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### THERMOGRAVIMETRIC STUDIES ON CATALYTIC AND NON-CATALYTIC PYROLYSIS OF PITCH DERIVED FROM HYDROCRACKED ATHABASCA BITUMEN

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THERMOGRAVIMETRIC STUDIES ON CATALYTIC AND NON-CATALYTIC  
PYROLYSIS OF PITCH DERIVED FROM HYDROCRACKED ATHABASCA BITUMEN

by

M.V.C. Sekhar\* and M. Ternan\*\*

ABSTRACT

The pyrolytic behaviour of a hydrocracked vacuum residuum was studied in an inert atmosphere in the presence and absence of an alumina catalyst, using thermogravimetric techniques. The non-catalysed pyrolysis proceeded in two stages. The first half of the pyrolysis obeyed overall first order kinetics while in the second half the kinetics became complex. When the gamma alumina catalyst was used, the total yield of distillate products increased. In addition the catalysed reaction was first order with respect to the reactant throughout the entire pyrolysis. In the first-order regime of both the catalytic and non-catalytic pyrolysis, the activation-energy and the pre-exponential factor increased with increasing extent of reaction. This was explained in terms of a compensation effect between the two Arrhenius parameters.

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## INTRODUCTION

The increasing demand for oil and gas coupled with the predicted decline in their supply, has in recent years stimulated research into the development of means and techniques for better utilizing the raw materials already available. For a number of years our laboratories (1) have been engaged in developing processes for upgrading the bitumen recoverable from the large oil-sands deposits of the Athabasca basin in northeastern Alberta, Canada. The main objective of the upgrading process is to effect molecular weight reduction and thereby convert the (50%) non-distillable residue to distillate hydrocarbons. Studies on hydrocracking processes (2) have shown that it offers a significant improvement over conventional coking processes for upgrading the bitumen, with 10 to 15% higher yields of usable liquid products. However, the hydrocracking process also produces 5 to 10% of non-distillable pitch, boiling above 525°C. Optimum use of the oil sands resource requires the utilization of this pitch by-product, in accordance with environmental constraints.

The pitch material contains sulfur, finely divided minerals and organo-metallic vanadium and nickel. Combustion of the pitch is one method of making use of its energy content. Unfortunately combustion processes will produce large quantities of sulphur dioxide which are environmentally unacceptable. One alternate option for utilization of pitch may be to gasify it to either a low-Btu gas or to hydrogen to supplement the energy and hydrogen requirements of the upgrading process, respectively.

When considering gasification processes it became apparent that at low temperatures pyrolysis of the pitch would occur. The pyrolytic reactions would take place prior to or concurrent with other reactions in a gasifier. It was therefore felt desirable to study and establish the behaviour of pyrolysis before attempting to understand the gasification characteristics.

## EXPERIMENTAL

A schematic diagram of the equipment is shown in Figure 1. Samples of pitch with or without added catalyst were placed in a cylindrical quartz basket (15 x 40 mm) which was suspended from one arm of a Cahn RG electro-balance. A stream of helium or nitrogen flowed through the reactor sweeping away the products formed during the pyrolysis. The volatile products carried by the inert carrier were condensed in traps maintained at dry ice temperatures while the non-condensable gases were collected in sampling bulbs for gas chromatographic analysis. The reactor was surrounded by a tubular furnace which could be operated either isothermally or in a temperature programmed mode. The sample temperature was monitored using a thermocouple (Type K) positioned in close proximity to the sample basket. Both the weight of the sample and its temperature were continuously monitored and recorded as a function of time.

The pitch used in these experiments was the portion of the liquid product boiling above 525°C, obtained by thermally hydrocracking Athabasca bitumen in a pilot plant reactor. The Athabasca bitumen was obtained from Great Canadian Oil Sands Ltd., Fort McMurray, Alberta. The properties of the pitch used in this study are shown in Table 1. In the case of the non-catalytic experiments, the pitch sample was used in lumps and the sample sizes were in the 20-100 mg range. For the catalytic case, the catalyst pellet ( $L=D=1.25$  mm) was dipped in hot pitch (150°C) resulting in a thin coating of the pitch around the pellet. The catalyst/pitch weight ratio in these experiments varied from 1 to 4. The gamma alumina catalyst used in this study, has been described previously (3).

Several experiments were performed with heating rates of 1, 2.5, 5, 10, 20°C per minute. Each experiment began at room temperature and the furnace was heated at the desired rate to a final temperature of 850°C. In the majority of cases, the run was terminated 10 to 15 minutes after reaching the final temperature. Some experiments were also performed with non-linear heating rates. The furnace temperature was set at the desired final level and the furnace allowed to reach this temperature. The heating rate in these experiments varied from a maximum of 50°C/min to essentially zero, as the final temperature was reached. In all the experiments, the inert carrier gas

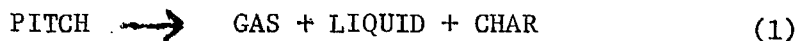
flow was maintained at 150 ml/min.

In order to obtain product samples required for all the analyses, some experiments were performed with approximately 5 g of pitch. These experiments were carried out under isothermal conditions without the electrobalance attached to the sample basket.

The pyrolysis products were analysed by several techniques. The gas samples collected were analysed by gas chromatography and mass spectrometry. Elemental analysis and proton n.m.r. and  $^{13}\text{C}$  n.m.r. analysis were performed on the initial reactant and the final distillable liquid products.

## RESULTS

Since pitch is a multi-component material, it is difficult to identify and study the various pyrolytic reactions separately. One simple representation of the overall pyrolysis process is



The products of the pyrolysis are grouped under three categories: a gas phase material, distillable liquid and a non-distillable char, all at ambient conditions. At any time during the course of the reaction, the material in the microbalance reactor would be a combination of the incompletely reacted pitch and the char reaction product, which combination will be referred to as the residue.

Typical experimental data from the microbalance reactor are shown in Figures 2 and 3. As is evident from Figure 2, very little reaction resulting in weight loss occurred up to approximately 400°C. Above 500°C, the rate of weight loss is small but relatively constant. In Figure 3, the weight of the residue is shown as a function of time for both the catalysed and non-catalysed cases. The furnace temperature, in both of these two cases, increased non-linearly, reaching 500°C in about 20 minutes and 850°C in about 120 minutes remaining constant thereafter. The difference in the shape between the curves in Fig. 2A and 3 are due to the widely different heating rate. As can be seen from Figure 3, the weight-loss pattern with and without added catalyst is identical up to about 28% total weight loss. The catalytic effects come into force thereafter and the rate of weight loss in the presence

of the catalyst is significantly higher than in the case when no catalyst was present.

Values illustrating product yields and gas compositions from isothermal experiments are shown in Table 2. The yield data shown were obtained after a reaction period of two hours at a reaction temperature of 450°C. The gas and liquid yields are higher and the residue yield lower when a catalyst is present. The gas compositions with and without catalyst are fairly similar. However <sup>13</sup>C n.m.r. analyses showed that the liquid products obtained in the catalysed experiment have a higher aromatic content than those formed in the absence of the catalyst.

The effect of the heating rate on the cumulative weight loss with and without added catalyst is shown in Table 3. The weight loss in both cases increases with decreasing rate of heating. Similar behaviour has been observed with decompositions of petroleum residuum. Other workers (4) have concluded that decreasing extent of reaction with increasing rate of heating is characteristic of decomposition reactions, which are the ones occurring in this system.

## DISCUSSION

The results can be interpreted in terms of standard kinetic expressions. A simple nth order equation which describes the rate of loss of pitch would be given by

$$-\frac{dW_p}{dt} = k W_p^n \quad (2)$$

where  $W_p$  refers to the weight of the reactive portion of the residue expressed as a percentage of the original sample and  $k$  is the rate constant. The Arrhenius equation

$$\ln k = \ln A - E_a/RT \quad (3)$$

can be substituted in Equation 2 after taking logarithms to give

$$\ln (-dW_p/dt) = \ln A + n \ln W_p - E_a/RT \quad (4)$$

In the above equation,  $A$  is the Arrhenius constant,  $E_a$  is the overall activation energy for the pyrolysis process and  $R$  is the gas constant.

A method of relating the extent of reaction to the amount of residue remaining in a microbalance reactor was described previously (5). An important part of that method involved the calculation of  $W_p$  from  $W_R$ , the weight of the residue expressed as a percentage of the original sample. Briefly it involved relating the magnitude of  $W_p$  to the hydrogen content of the residue, assigning the char a hydrogen content of zero, and performing material balance calculations. The same procedure was followed for this work.

In Figure 4 are shown the rates of change in  $W_p$  as a function of the total residue weight  $W_R$ , for three different heating rates. The faster heating rates produced higher temperatures and greater reaction rates for any given amount of residue. With this representation it is easy to compare reaction rates at constant amount of residue. Each unique value of the amount of residue has been equated to a unique reactant composition. A comparison at a specific value of the amount of residue is then equivalent to a comparison at a specific reactant composition. An inspection of Equation 4 shows that the first two terms on the right hand side would be a constant for a specific reactant composition. Therefore a plot of the rate of weight loss,  $(-dW_p/dt)$  versus the inverse of the corresponding temperature,  $(1/T)$  should result in a straight line whose slope is related to the activation energy,  $E_a$ .

In Figure 5 are shown four such straight lines corresponding to two different reactant compositions with and without added catalyst. It is immediately apparent from Figure 5 that the activation energy varies as a function of the reactant composition.

Figure 6 shows the variation in activation energy with extent of reaction. In the case of the non-catalysed experiment, the activation energy increases initially as the extent of reaction increases and approaches a maximum when about 20% of the sample has decomposed. During the course of the remainder of the pyrolysis the activation energy was found to decrease with increasing reaction. In the presence of the catalyst on the other hand, there is a continual increase in the activation energy with increasing extent of reaction. The apparent activation energies from the temperature-programmed data shown in Figure 6 varies from 80 to 170 kJ/mol for the uncatalysed experiments and 120 to 300 kJ/mol for the catalysed experiments.

According to Equation 4, the intercept, I, from Figure 5 is given by

$$I = \ln A + n \ln W_p \quad (5)$$

It was found that the intercept, I, also varied with the extent of reaction in an analogous manner to the activation energy. Both the catalytic and non-catalytic results formed curves for I which were similar in shape to those curves for  $E_a$  shown in Figure 6.

Since the intercept, I, which includes the Arrhenius constant A and the apparent activation energy  $E_a$  exhibit a similar pattern of variation as a function of the extent of reaction, it was decided to explore the existence of a compensation effect between A and  $E_a$ . Such compensation effects have been observed with many solid state decomposition reactions (6,7,8).

The compensation effect is usually expressed as

$$\ln A = \ln k_{iso} + \frac{E_a}{RT_{iso}} \quad (6)$$

where  $k_{iso}$  is the iso-kinetic rate constant and  $T_{iso}$  is the iso-kinetic temperature. Introduction of Equation 6 into Equation 5 followed by rearrangement gives

$$I - \ln k_{iso} - \frac{E_a}{RT_{iso}} = n \ln W_p \quad (7)$$

A multiple linear regression was performed on Equation 7 to obtain values of  $k_{iso}$ ,  $T_{iso}$  and n.

Pyrolysis in the presence of catalyst produced a value of n close to 1.0, indicating a first order reaction. No variation in order of reaction was apparent as a function of  $W_R$ . Non-catalytic pyrolysis produced a value of n close to 1.0, for  $100\% > W_R > 80\%$ . For smaller values of  $W_R$ , a value of 4.1 for n fitted the data. The values for  $k_{iso}$  and  $T_{iso}$  corresponding to a first order reaction are shown in Table 4.

Figure 7 shows the relationship between the left hand side of Equation 7 and  $\ln W_p$ . The straight lines in this figure have been drawn with a slope of  $n=1$ . It is apparent that the data can be represented by first order kinetics although there is some scatter.



The compensation effect is normally observed when different catalysts are used. The reaction data for a single catalyst are usually plotted in the form of the Arrhenius equation, Equation 3, to obtain a value for  $E_a$  and a value for A. When a number of catalysts with widely varying properties are tested they can produce different activation energies  $E_a$  (9,10,11) which lead to the compensation effect.

If the expression for  $\ln A$  in Equation 6 is substituted into Equation 3, the following expression is obtained

$$\ln k = \ln k_{iso} + \frac{E_a}{RT_{iso}} - \frac{E_a}{RT} \quad (8)$$

Equation 8 is a modified Arrhenius equation with two variables  $E_a$  and T.  $E_a$  is a variable which will only be constant for a specific catalyst and a specific reactant molecule.

In the present study the compensation effects were observed both with a single catalyst and without a catalyst. These compensation effects may be attributed to differences in  $E_a$  associated with different reactant molecules. As  $W_R$ , the residue weight, changed the reactant composition also changed. Initial pyrolysis of the reactive species was followed by the pyrolysis of less reactive species, with increasing reaction temperature. The less reactive species have higher activation energies as may be seen from the data in Figure 6, for all the catalytic results and for the non-catalytic results at values of  $W_R$  greater than 80%. These changes in  $E_a$ , when considered in conjunction with Equation 6, completely explain the observed compensation effect.

## CONCLUSION

In summary, it was observed that the alumina catalyst increased the extent of pitch pyrolysis at long reaction times, accompanied by some changes in the product distribution. The pyrolysis reaction was found to be first order with respect to the pitch reactant. A compensation effect was observed in which the Arrhenius parameters  $E_a$  and  $A$  were found to vary with the residue weight,  $W_R$ . This effect was explained in terms of a modified Arrhenius equation and the increasing activation energy  $E_a$  associated with the less reactive molecular species.

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### CAPTIONS AND FIGURES

- Figure 1: Schematic Diagram of the Microbalance Reactor.
- Figure 2: Amount of Residue (wt. %), Time Derivative of the amount of pitch,  $-\Delta W_p/\Delta t$  (wt. %/min), and Temperature ( $^{\circ}\text{C}$ ) versus Time (Min).
- Figure 3: Amount of Residue (wt. %) versus Time (Min).  
Final Temperature,  $850^{\circ}\text{C}$ , in 120 minutes  
Solid Line: no catalyst; dotted line:  $\gamma\text{Al}_2\text{O}_3$   
Catalyst, Catalyst/Pitch = 3.5
- Figure 4: Rate of change of Amount of Pitch -  $\Delta W_p/\Delta t$ , (weight percent per Min) versus Amount of Residue,  $W_R$  (Weight Percent) for Catalytic Pyrolysis. Heating rates were 1, 5,  $20^{\circ}\text{C}$  per minute for cuves 1, 2 and 3 respectively.
- Figure 5: Natural logarithm of  $-\Delta W_p/\Delta t$  versus Inverse Temperature ( $\text{K}^{-1}$ ).  
Solid line: no catalyst; dotted line:  $\gamma\text{Al}_2\text{O}_3$  catalyst. Squares and triangles represent a value for  $W_R$  of 66.5 weight percent and solid circles and open circles a value for  $W_R$  of 87.5 weight percent.
- Figure 6: Activation Energy as a function of weight of Residue. Solid and open circles represent non-catalytic and catalytic data respectively.
- Figure 7:  $(I - E_a/RT_{\text{iso}})$  versus  $\ln W_p$ . The straight lines have a slope of  $n = 1$ . Solid and open circles represent non-catalytic and catalytic data respectively.

TABLE 1

Feedstock Properties

Proximate Analysis, wt. %	
Moisture	Nil
Ash	5.2
Volatile Matter	42.4
Fixed Carbon (by diff.)	52.4
Ultimate Analysis, wt. %	
Carbon	79.6
Hydrogen	6.8
Sulphur	5.4
Nitrogen	1.5
Ash	5.2
Oxygen (by diff.)	1.5
*Pentane Insolubles, wt. %	70.1
*Benzene Insolubles, wt. %	27.1
*Tetrahydrofuran Insolubles, wt. %	10.4
Conradson Carbon Residue, wt. %	63.5
Percent aromatic carbon	67
Ash Analysis, wt. %	
SiO <sub>2</sub>	43.3
Al <sub>2</sub> O <sub>3</sub>	24.7
Fe <sub>2</sub> O <sub>3</sub>	11.4
Mn <sub>3</sub> O <sub>4</sub>	0.3
TiO <sub>2</sub>	6.6
P <sub>2</sub> O <sub>5</sub>	0.3
CaO	2.8
MgO	1.6
SO <sub>3</sub>	1.2
Na <sub>2</sub> O	0.2
K <sub>2</sub> O	1.7
V <sub>2</sub> O <sub>5</sub>	3.1
NiO	0.8

\* on ash-included basis

TABLE 2

Product Distribution and Gas and Liquid Analysis

Reaction Temperature 450°C

Reaction Time 2 hours

	Uncatalysed	Catalysed $\frac{\text{catalyst}}{\text{pitch}} = 0.6$
Residue, wt. %	70.8	61.2
Liquid, wt. %	22.0	25.8
Gas, wt. %	6.0	12.0
Unaccounted, wt. %	1.2	1.0
% Reacted	29.2	38.8

Gas Analysis (Vol. %)

H <sub>2</sub>	60	66
H <sub>2</sub> S	16	12
C <sub>1</sub>	10	12
C <sub>2</sub>	7	5
C <sub>3</sub>	4	4

Liquid Product Analysis

Hydrogen, wt. %	88.84	89.18
Carbon, wt. %	84.0	84.9
% saturate carbon	62	52
% aromatic carbon	38	48
olefins	trace	trace

TABLE 3  
Effect of Heating Rates on the Cumulative Weight Loss  
Final Temperature 500°C

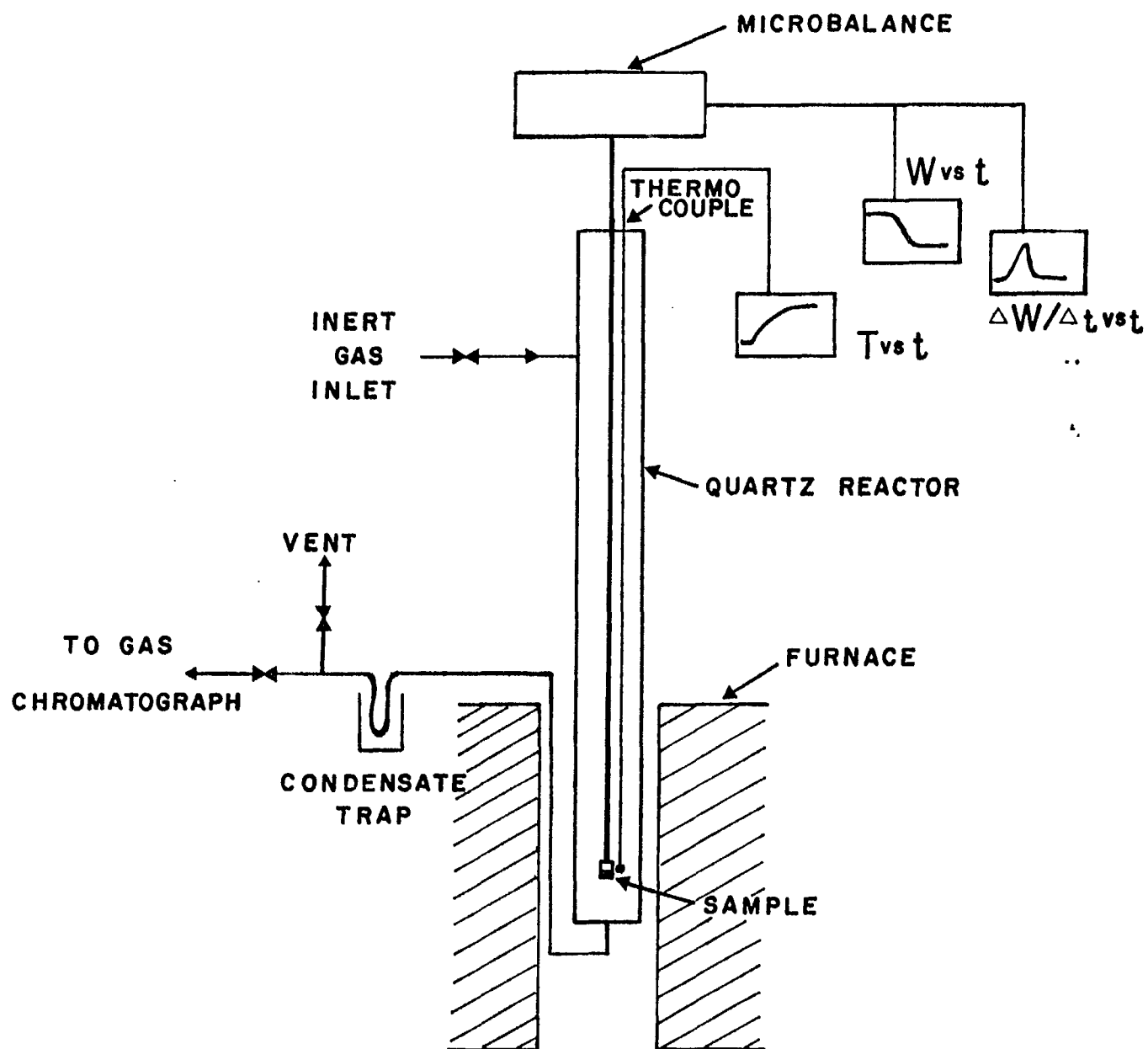
Heating Rate (°C/min)	Uncatalysed (Percent weight of original sample)	Catalysed
1	-	39
2.5	43	-
5	43	39.5
10	40	-
15	-	35.5
20	32	36

TABLE 4

Kinetic Parameters from Equation 7

Parameter	Catalytic Pyrolysis	Non-Catalytic Pyrolysis	
	$W_R > 66$	$W_R > 80$	$W_R < 72$
$n$	1.05	1.05	4.10
$k_{ISO}, s^{-1}$	$3.2 \times 10^{-2}$	$2.9 \times 10^{-4}$	$2.0 \times 10^{-7}$
$T_{ISO}, K$	805	679	805





**SCHEMATIC DIAGRAM OF THE MICROBALANCE REACTOR**

