

# INFLUENCE OF METAL IONS AND PYROLYSIS CONDITIONS ON CARBON DIOXIDE GASIFICATION OF WOOD CHAR

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## INTRODUCTION

The rate of biomass gasification is limited by the reaction rate of the thermally stable char which forms as a result of the initial pyrolytic degradation. This char also represents a large proportion of the energy content of the original biomass (1), and efficient conversion of the biomass should recover the energy value of this fraction. This can be achieved by reaction with oxygen, steam, or carbon dioxide, and the intent of this research was to investigate the effects of reaction conditions and inorganic catalysts on the gasification of wood chars. These chars also provide an excellent model for studying the gasification reactions of coal, since sample pretreatment and pyrolysis conditions can be varied to provide a wide range of chemical functionality in the resulting chars. Studying the chemical structure and reactivity of these chars can provide important insight into parallel reactions in coal and other carbonaceous materials.

Previous work in our laboratory on the gasification of biomass chars indicated that the inorganic species naturally present in wood were effective gasification catalysts (2), and that some of the natural inorganic species were exchangeable with cations of salts added to the wood in solution. We have studied this ion exchange process further and have found that the wood sample used in these studies contains approximately 8 meq/100 g of carboxylic acid groups, primarily as 4-O-methylglucuronic acid groups associated with the hemicellulose fraction of the wood (3). In this study we have added catalysts to previously acid-washed wood through ion exchange in order to incorporate a single catalytic species in a highly dispersed form and at a reproducible level. Selected samples were also treated beyond the ion exchange capacity in order to distinguish the effects of exchanged cations as opposed to adsorbed salts.

## EXPERIMENTAL

The wood sample used in this study was black cottonwood (*Populus trichocarpa*), a low-grade western hardwood. The heartwood and sapwood were separated and the sapwood was the primary sample studied. The wood was ground in a Wiley mill, and the 20/30 mesh fraction was retained for analysis.

Acid-washing ( $H^+$ -exchange) and ion exchange treatments were carried out by column percolation. The wood was degassed in a small quantity of the solution used for ion-exchange and transferred to a glass chromatography column. A 0.01 M solution of the acetate salt of the cation to be exchanged (at least a ten-fold excess) was then washed slowly through the column. The column was washed thoroughly with distilled, deionized water to remove any of the salt which was not bound by ion exchange. In order to add catalytic species beyond the exchange capacity of the wood, the wood was soaked in a 0.01 M solution of the acetate salt and then air-dried. All of the catalyst treatments were carried out using acid-washed wood in order that the treated samples contain only a single catalytic species.

The inorganic constituents of the wood samples were analyzed by inductively coupled argon plasma (ICP) emission spectroscopy, except for nickel which was analyzed by atomic absorption (AA) spectroscopy. Ash contents were determined by thermogravimetry (TG) at 550°C in air.

Chars were prepared in a tube furnace purged with flowing nitrogen. The wood sample was held in a porcelain boat which was pulled into the preheated furnace. After heating for a prescribed time the sample was pulled into a water condenser at the downstream end of the furnace tube, where it was cooled to approximately 10°C before being exposed to the air. Samples were stored in nitrogen- or argon-purged containers.

Cross polarization/magic angle spinning  $^{13}\text{C}$  nuclear magnetic resonance spectrometry (CP/MAS  $^{13}\text{C}$  n.m.r.) of the chars was carried out at the Colorado State University Regional N.M.R. Center.

Gasification was carried out in the gasification reactor/detector system depicted in Figure 1. The reactor consisted of a 1/8" I.D. alumina tube (99.8% alumina) heated by an external nichrome wire coil. The sample (3-10 mg) was confined within a 1.0 cm section of the tube by 1/8" O.D. 4-hole ceramic insulators, which also carried gas flows into and out of the reactor. The lower insulator contained a chromel-alumel thermocouple that extended 3-4 mm into the reactor and provided a reliable measure of the sample temperature throughout the reaction. The reactor was purged with a 30 cc/min flow of  $\text{N}_2$  for inert conditions and an equivalent flow rate of  $\text{CO}_2$  for gasification. Switching of gas flows and reactor temperature were under control of a data acquisition/control system.

Effluent gases from the reactor were mixed with a 10 cc/min air flow, causing the oxygen level of the air flow to be reduced by the stoichiometric quantity of oxygen required for combustion of any combustible gases formed by pyrolysis or gasification of the sample. The oxygen concentration of the combined gas streams was monitored by a 1/4" O.D. zirconium oxide oxygen sensor tube maintained at 900-950°K. This sensor was enclosed in a 1/2" O.D. quartz tube and produced an output proportional to the differential pressure of oxygen across its inner surface (flowing air reference gas) and outer surface (combined reactor and combustion air flows). The output of the oxygen sensor was converted to oxygen concentration during data acquisition according to the Nernst equation:

$$E = \frac{RT}{4F} \ln(P/P_{\text{ref}})$$

where R and F have their usual meanings, T is the detector temperature (°K) and P and  $P_{\text{ref}}$  are the partial pressures of oxygen in the sample and reference gases, respectively.

For the purposes of this study it was assumed that all of the combustible gases produced were CO, and the removal of one molar equivalent of  $\text{O}_2$  from the gas stream was therefore due to the gasification of one molar equivalent of carbon. The extent of gasification determined in this manner was consistently within 10% of the measured change in char weight.

The rate of gasification of a char (HTT 800°C) prepared from cottonwood is shown in Figure 2. The detector output can be integrated over the entire run to give the total extent of gasification, or it can be integrated above the baseline defined by the rate of pyrolytic gasification to give the extent of gasification due to reaction with  $\text{CO}_2$ .

## RESULTS AND DISCUSSION

The ash contents and composition of the inorganic fraction of the samples used in this study are shown in Table 1. The heartwood of the cottonwood has a very high ash content, approximately four times higher than the sapwood taken from the same tree. The main components of the natural inorganic fraction are calcium, potassium, and magnesium; in addition to these elements the lignite sample has a high concentration of iron. All of these elements are potentially active gasification catalysts.

Table 1. Composition of cottonwood, treated cottonwood and lignite samples.

Sample	% Ash	Composition of Ash (% dry weight)						
		K	Mg	Ca	Fe	Co	Ni	Cu
<b>COTTONWOOD</b>								
<u>Untreated</u>								
Heartwood	2.01	0.32	0.08	0.50	--	--	--	--
Sapwood	0.51	0.10	0.02	0.12	--	--	--	--
<u>Ion-exchanged</u>								
<u>Sapwood</u>								
Acid-washed	0.02	--	--	0.01	--	--	n.d. <sup>b</sup>	--
K <sup>+</sup> -exchanged	0.41	0.28	--	0.02	--	--	n.d.	--
Mg <sup>2+</sup> -exchanged	0.17	--	0.09	0.01	--	--	n.d.	--
Ca <sup>2+</sup> -exchanged	0.34	--	--	0.14	--	--	n.d.	--
Co <sup>2+</sup> -exchanged	0.34	--	--	0.01	--	0.23	n.d.	--
Ni <sup>2+</sup> -exchanged	0.33	--	--	--	--	--	0.21	--
Cu <sup>2+</sup> -exchanged	0.42	--	--	--	--	--	n.d.	0.32
<u>Acetate Salt-treated</u>								
<u>Sapwood (0.01 M)</u>								
KAc	0.91	0.38	--	0.02	--	--	n.d.	--
Ca(Ac) <sub>2</sub>	0.83	--	--	0.36	--	--	n.d.	--
Co(Ac) <sub>2</sub>	0.89	--	--	0.01	--	0.40	n.d.	--
LIGNITE <sup>c</sup> (PSOC-837)	11.88	0.04	0.64	1.81	0.39	--	--	--

<sup>a</sup>Ion-exchanged samples were acid washed (H<sup>+</sup>-exchanged) prior to treatment.

n.d. = "not determined"; no value (--) = <50 ppm.

<sup>c</sup>Lignite sample and analysis provided by the Penn State Coal Data Base.

Table 2. Conversion due to pyrolysis (P) and gasification (G) of chars prepared from cottonwood and lignite at various heat treatment temperatures (HTT) and pyrolysis times. Chars were gasified for 30 minutes at 800°C in 90.9 kPa CO<sub>2</sub>.

Sample	HTT (°C)	Time (min)	Char Yield (%)	% Conversion at 800°C		
				P	G	Total
<b>COTTONWOOD</b>						
<u>(Sapwood)</u>						
	800	10	13.1	1.6	32.5	34.1
	900	10	11.5	1.7	30.9	32.6
	1000	10	10.4	1.2	15.9	17.1
	800	5	13.2	3.2	32.9	36.1
	800	30	12.6	1.7	31.9	33.6
	800	60	12.3	1.2	34.0	35.2
<b>LIGNITE</b>						
	800	10	61.5	3.6	66.5	70.1
	900	10	59.0	1.9	51.8	53.7
	1000	10	58.0	1.6	34.7	36.3

Acid-washing of the cottonwood sapwood removed most of the inorganic fraction, with the exception of a small quantity of residual calcium. When the acid-washed wood was treated by ion exchange with dilute salt solutions, the resulting samples contained 7-8 milliequivalents/100g with the exception of the  $\text{Cu}^{+2}$ -exchanged sample, which was treated at the 10 meq/100 g level. This is in agreement with the carboxyl content of 8 meq/100 g found previously for this sample, and indicates that ion exchange provides a high level of control for addition of inorganic cations to wood. The overall ash contents of the treated samples were all lower than that of the untreated sapwood. When the salt solution was dried onto the acid-washed wood without removing the free salts, the level of cation addition was 1.5-2.5 times higher than in the ion-exchanged samples.

Table 2 shows the effects of heat treatment temperature (HTT) and pyrolysis time on the char yields and reactivities of the resulting chars toward  $\text{CO}_2$  gasification at 800°C. The char yields of the wood and lignite do not vary significantly within the temperature range and pyrolysis times studied. However, it is important to notice the differences in char yields between the wood and lignite samples, especially with respect to the concentration of inorganic species in the chars. The char yields from wood suggest that the ash is concentrated by a factor of 7-10, resulting in an ash content of 4-5% in the char. Similarly, the ash content of lignite char would be concentrated to nearly 20% of the weight of the char.

Reactivities of both the wood and lignite chars decreased by a factor of approximately two as the HTT was increased from 800°C to 1000°C. The contribution of pyrolysis to the gas yields in both samples was relatively small and it did not vary significantly under the conditions shown. Lignite char reactivity decreased approximately linearly between 800° and 1000°C. The reactivity declined more sharply above 900°C in the wood sample. This may indicate that one of the natural catalytic species in wood undergoes a specific transformation above 900°C, rendering it inactive, and that the reactivity of wood char is otherwise less dependent on HTT than is that of coal char. The extent of wood char gasification is independent of time of pyrolysis between 5 and 60 minutes. The dependence of reaction rate on HTT found in this study is somewhat less than that reported by Hippo *et al.* for a raw lignite gasified in steam (4). These workers report nearly a three-fold increase in reactivity in steam at 750°C as the HTT is reduced from 900° to 800°C.

The rates shown in Table 2 for the lignite char gasification are similar to data reported previously by other workers for  $\text{CO}_2$  gasification of lignite chars prepared under similar conditions (5,6). Rates of wood char gasification indicate a substantially higher reactivity than reported previously for another lignocellulose-derived char gasified in  $\text{CO}_2$  at 900°C (7). The lignite char was nearly twice as reactive as the wood char over the temperature range studied, which is no doubt due in part to its higher ash content. The lower reactivity of the wood char is also explained in part by the CP/MAS  $^{13}\text{C}$  n.m.r. spectrum of the char prepared by 10 minutes pyrolysis at 600°C, shown in Figure 3. This spectrum contains a single peak centered at 130 ppm, corresponding to aromatic carbon. The spectrum is nearly identical to that of an anthracite coal (8), and anthracite coals have been shown to be more than ten times less reactive than lignite under gasification by  $\text{CO}_2$  (5). Wood chars prepared at higher temperatures contained insufficient hydrogen to provide for transfer of spin polarization to carbon, as required in the cross-polarization n.m.r. technique, and they did not give well-resolved spectra. However, it is clear that chars prepared above 600°C are highly aromatic and their gasification will require effective catalysis if it is to be carried out at lower temperatures. These n.m.r. data are somewhat surprising in view of earlier work on the n.m.r. spectroscopy of wood chars which showed a significant aliphatic component in chars prepared at temperatures up to 400°C (9).

The char yields and reactivities of chars (HTT 800°C) prepared from untreated cottonwood and catalyst-treated samples are shown in Table 3. The catalysts were added by ion exchange to the acid-washed sapwood as described earlier. Acid washing had a dramatic effect on the char yield, reducing it by a factor of more than two. Addition of transition metal and alkaline earth metal catalysts had little effect on the char yield, but the alkali metal catalysts restored the char yield to near the level found for the untreated wood. Acid-washing also resulted in complete loss of the cellular structure of the wood during pyrolysis. All of these effects parallel those reported previously for the effects of inorganic species on the carbonization of the cottonwood (10).

Table 3. Ash content and char yields (HTT 800°C) of untreated and ion-exchanged cottonwood samples and extents of conversion due to pyrolysis (P) and gasification (G) of cottonwood chars gasified for 30 minutes at 800°C in 90.9 kPa CO<sub>2</sub>.

Sample	Ash Content (%, d.a.f.)	Char Yield (%, d.a.f.)	Percent Conversion		
			P	G	Total
Cottonwood Heartwood Untreated	2.01	16.8	(100% in <20 min)		
Cottonwood Sapwood Untreated	0.51	14.8	2	40	42
Acid-washed	<0.02	7.1	2	<1	2
Na <sup>+</sup> -exchanged	0.31	14.0	4	16	20
K <sup>+</sup> -exchanged	0.40	13.9	2	13	15
Mg <sup>+2</sup> -exchanged	0.17	9.4	3	15	18
Ca <sup>+2</sup> -exchanged	0.34	9.7	5	102	107 <sup>a</sup>
Co <sup>+2</sup> -exchanged	0.33	9.5	9	73	82
Ni <sup>+2</sup> -exchanged	0.32	8.0	3	34	37
Cu <sup>+2</sup> -exchanged	0.40	7.3	1	3	4

<sup>a</sup>Percent of conversion determined by integration of combustible gas detector signal was consistently 100-110% of weight of samples which gasified completely.

The most reactive sample was found to be the untreated cottonwood heartwood. The reactivity of this char reflects its higher ash content, and further illustrates the catalytic properties found previously for the natural inorganic fraction (2). The most effective ion-exchanged catalysts were found to be calcium and cobalt, which gave reactivities intermediate between the untreated sapwood and heartwood samples. Chars containing alkali metal catalysts were surprisingly unreactive in view of the excellent catalytic properties of these catalysts for lignite chars gasified in steam (4) and in air (11). Alkali metals are known to be lost during pyrolysis and gasification at these temperatures (12), but the char from potassium-treated wood contained 2.3% of ash by TG, suggesting that a large proportion of the catalyst was retained, at least during char formation.

The catalytic activities of the alkaline earth metals in wood gasification more closely parallel effects reported in the CO<sub>2</sub> gasification of coal char (5). The high catalytic activity of calcium suggests that it is the dominant factor controlling the reactivity of the untreated cottonwood sapwood and heartwood samples (see metals analysis in Table 1).

The transition metals are known to be active catalysts of CO<sub>2</sub> gasification, although they are often deactivated by oxidation during reaction (13). We have previously found this to be the case in the CO<sub>2</sub> gasification of wood chars (HTT 1000°) as well (2). The wide range of reactivities shown in Table 3 for the gasification of wood chars catalyzed by transition metals could, therefore,

represent the inherent activity of the catalyst or the activity of the catalyst under these specific conditions of pyrolysis and gasification. However, the high catalytic activity of the cobalt indicates the potential utility of these catalysts, and we are continuing to investigate the effects of pyrolysis and gasification conditions on catalysis of wood char gasification by cobalt.

The effects of different catalyst treatments are further illustrated by the reaction rate profiles shown in Figures 4-6. Figure 4 shows the rate of CO<sub>2</sub> gasification of char prepared from K<sup>+</sup>-exchanged wood. The rate is nearly constant throughout the reaction, suggesting that the reaction is zero order with respect to the mass of the char. The reaction does not appear to undergo the initial induction period which is often observed in gasification reactions. By contrast, Figure 5 shows that the gasification of the char containing calcium does exhibit an induction period, and the rate decays in a more nearly first order manner following the induction period. The char was completely gasified in this case. A third type of behavior is exhibited in catalysis by cobalt, as shown in Figure 6. In this case the reaction is very rapid at the outset and decays more rapidly than would be expected for a reaction which is first order with respect to the char. The rate approaches zero well before the char is depleted, indicating that the catalyst is being deactivated during reaction, and that a very high level of catalysis could be attained if this deactivation could be avoided.

We have also determined the rates of gasification of chars prepared from wood treated beyond the exchange capacity with the acetate salts of potassium, cobalt and calcium. Gasification rates of these chars are compared to those of the chars from ion-exchanged wood in Figure 7. In all three treatments the reactivity increased at least linearly with the quantity of added catalyst. This implies that the catalyst dispersion afforded by ion exchange is lost during carbonization, or that the catalyst added as the aqueous salt solution was equally well dispersed, presumably on the hydrophilic carbohydrate portions of the wood cell wall.

Loss of dispersion of ion-exchanged catalysts has been conclusively demonstrated in calcium-exchanged coals heated at 1000°C (14). Although the temperatures employed in the current study were somewhat lower, it is possible the same processes occur, and the potential advantage of the ion-exchanged catalyst is lost due to catalyst agglomeration. If this is the case, the relative effectiveness of the ion-exchanged catalyst should be enhanced by reducing the carbonization temperatures, and studies now underway should provide additional information on the nature of these processes.

The most surprising feature of Figure 7 is the dramatic increase in reactivity of chars prepared from wood treated beyond the ion exchange capacity with cobalt acetate. This sample was so reactive that the reaction rate at 800°C could not be accurately measured in our system. The two cobalt-treated chars (HTT 800°C) were therefore gasified at 600°C with similar results, as indicated by the dotted line in Figure 7. It is difficult to envision a mechanism whereby the acetate salt would be a more effective catalyst than ion-exchanged carboxylate salts. It is possible that the two forms of the catalyst decompose to different products, which could have different catalytic activities, although it is not clear at this time what these forms might be. In any case, the catalytic efficiency of the higher level of cobalt treatment is very promising. The reactivity at 600°C is much higher than that found previously for CO<sub>2</sub> gasification at 650°C of wood chars treated with even higher levels of iron and nickel salts (2), and it appears to be less subject to deactivation during gasification. Cobalt has previously been studied with respect to its effects on CO<sub>2</sub> gasification of graphite (13) and a highly carbonized cellulose char (HTT 1000°C) (15). In each case it was found to be similar in effectiveness to nickel and iron catalysts. The results reported here indicate a unique catalytic capacity for cobalt, which may also indicate unique properties of wood chars formed in the temperature range employed in this study.

#### ACKNOWLEDGEMENT

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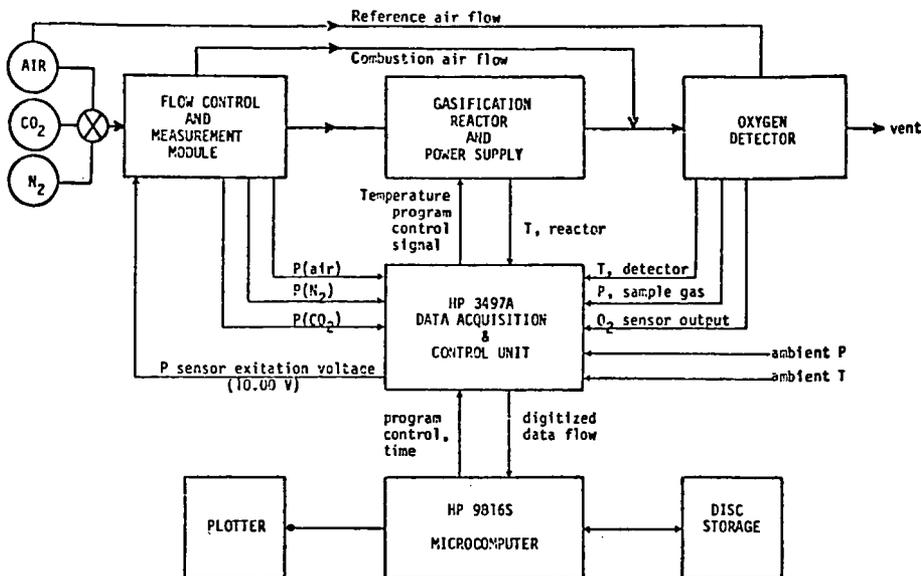


Figure 1. Schematic diagram of gasification reactor and combustible gas detector system.

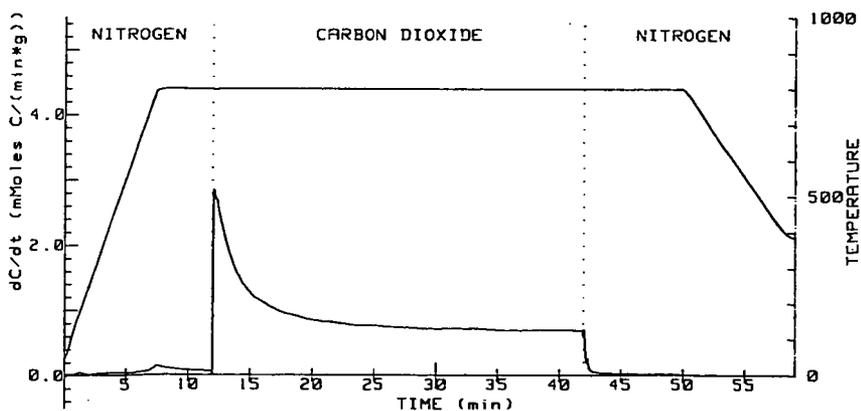


Figure 2. Reaction rate profile for the gasification of untreated cottonwood char in 90.9 kPa CO<sub>2</sub> at 800°C.

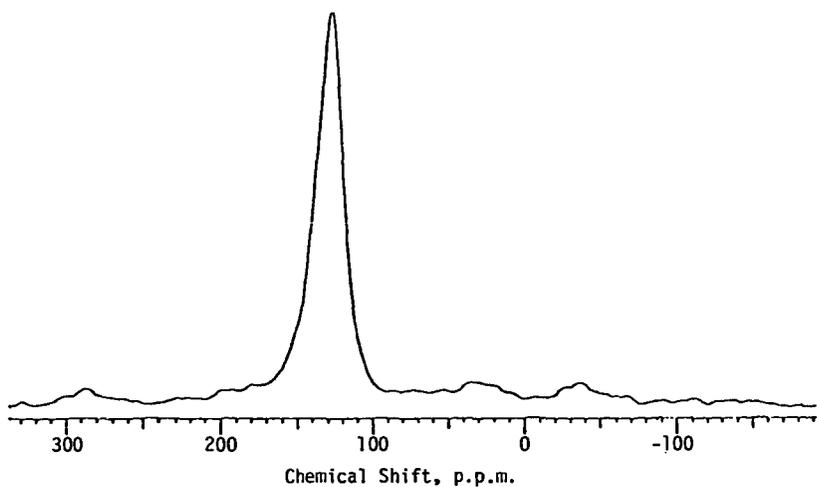


Figure 3. CP/MAS  $^{13}\text{C}$  n.m.r. spectrum of char prepared from untreated cellulose (HTT 600°C).

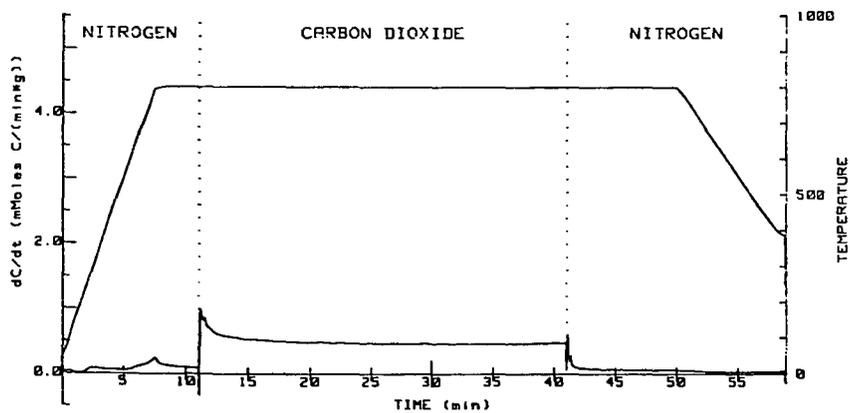


Figure 4. Reaction rate profile for the  $\text{CO}_2$  gasification of char (HTT 800°C) prepared from  $\text{K}^+$ -exchanged cottonwood.

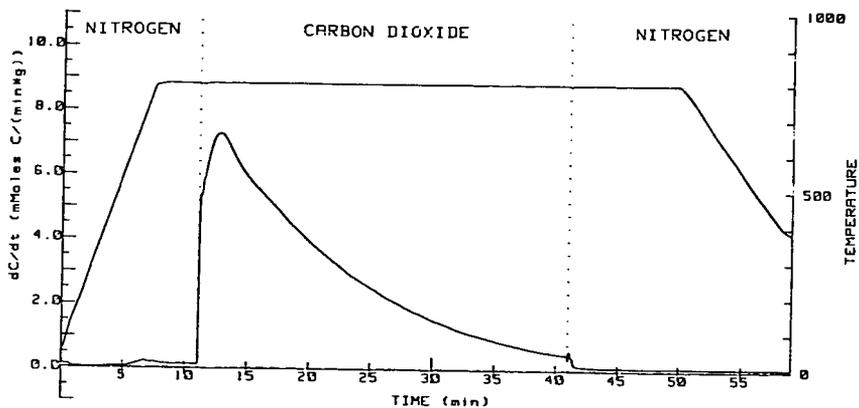


Figure 5. Reaction rate profile for the  $\text{CO}_2$  gasification of char (HTT  $800^\circ\text{C}$ ) prepared from  $\text{Ca}^{+2}$ -exchanged cottonwood.

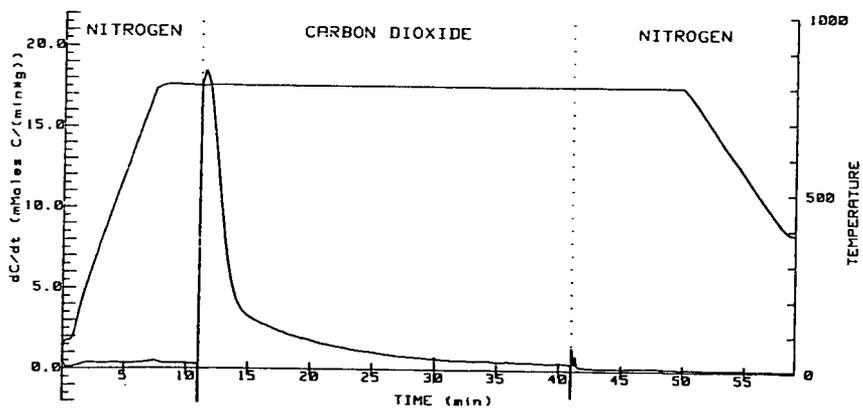


Figure 6. Reaction rate profile for the  $\text{CO}_2$  gasification of char (HTT  $800^\circ\text{C}$ ) prepared from  $\text{Co}^{+2}$ -exchanged cottonwood.

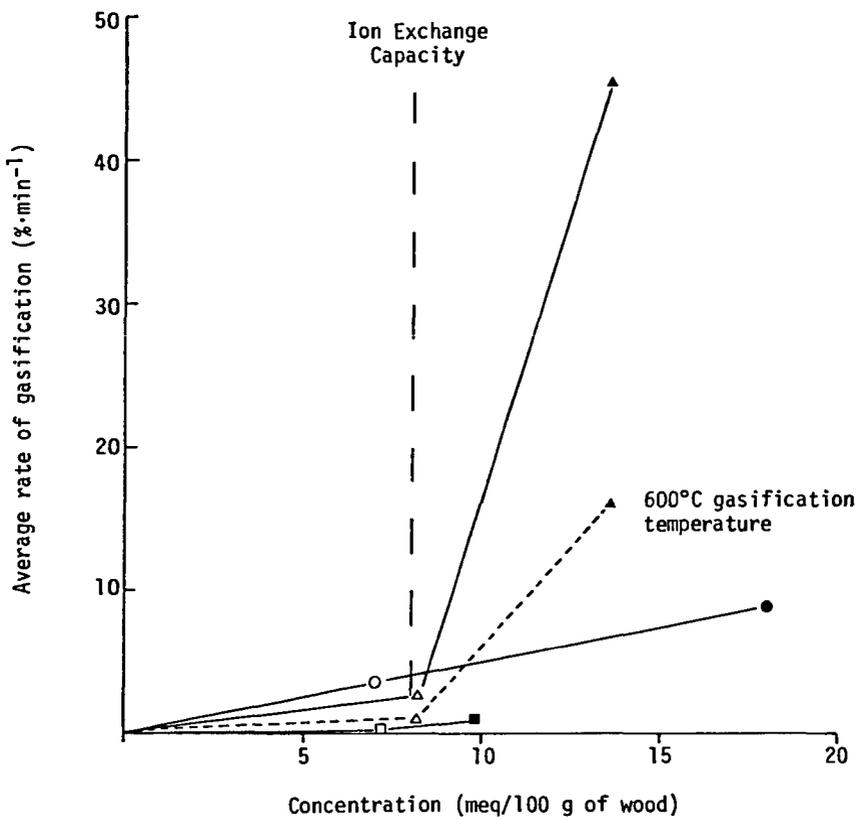


Figure 7. Average rate of  $\text{CO}_2$  gasification at  $800^\circ\text{C}$  of chars prepared from cottonwood treated with inorganic catalysts at the ion exchange capacity (open symbols) and beyond the ion exchange capacity (solid symbols): potassium ( $\square, \blacksquare$ ); cobalt ( $\triangle, \blacktriangle$ ); calcium ( $\circ, \bullet$ ).