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GASIFICATION KINETICS OF CANADIAN COALS AND WOOD IN A FIXED BED REACTOR

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by

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ABSTRACT

The chemical reactivity and kinetics of nine Canadian coals and one wood were examined in a fixed bed gasifier in the presence of air and steam at 950-1000°C. It has been found that the reactivity of coal decreases with increase in the carbon content, but increases with increase in the oxygen content of the parent coal. The reaction velocity decreases with increase in the carbon content of the parent coal.

With the shrinking core model, the coal-steam-air reaction systems have been found to be under chemical reaction control; the wood-steam-air, however, were found to be ash film resistance controlled. It has been also demonstrated that the present reaction system favours the water-gas shift reaction over the carbon-steam reaction as shown by the chemical composition of the product gas from the gasification.

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LA CINÉTIQUE DE LA GAZÉIFICATION DE DIVERS CHARBONS ET BOIS CANADIENS DANS UN RÉACTEUR À LIT FIXE

par

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RÉSUMÉ

On a étudié la réactivité chimique et la cinétique de neuf charbons et bois canadiens dans un réacteur à gazéification à lit fixe en présence d'air et de vapeur, à des températures variant de 950 à 1000°C. On a pu établir que la réactivité du charbon décroît lorsque la teneur en carbone augmente, mais qu'elle augmente lorsque la teneur en oxygène du charbon père augmente. La vitesse de réaction diminue avec l'augmentation de la teneur en carbone du charbon père. A l'aide du modèle de rétrécissement de carottes, on a pu établir que la réaction du charbon avec l'air et la vapeur d'eau est réglée par la chimie de la réaction, alors que la réaction du bois avec l'air et la vapeur d'eau est déterminée par la phénomène de diffusion des cendres. De plus, par l'analyse de la composition chimique des gaz obtenus par gazéification, on a pu démontrer que le système de réaction utilisé dans le cas présent favorise le passage de l'eau en gaz au détriment de la conversion du charbon en gaz.

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CONTENTS

TABLES

FIGURES

For the past several years, the Department of Energy, Mines and Resources Canada has been sponsoring research and development of coal and biomass conversion projects under the National Energy Program. One objective of this program to achieve energy self-reliance for Canada by 1990 is the development of new energy sources and conversion methods. Some of these projects are conducted in-house at the Energy Research Laboratories [1,2] and others are contracted out to the industrial sector[3].

In-house research at the Energy Research Laboratories is directed toward compiling gasification reactivity data for various Canadian coals in a laboratory gasifier. This data will be used to test the technical and economic feasibility of producing specific gaseous products from coals of different chemical reactivities via the gasification process.

The gasification reactivity of Canadian coals and chars at different experimental conditions has been reported previously [1,2,4] Kinetic parameters for these solid fuels have been established and the shrinking core model was used to explain the gasification mechanisms of nine coals and their chars [2,4]. This paper reports new gasification reactivity data for nine Canadian coals and one wood at 950 - 1000°C in the presence of air and steam. Results from this study further strengthen the validity of the shrinking core model for the interpretation for the gasification mechanism of carbonaceous materials. The reactivity data for wood provides a base in the study of the relationship between the reactivity and the carbon content of a solid fuel such as wood, peat, coal and char.

EXPERIMENTAL

Materials

All the samples (3 to 6 mm) were air-dried, then oven dried for two hours at 105°C before use for gasification. Chemical analyses of the coal and wood samples are given in Table 1. The wood sample contained 85 wt% Spruce wood and 15 wt% bark.

Gasification unit

The gasification procedure in a fixed-bed reactor was presented in detail in a previous communication[1]. Briefly, a coal sample (50 g) mixed with Berl saddles as an inert material was gasified in a sample holder which had an opening (6 mm diam.) for the incoming reacting gases at the bottom of the holder. The reacting gas is a mixture of air (2.0 l/min.) and steam (3 g/min. water rate). The gasification temperature ranged from 950 - 1000°C.

Duplicate experiments were carried out for the wood and coal samples. After a gasification run of 30 minutes at atmospheric pressure, the residue in the reactor was cooled with a stream of N_2(0.9 l min.^{-1}) for two hours before it was removed and weighed.

Gas sampling and analysis

A total of 15 samples of the product gas were collected at 2 min. intervals over a period of 30 min. by means of a commercial Valco 16-port valve system. The samples were analysed by a gas chromatograph (Perkin-Elmer Sigma 1) with porapak N and molecular sieve 5A columns. Carrier gas was a mixture of helium and hydrogen with a flow rate of 45 $\text{cm}^3\text{min}^{-1}$ at column temperature programming at a rate of 15°C min^{-1} from 40 to 75°C.

Results and Discussion

The rate of gasification and combustion was calculated from the chemical composition of the coal, concentration and volume of the product gas. In a typical plot of carbon conversion versus time, a maximum conversion of each fuel sample occurs in the linear region at the initial stage of the reaction as shown in Figure 1. The conversion curves for all the coal and wood samples studied exhibit a linear portion which represents about 20 to 60% conversion. The reactivity, R , can be calculated from the maximum slope of the conversion curve with the following equation [2]:

$$R = -\frac{1}{W}\left(\frac{dc}{dt}\right) \qquad (1)$$

R is the maximum reactivity, g/h/g, W the initial mass of coal sample on a dry ash free basis and dc/dt the carbon weight loss rate, g/h.

Using equation (1), the maximum reactivities of 9 Canadian coals and one wood were determined. The reactivities varied from 4.11 to 0.36 g/h/g from wood to semianthracite under the gasification condition used in this study. In general, the chemical reactivity decreases with increase in the carbon content or the rank of the parent coal [2,5,6,7] (Figure 2a). This finding is in agreement with two previous gasification studies of coals and chars under different experimental conditions [2,4]. The low reactivity of the higher rank coal is attributed to poor utilization of the small surface area in the micropores during the gasification reaction[7]. In contrast, the higher reactivity of the lower rank coals is believed to be due to the larger pore volume which provide better utilization of the micropore surface area for the reaction[6].

Since the oxidation reaction of the carbonaceous material is involved in the present coal-steam-air gasification system, the oxygen content of the parent coals and wood will influence the chemical reactivity of the material and the rate of the gasification. As can be seen in Figure 2b the reactivity of the carbonaecous material has been found to increase with increase in the oxygen content[8] of the parent coals and wood. It has been demonstrated that addition of oxygen to the steam gasification reaction enhances the chemical reactivity of the higher ranking coals when compared to a similar study at 800 - 840°C with a higher oxygen content[2].

Chemical composition of product gas

The chemical composition of the product gas from the present air-steam gasification at 950 - 1000°C of nine coals and wood at constant condition

.../4

are listed in Table 2. Hydrogen, carbon dioxide and carbon monoxide are produced in a relatively large amount from all the samples studied. These results suggest that the major reactions involved in the gasification are as follows:

$$C + H_2O \rightarrow CO + H_2 \qquad (A)$$

$$CO + H_2O \rightarrow CO_2 + H_2 \qquad (B)$$

It is believed that these two reactions are taking place at the solid-gas interface. The second reaction may also occur in the gas phase.

The effect of the carbon content of the parent coal on product gas (H_2, CO_2, CO and CH_4) can be seen in Table 2. Since the methane formation from the carbon-steam reaction at atmospheric pressure is not thermodynamically favourable, its formation is therefore independent of the carbon content of the coal. In general, carbon dioxide formation increases somewhat with increase in the carbon content of the coal but decreases with increase in the oxygen content of the parent coal. However, hydrogen formation decreases slightly with increase in carbon content of coal. In contrast, the carbon content does not have any effect on the carbon monoxide formation until it reaches 87 wt% as in the case of the Devco coal. Thereafter, carbon monoxide formation increases with increase in the carbon content of the coal.

The molar ratio of CO_2/CO increases as the carbon conversion increases and this ratio varies from 0.5 to 2.0 for temperature 950 - 1000°C (Figure 3). This may suggest that the water-gas shift reaction (Reaction B) is more predominant than the carbon - steam reaction (Reaction A) for the present reaction system. The predominance of the water-gas shift reaction over the carbon-steam reaction has also been observed in a previous study[2].

Reaction Kinetics

When the rates of diffusion through a fluid-film and a porous solid are both very fast, the overall rate of a solid-fluid reaction is entirely controlled by the inherent chemical reactivity of the solid reactant [2,9]. Since the reactions between coal-steam and coal-oxygen are controlled by the chemical reactivity, the shrinking core model [2,9,10,11] can be used for the interpretation of the present conversion data of coals and wood.

..../5

In the shrinking core model, where chemical reaction is the rate controlling step, the following equation can be applied [9,11].

$$t/t^* = 1-(1 - X)^{1/3} \qquad (2)$$

where t is the reaction time, X the carbon conversion fraction and t* the time for complete conversion as defined by the following equation

$$t^* = RC_{so}/KP^n \qquad (3)$$

in which R, C_{so}, K and P are mean radius (cm) of the particles, initial concentration (mole cm^{-3}) of carbon, specific velocity per reaction surface (mole $cm^{-2} atm^{-n} min^{-1}$) and pressure (atm) respectively. When ash film resistance is the controlling step, the following equation can be applied:

$$t/t^* = \left[1 - (1 - X)^{1/3}\right]^2 \qquad (4)$$

It can be determined from equation (3) and (4) that, when a log-log plot of $\left[1 - (1 - X)^{1/3}\right]$ versus t is made, the slope of the line determines whether the reaction is chemical controlling or ash film resistance controlling. If a straight line is obtained with a slope of unity, the chemical reaction is a rate controlling step. A slope of 2 indicates that the reaction is controlled by ash film resistance.

Figure 4 is a log-log plot of the reaction time t versus $\left[1 - (1 - X)^{1/3}\right]$. The solid lines represent model lines. It can be seen from this figure that the carbon conversion data points of the coals fall on the lines all of which have a slope of one. This indicates that the gasification reaction of the coal is chemical reaction controlling. On the contrary, the slope of the line for the carbon conversion of wood is two and the reaction is controlled by ash film resistance. This means that the gasification mechanism for wood is different from that of coal in which chemical reaction control predominates. One may say that the char ash layers formed during wood gasification increase diffusion resistance to the reacting gas passing through the layers as postulated by the shrinking core model[9].

.../6

The value of t* for each sample can be obtained by extrapolation of the model lines to complete conversion ($X = 1.0$) in Figure 4. From the t* values, the specific reaction velocity per reaction surface, K, of each sample, can be determined from equation (3) with the knowledge of R, C_{so} and P. It can be seen from Figure 5 that the specific reaction velocity K of the coal samples decreases with increase in the carbon content of the parent coal.

Figure 6 is a model line plot between the carbon conversion fraction X, and the reaction time, t, of the coal and wood samples studied. The carbon conversion was calculated from equations (2) and (3) using the t* value (in bracket) extrapolated from the plot in Figure 4. One can see that there is agreement between the experimental data points and the model (Figure 6). This agreement leads us to believe that the shrinking core model can be utilized for predicting the carbon conversion with the knowledge of the time for complete conversion t*, for various coal and wood samples.

.../7

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..../8

TABLE 1 - Chemical Analysis of Coal Samples (moisture free)

Coal (Rank)	Proximate Analysis (wt %)			Ultimate Analysis (wt %)				
	Ash	Volatile Matter	Fixed Carbon	C	H	S	N	O^a
Canmore (semi-anthracite)	15.1	11.9	73.0	78.6	3.6	0.8	1.5	0.4
McIntyre (low volatile bituminous)	8.2	18.1	73.7	83.1	4.3	0.6	1.2	2.6
Devco (high volatile bituminous)	2.9	35.4	61.7	84.7	5.6	1.3	1.3	4.2
Byron Creek (med. vol. bituminous	15.3	26.2	58.5	74.4	4.3	0.8	1.2	4.0
Prince (high volatile bituminous	15.6	43.6	49.8	66.0	4.5	4.9	1.4	7.6
Coalspur (sub-bituminous B)	9.5	37.1	53.4	71.9	4.7	0.2	1.1	12.6
Bienfait (lignite)	12.5	41.4	46.1	66.1	2.2	0.6	1.3	17.3
Coronach (lignite)	13.4	43.5	43.1	61.1	3.6	1.1	1.0	19.8
Onakawana (lignite)	26.8	40.0	33.2	49.7	3.3	5.4	0.7	14.1
Wood	1.7	76.4	21.9	50.5	5.3	0	0.1	42.4

[a] Determined by difference

.../9

Table 2 - Chemical Composition of Product Gas from Steam Gasification

Sample	Chemical composition, vol % (N_2 free basis)				
	H_2	O_2	CH_4	CO_2	CO
Canmore	36.1	2.3	0.3	32.2	29.1
McIntyre	39.3	2.0	0.3	33.5	23.9
Devco	43.3	1.9	1.4	33.1	20.3
Byron Creek	35.1	2.5	0.6	38.9	22.8
Prince	37.3	1.7	1.0	38.6	21.4
Coalspur	53.5	0.8	1.6	25.2	18.9
Bienfait	52.9	0.0	1.5	25.0	20.6
Coronach	48.6	0.7	0.7	28.0	22.0
Onakawana	51.5	0.0	1.5	25.0	22.0
Wood	49.2	0.8	0.8	27.9	21.3

..../10

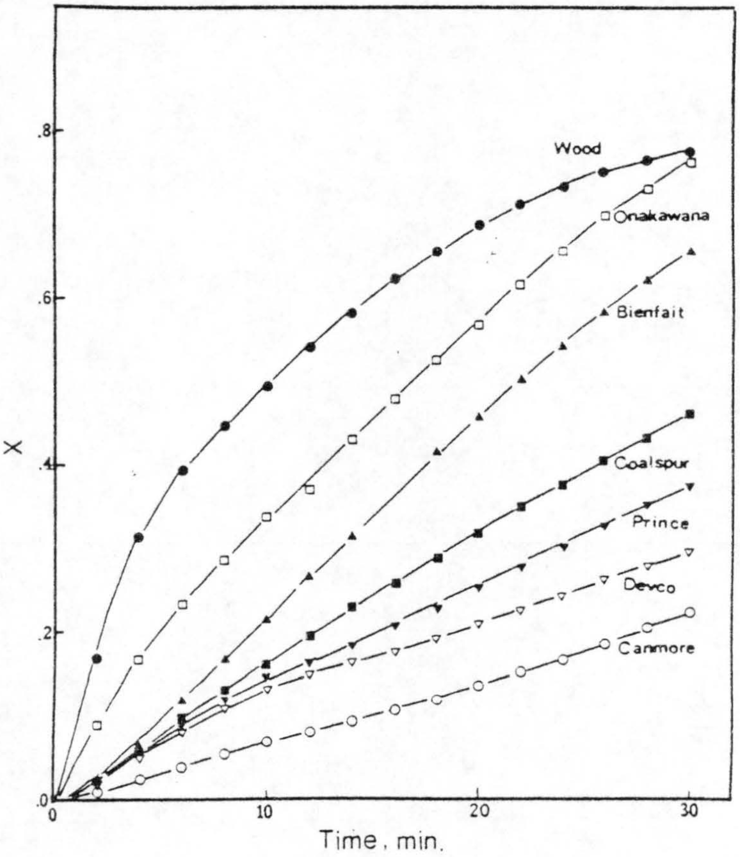

Figure 1. Carbon Conversion of Coals and Wood with Reaction Time at 950°C - 1000°C.

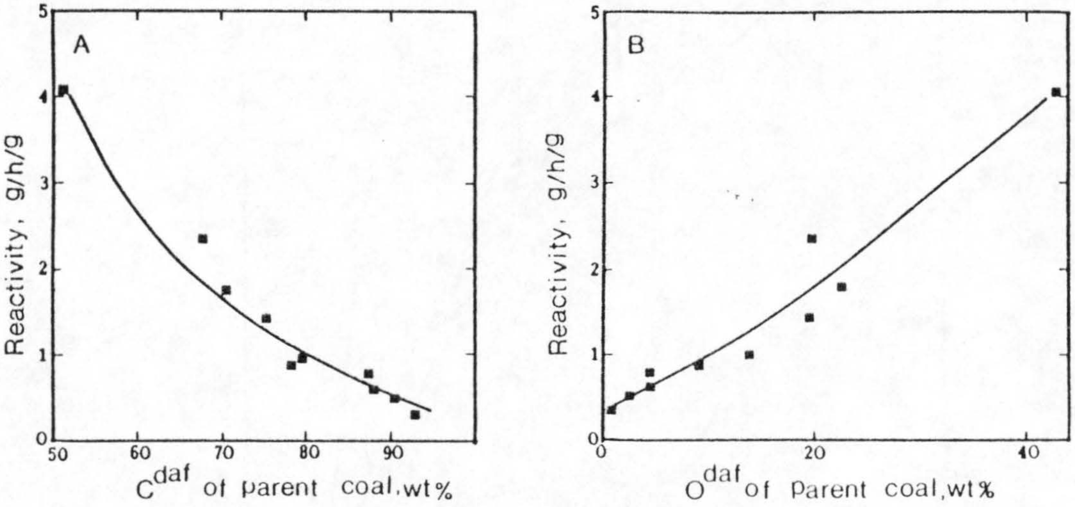

Figure 2. A) Correlation between Reactivity of Coals and Wood and Carbon Content of Parent Coal

B) Correlation between Reactivity of Coals and Wood and Oxygen Content of Parent Coal

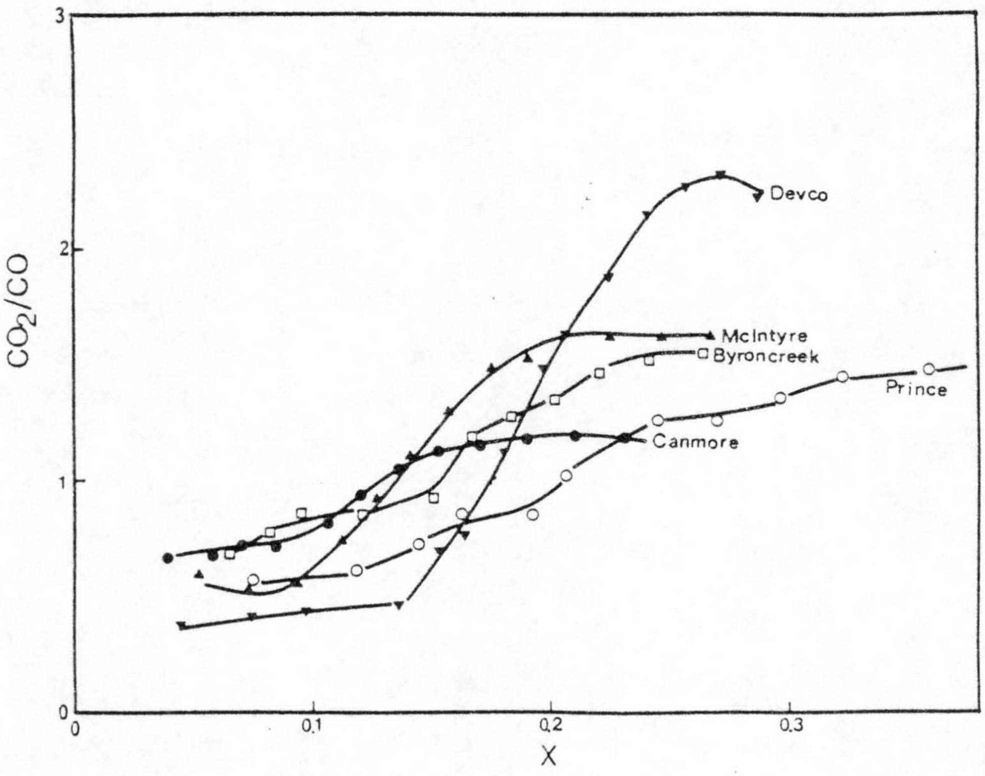

Figure 3. Composition of Product Gas as function of Conversion

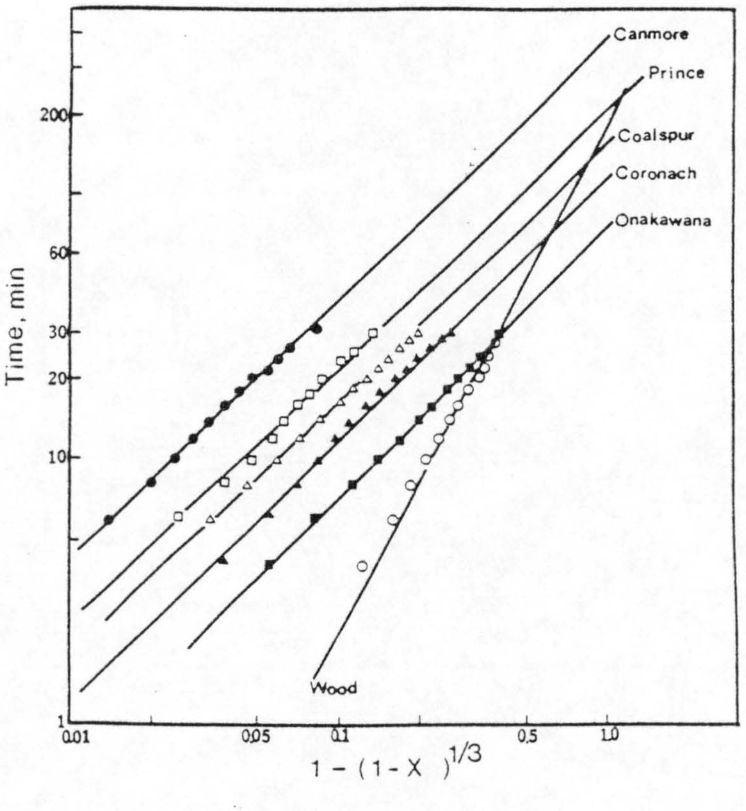

Figure 4. Carbon Conversion versus Reaction Time in the Shrinking Core Model

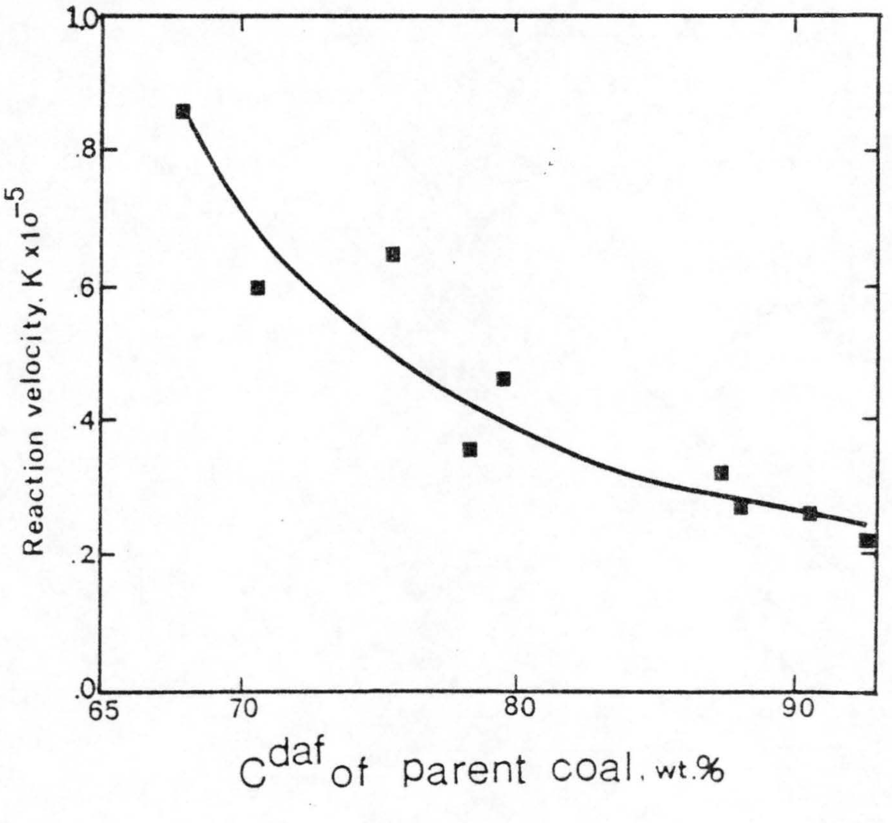

Figure 5. Correlation Between Reaction Velocity of Coals and Carbon Content of Parent Coal.

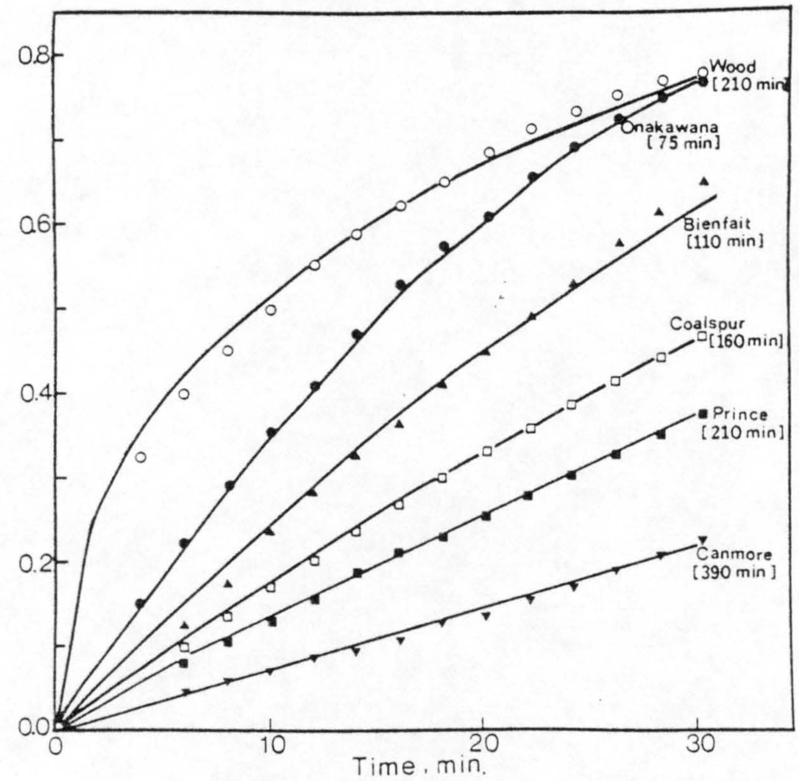

Figure 6. A Comparison of the Model and Experimental data On Carbon Conversion.