

ORIGINAL ARTICLE

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Hydrogasification of wood for high heating-value gas production X: Effect of pretreatment of Japanese oak bark by HNO₃ oxidation on subsequent iron-catalyzed hydrogasification

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Abstract Japanese oak bark, which is one of the most difficult woody biomass materials for iron-catalyzed low-temperature (<700°C) hydrogasification, was subjected to HNO₃ oxidation as the pretreatment after prewashing with water. The effect was compared with that of HCl demineralization from four points of view: (1) removal of catalyst poisons; (2) development of porosity in the cell tissue; (3) introduction of ion-exchanged iron; and (4) reduction of nitrogen and sulfur. It was found that HNO₃-oxidized oak bark char loaded with iron by the ion-exchange method gave a satisfactory reactivity in agreement with the corresponding larch bark char previously used. Also, the oak bark char contained only small amounts of nitrogen and sulfur. These situations confirmed the high suitability of oxidation pretreatment combined with water prewashing for woody biomass.

Key words Oak bark · Hydrogasification · HNO₃ oxidation pretreatment · Iron catalyst

Introduction

Conversion of bark into fuel and synthesis gases has lately attracted little attention, although it is an important subject in the production of fluid energy from woody biomass. A main reason for abated interest in the research is the difficulty of enhancing the reactivity of the waste-like material by catalyst loading, regardless of the atmosphere.^{1–6} According to our study of nickel- and iron-catalyzed low-temperature (<700°C) hydrogasification, smaller activities of these metals on bark chars than on wood chars are ascribed to the characteristics of raw bark^{6,7}: (i) a larger amount of catalyst poisons existing as indigenous mineral

matter and (ii) harder and thicker cell tissue leading to poor dispersion of metal precursor particles on wet impregnation, which is a popular catalyst addition method we have used. Thus, basically, (1) removal of catalyst poisons and (2) development of pore structure in the cell are the keys to catalyzed gasification of bark or its char.

In a previous paper, we described the effect of pretreatment with HNO₃ on larch bark for iron-catalyzed hydrogasification.⁸ Concerning the above problems, the acidic oxidation markedly diminished the amount of major poisons, such as calcium and silica,^{9–11} accompanying the collapse of cell structure to some extent. Such functions were, however, inadequate for increasing the activity of impregnated iron to a desired level. It was noteworthy that the concurrent increase of carboxyl content allowed us to increase an introducible amount of ion-exchanged iron with more activity than impregnated iron,⁹ whereby the iron-loaded bark char could provide sufficient reactivity in the low temperature region. This indicated enough compensation by (3) chemical modification to enable better dispersion of loaded iron for the lack of ability relating to (2).

However, whether HNO₃ oxidation likewise becomes effective for hardwood bark is still uncertain, because this material is considered more difficult to gasify than softwood bark from the same reasons as (i) and (ii). Actually, HCl-demineralized oak bark char with impregnated iron gave less conversion in hydrogen than the corresponding larch bark char.¹¹ The utility of the pretreatment should thus be judged only after examination on hardwood bark. Its success with the most difficult material warrants such high adaptability that the technique can be used for all the kinds and types of woody biomass. This is the significance of tests on hardwood bark.

The present work deals with low-temperature hydrogasification of HNO₃-oxidized Japanese oak bark char loaded with iron. The oxidation-demineralization synergy is discussed in comparison with the effect of HCl demineralization, by placing emphasis on (1), (2), and (3). It was also assessed from a viewpoint of the influence on environment, such as (4) the emission of NO_x and SO_x during the carbonization of bark to prepare char.

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Experimental

Bark material

Powdered bark of mizunara (Japanese oak, *Quercus crispula* Bl.), 0.25–0.35 mm in diameter, was prewashed with distilled water to remove sand and mud attached to the surface. The cleaned powder was vacuum-dried at 50°C and used as raw bark (RB).

HNO₃ oxidation and HCl demineralization

For HNO₃ oxidation (OX), RB was soaked in a 4N solution with stirring at 40°C for 1h. HCl demineralization (DM) was made by stirring RB with 1N HCl at room temperature for 24h. The characteristics of OX and DM were similar to that previously used.⁸ After filtering off, the barks were rinsed with aqueous alkali for neutralization and washed exhaustively with warm distilled water. They were designated OB and DB for OX and DM, respectively.

Properties of barks

All of the barks were analyzed for ash; metal composition; sulfur; C, H, O, and N composition; and carboxyl content, as described in previous papers.^{6–8,11} Fourier transform infrared spectroscopic (FT-IR) spectra were taken by the KBr disk method (Shimadzu FTIR-8200). For a specially dried specimen, the specific surface area (S_A) was measured by the BET method (Shibata P-700) using an adsorption amount of CO₂ at –78°C; and the cell tissue was observed by scanning electron microscopy (SEM) (JOEL JSM-T200) in which the beam was accelerated at 25kV. To prepare the sample, the containing water was replaced with mixtures of ethyl alcohol-*iso*-amyl acetate of varying ratios, followed by critical-point drying (Eiko Engineering DX-1) with solid carbon dioxide at –78°C.¹¹

Loading of iron catalyst

Each bark was loaded with Fe(NO₃)₃ · 9H₂O as the iron catalyst precursor by usual wet impregnation.^{6–8} For ion exchange, OB was washed successively with distilled water, 0.01M solution of the iron salt, and deionized water.⁸ The same ion exchange was done on DB for comparison. The ion-exchange loading was denoted by the suffix “-Ion” to differentiate from impregnation. The amount of iron was adjusted to less than 5 wt% as metal in char for either loading method.

Preparation and characterization of char

Bark was all carbonized at 500°C in a fixed-bed vertical tube reactor for 1h under a flow of nitrogen. The resulting char was subjected to ultimate analysis, S_A measurement, FT-IR, and laser Raman spectroscopic analysis (LRS, JASCO NR-1800KS), and X-ray diffraction (XRD, Rigaku RINT 1200), in addition to quantification for ash and iron. In LRS analy-

sis, the R value,¹² which is given as the ratio of the absorption of amorphous carbon at 1360cm⁻¹ to that of graphitic carbon at 1580cm⁻¹, was determined to estimate the crystallinity of carbon, from which chemical reactivity of carbon itself can be judged. In XRD, Cu-K α ray was radiated at 40kV and 30mA for identifying the chemical state of the iron. Several chars were observed by SEM equipped with an energy-dispersive X-ray spectrometer (EDX, JOEL JED-2001) to examine the distribution of iron, calcium, and silicon particles. This was undertaken with each K α line (6.40, 3.69, and 1.74eV for Fe, Ca, and Si, respectively) at a fixed exposure time (450s) and dead time (7%). When the mapping was preliminarily checked on wood and bark chars with varying amounts of these three metals loaded by wet impregnation, a difference of more than 0.5 wt% in the bulk concentration for each metal species gave visibly different numbers of spots on a cross section of char. The SEM-EDX observation suggested its convenience for estimating the dispersion of metal particles, as described later.

Hydrogasification reactivity of char

Char was hydrogasified in a thermobalance (Shinku-Riko TGD-5000RH) at ambient pressure to evaluate the reactivity. The conditions were as follows: sample weight 10mg, hydrogen flow 100ml (stp) min⁻¹, heating rate 10°C min⁻¹, and maximum temperature 1000°C. All the char samples were vacuum-dried overnight at 50°C prior to the test. Weight loss up to 700°C (W_{700}) on a dry ash-free, catalyst-free basis was determined as reactivity parameter in the low temperature region. A derivative thermogravimetric (DTG) curve also was obtained.

Dispersion of metallic iron on hydrogasified char

Isothermal hydrogasification for all the types of chars with 3 wt% iron was carried out in a downflow fixed-bed reactor at 700°C for 10–30min. The detailed procedures are given elsewhere.^{11,13} The reaction residue was weighed to determine the conversion (dry ash-free, catalyst-free basis) and then irradiated with Cu-K α ray. Specific intensity, which is defined as the peak height per unit weight of iron in char and expressed as I_{Fe}/W_{Fe} , was calculated from the intensity of the XRD line at 2θ of about 45°. This can be an index for estimating the dispersion of metallic iron,^{8,11} as well as the metallic nickel,¹³ on the char. The following interpretation can be made: More highly dispersed metallic iron gave smaller specific intensity at an equal loading onto char containing ash of similar quantity and composition.

Results

Different influence on bark for HNO₃ oxidation and HCl demineralization

Table 1 summarizes the recovery and properties for three types of bark. Compared to DM, OX caused a greater loss

Table 1. Recovery and properties of raw, HCl-demineralized, and HNO₃-oxidized oak barks

Barks ^a	Recovery ^b (%)	Ash ^c (wt%)	Metals in ash ^d (%)							COOH ^e (mEq/g)	Ultimate analysis (dry, wt%)				SA ^g (m ² /g)
			Na	K	Mg	Ca	Fe	Al	Si		C	H	N	O ^f	
RB	100	6.6	0.4	0.5	1.2	27.7	0.5	0.6	26.7	0.6	49.0	5.7	0.4	38.3	52
DB	77	0.5	0.8	1.3	0.3	12.5	1.3	2.1	34.4	0.7	50.8	5.8	0.1	42.7	61
OB	70	0.7	1.0	1.1	0.2	9.2	1.5	2.3	38.5	1.2	47.7	5.6	0.1	45.9	73

^a RB, raw; DB, HCl-demineralized; OB, HNO₃-oxidized. All these barks contained less than 0.1 wt% sulfur.

^b Expressed relative to RB.

^c Incombustible residue at 600°C.

^d Determined by atomic absorption and ICP emission methods on HF-HCl-HNO₃ solution of ash.

^e Determined by the method of described by Onabe and Kuga.¹⁴

^f Expressed as: 100 - (ash + C + H + N).

^g Specific surface area. On a dry ash-free basis

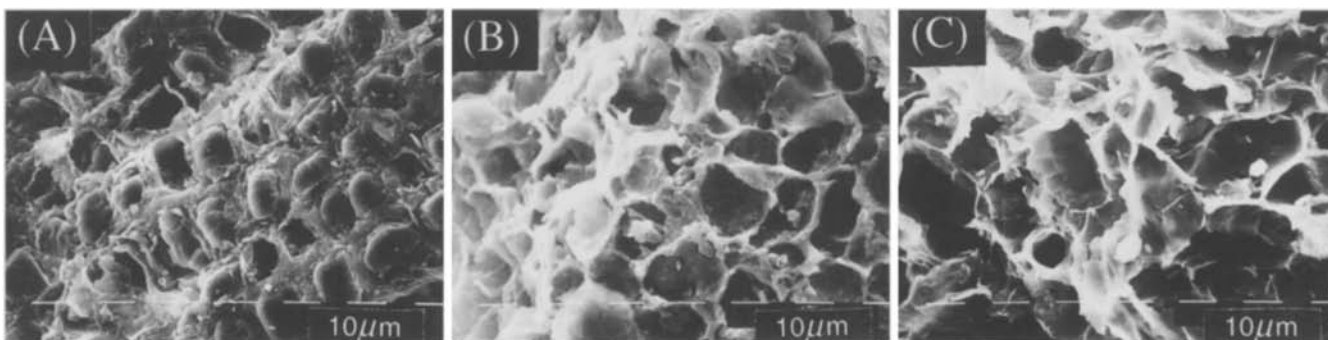


Fig. 1. Scanning electron micrographs (SEM) of oak bark. **A** Raw. **B** HCl-demineralized. **C** HNO₃-oxidized

of organic constituents with slightly less removal of mineral matter, particularly silica. Thus the selectivity of ash removal was lower for OX than for DM, but OB was on an equal basis with DB in terms of the amount of calcium remaining. Sulfur was negligible even for RB. Nitrogen was reduced by OX to the same degree as did DM. OB had larger carboxyl and oxygen contents than RB and DB, as expected. S_A was OB > DB > RB and was in the reverse order of recovery.

According to SEM observation, most of the lumina for RB were clogged with solid substances, perhaps composed of starch, calcium oxalate, and other substances,¹⁵ whereas DB and OB had empty and broader lumina, as seen in Fig. 1. Also, the tissue of OB was observed to be more heavily destroyed to yield thinner cell walls compared to that of DB. Such situations would lead to the difference in S_A , as well as the recovery, among three barks. The FT-IR spectra illustrated in Fig. 2 indicated smaller absorptions at 1500, 1325, and 1270 cm⁻¹ for OB than those for DB, suggesting that the lignin in OB is degraded to a greater extent. Although three barks were almost equal in terms of the intensity of absorption at 1730–1740 cm⁻¹, 1400 cm⁻¹ absorption possibly assigned to carbonyl stretching was stronger for OB. The strengthened absorption may be therefore evidence for the increased carboxyl and oxygen contents. NO₂ and NO groups were not found in OB, as could be predicted because the nitrogen content is equal to that in DB.

Characteristics of bark chars

Table 2 lists char yields of bark and properties of the chars. For all of the chars except DB-Ion char, the yield and oxygen content increased with iron loading. A similar tendency has been observed for other woody materials.^{6,7,10} Ash, whose metal composition was unchanged before and after carbonization, deservedly decreased with increasing char yield. At an equal loading of iron, DB, OB, and OB-Ion chars with smaller oxygen and ash contents were obtained in lower yields than RB char. The former three chars did not differ much from one another in terms of their oxygen and ash contents, although the yield of DB char was somewhat larger. Nitrogen and sulfur remained negligible for all chars. Judging from the R-value determined by LRS, the difference in the crystallinity of carbon among the four types of chars was only slight. S_A varied largely without dependence on the initial value of each bark and iron loading. Nevertheless, it seems unimportant for the reactivity of iron-loaded char, to our knowledge.^{6–11,13}

FT-IR spectra of DB, OB, and OB-Ion chars were alike, despite iron loading, although RB char gave a different spectrum because of enrichment with ash. None of iron-loaded chars gave XRD lines due to iron species chiefly by interference from ash, and so the chemical state of the iron was unidentified. A noticeable difference among four chars appeared in the map of iron particles. As is shown by typical

Fig. 2. FT-IR absorption spectra of oak bark. **A** Raw. **B** HCl-demineralized. **C** HNO₃-oxidized

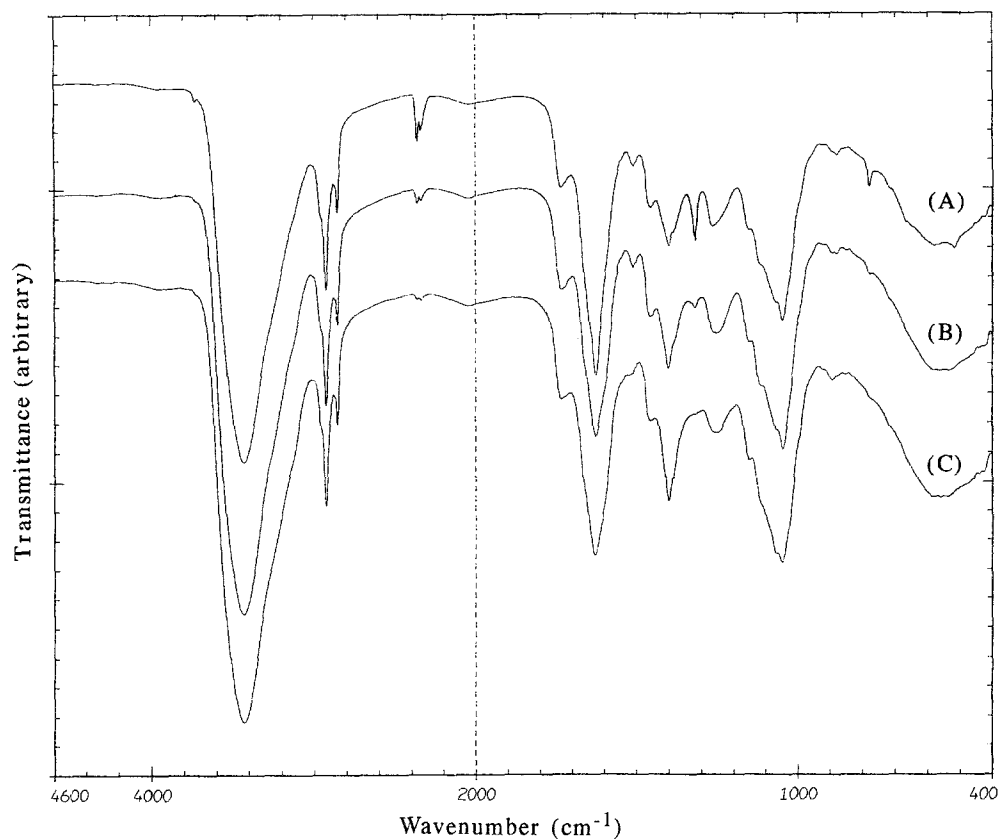


Table 2. Char yields of oak bark and the properties of chars

Barks ^a	Iron loaded (wt%)	Char yield ^c (%)	Ash ^d (wt%)	Ultimate analysis (%)				R value ^f	S _A ^g (m ² /g)
				C	H	N	O ^e		
RB	0.0	29.1	19.8	61.4	2.7	0.1	15.8	0.98	330
	0.9	30.6	18.1	61.2	3.0	0.1	17.4	1.00	293
	2.8	32.5	17.4	60.8	2.9	0.1	18.6	1.00	278
	4.8	34.2	15.9	60.7	3.6	0.1	19.4	1.01	285
DB	0.0	29.7	2.5	79.7	3.2	<0.1	14.6	0.95	262
	0.9	30.7	1.9	79.5	3.1	<0.1	15.4	0.97	276
	3.1	31.4	1.6	79.6	3.0	<0.1	15.8	0.98	312
	4.8	33.4	1.3	79.4	2.8	<0.1	16.3	0.99	298
OB	1.0 ^b	30.5	1.9	79.4	3.0	<0.1	15.8	0.96	284
	0.0	27.9	2.7	79.5	3.4	<0.1	14.3	0.96	268
	1.2	28.8	2.1	78.8	3.3	<0.1	15.8	1.01	285
	2.8	29.5	1.8	78.2	2.9	<0.1	17.0	1.02	279
	4.5	31.4	1.5	77.0	2.9	<0.1	18.5	1.01	256
	1.8 ^b	27.0	2.4	79.0	3.0	<0.1	15.6	0.98	291
	2.9 ^b	28.6	2.1	78.7	2.8	<0.1	16.3	1.00	282

^{a,d,e,f} Same as in Table 1.

^b Iron loading by ion-exchange method.

^c On a dry ash-free, catalyst-free basis.

^g Index of the crystallinity of char carbon. Defined as the ratio of the Raman absorption at 1360 cm⁻¹ to that at 1580 cm⁻¹

SEM-EDX photographs in Fig. 3, the number of spots increased in the order of OB-Ion ≤ OB < DB < RB. Calcium was abundant in the RB char and occurred in only slight amounts in the other chars. As for silica in these fields, all of the chars had similar distribution, spreading widely and nearly uniformly. RB had a greater number of spots than the other chars.

Hydrogasification reactivity and specific intensity of metallic iron

Figure 4 displays the relation between W₇₀₀ and iron loading, from which the reactivity of OB-Ion > OB > DB > RB was established at more than 1wt% iron. It is noteworthy that W₇₀₀ of OB-Ion char with 3wt% iron reached 90%,

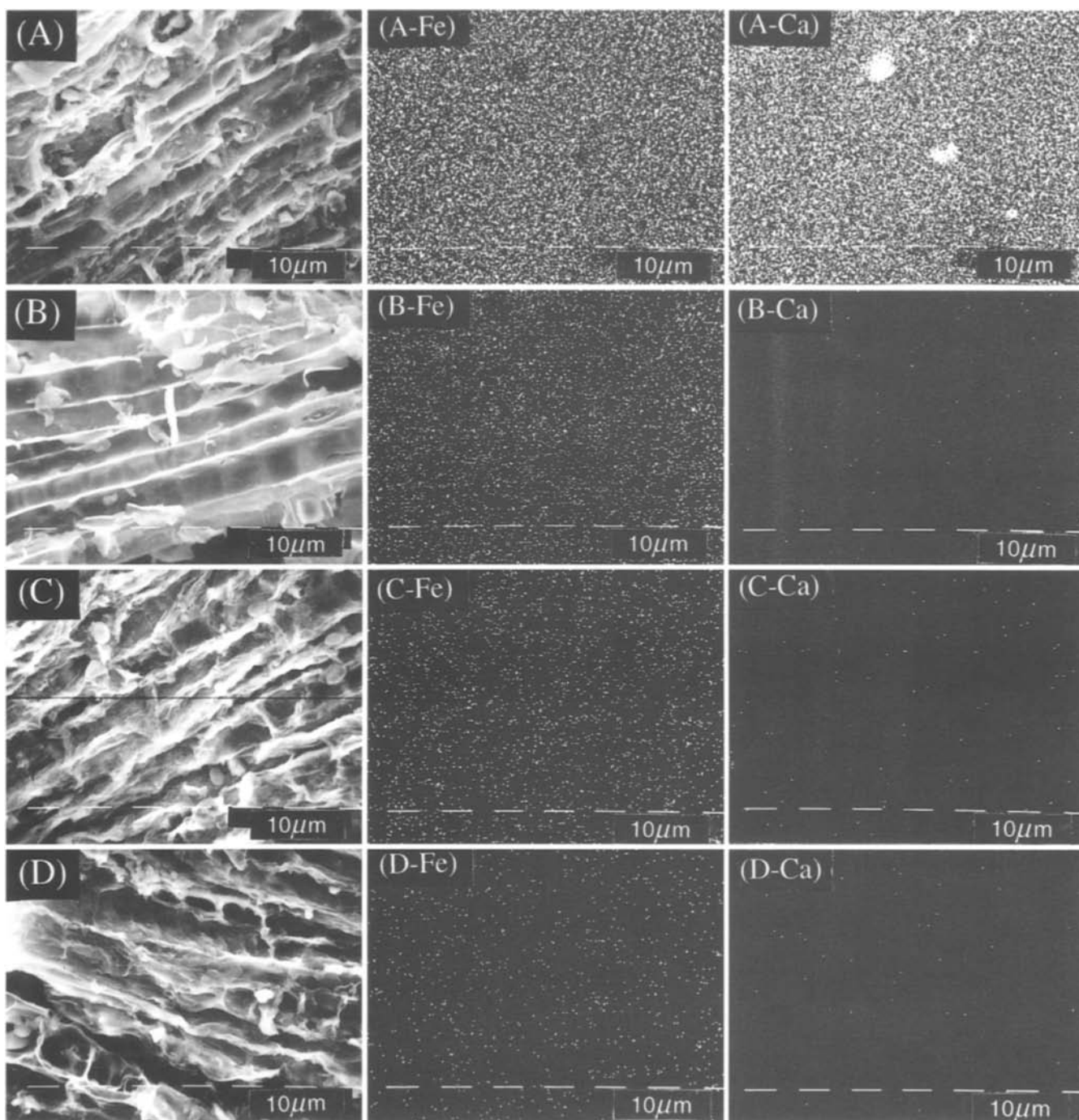


Fig. 3. SEM–energy dispersive X-ray spectrometry (EDX) photographs of 3% iron-loaded oak bark char. **A** Raw. **B** HCl-demineralized. **C** HNO₃-oxidized. **D** HNO₃-oxidized (ion). Iron was loaded by wet impregnation for **A**, **B**, and **C** and by ion-exchange for **D**

which is our customary standard for successful low-temperature gasification.^{7–11} This amount of iron was two-thirds that required for OB char to have the same W_{700} . DB-Ion char could not hold more iron than 1 wt%, and its reactivity was the same as that of DB char at this loading level. The increase in iron loading for RB char was scarcely beneficial, though without iron its W_{700} surpassed those of the other chars.

Figure 5 compares DTG curves of four chars with about 3wt% iron. A maximum rate (R_{\max}) appeared at between 600° and 700°C for OB-Ion, OB, and DB chars, with the value ascending in the sequence, whereas RB char gave two R_{\max} values, at 600° and above 700°C. Increasing the amount of iron usually lowered the temperature, affording R_{\max} for the three chars and did not appreciably alter those of RB char.

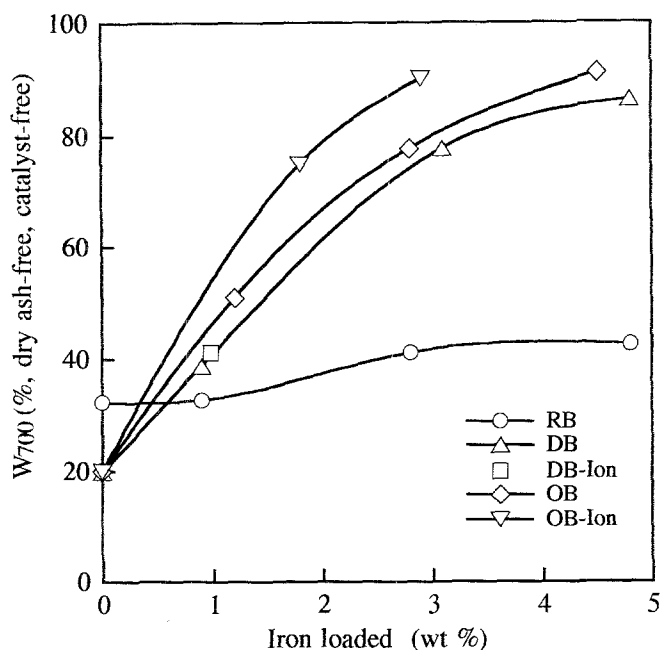


Fig. 4. Low-temperature hydrogasification reactivity (weight loss up to 700°C, W_{700}) for various kinds of oak bark chars. *RB*, row; *DB*, HCl-demineralized; *OB*, HNO_3 -oxidized

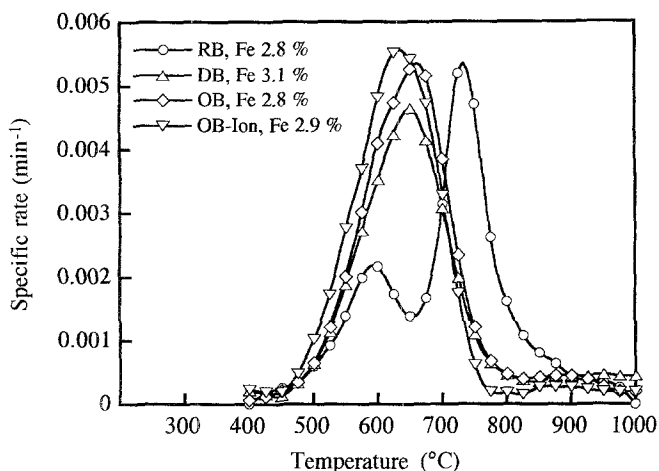


Fig. 5. Derivative thermogravimetric curve for various kinds of oak bark chars

Figure 6 presents plots of conversion and specific intensity ($I_{\text{Fe}}/W_{\text{Fe}}$) versus the reaction time at 700°C gasification for 3 wt% iron-loaded chars. The order of these chars in the conversion agreed with that in W_{700} , indicating that the same factors would determine the reactivity order during both types of hydrogasification. $I_{\text{Fe}}/W_{\text{Fe}}$ for each char increased similarly to the conversion with the time, to give the order of $\text{DB} > \text{OB} > \text{OB-Ion} > \text{RB}$. With the exception of RB, the specific intensity was smaller for more-reactive char. This gave evidence of a close relation between the dispersion of iron metal particles and the reactivity for the three chars.

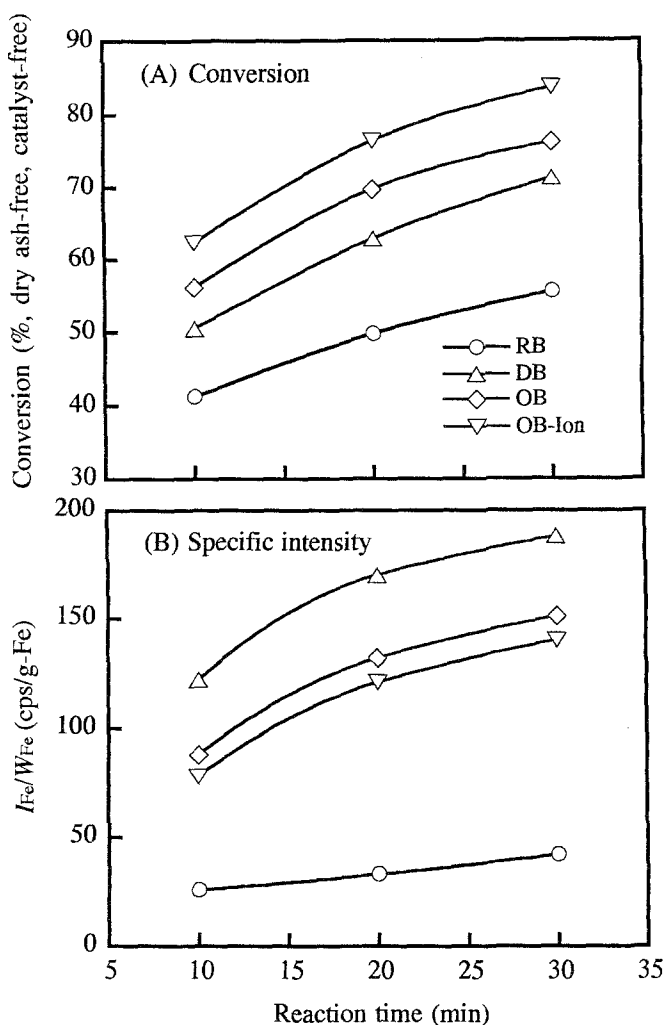


Fig. 6. Conversion (A) and specific intensity (B) for 3% iron-loaded oak bark chars isothermally hydrogasified at 700°C for 10–30 min

Discussion

The reactivity measurement of oak bark chars demonstrated the superiority of OX to DM as pretreatment. Also, the reactivity of OB-Ion char manifested that the combination of OX with iron loading by ion-exchange was a skillful method for obtaining high catalytic activity of the metal. It is thus certain that through OX, oak bark turned, in a manner similar to larch bark,⁸ into a suitable material for hydrogasification. The great efficacy of OX can be well elucidated by comparing it with the effect of DM from the four points of view stated at the beginning.

The first is the capability of OX to eliminate poisons for iron catalyst. Of three major poisons, sulfur was adequately lost by prewashing with water. Such was also the case in previous work with larch and oak barks.^{8,11} There is thus no denying the significance of the prewashing, but it is also true that high iron activity was not obtained by the mere removal of sulfur. The poor activity of iron on RB char reflected serious poisoning by the remaining calcium and

silica. Because calcium is considered more harmful than silica,^{8,9,11} removal of the alkaline earth metal to the same level as accomplished by DM must be an important function of OX. The effect was perceived as the change in the DTG profile: the activity of iron on DB, OB, and OB-Ion chars so restored as to join two R_{\max} of the RB char into one with a larger rate. The less efficient removal of silica by OX than by DM was not a great disadvantage, as OB char had more reactivity than DB char at an equal loading of iron. In other words, the inferior ability to remove silica could be fully compensated by the benefit given below.

The second is concerned with structural change in the cell of oak bark. OX involving oxidation gave a larger S_A than did DM in return for a larger mass loss by expanding the cell tissue to a greater extent. In brief, the cell structure of OB became more porous than that of DB. The promoted development of porosity was helpful for improving the dispersion of impregnated iron, as supported by the fact that the larger S_A of bark, the fewer spots of iron detected by SEM-EDX. The result of SEM-EDX did not always mean a lower concentration of iron, because the mapping obtained would be influenced by the physical state of the char, which differed among the chars. However, the above-mentioned preliminary test suggested the possibility that the map of iron, as well as of calcium and silica, would have a fairly close relation to its concentration on the char surface, even if an accurate determination of surface iron was not made. This can be reinforced by the interpretation of $I_{\text{Fe}}/W_{\text{Fe}}$ described later. That is, a smaller quantity of iron on the outer surface equivalent to its larger quantity in the inner part should amount to wider distribution or higher dispersion throughout the char. A similar dependence of the dispersion of iron particles in char on the surface area of the starting material has been recognized for oak bark.¹¹ From these statements, it follows that, compared to DB, OB allowed impregnated iron to be better dispersed in the char because of its higher porosity. This was another noteworthy function of OX, explaining why OB could produce more reactive iron-loaded char than DB. Actually, no great difference in the other properties was found between OB and DB chars, and the char reactivity of OB > DB > RB was in the same order as that for the S_A of bark.

The accompanying increase in oxygen and carboxyl contents for OB, although it would have no direct bearing on the above situation, presented some problems as the third point. Unexpectedly, OB char had a lower content of oxygen than RB char. This signified a great discrepancy in the pyrolytic behavior between oak and larch⁸ barks, but the importance of oxygen in char for gasification reactivity^{8,16-20} was reconfirmed by the smaller W_{700} for OB char and DB char than for RB char at a null loading of iron. It is more important to note that OB gained cation exchangeability to have a new function, and the resulting benefit more than offset the demerit of a smaller amount of oxygen. OB had an aptitude for accommodating the proper amount of ion-exchanged iron, which can produce finer or better-dispersed metallic particles with larger activity than impregnated iron.^{8,9} This was the reason for OB-Ion char exceeding OB char in reactivity. In contrast, DB-Ion and DB chars had

almost equal W_{700} at 1 wt% iron. The lack of advantage of ion exchange over impregnation would be due to an insufficient amount of ion-exchanged iron, as suggested by the upper limit of iron loading for DB-Ion char. The evidence of ion-exchanged iron on OB-Ion char was provided by the smaller $I_{\text{Fe}}/W_{\text{Fe}}$ and thus better dispersion than that for OB char. The different intensity for DB and OB chars also could be interpreted as their difference in the dispersion of metallic iron. It is thus reasonable to deduce that for OB-Ion, OB, and DB chars, the dispersion of iron metal played a dominant role in determining the reactivity order. For RB char, the same correlation of specific intensity with the dispersion of iron metal did not hold because of the extremely large quantity of ash. The smallest intensity for RB char would result from the depressed formation of metallic iron by strong interference from poisons, by which the poor reactivity was accounted for.

As the fourth point, the practicability of OX was assessed in terms of the influence on the environment. Although nitrogen in RB was not abundant, its smaller quantity is more desirable for thermochemical utilization, because the possibility of NO_x emission cannot be ignored. It is to be noted that against the fear of containing a large amount of nitrogen, OB equaled DB in its content. This disclosed little different ability in eliminating the element for OX and DM, thus convincing us that hardly any amount of NO_x due to OX would be emitted during the carbonization of OB and OB-Ion. The fact that sulfur in any oak bark was as low as 0.1 wt% predicts no serious evolution of SO_x after prewashing with water. Thus, the pretreatment by OX incorporated with the prewashing is effective also for converting oak bark to less pollutant-containing, or more environmentally friendly, material. With wet impregnation, the use of iron nitrate containing nitrogen as the catalyst precursor is the problem to be settled first. However, ion-exchange, in principle, is independent of anion species of iron resources and is likely to escape the trouble. This explains another significant aspect of iron loading by ion-exchange associated with OX.

Conclusions

Pretreatment of oak bark by OX was carried out for subsequent iron-catalyzed low-temperature hydrogasification, and the effect was examined by comparing the results with those attained by DM. Although OX was equal to DM in the ability to remove calcium as a typical poison for iron catalyst, the former could develop porosity in the cell tissue to a greater extent than the latter. As a result, a better dispersion of impregnated iron particles was achieved for OB char, resulting in improved gasification reactivity. OB-Ion char surpassed OB char in reactivity because of much higher dispersion of metallic iron, and it reached a satisfactory gasification level at a small iron loading of 3 wt%. These results were similar to those for previously conducted hydrogasification of larch bark char. In addition, OX, as well as DX, incorporated with prewashing with water was

helpful for decreasing nitrogen and sulfur in oak bark. The excellent reactivity of OB-Ion char containing only slight amounts of these two elements confirmed the high suitability of OX as pretreatment for woody biomass.

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