

Co-production of Functional Carbon and Fluid Fuels from Wood by Nickel-Catalyzed Carbonization

Kyoko Suzuki, Hiroshi Matsuzaki, Tetsuo Yamada, and Tsutomu Suzuki

Dept. Applied and Environmental Chemistry, Kitami Institute of Technology, Kitami, Hokkaido 090-8507, Japan

Fax: 81-157-24-7719, e-mail: suzuki@serv.chem.kitami-it.ac.jp

Carbonization of wood loaded with nickel at 900°C for 1h could effectively produce crystallized mesoporous carbon with good electroconductivity and liquid phase adsorption capacity. Concurrently oil fraction was decomposed and deoxygenated into small molecules and a large amount of hydrogen-rich gas was evolved. These situations indicated the successful co-production of highly functional carbon and upgraded fluid fuels, thus confirming that the catalyzed carbonization is promising as a thermochemical conversion means of wood.

Key words: wood, nickel-catalyzed carbonization, functional carbon, fluid fuels

1. INTRODUCTION

Conversion of wood that is a typical renewable and carbon-offset resource into liquid and gaseous fuels has grown in importance from the anxiety about global warming by CO₂ emission. To date many liquefaction and gasification processes have been developed,^{1,2} but their current technologies are still not satisfactory in terms of commercial operation. A chief problem lies in the difficulty of complete and selective conversion into tar (oil) or gases, so that the total operating cost becomes very high. These situations justify the opinion that full conversion into fluid energies is never reasonable. On the other hand, petroleum is predicted to be exhausted in about 40 years.³ This prediction should stress the need of wood, a high quality biomass, for utilization as not only fluid fuels but also chemicals and/or materials as substitutes for fossil resources.

As is generally known, carbonization of wood affords considerable amounts of oil and gases as by-products. Although the technology is inferior to liquefaction and gasification in both yield and fuel quality of the corresponding product, it has industrial advantages of easy operation and low running cost. Furthermore, the main product, wood char, is widely used particularly in Japan as soil improver, fodder, moisture conditioner, deodorant, etc.,⁴ in addition to solid fuel. Thus, while carbonization is an approach that makes useful solid products, the potential will not expand as long as the use of wood char is limited to the present state. To raise the value of this technology, it is necessary to identify new uses for the resulting char along with improvement in fuel quality for the derived oil and gases.

Such circumstances motivated us to develop the entitled nickel-catalyzed carbonization, and several new functions for the metal-containing wood char obtained at various temperatures have been reported so far.⁵⁻¹⁰ The present work describes the effective production of crystallized mesoporous carbon with dual function by the treatment at 900°C in concurrence with liquid and gaseous fractions improved in fuel quality. The feature confirms that this process can serve the above purpose and thus is promising as a thermochemical conversion means of wood.

2. EXPERIMENTAL

2.1 Wood material and nickel loading

Powdered Japanese larch with the size of 0.50-1.40 mm was chosen as the raw wood material. It had the composition of C 50.5%, H 6.3%, N 0.2%, ash 0.15%, and O 42.9 % (by difference), and the net calorific value calculated by the Dulong's equation was 17.23 kJg⁻¹. As the nickel precursor, (CH₃COO)₂Ni·4H₂O was loaded by aqueous impregnation in a rotary evaporator. The amount of nickel was adjusted to 2 and 4 wt% as metal in wood. These Ni-woods were vacuum dried at 50°C before carbonization.

2.2 Carbonization

A stainless steel vessel packed with 2 g of each dried Ni-wood was placed in a vertical quartz tube reactor, and the reactor was electrically heated at a rate of 10°C min⁻¹ in a He flow of 23.2 mlSTPcm⁻²min⁻¹ to 900°C and the temperature was kept for 1 h. For comparison, the same carbonization was made with raw (Ni 0%) wood. Gas stream exited from the reactor entered glass traps cooled with iced water where liquid fraction was condensed, and the incondensable portion containing He was stored in rubber-made sampling bags, as previously described.¹¹ The collection of gases was made according to the following divisional regions: 100-300°C, 300-500°C, 500-700°C, 700-900°C, and 900°C-1 h.

2.3 Characterization of char carbon

After weighing, the resulting char was subjected to measurements of X-ray diffraction (XRD, Rigaku RINT 1200) and adsorption/desorption isotherms of nitrogen at -196°C (ThermoQuest Sorptomatic 1990). In XRD with Cu-Kα radiation, the average crystallite size of carbon indicating the thickness of the hexagonal layer, *L_c*, and the spacing of the plane, *d*₀₀₂, were calculated from the profile. Peak intensity at the (002) plane was given relative to that of artificial graphite, Lonza, and the value was expressed as relative peak intensity (RPI). In judgment of the crystallization, practical standards of electromagnetic shielding capacity, 8.5 nm and 15 × 10⁻³ for *L_c* and RPI, respectively,¹¹ were adopted. For the

nitrogen isotherms obtained, BET¹² and BJH¹³ methods were applied to determine BET surface area (SBET), BJH mesopore (pore with diameter of 2-50 nm) surface area (Sm), BJH mesopore volume (Vm), and BJH total pore volume (Vt). Sm and Vm were parameters employed for evaluating mesoporosity and their standards were settled on $140 \text{ m}^2 \text{ g}^{-1}$ and $0.17 \text{ cm}^3 \text{ g}^{-1}$, respectively, by assuming the application to liquid phase adsorption of macromolecules.^{14,15} In addition, the selectivity of mesopore was checked by Rv, defined as the ratio of Vm to Vt.

2.4 Analysis of liquid fraction

Liquid in cold traps was extracted with moisture-free acetone for separation from water. Next the extracted solution was carefully heated in a rotary evaporator to remove the solvent, and the resulting acetone soluble was recovered as 'oil'. For oil, GC-MS (Shimadzu GC-17A/QP 5000, equipped with SPB-1, 30 m x 0.25 mm Φ , as the column) and ¹H-NMR were applied to identify major constituents and to calculate the amount of acetic acid, respectively. To quantify the carboxylic acid, acetophenone was chosen as the internal standard. Elemental analysis (Elementar vario EL) also was made to determine the proportion of C, H, N, and O, and from the composition, net calorific value was obtained.

2.5 Analysis of gaseous fraction

For gas fraction collected in each temperature region, the composition was analyzed by TCD-GC (HITACHI G-3900) equipped with an active carbon column after the whole volume was measured at room temperature. Chief gas species detected were H₂, CO, CH₄, and CO₂, and their productions in the region were determined. The individual productions were summed up to obtain the total production in the whole period. For the total production, the net heating value was calculated on the basis of the standard value of H₂, CO, and CH₄ (12.77, 12.64, and 39.85 J/Nml, respectively).

2.6 Heat treatment of (CH₃COO)₂Ni·4H₂O

In the above carbonization of Ni-woods, the loaded nickel salt decomposed into certain amounts of oil and gases. These amounts must be subtracted from the whole amounts for evaluating the net productions of oil, acetic acid, and gases from wood. By this reason, the nickel salt impregnated onto Al₂O₃ (JRC-ALO-1, a reference alumina from Catalysis Society of Japan) was heat treated under the same conditions of carbonization. Thus correction was made for relevant values given in Tables II, III, and IV that are presented later.

3. RESULTS AND DISCUSSION

3.1 Characteristics of char carbon

Fig. 1 illustrates XRD profiles of Ni 4%-, Ni 2%-, and Ni 0%-chars. Ni 4%- and 2%-chars gave relatively sharp peaks at about 26° assigned to crystallized T component, whereas Ni 0%-char was amorphous. Fig. 2 shows isotherms of nitrogen adsorption/desorption for the same set of chars in Fig. 2. The hysteresis at about 0.5-0.9 of P/P₀ for two Ni-chars implied a considerable proportion of mesopore, in contrast to Ni 0%-char, which was mostly occupied by micropore (pore diameter < 2 nm).

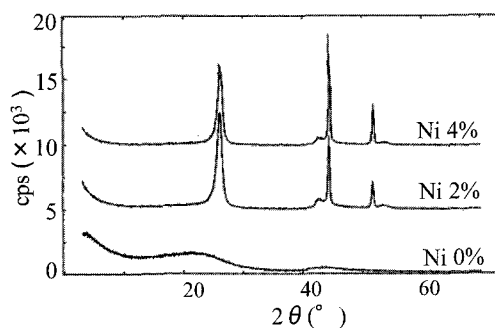


Fig. 1 XRD profiles of Ni 0%-, Ni 2%-, and Ni 4%-wood chars.

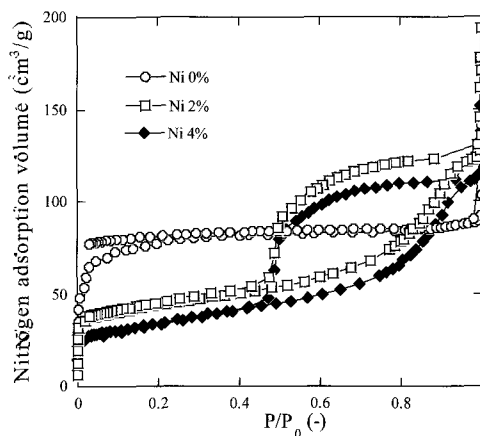


Fig. 2 Nitrogen adsorption/desorption isotherms for Ni 0%-, Ni 2%-, and Ni 4%-wood chars.

Table I Yield and properties for Ni 0%-, Ni 2%-, and Ni 4%-wood chars.

Carbon	Yield (%) ^{a)}	Crystal structure		
		<i>l</i> _c (nm)	<i>d</i> ₀₀₂ (nm)	RPI (x 10 ⁻³) ^{b)}
Ni 0%	23.8	< 1.0	---	---
Ni 2%	25.3	10.1	0.342	23.4
Ni 4%	26.7	9.5	0.341	20.7

Carbon	Pore structure			
	SBET (m ² /g) ^{c)}	Sm (m ² /g) ^{d)}	Vm (cm ³ /g) ^{e)}	Rv (%) ^{f)}
Ni 0%	237	29	0.011	16
Ni 2%	140	188	0.203	71
Ni 4%	112	142	0.204	86

^{a)} Dry ash-free, additives-free basis, ^{b)} Relative peak index, ^{c)} BET surface area, ^{d)} BJH surface area, ^{e)} BJH mesopore volume, ^{f)} Ratio of Vm to Vt (total pore volume), used as the selectivity of mesoporosity

Table I summarizes properties relating to crystallinity of carbon and pore structure for three chars, together with yield. Both Ni-chars surpassed the above-mentioned standards of *l*_c and RPI, and these parameters were larger for Ni 2% than for Ni 4%, as expected from Fig. 2. Besides, these chars satisfied the standards of Sm and Vm. Ni 2% was superior to Ni 4% in Sm, although Rv and the increment of yield were smaller for the former. The larger Sm for Ni 2% is consistent with the more

crystallized carbon because the development of mesopore would have a close relationship with the crystallinity of carbon.¹¹ It can thus be judged that Ni 2% was more adequate than Ni 4% in terms of dual function.

3.2 Production of oil

For any carbonization, liquid began to occur at below 200°C and almost ceased at 500°C. In Figs. 3 and 4, GC-MS total ion chromatograms and ¹H-NMR spectra were displayed for Ni 0%- and Ni 2%-oils, respectively. Fig. 4 disclosed that Ni 2%-oil was enriched with lower molecular weight constituents than Ni 0%-oil, because of more numerous peaks in less retention time than 4

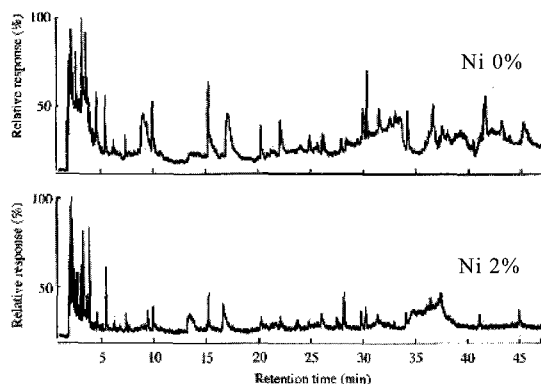


Fig. 3 GC-MS chromatograms for Ni 0%- and Ni 2%- oils.

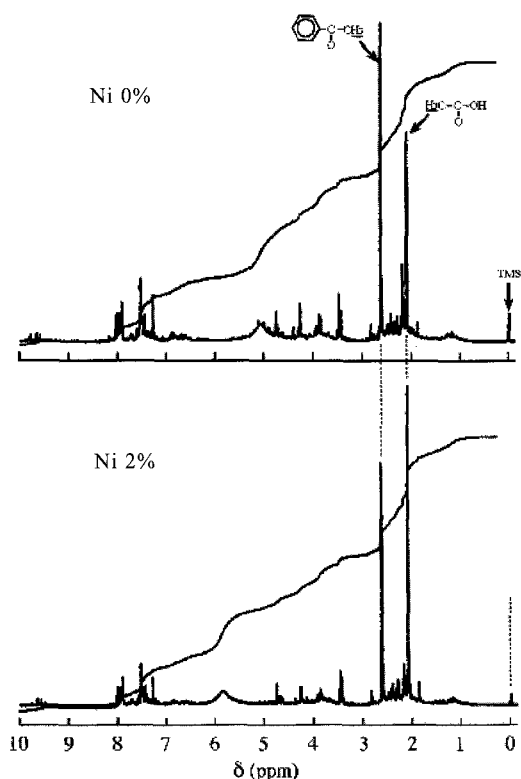


Fig. 4 ¹H-NMR patterns for Ni 0%- and Ni 2%-oils

min with smaller peaks in over 10 min for the former. For acetic acid, the concentration was higher for Ni 2%-oil than for Ni 0%-oil, as was obvious in Fig. 4. Compared to Ni 2%, Ni 4% gave lighter oil with acetic acid denser. Table II lists yield and properties for three oils. It is evident that the increased loading of nickel

Table II Yield and properties for Ni 0%-, Ni 2%-, and Ni 4%-oils.

Oil	Yield (%) ^a	Elemental composition (%)			
		C	H	N	O ^b
Ni 0%	26.8	59.5	7.3	0.1	33.1
Ni 2%	24.9	64.6	6.6	0.1	28.7
Ni 4%	23.9	66.6	6.9	0.1	26.4

Oil	Net calorific value (kJ/g) ^c	Net calorific value (kJ) ^d	Acetic acid	
			Conc. (mg/g-oil)	Yield (%) ^e
Ni 0%	20.55	5.51	72.1	1.9
Ni 2%	22.26	5.54	137	3.4
Ni 4%	23.01	5.50	160	3.8

^a On the basis of dry wood, ^b By difference, ^c Calculated on the composition of C, H, and O, according to the Dulong's equation, ^d (The amount of oil, g) x (the value per unit gram, kJ/g)

promoted decomposition and deoxygenation of oil at the cost of yield, thereby increasing the net calorific value per unit weight. The amount of acetic acid was Ni 0% < Ni 2% < Ni 4%, and this order would reflect a larger production of smaller oil molecules for a larger loading of nickel. These aspects proved the efficient upgrading of oil by the catalysis of nickel, even though the quality was still inadequate for motor fuel.

3.3 Production of gas

Evolution of gases began at near 200°C and continued until the end of carbonization. Fig. 5 represents the production of each gas species from Ni 0%-, Ni 2%-, Ni 2% afforded much larger amounts of gases particularly H₂ than Ni 0% at above 500°C. Even at 300-500°C, the evolution of H₂ was prompted by nickel. Ni 4% had a larger effect than Ni 2% on the promotion of H₂ evolution, as well as CO₂ evolution. The total gas production is given in Fig. 6, and the overall aspect is

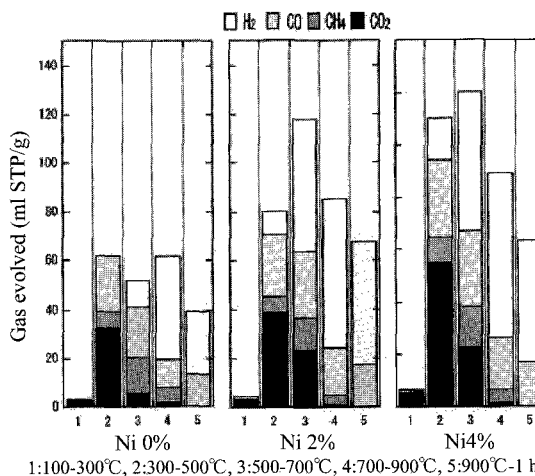


Fig. 5 Gas evolution from Ni 0%-, Ni 2%-, and Ni 4 %-woods in various temperature regions.

presented in Table III. These situations made clear that increase in the loading of nickel favored both gas yield and the net heating value, as opposite to the production of the functional carbon.

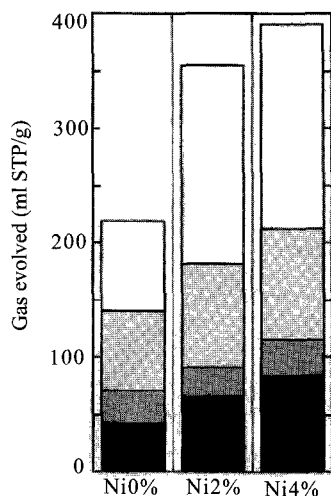


Fig. 6 Total gas evolution from Ni 0%-, Ni 2%-, and Ni 4%-woods.

Table III Gas production from Ni 0%-, Ni 2%-, and Ni 4%-woods.

Gases	Gases produced (mlSTP/g-dry wood) and the proportion ^{a)}				Total
	H ₂	CO	CH ₄	CO ₂	
Ni 0%	78.9 (36.2)	68.8 (31.5)	27.8 (12.7)	42.9 (19.6)	218.4
Ni 2%	174.4 (49.1)	89.7 (25.2)	25.0 (7.0)	66.2 (18.7)	355.6
Ni 4%	178.9 (45.8)	96.6 (24.8)	31.0 (7.9)	83.8 (21.5)	390.3

Gases	Net heating value (kJ/g) ^{b)}	Amount of gases (mg/g-dry wood)		Yield (%) ^{c)}
		H ₂	CO	
Ni 0%	2.99	6.56H ₂ + 80.13CO - 18.50CH ₄ + 78.52CO ₂	18.3	
Ni 2%	4.36	14.54H ₂ + 104.47CO - 16.64CH ₄ + 121.16CO ₂	25.6	
Ni 4%	4.74	14.88H ₂ + 112.51CO - 20.63CH ₄ + 155.37CO ₂	30.3	

^{a)} Figures in parenthesis, ^{b)} Calculated by using the standard value (kJ/molSTP) of each combustible gas species: 12.77, 12.64, and 19.85 for H₂, CO, and CH₄, respectively. ^{c)} On the basis of dry wood

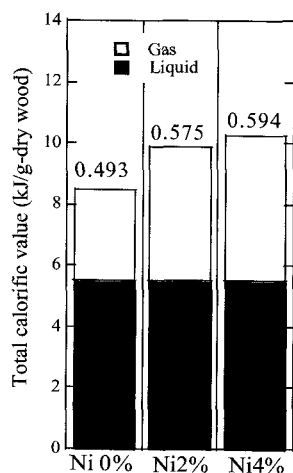


Fig. 7 Total conversion into fluid energies for carbonization of Ni 0%-, Ni 2%-, and Ni 4%-woods at 900°C.

3.4 Total conversion into fluid fuels

Fig. 7 compares the total calorific value of oil and gas fractions among three woods. Figures on columns stand original wood, 17.23 kJg⁻¹. Although little difference was found for oil fraction, the total value was Ni 0% < Ni 2% < Ni 4% in accord with the order of gas fraction. The larger profit of gas production can be accepted as the great feature of nickel-catalyzed carbonization when used for energy conversion of woody biomass.

4. CONCLUSIONS

Nickel-catalyzed carbonization of wood at 900°C was performed to examine the properties of the resulting carbon and the yield and composition for oil and gaseous fractions. The results obtained showed the successful co-production of functional carbon and fluid fuels. This confirmed that the catalyzed carbonization is promising as a conversion means of wood to energy and material, although oil is required to be further upgraded for the use as motor fuel.

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