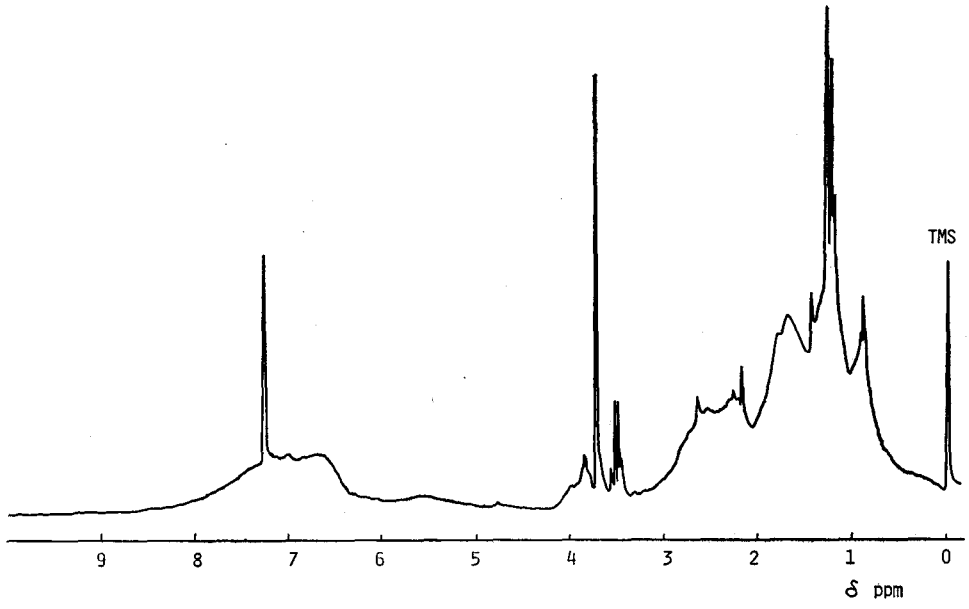

Fig. 9. ^{1}H-NMR spectra of acetylated ether soluble residual oils of Ex. no. 24.

and of extended conjugate systems of aliphatic chains. In the spectrum of ex. no. 24, such a peak is not observed. In case of ex. no. 24, deoxygenation would be preferencial because of much more carbon monoxide, on the other hand, in ex. no. 23, small amount of carbon monoxide may cause dehydration to form conjugated double bonds in the molecule. A peak at δ 3.6 corresponds to protons of methoxyl which are much more abundant in ex. no. 23 from the same reason described above. A peak at δ 0.6 is observed in the spectrum of ex. no. 24, but not in that of ex. no. 23. It is clearly assigned to protons of aliphatic end methyl which may be formed by deoxygenation of C_6 carbinol in carbohydrates or C_γ-hydroxyl groups of lignin. A shoulder at δ 2.0 in ex. no. 24 may originate from protons on carbon atoms adjacent to carbonyl.

^{1}H-MNR spectra of acetylated ether soluble residual oils of ex. no. 21 and 24 are shown in Fig. 8 and 9, respectively. In these spectra, many sharp signals are observed. It is obvious from all these spectra that aliphatic protons are much more abundant comparing to aromatic protons, indicating that reduction ocurred intensively.

vi) ^{13}C-NMR spectrum

^{13}C-NMR spectrum of residual oils from ex. no. 24 is shown in Fig. 10. A large triplet at δ 80 originates from the solvent of deuterochloroform. The region of δ 140–160 is attributed to aromatic carbons, and that of δ 120–140 with peak at 130 may correspond to carbons of -CH=CH-. The range δ 60–100 should correspond to signals of side chain carbons attached to hydroxyl which, however, cannot be observed and the peaks of methoxyl are ambiguous, indicating deoxygenation and dehydration. Most intensive peak groups at δ 20–40 are attributed

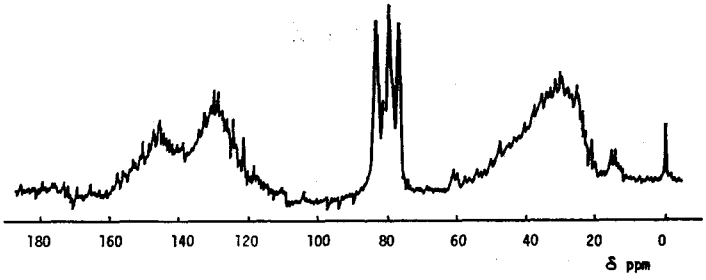

Fig. 10. ^{13}C-NMR spectrum of residual oil from Ex. no. 24.

to methylene $-CH_2-$ in side chains, suggesting advance reduction to polysaccharides and lignin. A small peak at δ 15-18 is clearly assigned to end methyl $-CH_2-CH_3$.

v) Gas chromatography of product oils

Fig. 11 and 12 show chromatograms of phenol and neutral fractions from product oils, respectively. In phenol fraction, guaiacol, p-cresol, guaiacyl ethane, dihydroeugenol and dihydroconiferyl alcohol are identified. Neutral fraction could not be identified because of its complexity.

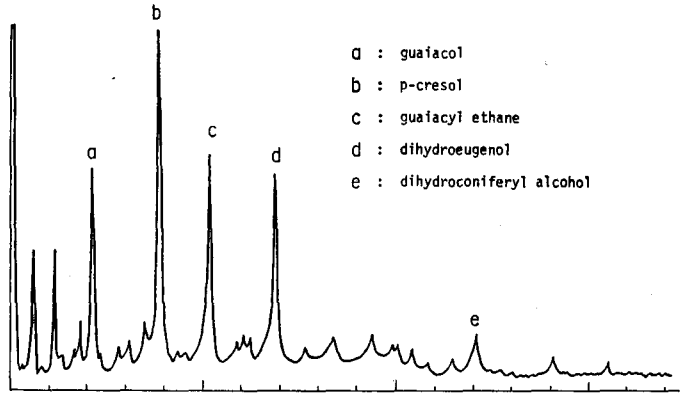

Fig. 11. Gas chromatograms of phenol fraction of product oils from Ex. no. 23.

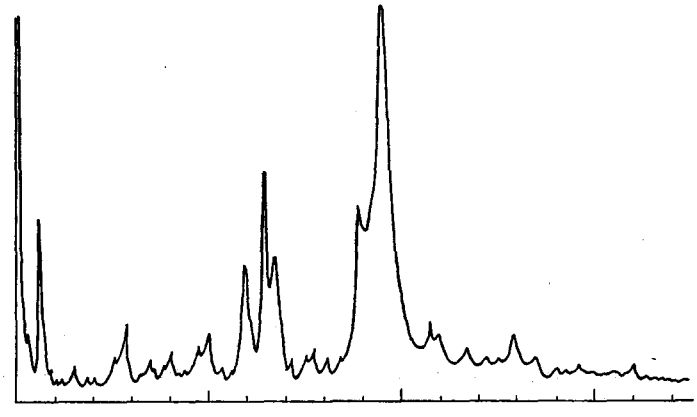

Fig. 12. Gas chromatograms of neutral fraction of product oils from Ex. no. 23.

4. Conclusion

It was found that synthesis gas is effective enough to liquefy wood, and it is much more practical to react wood in organic solvent such as heavy oil from product oils in practice under the pressure of synthesis gas over the cheapest catalyst such as Fe_2O_3. In this case, synthesis gas rich in carbon monoxide is more effective.

The product oils are, however, still heavy, thus it would be necessary to send them to further processing such as hydrocracking to produce gasoline or diesel fuel.

As feed stock, wood waste of even the lowest quality would be enough for production of oil. And it should be noted that all kinds of lignocellulosic materials can be applied for this process.

Summary

Cellulose and wood powder of hard- and softwoods were converted to oil by heating at 300–350°C under the pressure of carbon monoxide or synthesis gas (mixture of CO and H_2) in water and organic solvent over catalysts. Carbon monoxide liquefied wood effectively by deoxygenation from polysaccharides to give carbon dioxide. Some oils obtained from the reaction with carbon monoxide were characterized by means of distillation, elementary analysis, IR and NMR spectra, and also gas chromatography. The products obtained were still heavy oil which must be further subjected to hydrocracking to convert to gasoline or diesel fuels. Wood powder was also liquefied effectively by synthesis gas over the catalyst Fe_2O_3 in cyclohexanol. In this case, CO : H_2 ratio was an important factor to obtain distillable oil. The distillable oil yields were 4.5–32.5% of wood (larch) and were mainly composed of neutral oil containing small amounts of phenols and carboxylic acids. The process using synthesis gas is more practical, because the gas price is much lower than that of carbon monoxide.

Acknowledgement

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References

1. APPELL, H. R. *et al.*: Conversion of Cellulosic Waste to Oil, RI 8013, U. S. Bureau of Mines (1975).
2. APPELL, H. R., I. WENDER and R. D. MILLER: Conversion of Urban Refuse to Oil, U. S. Bureau of Mines Tech. Prog. Rept. **25**, 5 (1970).
3. YOUNGQUIST, G. R., L. G. DONARUMA, R. PARTCH, S. ARCIERO and D. CENTRY: Conversion of Organic Wastes to Oil, 82nd National AICh Meeting, Atlantic City (1976).
4. STEPHUR, M. K., P. M. BARHORDAR, F. A. SCHOOLEY and R. L. DICKENSON, 1979. Production of oil by catalytic liquefaction of wood, In: Mission Analysis for the Federal Fuels from Biomass Program, Vol. IV. Thermochemical Conversion of Biomass to Fuels and Chemicals, SRI International, 87–103.

要　　約

セルロースおよび針・広葉樹木粉を触媒存在下に水および有機溶媒中に懸垂し，一酸化炭素または合成ガス（CO と H_2 の混合ガス）加圧下に 300～350°C で加熱して油状物に変換した。

一酸化炭素は多糖類から酸素を奪って二酸化炭素に変化し，効果的に木材を液化した。一酸化炭素との反応で得られた油のあるものについて，蒸留，元素分析，IR，NMR スペクトルおよびガスクロマトグラフィによって特性づけがなされた。これらの生成油はなお重質であるから，ガソリンあるいはディーゼル燃料とするためには，さらにハイドロクラッキングにより軽質化をはからねばならない。

木粉は Fe_2O_3 触媒存在下に，シクロヘキサノール中で合成ガスによっても効果的に液化した。この場合，$CO:H_2$ 比は蒸留可能な油分を得るための重要な因子であることがわかった。カラマツ材の場合，蒸留可能な油の収率は 4.5 から 32.5% であり，主として中性油からなっているが，少量のフェノール類およびカルボン酸類を含有している。

合成ガスの価格は一酸化炭素のそれよりも遥かに低廉であるから，合成ガスを用いるプロセスの方がより実際的である。