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Nickel-catalyzed carbonization of wood for coproduction of functional carbon and fluid fuels II: improved fuel quality of oil fraction and increased heating value of gas fraction

Abstract The yields and properties of oil and gas fractions coproduced during carbonization of larch wood loaded with Ni 2%, Ni 2%+Ca 1%, and Ni 4% and without catalyst (None) at 700°–900°C were examined to clarify the catalytic effect in terms of conversion into fluid fuels. The net calorific value of oil occurred mainly below 500°C and increased in the order None < Ni 2% < Ni 4% < Ni 2%+Ca 1%, while the yield decreased in this order. The same order held for the production of gases enriched with hydrogen at 500°–700°C. Even above 800°C, markedly promoted evolution of hydrogen took place for all catalyst systems. These observations confirmed the effectiveness of nickel-catalyzed carbonization at 900°C, particularly Ni 2%+Ca 1%, for both upgrading of oil and gaseous fractions, although the quality of oil was not satisfactory. The catalysis of nickel with and without calcium is discussed on the basis of the modified Broid-Shafizadeh scheme, and the scheme was altered to adapt to the high temperature region where oil was no longer produced.

Key words Nickel-catalyzed carbonization · Upgraded oil · Hydrogen-rich gas · Broid-Shafizadeh scheme

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Introduction

Carbonization of nickel-loaded wood at about 900°C can effectively produce a crystallized mesoporous carbon with good electroconductivity and adsorption capacity in the liquid phase, as reported in our recent review[1] and articles.[2,3] Given that the production of such a value-added functional carbon uses no difficult techniques, commercial production is promising, even if the temperature used is higher than that for conventional carbonization. However, this nickel-catalyzed carbonization has been developed with another purpose of improving the fuel properties of liquid and gaseous fractions. In other words, this process aims to simultaneously produce the functional carbon and good-quality fluid fuels from woody biomass. This unique concept may achieve the desired result at much lower cost than currently used liquefaction (flash, fast, or rapid pyrolysis) and gasification processes.[4–6]

In biomass pyrolysis and/or gasification, nickel-based catalysts, mainly nickel metal supported on alumina, have been employed for decomposing liquid vapor by passing it through the packed bed into gases.[7–13] The moderate result of the usual treatment at 650°C or below leads to the expectation that nickel catalyst loaded on wood in the above carbonization, although it differs definitively from the packed catalyst in respect of contact with pyrolysis products, would play some favorable role in upgrading the fuel properties of the liquid fraction, as well as the gas fraction. Nevertheless, the nature of the process involved is still not clarified in detail, and the present work deals with this issue. Relevant data were obtained from previously conducted experiments with larch wood,[3] and they were analyzed to assess the effect of nickel with and without calcium on conversion into fluid energies. The obtained results demonstrated the potential of this catalytic carbonization process for the entitled goal.

Experimental

Samples

Liquid and gaseous products subject to analysis were those obtained by carbonizing powdered Japanese larch (*Larix leptolepis* Gord, particle diameter of 0.50–1.40 mm) loaded with $(CH_3COO)_2Ni·4H_2O$ and both the nickel salt and $(CH_3COO)_2Ca·H_2O$ and untreated samples, denoted as "Ni-," "Ni+Ca-," and "None-," respectively. The conditions were: weight of wood specimen, 2 g (dry); maximum temperature, 700°C, 800°C, and 900°C; holding time at maximum temperature, 1 h; heating rate to maximum temperature, 10°C min^{-1}; helium flow, 23.2 ml STP (standard temperature and pressure, 0°C and 101.3 kPa) cm^{-2} min^{-1}. The wood powder had the composition of C 50.5%, H 6.3%, N 0.2%, ash 0.15%, and O 42.9 % (by difference) on a dry basis, and the calorific value calculated by Dulong's equation described below was 17.23 kJ g^{-1}. For Ni- and Ni+Ca-loadings, nickel was adjusted to 2% or 4% as metal in wood for the former, and nickel 2% and calcium 1% for the latter. Details of metal impregnation and the reaction apparatus were given elsewhere.[3] The liquid fraction was condensed in two glass cold traps where the outlet gas stream was cooled with iced water during the carbonization. For the gaseous fraction, it was collected in fractions together with the carrier gas in rubber sampling bags placed after the traps according to the following regions: 1, 100°–300°C; 2, 300°–500°C; 3, 500°–700°C; and 4a, 700°C for 1 h; or 4b, 700°–800°C followed by 5b, 800°C for 1 h; or 4c, 700°–900°C followed by 5c, 900°C for 1 h. That is, 1, 2, and 3 were common, and 4a, 4b-5b, and 4c-5c were adopted for 700°C, 800°C, and 900°C carbonizations, respectively.

Analysis of liquid product

After mixing the two liquids from the first and second traps, the mixture was extracted with dry acetone and dehydrated with $MgSO_4$ for separation from tar-like substance and water. The extracted and dehydrated solution was then carefully heated in a rotary evaporator to remove the solvent, and the resulting acetone-soluble fraction was weighed and recovered as oil. For oil, gas chromatography-mass spectrometry (GC-MS; Shimadzu GC-17A/QP-2010) was used to identify major constituents with the aid of a computerized searching program and ^1H nuclear magnetic resonance (NMR) spectroscopy (JEOL ECX-400) was used to elucidate the chemical structure and for determination of acetic acid. Elemental composition was also determined for C, H, N, and O by elemental analysis (Elementar Vario EL). For GC-MS analysis, a fused silica capillary column (GL Science TC-1, 30 m × 0.25 mm i.d.) was used for component separation and the electron-impact ionization mass spectrum was recorded as a total ion chromatogram (TIC). The system was operated at 50°C for 5 min, after which the temperature was raised to 230°C at a rate of 6°C min^{-1}. The injection and detector temperatures were fixed at 250°C. The sample was prepared as a 1% solution of the raw oil in

acetonitrile; 1.0 µl was injected with a split ratio of 1/10. Helium was used as carrier gas at a flow rate of 0.9 ml STP min^{-1}. NMR spectra were measured at room temperature in the usual pulse Fourier mode. To prepare the sample, oil was dissolved in $CDCl_3$ to give a 5% (v/v) solution. Furthermore, known amounts of tetramethylsilane (TMS) and acetophenone $(C_6H_5COCH_3)$ were added to the solution as standards for chemical shift and for quantifying acetic acid, respectively. In elemental analysis, oxygen was given by difference, and from the determined composition, net calorific value (NCV) was calculated by using Dulong's equation:

$$NCV = 33.9C + 12[H - (O/8)] + 9.2S$$

where C, H, O, and S indicate the fractional weights of carbon, hydrogen, oxygen, and sulfur, respectively, and NCV is given in units of kilojoules per gram. S was zero for all oils obtained in this study.

Analysis of gaseous products

For gases collected in each temperature region, the whole volume containing the carrier gas was measured at room temperature by drawing it out through a needle connecting to a calibrated gastight syringe. The composition was then analyzed by GC with thermal conductivity detection (Hitachi G-3900) equipped with a packed column of activated carbon (1.5 m × 3 mm i.d.). The apparatus was operated at 120°C under a flow of helium (20 ml STP min^{-1}). The chief gas species detected were H_2, CO, CH_4, and CO_2 with retention times of 0.9, 1.7, 3.0, and 5.4 min, respectively, irrespective of wood sample and the temperature region. Hydrocarbons of C2 or C3 were neglected on account of their low proportions (usually <1.0% v/v in all regions). For the four gas species, their production in the specified temperature region was determined and individual productions were summed to give the total production for the entire period. For total production, the net heating value was calculated by using the standard value of each gas: 12.77, 12.64, and 39.85 MJN m^{-3} for H_2, CO, and CH_4, respectively.

Heat treatment of nickel acetate $[(CH_3COO)_2Ni·4H_2O]$ and calcium acetate $[(CH_3COO)_2Ca·H_2O]$

In the above carbonization of Ni- and Ni+Ca-wood specimens, loaded nickel and calcium salts decomposed into the oils and gases produced. Therefore, the amount of material derived from the metal salts should be subtracted to give the net production of oil, acetic acid, and gases from wood. To achieve this, the nickel salt was impregnated singly and together with the calcium salt onto Al_2O_3 (JRC-ALO-1, a reference alumina supplied from Catalysis Society of Japan) for heat treatment under the same conditions of carbonization. The alumina was selected as an inactive support, and loadings of nickel and calcium were the same as those used for wood. The specimens are designated as Ni 2%-, Ni 2%+Ca 1%-, and Ni 4%-Al_2O_3.

Results

Yields and properties of oil

The production of liquid, including water, appeared below 200°C and almost ceased at around 500°C. The liquid was colorless at the beginning, changed to yellow, and finally became light brown and contained some brown tar-like substance. These observations were recorded in all carbonizations.

Figure 1 shows TICs of oils from None- and Ni 2%-loading, which were produced by carbonization at 900°C. It is obvious that both oils had complex compositions with appreciably different proportions of constituents. Table 1 lists the main compounds commonly detected for all of the oils together with peak numbers and retention times corresponding to those given in Fig. 1. Although exact determination of each compound was not made, the ratio of the peak area for three Ni-oils and None-oil was obtained as relative peak area, as is graphically shown in Fig. 2 for typical constituents. It revealed that although carbonization temperature had no significant influence on the composition of any oil, the peak areas of furfurals (No. 1, 5, 7, and 11) and phenol (No. 6) were in the order of None (= 1) < Ni 2% < Ni 4% < Ni 2%+Ca 1%. The peak areas of guaiacols (No. 10, 12, and 14) were larger for None-oil than for three Ni-oils, and the differences among the Ni-oils were ambiguous.

^{1}H NMR spectra for the set of oils in Fig. 1 are illustrated in Fig. 3; each includes a large signal at 2.61 ppm due to the internal standard acetophenone. The overall shapes of the spectra were similar with a small proportion of signals in the aromatic region at 7–8 ppm. However, the signal for acetic acid at about 2.1 ppm and a broad signal in the region of 5–6 ppm differed in relative strength and in position, respectively. Three Ni-oils showed little difference in the whole spectrum, except that the signal strength of acetic acid for Ni 2%+Ca 1%-oil and Ni 4%-oil was a little larger than that for Ni 2%-oil. The spectral pattern for None-oil

and Ni-oils scarcely varied with carbonization temperature, as was the case for the TIC profiles.

Table 2 summarizes the analytical results of four oils, in addition to amounts of oil and acetic acid derived from
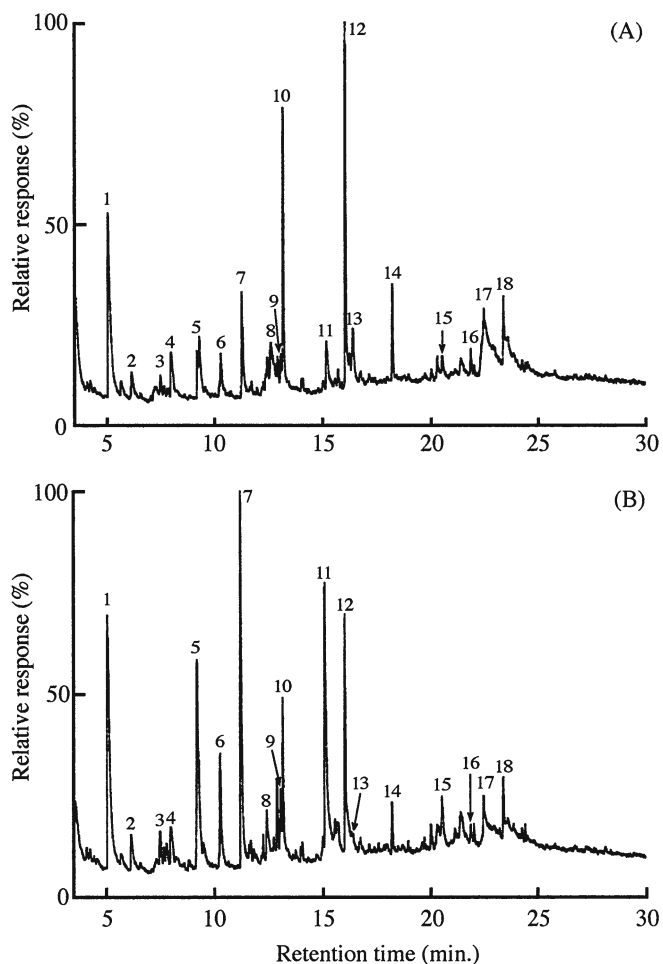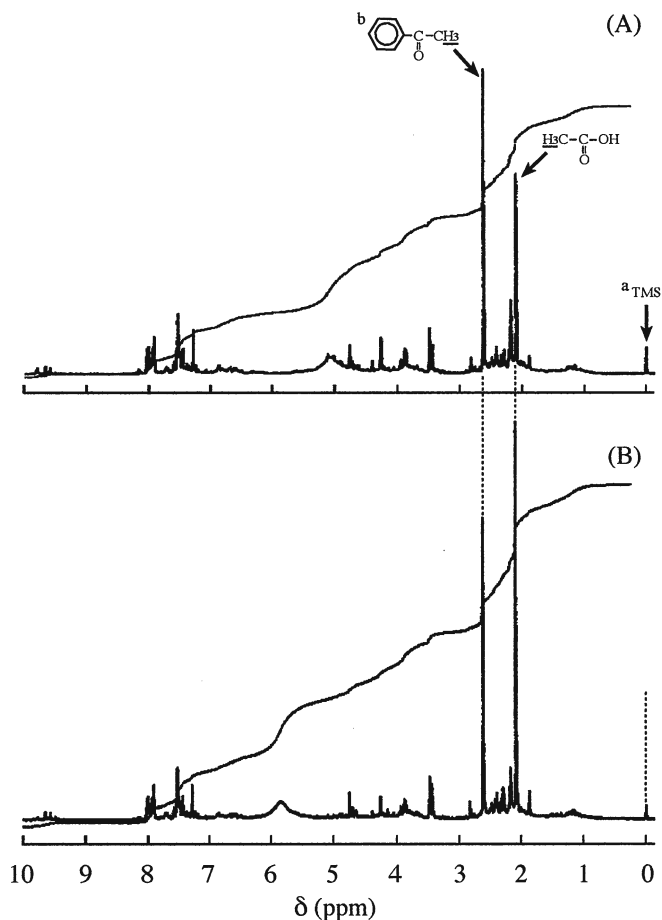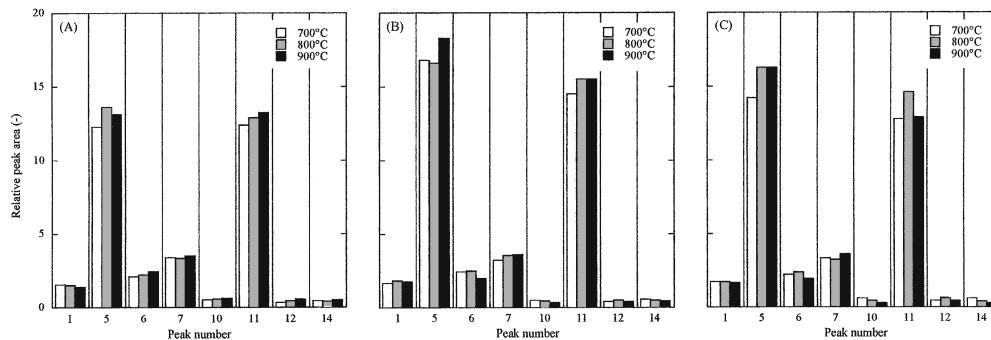

Fig. 1A, B. Total ion chromatograms of **A** None-oil and **B** Ni 2%-oil. Peak numbers and their identification are the same as those given in Table 1

Table 1. Main constituents commonly detected in all oils

Peak number	Retention time (min)	Compound	Group	Formula
1	5.1	Furfural	F	$C_5H_4O_2$
2	6.1	Hydroxyacetone	C	$C_5H_8O_3$
3	7.5	2-Methy-2-cyclopentene-1-one	F	C_6H_8O
4	8.0	1,2-Cyclopentanedione	F	$C_5H_6O_2$
5	9.2	5-Hydroxymethylfurfural	F	$C_6H_6O_3$
6	10.3	Phenol	P	C_6H_6O
7	11.2	3-Methy-1, 2-cyclopentanedione	F	$C_6H_8O_2$
8	12.4	*o*- or *m*-Cresol	P	C_7H_8O
9	13.1	*p*-Cresol	P	C_7H_8O
10	13.2	Guaiacol	P	$C_7H_8O_2$
11	15.2	4-Methyl-2,3-dihydrofuran	F	C_5H_8O
12	16.1	*p*-Methylguaiacol	P	$C_8H_{10}O_2$
13	16.4	2,3-Anhydro-D-mannosan	A	$C_6H_8O_4$
14	18.2	*p*-Ethylguaiacol	P	$C_9H_{12}O_2$
15	20.6	Vanillin	P	$C_8H_8O_3$
16	21.9	*p*-Propylguaiacol	P	$C_{10}H_{14}O_2$
17	22.5	Levoglucosan	A	$C_6H_{10}O_5$
18	23.4	4-Hydroxy-3-methoxyphenyl-2-propanone	P	$C_{10}H_{12}O_3$

F, Furans; C, carbonyls; P, phenols; A, anhydrosugars

Fig. 2A–C. Relative peak areas of typical constituents for **A** Ni 2%-oil, **B** Ni 2%+Ca 1%-oil, and **C** Ni 4%-oil. Peak numbers and their identification are the same as those given in Table 1

rific value per gram of oil was None < Ni 2% < Ni 4% < Ni 2%+Ca 1%, because C and O were increased and decreased, respectively, in that order. Thus, the order of calorific values was the same as that of the yields of acetic acid. However, the total calorific value of oil calculated as the product of net calorific value per gram by the yield was almost equal for the four oils.

Yields and composition of gases

The evolution of gases started at near 200°C and continued until the end of carbonization. Figure 4 represents the production of gases from None-, Ni 2%-, Ni 2%+Ca 1%-, and Ni 4%-woods in the individual temperature regions. The quantity of each gas species for three Ni-woods was corrected in the same manner as mentioned for oil and acetic acid. As the production from any metal salt-Al_2O_3 loading was negligibly small above 700°C, the data obtained by treatment at 700°C was employed for correction. All of the Ni 2%, Ni 2%+Ca 1%, and Ni 4% loadings gave much larger amounts of gases than no loading (None), particularly because of the markedly increased production of H_2 between 500°C and 700°C with the order of Ni 2% ≤ Ni 4% < Ni 2%+Ca 1%. Even between 300°C and 500°C, any nickel loading induced considerable evolution of H_2. The promoted production of H_2 accompanied by an increased proportion continued over 700°C, and the gas produced above 800°C comprised only H_2 and CO with a volume ratio of 3:1, irrespective of the catalyst system. The evolution of CO between 300°C and 500°C was likewise increased with amounts in the order of None < Ni 2% < Ni 4% < Ni 2%+Ca 1%. Although the order changed between 500°C and 700°C and above 700°C, the quantity of CO in these regions was still larger for Ni-woods than for None-wood. For CH_4, which evolved mainly below 700°C, the production was in the order of Ni 2% < Ni 2%+Ca 1% < None < Ni 4% without great difference. The amount of CO_2 produced was almost parallel with CH_4 in the order of None < Ni 2% < Ni 4% ≤ Ni 2%+Ca 1% between 300° and 500°C, and this order was the same as for H_2 and CO in the corresponding region. The quantities of CO_2 evolved between 500° and 700°C for the three Ni-woods were almost equal, although they were much larger than that for None-wood.

The overall aspect of gas production for carbonizations at 700°, 800°, and 900°C is presented in Table 3. It became

Fig. 3A, B. ^{1}H nuclear magnetic resonance (NMR) spectra of **A** None-oil and **B** Ni 2%-oil. *a*, tetramethylsilane; *b*, acetophenone

heating metal salts-Al_2O_3 for correction of the contribution of the metal salts. Insignificant variations of both yields of oil and acetic acid, corrected for relevant nickel loadings, with temperature were found for all four oils, and the deviation of each yield at the individual temperature from the corresponding average was less than ±8%. From similar conditions, averages were taken to enter in the table for elemental composition and net calorific value, as well as oil and acetic acid used for correction. As a result, the yield of oil was in the order: Ni 2%+Ca 1% < Ni 4% < Ni 2% < None, and that of acetic acid was the very reverse. Net calo-

Table 2. Yields and properties for oils obtained by noncatalyzed and nickel-catalyzed carbonizations of wood

Sample[a]	Treatment temperature[a] (°C)	Oil[b,c] (%) or amount[d] (g)	Elemental composition (%)				NCV[a] (kJ/g oil)	TCV[a] (kJ)	Acetic acid	
			C	H	N	O[f]			Concentration (mg/g oil)	Yield[b,c] (%) or amount[d] (g)
None-wood	700	25.8							77.9	2.1
	800	27.2 (26.8)[e]	59.5	7.3	0.1	33.1	20.55	5.51	65.9 (72.1)[e]	1.7 (1.9)[e]
	900	27.6							72.5	1.9
Ni2%-wood	700	24.3							141	3.5
	800	24.8 (24.9)[e]	64.6	6.6	0.1	28.7	22.26	5.54	126 (137)[e]	3.1 (3.4)[e]
	900	25.6							144	3.6
Ni2%+Ca1%-wood	700	23.4							162	3.8
	800	24.3 (23.2)[e]	67.8	6.9	0.1	25.2	23.43	5.44	180 (168)[e]	4.2 (3.9)[e]
	900	21.9							162	3.8
Ni4%-wood	700	25.3							159	3.8
	800	23.6 (23.9)[e]	66.6	6.9	0.1	26.4	23.01	5.50	172 (160)[e]	4.1 (3.8)[e]
	900	22.8							149	3.5
Ni2%-Al$_2$O$_3$	700, 800, 900	0.058[d]							758[d]	0.044[d]
Ni2%+Ca1%-Al$_2$O$_3$	700, 800, 900	0.079[d]							873[d]	0.070[d]
Ni4%-Al$_2$O$_3$	700, 800, 900	0.123[d]							797[d]	0.100[d]

NCV, Net calorific value per gram of oil; TCV, total calorific value calculated as (kJ/g oil) × yield (g oil/g dry wood)
[a] See the text
[b] Expressed on the basis of dry wood
[c] Obtained by the following correction: (the whole weight – the corresponding weight with superscript d/dry wood weight) × 100
[d] Average production from metal salt(s)
[e] Average for three temperatures
[f] By difference

Fig. 4A–D. Gases evolved from **A** None-, **B** Ni 2%-, **C** Ni 2%+Ca 1%-, and **D** Ni 4%-woods in each temperature region: *1*, 100°–300°C; *2*, 300°–500°C; *3*, 500°–700°C; *4a*, 700°C for 1 h; *4b*, 700°–800°C; *4c*, 700°–900°C; *5b*, 800°C for 1 h; *5c*, 900°C for 1 h. *Temperatures* listed on horizontal axes indicate final temperatures
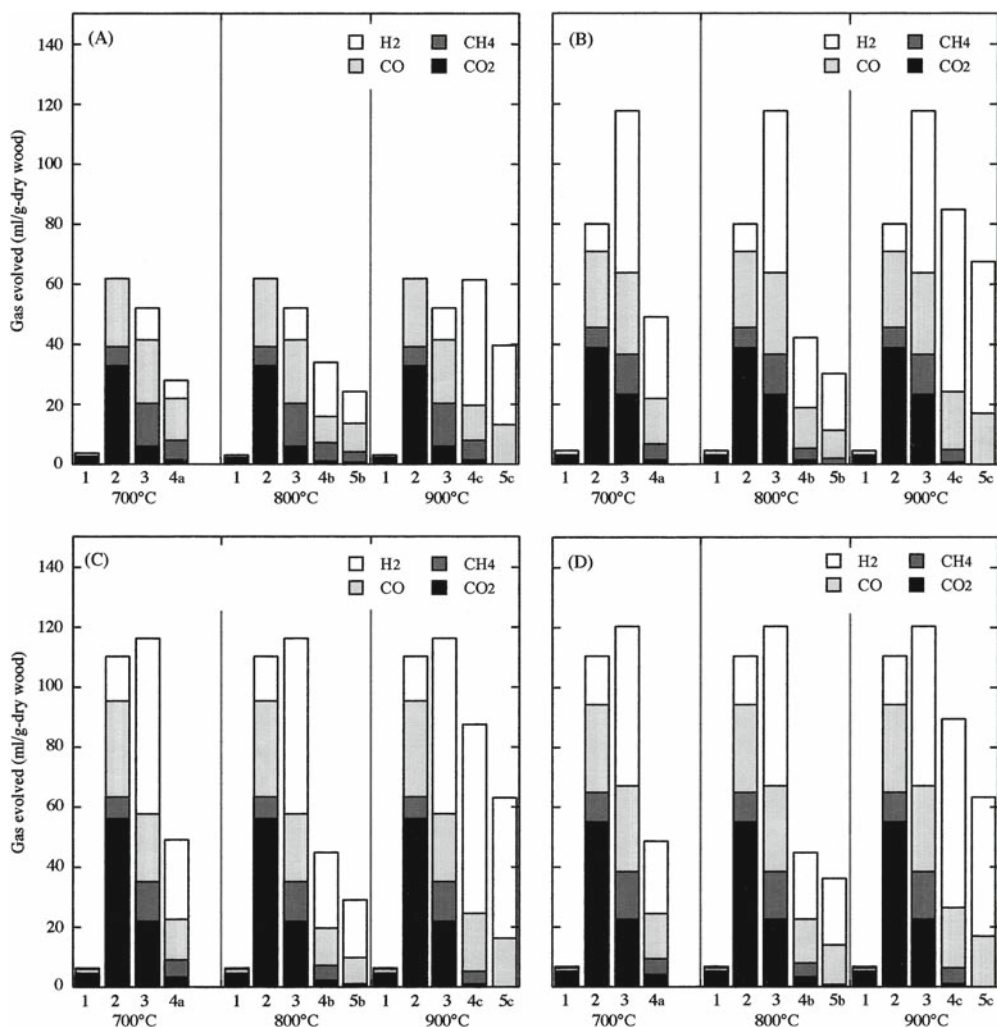
Table 3. Gases produced by noncatalyzed and nickel-catalyzed carbonizations of wood

| Sample[a]	Treatment temperature[a] (°C)	Gas produced[b,c] (mlSTP/g dry wood)					Net heating value[a,e] (kJ)	Yield[f] (%)
		H_2	CO	CH_4	CO_2	Total		
None-wood	700	16.9 (11.6)	57.9 (39.8)	27.9 (19.3)	42.6 (29.3)	145.3	2.06	16.5
	800	38.9 (22.2)	62.7 (35.8)	30.6 (17.5)	43.0 (24.5)	175.2	2.51	17.5
	900	78.9 (36.2)	68.8 (31.5)	27.8 (12.7)	42.9 (19.6)	218.4	2.99	18.3
Ni 2%-wood	700	90.6 (36.1)	68.4 (27.2)	25.5 (10.1)	67.0 (26.6)	251.5	3.04	22.6
	800	106.3 (38.6)	76.4 (27.7)	25.5 (9.2)	67.2 (24.5)	275.4	3.34	23.8
	900	174.7 (49.1)	89.7 (25.2)	25.0 (7.0)	66.2 (18.7)	355.6	4.36	25.6
Ni 2%+Ca 1%-wood	700	100.4 (35.6)	69.2 (24.5)	26.5 (9.4)	85.8 (30.5)	281.9	3.21	26.4
	800	118.4 (38.6)	77.2 (25.2)	25.7 (8.4)	85.6 (28.0)	306.9	3.51	27.3
	900	183.5 (47.9)	91.3 (23.8)	24.7 (6.4)	83.6 (21.9)	383.1	4.48	29.1
Ni 4%-wood	700	94.0 (32.8)	74.5 (26.0)	31.4 (10.9)	86.9 (30.3)	286.8	3.39	27.4
	800	114.3 (35.8)	87.3 (27.4)	30.9 (9.7)	86.3 (27.1)	318.8	3.79	29.0
	900	178.9 (45.8)	96.6 (24.8)	31.0 (7.9)	83.8 (21.5)	390.3	4.74	30.3
Ni 2%-Al_2O_3	700	3.9[d]	2.2[d]	1.8[d]	4.2[d]	12.1		
Ni 2%+Ca 1%-Al_2O_3	700	5.7[d]	3.0[d]	2.6[d]	6.1[d]	17.4		
Ni 4%-Al_2O_3	700	7.6[d]	4.2[d]	3.5[d]	8.4[d]	23.7		

[a] See the text
[b] Given as a corrected amount, and the correction was made by subtracting the corresponding amount with superscript d from the whole amount
[c] Proportion of gas produced given in parentheses as a percentage
[d] Produced from metal salt(s)
[e] Calculated for total gas production
[f] Expressed on the basis of dry wood

clear that for total gas production, net heating value, and gas yield, each was in the order of None < Ni 2% < Ni 2%+Ca 1% < Ni 4% at a given temperature. Although the promoted gas production between 700°C and 900°C was common to all wood specimens, both increments of the heating value and gasified yield were None < Ni 2%+Ca 1% < Ni 4% ≤ Ni 2% due to their different production of CO and H_2 in this period. With carbonization at 900°C, the heating value of gases for Ni 4%, Ni 2%+Ca 1%, and Ni 2% were 1.57, 1.44, and 1.43 times, respectively, larger than that for None.

Total conversion into fluid energies and overall product distribution

Figure 5 compares total calorific value of oil and gas fractions among four wood specimens. Figures on individual columns indicate total energy conversion into oil and gases, namely, the total value relative to the calorific value of original wood (17.23 kJ g^{-1}). The total conversion was in the order of 700°C < 800°C < 900°C for any wood and None < Ni 2% < Ni 2%+Ca 1% < Ni 4% at a given temperature. Evidently these orders were dominated by the value for the gas fraction, because the oil fraction was almost the same for the four specimens with no dependence on the carbonization temperature. Although the gas fraction was smaller than the oil fraction, which made up about 32% of the original value of wood for any carbonization, in the proportion of calories, the ratio of gas to oil varied from 0.374 (None, 700°C) to 0.864 (Ni 4%, 900°C). The increment of total conversion due to the presence of catalyst was 5.9%–7.7%, 5.0%–7.4%, and 8.2%–10.1% for 700°, 800°, and 900°C, respectively.
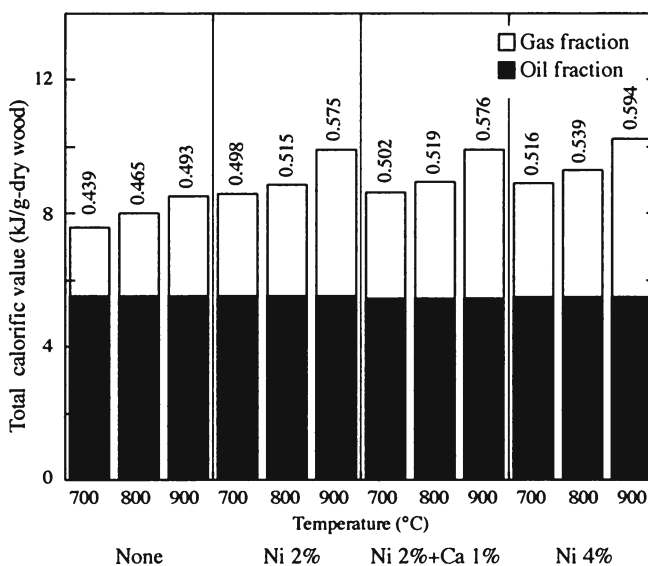
Fig. 5. Total calorific value of oil and gas fractions for None-, Ni 2%-, Ni 2%+Ca 1%-, and Ni 4%-woods. Figures on individual columns indicate total energy conversion into oil and gas

Table 4 shows the overall product distribution including char, the part of which was previously reported.[3] The proportion of "water + loss" was given by subtracting the sum of oil, gases, and char from 100. Most of the loss corresponded to tar-like substance that deposited to solidify near the bottom of the reactor or adhered to the inside of a glass pipe connecting to the first trap, partly transferring into the trap as acetone insoluble. Because of the difficulty in achieving complete recovery, this fraction was combined with water as water+loss. The quantity of this combined fraction was Ni 4% < Ni 2%+Ca 1% < Ni 2% < None and decreased

Table 4. Product distribution for noncatalyzed and nickel-catalyzed carbonizations of wood

Sample[a]	Carbonization temperature[a] (°C)	Oil[b] (%)	Gas[b] (%)	Char[b] (%)	Water+loss[c] (%)
None-wood	700	25.8	16.5	24.5	33.2
	800	25.8	17.5	24.1	32.6
	900	25.8	18.3	23.8	32.1
Ni 2%-wood	700	24.9	22.6	26.6	25.9
	800	24.9	23.8	26.0	25.3
	900	24.9	25.6	25.5	24.0
Ni 2%+Ca 1%-wood	700	20.9	26.4	27.6	25.1
	800	20.9	27.3	26.7	25.1
	900	20.9	29.1	26.1	23.9
Ni 4%-wood	700	21.9	27.4	28.7	22.0
	800	21.9	29.0	27.9	21.2
	900	21.9	30.3	26.7	21.1

[a] See the text
[b] Expressed on the basis of dry wood
[c] Given as 100 − (oil + gas + char)

with increasing temperature for all carbonizations. For char, when obtained at higher temperature, the yield became lower for the four wood specimens, as usually observed. However, the order of None < Ni 2% < Ni 2%+Ca 1% < Ni 4% at an identical temperature was similar to that of gas yield and thus was opposite to the proportion of water+loss. The increase of char yield in the presence of nickel was in agreement with our earlier findings.[14–16]

Discussion

Catalytic pyrolysis of wood, as well as noncatalytic pyrolysis, is mechanistically complicated, because various reactions occur simultaneously and/or consecutively. To better understand the process, it is convenient to assume a proper scheme. The modified Broid-Shafizadeh (abbreviated as mBS) scheme[17,18] depicted in the upper part of Fig. 6 is a widely accepted kinetic model for dealing with noncatalytic isothermal pyrolysis of cellulose. Recently, the mBS scheme was adapted to fast pyrolysis of biomass.[4] The basic concept will also hold at least qualitatively within the limitation of temperature for the present nonisothermal catalyzed carbonization. According to the mBS model, primary volatile, equivalent to liquid vapor, can be converted into char, gas, and secondary tar in the secondary pyrolysis step. It is a valuable and useful postulation in the mBS model that the decomposition of liquid vapor will thus affect both yields of char and gas. As described below, the first catalysis of nickel with and without calcium was supposed to participate only in the secondary pyrolysis step for reasons of simplicity. The second catalytic effect was, however, the promotion of gas evolution affording no oil at higher temperatures. Because the mBS scheme does not consider the second catalysis stage, the overall temperature was divided into two separate regions: one is the low temperature region where oil was produced and the other is the higher region lacking oil production. Such a separation led inevitably to the proposal of a moderately altered mBS model, as presented in the lower part of Fig. 6.
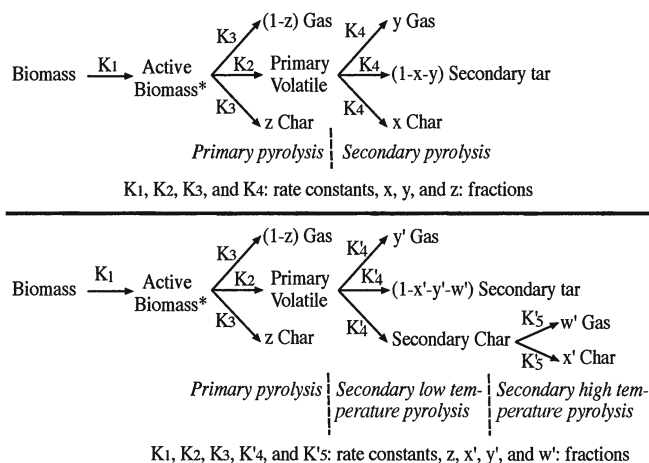
Fig. 6. The modified Broid-Shafizadeh scheme (*upper*) and its alteration for the present catalyzed-carbonization (*lower*). *Asterisk* indicates the original term of "cellulose" was changed to "biomass"

For oil, there was no significant influence of carbonization temperature from 700°C to 900°C on the yield and composition, including the yield of acetic acid (Fig. 2 and Table 2). This was interpreted as complete disappearance of liquid vapor up to 700°C. This can be expected from the operation temperature scarcely exceeding 600°C[19] for ordinary pyrolysis liquefaction. The substantial production of oil below 500°C judged by visual observation was in accord with conventional noncatalytic pyrolysis.[20] Therefore, nickel with and without calcium did not vary the temperature range of oil production significantly. This was ascertained by the fact that four oils comprised a number of common constituents (Table 1) without much difference in the net heating value (20.55–23.43 kJ g^{-1}, Table 2). Additional support was provided by the close resemblance of the entire ^{1}H NMR spectra of None-oil and Ni 2%-oil (Fig. 3). It follows that without changing the fundamental formation and decomposition pathways of the primary volatile, the nickel catalyst affected at least the secondary pyrolysis step

into secondary tar to result in the oil yield order of Ni 2%+Ca 1% < Ni 4% < Ni 2% < None. This order allows the interpretation that the yield decreased in the reverse order. The decrease accompanied by increasing the heating value per unit weight of None < Ni 2% < Ni 4% < Ni 2%+Ca 1% (Table 2) evidenced the effect of Ni 2% < Ni 4 % < Ni 2%+Ca 1% on deoxygenation of oil to improve the fuel quality at the cost of the yield. The liquid fraction water+loss in the order of Ni 4% < Ni 2%+Ca 1% < Ni 2% < None (Table 4) with nearly the same order for oil yield suggested concurrent cracking of tar-like substance as a precursor to oil according to the catalytic activity. The detailed catalytic action can be interpreted from GC-MS data (Table 1, Figs. 1 and 2) and ^1H NMR data (Fig. 3). For example, the striking resemblance of relative peak areas of furfurals to the heating value in the given order disclosed that the oil quality was enhanced by enriching carbohydrate moieties with the decrease of lignin-derived fragments. Major constituents such as furfural, 5-hydroxymethylfurfural, and guaiacols are reported to be typical decomposition products of hemicellulose, cellulose, and softwood lignin, respectively.[21] Such upgrading of oil was supported by the yield of acetic acid derived from hemicellulose[21] in the order None < Ni 2% < Ni 4% < Ni 2%+Ca 1%. A relatively small proportion of aromatic protons common to all of the oils resulted from the abundance of carbohydrate fragments and thus suggested little difference in the heating value among the four oils. In connection with this, the different position of a broad signal at 5–6 ppm for None- and Ni 2%-oils was due to the quantity of compounds containing OH groups, mostly acetic acid.

As is generally accepted, thermally unstable carbohydrate components are more susceptible to liquefaction than lignin. This in turn implies that lignin is more resistant to catalysis, thus accounting for the larger proportion of guaiacols in None-oil than in Ni-oils. However, the degradation of lignin was not trivial, because the trend for the relative area of phenol was None < Ni 2% < Ni 4% < Ni 2%+Ca 1%, which is identical to the order for furfurals. No clear difference in the peak areas of guaiacols among the three Ni-oils reflects considerable conversion into gases by the individual catalysts, as mentioned below. Consequently, it is reasonable to conclude that pyrolytic behavior of wood components combined with the catalytic activity brought about the above-mentioned difference in the yield and composition of the four oils. It is also necessary to emphasize that deoxygenation accompanied by decreased yield of oil was the desired upgrading, because upgrading oil to a higher degree necessarily involves a larger decrement in the yield. In this respect, Ni 2%+Ca 1% was more effective than other catalyst systems, even though the calorific value of the former oil was still unsatisfactory for use as motor fuel. The superiority of Ni 2%+Ca 1% to Ni 4% in the upgrading effect was interesting, considering that the effect of coloading of Ca with Ni surpassed that observed with twice the amount of Ni. It is likely that calcium exerted an effective promotion action by preventing agglomeration of nickel particles,[15,22] thereby raising the catalytic activity in the region below 500°C. However, the increased activity of Ni

2%+Ca 1% was not always more favorable for the production of fuel gas at higher temperatures.

With gas fraction, the order of None < Ni 2% < Ni 4% < Ni 2%+Ca 1% for amounts of CO and CO_2 at 300°–500°C (Fig. 3) was in agreement with that for the yield of acetic acid and was thus opposite to that for oil yield. Therefore, it is likely that the upgrading of oil was achieved by deoxygenation. The evolution of H_2 in the order of None (null) < Ni 2% < Ni 2%+Ca 1% < Ni 4% in this region reinforced the positive relation with the catalytic upgrading of oil, although most of CH_4 seemed to occur via a noncatalytic route. Production of both of H_2 and CO between 500°C and 700°C consistent with the upgrading of oil in the stated order demonstrated that the aromatic structure of carbon was dependent on the catalytic effect of nickel. This situation furthermore demonstrated the advantage of nickel loading for the production of H_2, as likewise verified by its much larger amount compared with None. However, the generation of CO_2 and CH_4 had no precise relation to the catalytic effect, possibly due to their easy formation and release. The fact that nickel catalyst still promoted the production of H_2 above 700°C (Table 3) signifies the accelerated formation of carbon into polycondensed aromatics and/or crystallized T component.[2,3] Greater attention should be paid to a composition of 75% H_2 and 25% CO for gases produced between 800°C and 900°C, irrespective of the catalyst system. The larger production and higher proportion of H_2 for Ni-woods than for None-wood confirmed that nickel-catalyzed carbonization conducted at such a high temperature could serve as an effective means to make the composition of gas more valuable[23] in concurrence with production of functional crystallized mesoporous carbon.

As indicated by total gas production and net heating value (Table 3) and the calorific ratio of gas fraction to oil fraction (Fig. 4), the order of None < Ni 2%+Ca 1% < Ni 4% ≤ Ni 2% for the production of the H_2-rich gas above 700°C was no longer closely correlated with the catalytic effect. This would arise from the circumstances that the conversion into gases in this temperature range also depended on the residual amount of char. Therefore, the above order was not consistent with the char yield of None < Ni 2% < Ni 2%+Ca 1% < Ni 4% (Table 4). It was more scientifically interesting that the order of char yield was the same as that of gas yield (Table 4), and both orders of char and gas in their yields were opposite to the proportion of water+loss of Ni 4% < Ni 2%+Ca 1% < Ni 2% < None (Table 4). These aspects of the catalytic process can be explained by the following two steps: (1) appreciable amounts of water formed through the deoxygenation of oil and tar-like substance could be incorporated in the secondary char, assumed in the lower part of Fig. 6, in the low temperature zone of secondary pyrolysis, probably below 500°C, and (2) subsequently the secondary char was converted into char with increased production of gases at elevated temperature. According to this proposal, the m BS scheme needs only alteration for secondary high temperature pyrolysis. The alteration was limited to secondary pyrolysis steps according to the initial supposition. Although no assurance is offered for the small influence of the cata-

lytic action on other steps, it is to be noted that the minimum alteration was adequate to characterize the feature of the catalytic effect.

The larger catalytic effect of Ni 2%+Ca 1% compared with Ni 4% below 500°C was useful information on the upgrading of oil. When considering that the oil fraction had a higher proportion of the total calorific value than the gas fraction in all carbonizations (Figs. 4 and 5), the production and improvement of oil must be seriously considered. From the standpoint of a practical operation, the better result of Ni 2%+Ca 1% with less cost compared with Ni 4% is favorable, although the production of both fuel gas and functional carbon was a little unfavorable for the former. To achieve more efficient upgrading of the oil fraction by employing such a nickel-calcium catalyst is the subject for our future study, in addition to confirmation of the validity of the above postulation of secondary high temperature pyrolysis.

Conclusions

The yields and properties of oil and gas fractions coproduced by nickel-catalyzed and noncatalyzed carbonizations of larch wood at 700°–900°C were examined. Upgrading of oil occurred in the order of None < Ni 2% < Ni 4% < Ni 2% +Ca 1% by deoxygenation accompanied by decrease in yield. The production of gas enriched with hydrogen was markedly promoted in the same order up to 700°C. The catalyzed promotion of hydrogen production continued above this temperature. Thus, the nickel-catalyzed carbonization at 900°C was favorable for the production of not only functional carbon but also fluid energy sources. By altering the modified Broid-Shafizadeh scheme at high temperatures, the catalytic effect of nickel with and without calcium was well explained in the whole temperature region.

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