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### CATALYTIC BIOMASS GASIFICATION BY THERMOGRAVIMETRY

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## CATALYTIC BIOMASS GASIFICATION BY THERMOGRAVIMETRY

by

M.V.C. Sekhar\*

### ABSTRACT

Results of gasification of a wood waste from a pulp mill debarking process are described. Experiments were carried out with and without a gasification catalyst and at atmospheric pressure between 500 and 1000°C. The gasification process was followed by thermogravimetric measurements and the product gases were analyzed by infrared and thermal conductivity techniques. Gasification in the presence of steam increased the gas production by converting some of the intermediate devolatilization products to CO and H<sub>2</sub>. The potassium carbonate catalyst lowered the activation energy of the steam-carbon reaction from 121.8 to 93.4 kJ/mol.

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## INTRODUCTION

The concept of converting biomass to other energy forms, although not new, is appropriate to the times. It is estimated that the waste wood generated by lumber operations in Canada amount to 12 million tons per year (1), equivalent to 36 million barrels of crude oil or about 5-6% of Canada's crude oil use. It thus represents an important source of energy and if proper technologies are developed for its use, can make a significant contribution to our energy needs.

Conversion of this biomass to useful forms of energy can be accomplished by a number of processes such as pyrolysis, gasification and hydrogasification (2,3). Biomass offers many advantages for conversion to fuel for gas or oil furnaces or transportation.

Unfortunately, the synthetic gaseous and liquid fuels produced by these conversion processes are very expensive. A major factor responsible for this high cost is the high capital charges in building complex equipment and high operating costs necessitated by the high operating temperatures and pressures. However, suitable catalysts can lower the gasification temperatures and reduce reactor sizes, resulting in lower costs for the entire operation. This paper discusses results of catalytic and non-catalytic gasification of biomass to produce carbon monoxide and hydrogen.

## EXPERIMENTAL

The biomass material gasified in this study was a residue obtained from the Forest Engineering Research Institute of Canada, Pointe Claire, Quebec. This residue was the waste material stripped from full tree chips (consisting of equal amounts of white spruce and balsam fir) during the technical process known as debarking. It had an overall bark content of 70%. An analysis of this sample on a moisture free basis is given in Table I.

Potassium carbonate was used as the gasification catalyst. Two modes of catalyst addition were tested. In the first method, experiments were performed using a mechanical mixture of the dry catalyst and the biomass sample. The second method was an impregnation procedure, in which an aqueous

solution of  $K_2CO_3$  was prepared and the biomass soaked in this solution and dried overnight at  $60^\circ C$ . In both methods the catalyst concentration was in the range 8-12% by weight of the biomass.

A semi-batch reaction system was used to study the pyrolysis and gasification rates (4). Samples of biomass (with and without the catalyst) in the range 100-200 mg were placed in a cylindrical quartz basket, which was suspended from the weighing mechanism of a Cahn RG Electrobalance. A stream of nitrogen flowed through the hangdown tube containing the sample and carried away the products of gasification. Steam was added as a nitrogen-steam mixture produced by bubbling nitrogen through a trap filled with distilled water and maintained at  $23^\circ C$ . All the experiments were carried out at atmospheric pressure and at total gas flow rates in the range  $180-220 \text{ mL}\cdot\text{min}^{-1}$ . The hangdown tube was surrounded by a tubular furnace and the gasification temperature was varied in the range  $500-950^\circ C$ . Both the sample weight and the temperature of the interior of the hangdown tube were monitored and recorded continuously.

The products leaving the reactor tube were passed through a series of traps maintained at dry ice temperature to remove water vapour and condensables. The dried gases were then passed through a thermal conductivity cell and a Wilks Infrared Analyzer. The signal from the thermal conductivity cell measuring the overall thermal conductivity was correlated with the hydrogen concentration in the mixture while the IR analyzer was used to monitor CO concentrations. The products were also qualitatively analyzed at intervals by gas chromatography.

At the start of each experiment, the air in the apparatus was purged with dry nitrogen for two hours. After ensuring by gas analysis that the air had been removed, the furnace was moved into position and heating initiated. For those experiments where char gasification rates were determined, the sample was heated in the absence of steam to a final temperature of  $950^\circ C$  and maintained at that temperature until the sample had attained a constant weight. Next the furnace temperature was lowered to the desired value and char gasification initiated by introducing steam-nitrogen mixture. In all other experiments, the steam-nitrogen mixture was introduced at the beginning.

## RESULTS AND DISCUSSION

Wood, like coal, is a multi-component solid and its gasification therefore involves a number of different reactions which might be occurring simultaneously. The thermal decomposition of wood, in the absence of any reactive gases such as steam or air yields a gaseous, a liquid (tar) and a solid product. The gases evolved include  $\text{CO}_2$ ,  $\text{CO}$ ,  $\text{H}_2$  and small amounts of  $\text{CH}_4$  and higher hydrocarbons (5-7). If these primary pyrolysis products are not removed immediately from the hot reactor they undergo secondary reactions to form additional  $\text{CO}$ ,  $\text{CO}_2$ ,  $\text{H}_2$ , tars and char. In the presence of reactive gases, the products of the primary and secondary reactions undergo further reactions with these gases to form more  $\text{CO}$ ,  $\text{CO}_2$  and  $\text{H}_2$ .

Figure 1 shows the weight of the sample as a function of temperature with and without added steam. The solid curve represents the pyrolytic processes occurring in the system and accounts for the 80% weight loss observed. The bulk of this weight loss, as much as 65%, occurs at temperatures below  $500^\circ\text{C}$ . In the presence of steam, the weight vs. temperature curve is not appreciably different until a temperature of about  $800^\circ\text{C}$  is attained, above which the char-steam reaction begins, resulting in further weight loss.

Figure 2 shows the concentration of carbon-monoxide in the product gases as a function of time for the same set of experiments as in Figure 1. There is a five-fold increase in the amount of  $\text{CO}$  formed when the sample was heated in a steam-nitrogen mixture.

The two curves in Figure 3 show the reaction profile for gasification of the char residue by steam at constant temperature. For both cases shown in this figure, the samples were heated initially to  $950^\circ$  in the absence of steam till no further loss in weight was observed. It is apparent from the figure that the catalyst increases the reaction rate and reduces the total time required for complete gasification. Thus, after 70 min at  $865^\circ\text{C}$ , the catalyzed gasification is virtually complete whereas in the uncatalyzed case only 50% of the char has been gasified.

The mode of addition of catalyst was found to be unimportant, the catalyst being equally effective whether added as a dry powder or impregnated as an aqueous solution. In view of this, some experiments were performed using the residue from a previously catalyzed experiment to catalyze the gasification. As can be seen from Figure 4, the weight-loss patterns using recycled catalyst is very similar to the result obtained with fresh catalyst. It is therefore possible to recycle the used catalyst along with the ash residue without appreciable loss in activity. Similar results have been observed recently by Sealock et al. (8).

The effect of the catalyst in the gasification with steam becomes more apparent as shown in Figures 5 and 6. The presence of catalyst does not appreciably affect the pyrolytic portion of the weight-loss curve. However, the amounts of CO and H<sub>2</sub> formed differ appreciably as seen in Table II. At a temperature of 875°C and with no catalyst present about 45% of the total carbon present in the sample is converted to CO, whereas in the presence of a catalyst about 59% of the carbon appears in the form of CO.

The catalytic effect is also more apparent when one considers the total time required to completely gasify the biomass material. At 760° with no catalyst it takes 360 min to gasify the biomass leaving behind only the ash residue, whereas the catalyst reduces this time to 160 min. At approximately 875°C, these times reduce to 108 and 92 min (Table II).

Figure 7 is an Arrhenius plot showing the effect of temperature on the char-steam reaction rate. The data for this figure were obtained from experiments in which the samples were pyrolysed initially in the absence of steam, followed by gasification of the char according to the reaction:



Assuming the reaction to be of first order with respect to carbon and of order n with respect to H<sub>2</sub>O, (9), the rate of the reaction is given by:

$$\text{Rate} = - \frac{d[C]}{dt} = k_1 [H_2O]^n [C] \quad (2)$$

$$= k [C] \quad (3)$$

$$\text{where } k = k_1 [H_2O]^n$$

Since steam was present in excess in all the experiments the water concentration can be assumed to remain constant and  $k$  becomes a pseudo first order rate constant. Integrating equation 3 and taking logarithms, one obtains:

$$k = \frac{1}{t} \ln \frac{[C]_0}{[C]} \quad (4)$$

where  $[C]_0$  and  $[C]$  represent the concentrations of the char carbon at  $t=0$  and  $t=t$  respectively.  $[C]_0$  and  $[C]$  are related to the weight of the sample according to:

$$[C]_0 \propto (W_0 - W_\alpha) \quad (5)$$

and

$$[C] \propto (W_t - W_\alpha) \quad (6)$$

where  $W_0$ ,  $W_t$  and  $W_\alpha$  refer to the weight of the sample at  $t=0$ ,  $t=t$  and  $t=\infty$  respectively. Substitution of these values for  $[C]$  and  $[C]_0$  in equation (4) followed by rearrangement gives:

$$\ln (W_t - W_\alpha) = \ln (W_0 - W_\alpha) - kt \quad (7)$$

A plot of  $\ln(W_t - W_\alpha)$  vs.  $t$  gives a straight line having a slope of  $-k$ . These rate constants obtained at different temperatures are related by the Arrhenius equation:

$$\ln k = \ln A - \frac{E}{RT} \quad (8)$$

where  $T$  is the absolute temperature,  $R$  the gas constant and  $A$  and  $E$  the Arrhenius parameters. The slopes of the dotted and the solid lines in Figure 7 give the activation energies for the catalyzed and uncatalyzed reactions respectively. The catalyst lowers the activation energy of the steam-carbon reaction from 121.8 to 93.4 kJ/mol.

## CONCLUSIONS

The work described here has shown that  $K_2CO_3$  is an effective catalyst in the gasification of forest product wastes. At temperatures below  $700^\circ C$ , the rate of thermal conversion of the biomass to gaseous liquid and solid products is not influenced by the  $K_2CO_3$  catalyst or steam. With steam, the rate of decomposition markedly increases at temperatures above  $700^\circ C$  due to the onset of the steam-carbon reaction. Either steam or a  $K_2CO_3$  catalyst however, causes major changes in the product distribution. Both increases the selectivity for the formation of CO and  $H_2$ . The catalyst is equally effective whether added as a dry powder or impregnated as an aqueous solution; the catalyst can therefore be recovered along with the ash residue and reused without further treatment.

## ACKNOWLEDGEMENTS

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#### CAPTIONS TO FIGURES

- Figure 1: Thermogravimetric curves in  $N_2$  and  $N_2$ -steam mixture
- Figure 2: CO concentration in off-gas as a function of time. No corrections have been made for dispersion effects during the flow of gases from the reactor to the sample cell.
- Figure 3: Effect of catalyst on gasification of char with steam. Time was arbitrarily set at  $t=0$  when gasification was initiated.
- Figure 4: Comparison of the catalytic effects of fresh and recycled catalyst on char gasification.
- Figure 5: CO concentration in off-gas as a function of time.
- Figure 6:  $H_2$  concentration in off-gas as a function of time.
- Figure 7: Arrhenius plot of the pseudo first order rate constant for steam-char reaction vs. inverse temperature.

#### CAPTIONS TO TABLES

- Table I: Analysis of the dry biomass sample, wt %
- Table II: Comparison of the effects of catalyst in the gasification in presence of steam.

TABLE I

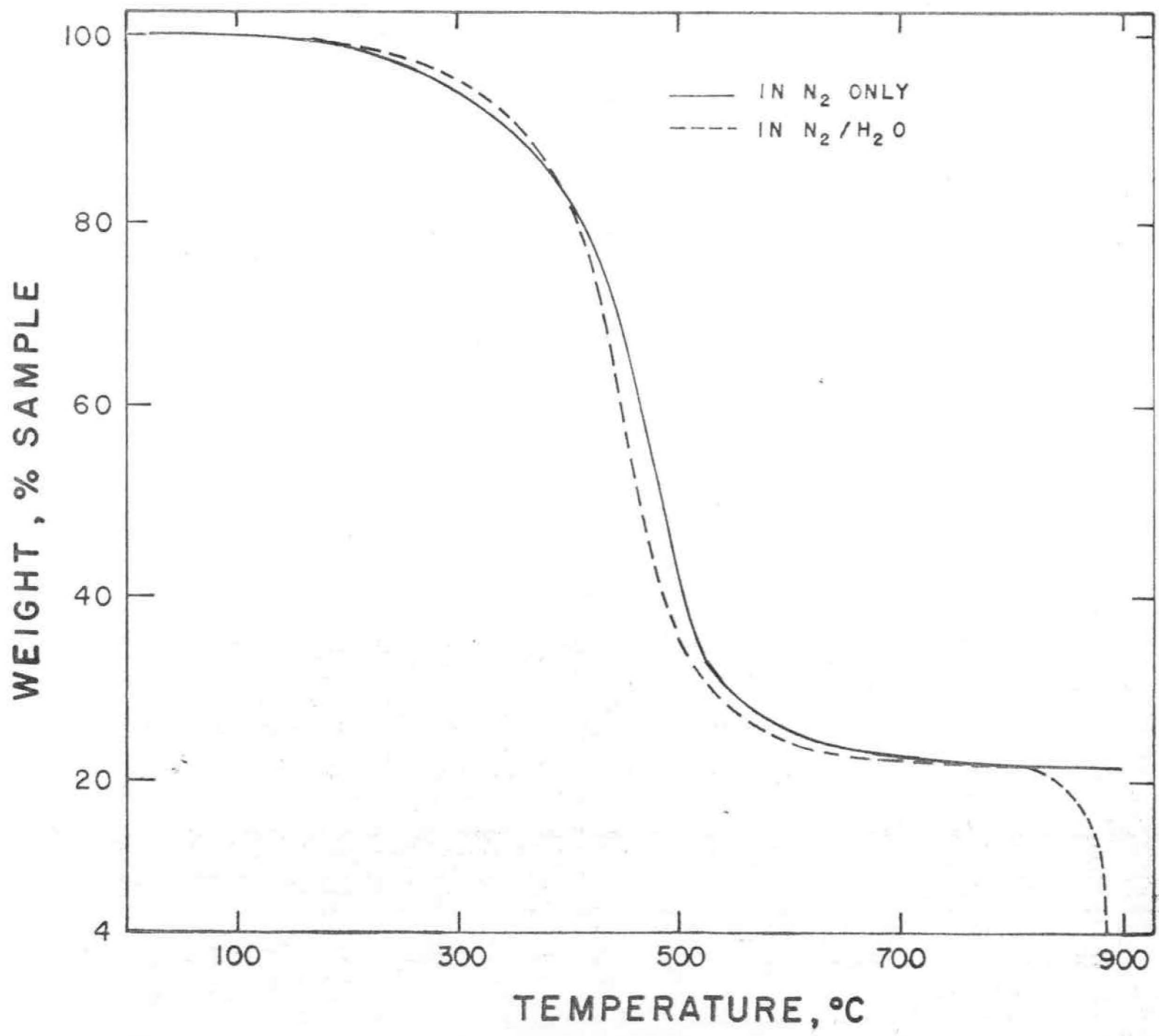
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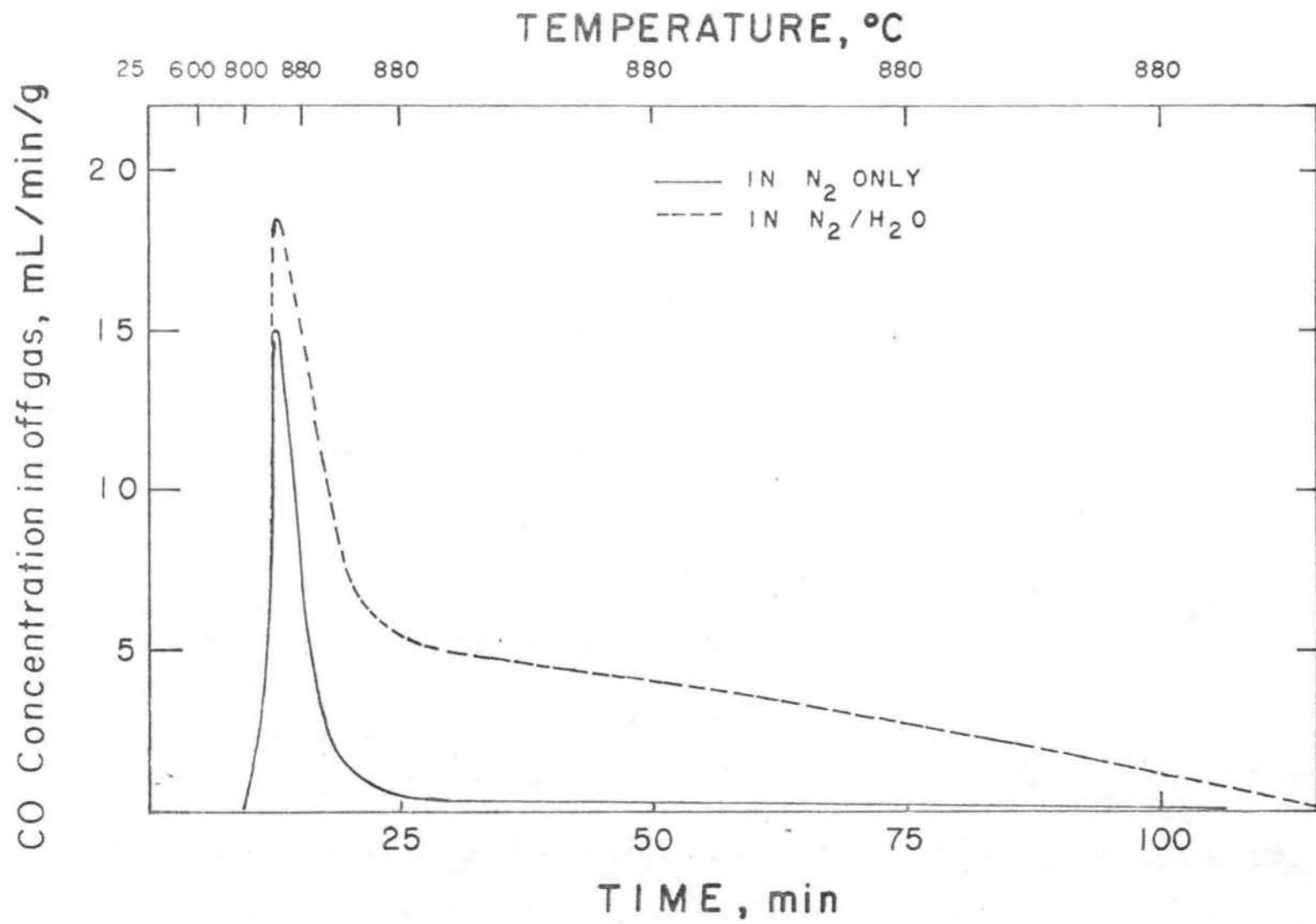
<u>Proximate Analysis</u>	
Volatiles	77.4
Fixed Carbon	19.1
Ash	3.5
<u>Ultimate Analysis</u>	
Carbon	51.2
Hydrogen	5.8
Sulphur	0.1
Nitrogen	1.1
Ash	3.5
Oxygen (by diff.)	38.3

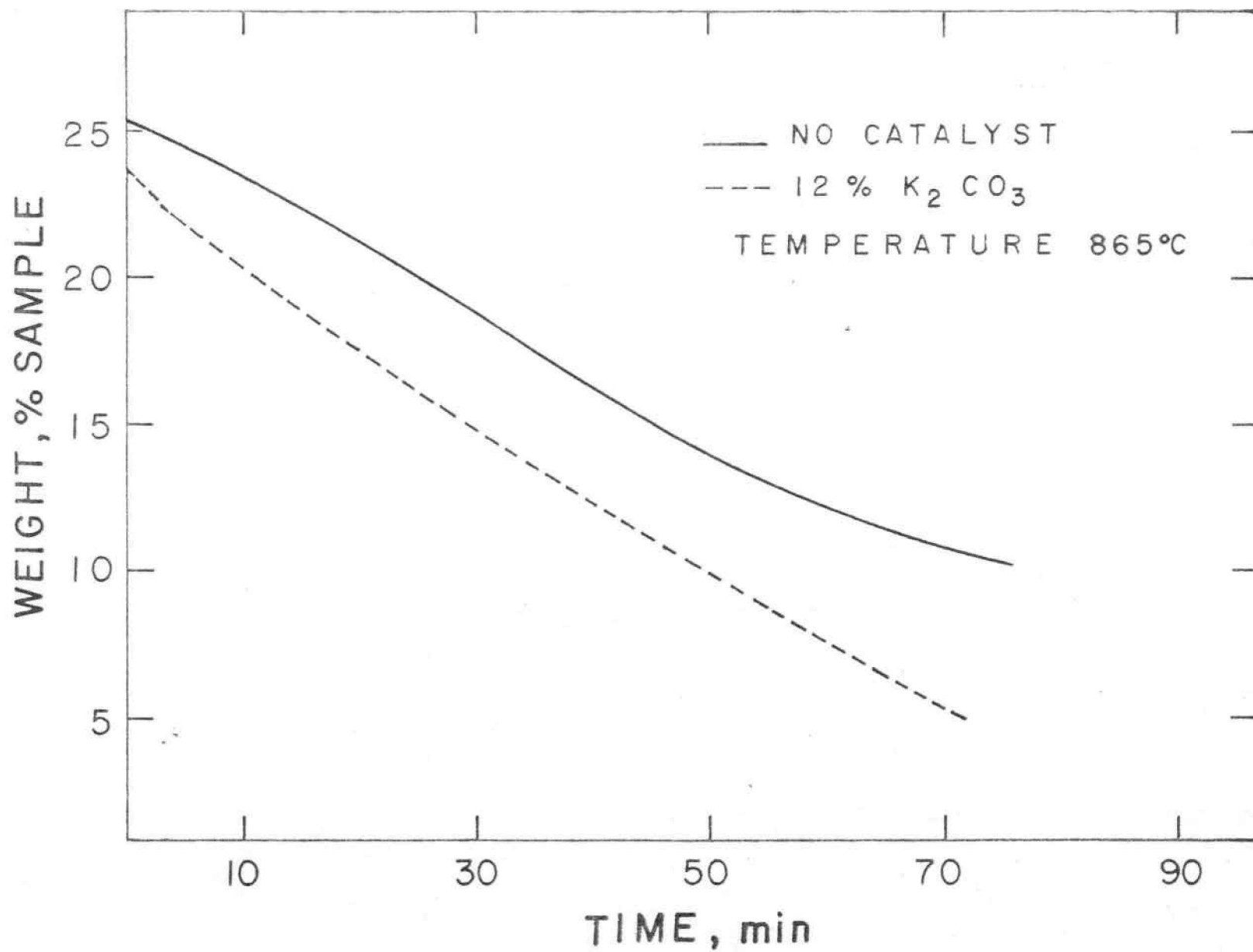
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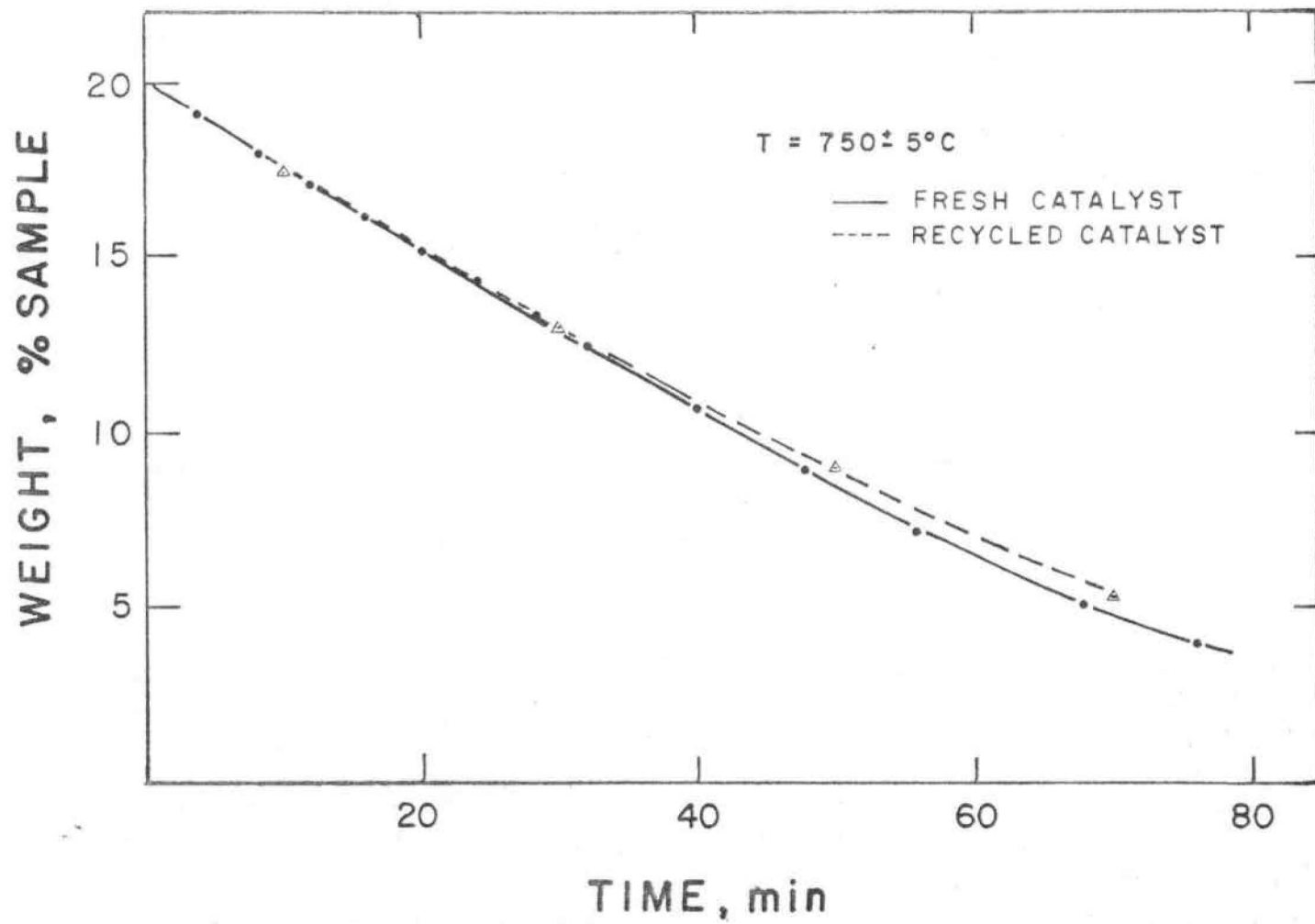
TABLE II

	No. 29	No. 31
Catalyst	nil	10 wt %
Total Loss, wt %	96.7	96.4
Fraction of Carbon Converted to CO	0.45	0.59
Amount of Hydrogen (millimole/g sample)	19.3	25.2
Final Temperature, °C	882	867
Time taken for Complete Gasification, min	108	92









# TEMPERATURE, °C

25 450 630 700 750 750 750 750

