

# CARBON FORMATION DURING PYROLYSIS IN THE PRESENCE OF HYDROGEN

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Recent interest has been focused on the conversion of heavy hydrocarbons to more amenable feedstocks, by using reactions such as hydrogasification (1), the pyrolysis of hydrocarbons in the presence of hydrogen. Although such reactions may be industrially feasible, they tend to lose efficiency as a result of carbon formation on the reactor walls. The present studies were designed to investigate this phenomenon in the context of hydrogasification of butane.

Experiments were carried out with a flow system involving a tubular reactor in which metal liners could be placed. A sample of copper (an inert metal) was hung in the reactor from one arm of a C.I. Mark 2B microbalance. A continuous record of carbon formation on the copper was obtained, and the exit gases and liquids were analysed gas chromatographically.

As shown in figure 1, variation of the metal liner had a significant effect on carbon formation on copper, inferring that the metal liner affected the composition of the gases responsible for carbon formation on copper. In general carbon formation involved an induction period, followed eventually by a reproducible rate of deposition (figure 1). The variation of gaseous, liquid and solid products was studied as a function of operating variables. Typical plots of yields vs. residence time are shown in figures 2 and 3.

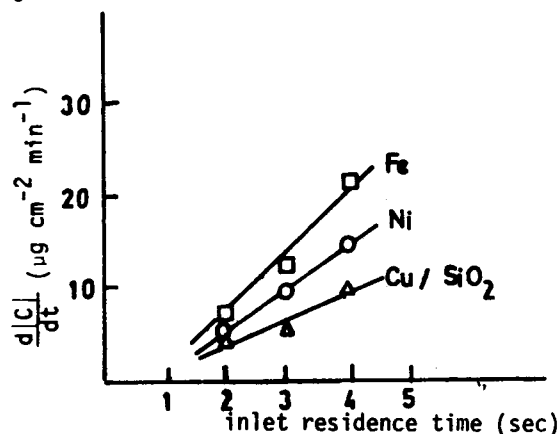


Figure 1. Carbon deposition vs metal liner

Butane: 800 °C

The presence of the induction period supported the concept of carbon formation involving intermediates such as polycyclic aromatics (2). Assuming a simple first order reaction

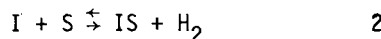


the integrated kinetic expression would be

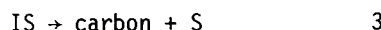
$$|I| = \alpha |RH_0| (1 - e^{-k_1 \tau}) \quad a$$

where  $\tau$  is the residence time.

If the intermediate adsorbs and dehydrogenates



and this reacts to give carbon



Then the sequence of reactions can be shown to predict the kinetics, at the steady state:

$$\frac{d|C|}{dt} = \frac{k_2 k_1 |I|}{(1 + \frac{k_1}{k_2} |I| + \frac{k_{-2}}{k_3} |H_2|)} \quad b$$

This equation may be tested against experimental results. Thus, for example, if  $|RH_0|$ ,  $\tau$  and  $T$  are held constant, the variation of carbon deposition with hydrogen can be expected to be

$$\frac{dt}{dC} = A_1 + A_2 |H_2| \quad c$$

Experimental results agreed with this prediction for  $A_1 = 500 \text{ mg cm}^{-2} \text{ min}^{-1}$ ,  $A_2 = 62.5 \text{ mole percent}^{-1} \text{ mg}^{-1} \text{ cm}^{-2} \text{ min}^{-1}$ . Similarly, the variation of carbon deposition with butane concentration should take the form

$$|RH_0| \frac{dt}{dC} = A_3 + A_4 |RH_0| \quad d$$

Again experimental results agreed with this prediction for  $A_3 = 200 \text{ mg cm}^{-2} \text{ min}^{-1}$ ,  $A_4 = 500 \text{ mg cm}^{-2} \text{ min}^{-1} \text{ mole fraction}^{-1}$  for  $|RH_0|$  expressed as mole fraction of butane in the feed.

When considering relatively short residence times, equation a can be expanded in a Taylor series to give, considering only the first power.

$$|I| = \alpha |RH_0| k_1 \tau \quad e$$

Substitution in equation b for constant inlet compositions and temperature gives

$$\tau \frac{dt}{dC} = A_5 + A_6 \tau \quad f$$

Application to results such as those summarised in figures 2 and 3 gives good agreement except at low temperatures and very low residence times. At 800°C,  $A_5 = 200 \text{ sec mg}^{-1} \text{ min cm}^2$  and  $A_6 = 50 \text{ mg}^{-1} \text{ min cm}^2$ .

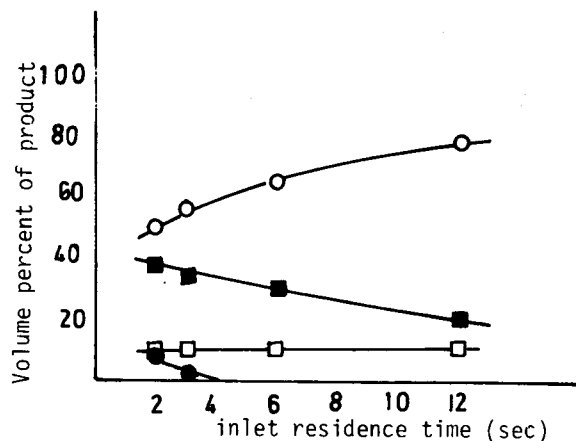


Figure 2. Effect of residence time on gas phase products  
T = 800 °C  
50 % Butane: 50 % Hydrogen

□ Ethane      ■ Ethylene  
○ Methane      ● Propylene

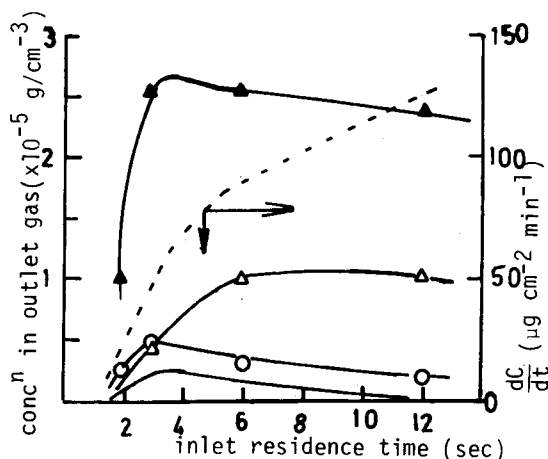


Fig. 3. Effect of residence time on the formation of aromatics and carbon. T = 800 °C  
50% Butane: 50% Hydrogen

▲ Benzene  
△ Naphthalene  
○ Toluene  
--- Carbon  
— Ethylbenzene + Acenaphthylene + Anthracene + Phenanthrene

Substitution of equation f in equation b gives

$$\frac{dC}{dt} = \frac{k_3 k_2 k_1 \alpha |RH_0| \tau}{\left(1 + \frac{k_2}{k_3} k_1 \alpha |RH_0| \tau + \frac{k_{-2}}{k_3} |H_2|\right)} \quad g$$

which predicts a complicated dependence of rate upon temperature. However, if the rate of carbon formation is compared in the presence and absence of hydrogen at differing temperatures, this equation can be rearranged to give

$$\left| \frac{dt}{dC} \right|_{+H_2} - \left| \frac{dt}{dC} \right|_{-H_2} = \frac{A_2}{A_3 A_2 A_1} \exp \frac{(2E_3 + E_2 + E_1 - E_2)}{RT} \frac{|H_{20}|}{\alpha |RH_0| \tau} h$$

where  $A_i$  is the pre-exponential factor of reaction i.

Experimental runs were carried out to study this prediction, which was found to hold over T = 800-950 °C, with  $(2E_3 + E_2 + E_1 - E_2) = 22.6$  kcal/mole.

It is also possible to extend the predictions of the model to include the effect of surface: volume ratio (figure 4)

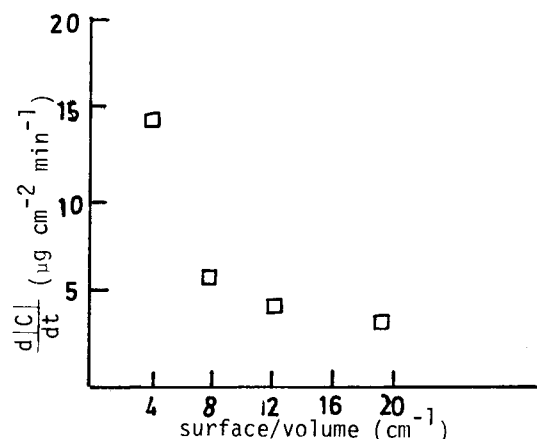


Figure 4. Carbon deposition as a function of S/V  
τ = 3 sec T = 800 °C  
Butane 50%: Hydrogen 50%

At large ratios, the model predicts that the rate of carbon formation should be inversely related to the surface: volume ratio, in close agreement with the experimental results.

Although the model is obviously very simplified, the predictions are thus seen to be in good agreement with experimental results. On the basis of results similar to those presented in figures 2 and 3, attempts were made to identify the intermediates. This showed that polycyclic aromatics did appear to be important, but it was not possible to characterize the reactivity of individual molecules.

#### References

- 1) Dent, F.J., Edge, R.F., Hebden, D., Wood, F.C. & Yarwood, T.A.: Trans. Inst. Gas Eng. 106, 194 (1956-57)
- 2) Brooks, C.T., Cunnings, C.P.R. & Peacock, S.J.: Trans. Farad. Soc. 67, 3265 (1971)