

MICROBALANCE STUDIES IN FLOW REACTORS: DESIGN OF EXPERIMENTAL EQUIPMENT*

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ABSTRACT

Studies have been made of the effect of the nature of the reactor surface on the gaseous, liquid and solid products of hydrocarbon pyrolysis at high temperatures. This has necessitated the development of a tubular and a jet-stirred reactor, which can be used together with a microbalance to record weight changes resulting from the formation of carbon.

The results show that there is a significant effect of the nature of the reactor surface on the kinetics of formation of different products. This effect tends to approach a common value as individual surfaces become covered with carbon. If carbon encapsulation is prevented, for example by gasification by hydrogen, the particular effect of an individual surface continues to influence the product spectra.

INTRODUCTION

The production of useful petrochemicals by the gas phase pyrolysis of various boiling point fractions of crude oil is of considerable industrial importance. Light fractions may be pyrolysed in the presence of steam (steam cracking) to produce light olefins and aromatics¹, while pyrolysis of heavier feedstocks in the presence of hydrogen (hydrogasification) leads to the production of methane and of aromatics².

One of the major problems in the operation of the processes is that significant amounts of tar and carbon are produced, resulting in reactor blockage over a period of time. The formation of this "coke" occurs both in the gas phase and on the metallic surfaces of the reactor, and the present studies were initiated in order to investigate some aspects of this problem.

Measurements of the kinetics of coke formation require a continuous record of weight uptake on a sample with time, and a microbalance was used to obtain these. However, the nature of the reaction is such that particular attention must be paid to

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the design of the reactor. Two problems are apparent. First, it is necessary to carry out the reaction in the presence of steam or of noxious gases such as hydrogen sulphide: these must be kept away from the microbalance head. Secondly, in order to simulate industrial conditions, it is necessary to work with high conversions of reactant. Under these conditions, it is necessary to define, accurately, factors such as gas flow patterns, gas residence times and sample and gas temperatures³.

As a result of these considerations, the use of a microbalance associated with two types of reactor has been developed. In order to carry out preliminary experiments, a tubular integral reactor has been used, while—for more quantitative work—a well-mixed jet-stirred reactor (4) is more suitable. The development of these two systems is described in this paper, together with experimental results obtained for the pyrolysis of hydrocarbons in the absence and presence of hydrogen and hydrogen sulphide.

EXPERIMENTAL

All experiments were carried out using a flow system in which premixed gases passed through a reactor maintained at a known temperature ($\pm 0.2^\circ\text{C}$) to an on-line chromatograph. Reactor assemblies are described below: a C.I. Mark 2B microbalance was used to record weight changes in both systems.

Gases were obtained from B.O.C. in the highest available purity. Metal foils were obtained from Goodfellow Metals (4N purity or better): before use they were reduced in situ with a nitrogen-hydrogen mixture (to constant weight) at the temperature to be used in the subsequent reaction.

The analysis of gases was carried out using an on-line gas chromatograph. Hydrogen and nitrogen were separated on a silica gel column at 25°C and detected with a Servomex micro-katharometer. Methane, ethane, ethylene, propane, propylene, butane, butenes, butadiene, cyclohexene, cyclohexadiene and benzene, were separated with an activated alumina column programmed from 75 to 300°C in a G.C.D. Pye gas chromatograph with dual flame-ionization detector. Aromatics, from benzene to 3-4 benzopyrene, were separated with a glass column packed with 3% OV-1 on Gas Chrom Q, 80-100 mesh, programmed from 35 to 350°C in the G.C.D. gas chromatograph.

Microbalance

Although the C.I. microbalance is a sturdy and reliable instrument, it is necessary to protect the head mechanism from corrosive gases in the reactor. This was achieved by a combination of techniques.

To ensure that the balance head was kept well away from the furnace, a long suspension was used for the sample. This consisted of a series of very thin silica fibres, hooked together at each end, to give a total length of 15 in. (2 or 3 sections).

This long suspension was hung from one arm of the microbalance and passed through an extension section (Fig. 1) in which were placed two flow directors: the

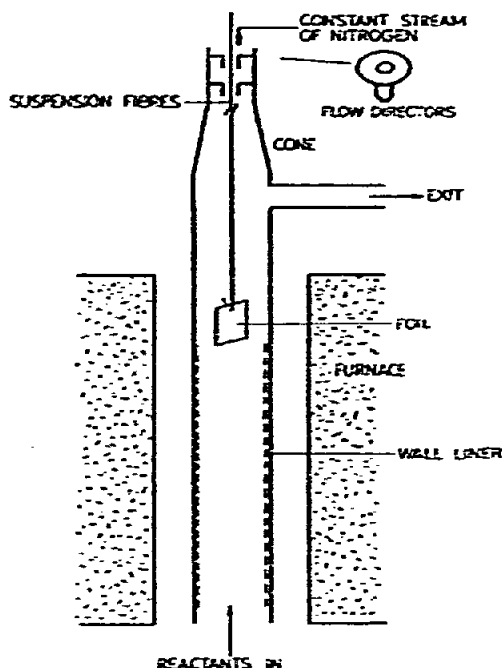


Fig. 1. Line diagram of the tubular reactor.

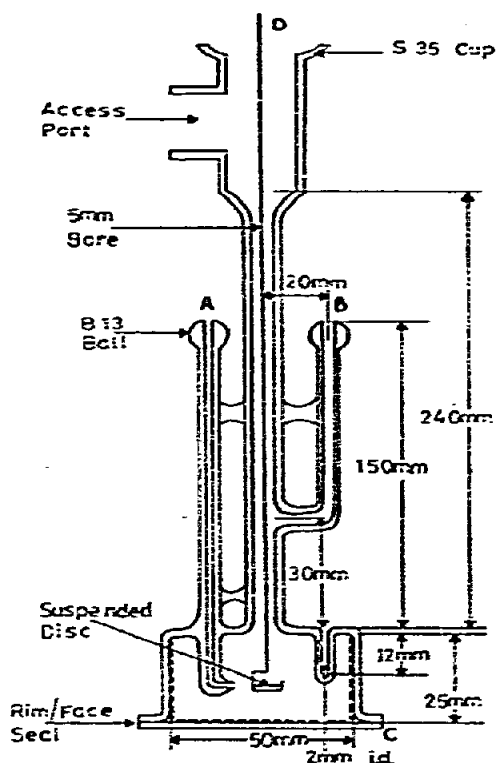


Fig. 2. Line diagram of the jet-stirred reactor.

location and design of these is shown in Fig. 1. A sample of silica or of metal, cut in the shape of a rectangle (the foil), hung on the end of the suspension inside the reactor.

Throughout the reaction a constant stream of nitrogen was passed from the balance head to the reactor exit. It was necessary to control this flow accurately in order to avoid pseudo-weight changes caused by buoyancy effects. With the long suspension, the flow directors and the constant flow of nitrogen, no corrosion of the balance head was observed, even with hydrogen sulphide in the reactor.

The tubular reactor

Several experiments were carried out with a tubular reactor as shown in Fig. 1. The sample was suspended at a known position in the reactor by adjusting the length of the suspension—contact with the wall did not occur unless heavy carbon deposits were formed. It was possible to place a metal liner in the reactor at the position shown by the broken lines in Fig. 1.

The jet-stirred reactor

Experiments were also carried out using a jet-stirred reactor⁴ as modified by I.C.I.⁵ A line diagram of the reactor is shown in Fig. 2. Premixed gases were injected

into the reactor through jet A and left the reactor at B. The reactor was constructed of quartz, with a removable base plate C held in position by spring loaded Inconel clamps: no leakage was observed across this flange. This flange was necessary in order to insert metal liners, as shown by the broken lines in Fig. 2.

Foils were cut in a circular form and were suspended horizontally in the reactor in a cruciform of thin silica fibre hanging from the microbalance arm at D. The position of the foil was found to be important (see later).

At the start of an experiment, the foil and liner were cut to size and placed in position. A constant stream of nitrogen (250 ml min^{-1}) was then passed through the microbalance head at D to the gas exit at B. The furnace was then raised into position and heated to the desired temperature, when the foil weight was balanced off on the other arm of the microbalance. After reducing the foil and the liner, the reactor was rinsed with nitrogen and the reactants were admitted.

The position of the cradle relative to the jet was found to affect the measurements, and this was investigated over a range of temperatures and residence times. Typical results are presented in Fig. 3, from which it is seen that the weight changes are independent of location, provided that the relative vertical positions of the jet and the foil are not more than 1.5 mm apart.

Experimental results

A typical trace of weight uptake against time for the jet-stirred reactor is shown in Fig. 4. Apart from the major fluctuation caused by operation of the sample valve of

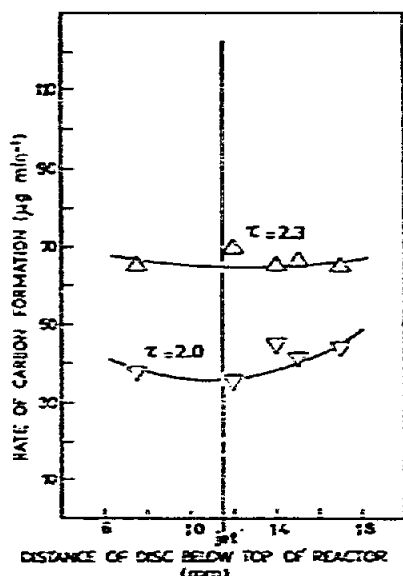


Fig. 3. The dependence of the rate of carbon formation on the relative vertical position of jet and foil. Jet-stirred reactor. Silica disc. Feed: pure propane, $T = 840^\circ\text{C}$. τ = inlet residence time (sec).

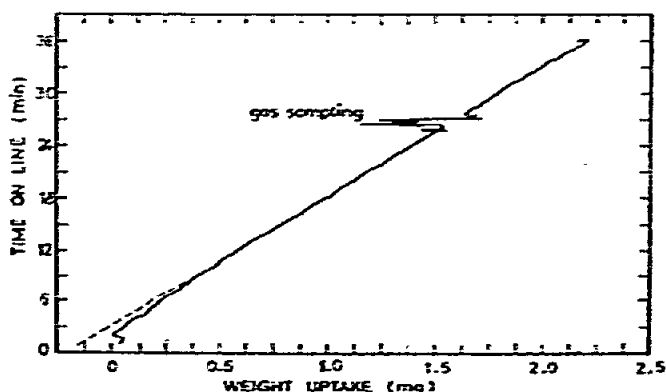


Fig. 4. Typical trace of weight uptake against time. Jet-stirred reactor. Silica disc. Feed: pure propane, $T = 840^\circ\text{C}$. Inlet residence time = 2.3 sec.

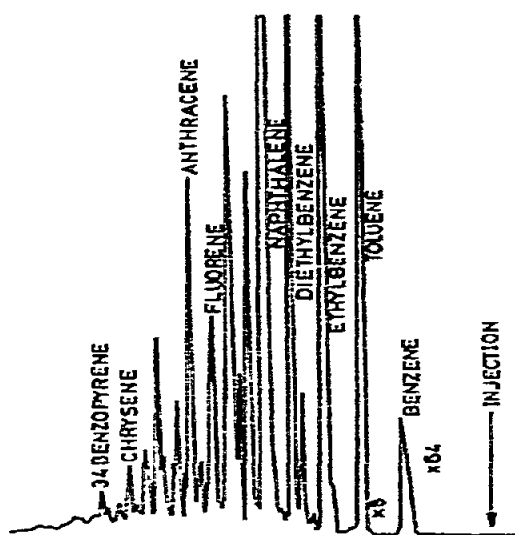


Fig. 5. Typical gas chromatographic trace of the analysis of heavy tars. Conditions as in text.

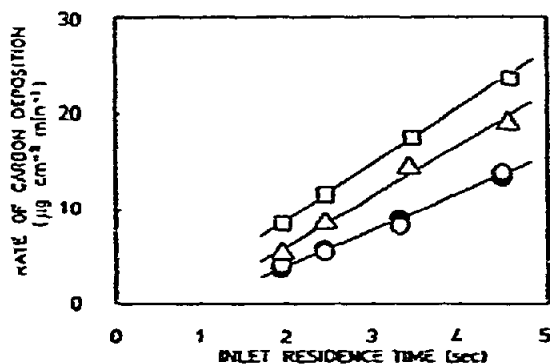


Fig. 6. Effect of the nature of the liner on carbon formation on a foil. Tubular reactor. Copper sample foil. Feed: pure butane, $T = 800^{\circ}\text{C}$. ○, silica liner; ●, copper liner; △, nickel liner; □, iron liner.

the gas chromatograph, the trace is seen to be stable enough to give a good measure of the rate of weight uptake.

Analysis of the light gases was conventional. Analysis of the tar products gave a trace such as is shown in Fig. 5.

RESULTS AND DISCUSSION

Although these high-temperature pyrolytic reactions are known to proceed mainly through a free-radical-chain reaction in the gas phase^{1, 6}, there is some evidence that the reactor surface can influence the product spectrum⁷. As a result, the present studies were intended to investigate this possibility by measuring the nature and kinetics of formation of gaseous, liquid and solid products as a function of reactor surface: silica, copper, nickel and iron were used as test surfaces.

Perhaps the most informative experiments were carried out in the tubular reactor using (a) a silica liner and various foils and (b) a copper foil and various liners. The results, summarised in Fig. 6, show that, although the nature of the foil does not have a large effect, the nature of the liner has a marked effect on the rate of carbon formation. As this is measured by weighing the foil, the nature of the liner must be affecting gas-phase reactions, at least some of which are responsible for carbon formation on the foil.

However, it is also known that carbon formation will occur on the liner and the foil under these conditions⁸. As a result, any individual effect of a particular material should tend towards a common value as the material becomes encapsulated by carbon.

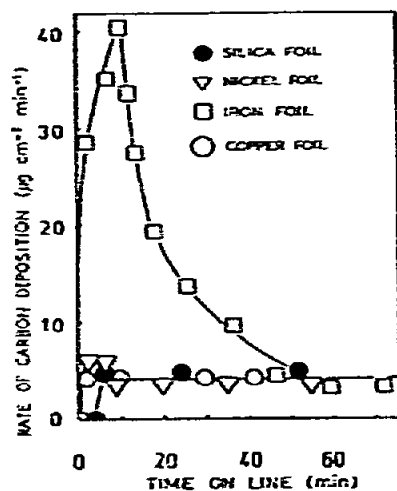


Fig. 7. Transient rates of carbon formation. Tubular reactor. Silica liner. Feed: pure butane, $T = 800^\circ\text{C}$. Residence time = 2 sec.

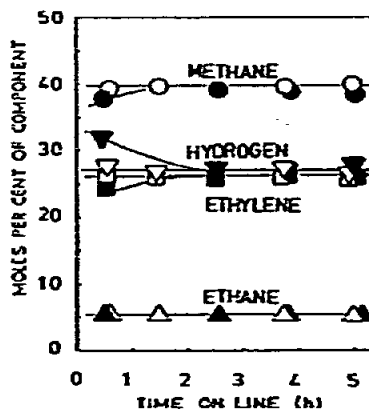


Fig. 8. Transient concentrations of gas products. Tubular reactor, Copper sample foil. Feed: 50% butane in hydrogen. $T = 800^\circ\text{C}$. Residence time: 6 sec. Open symbols, copper liner; closed symbols, iron liner.

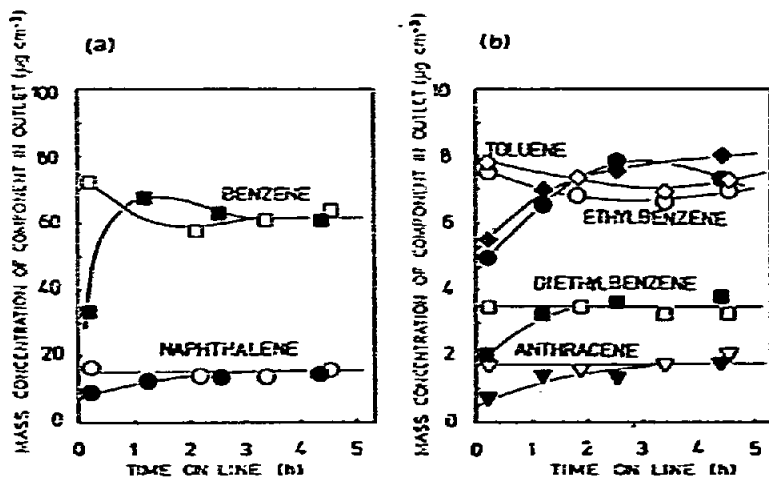


Fig. 9. Transient concentrations of aromatic products. (a) Major products. (b) Minor products.

As can be seen from Figs. 7, 8, and 9, this is indeed the case for the production of gases, tars and carbon.

If this concept is correct, then the nature of the metal liner would be expected to have only a small effect on measurements carried out in the jet-stirred reactor since this system, by definition, works in a near steady-state situation⁴. As can be seen from Fig. 10, this is indeed the situation, the rate of carbon formation falling as the reactor ages (points A, B, C) to a constant level for all liners with the exception of stainless steel.

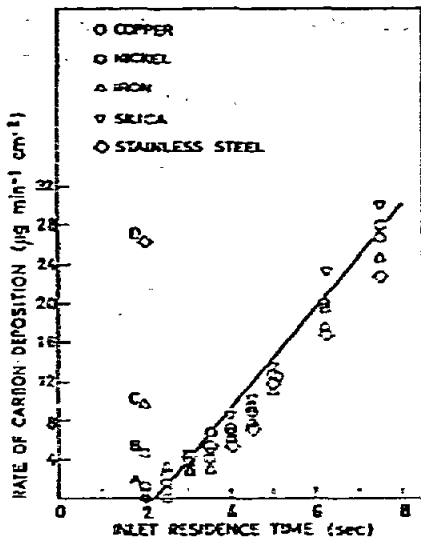


Fig. 10. Effect of the wall liner material on carbon formation in the jet-stirred reactor. Feed: pure propane, $T = 810^{\circ}\text{C}$. Copper sample foils. Points A, B, C and D indicate the initial rate of deposition with the corresponding liners.

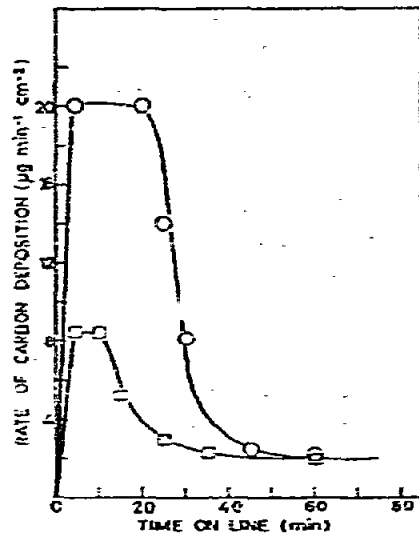


Fig. 11. Effect of sulphiding on the transient rates of carbon formation. Jet-stirred reactor. Iron sample disc. Feed: pure propane, $T: 807^{\circ}\text{C}$. Residence time = 2 sec. \circ , No sulphiding; \square , samples sulphided before the start of the reaction by passage of H_2S .

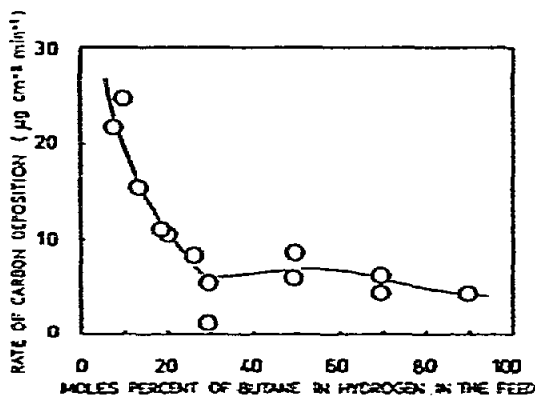


Fig. 12. Effect of hydrogen on the steady-state rate of carbon formation. Tubular reactor, Nickel sample foil. Feed: butane and hydrogen mixtures. $T = 800^{\circ}\text{C}$. Residence time = 1.66 sec.

This observation can be clarified by extending the argument. Since carbon formation on the foil depends on the nature of the surface of the liner, several effects may be expected. Firstly, the behaviour of a fresh surface should depend upon its chemical composition. As a result, sulphiding, for example, would be expected to affect carbon formation during the transient: this has been found to be correct (Fig. 11).

Secondly, if a surface does not become encapsulated with carbon—for any reason—then carbon formation on the foil should continue to be particular to that surface. Two general cases can be envisaged. If carbon deposited on the liner is

gasified, for example by hydrogen⁹, so that encapsulation does not occur, then the particular effect of the surface should continue. Measurements of the steady-state rate of carbon formation on nickel in the presence of different amounts of hydrogen (Fig. 12) shows that this is indeed the case.

One other phenomena could ensure that at least some of a metal remains active. It is known that metal can migrate through carbon deposits if the conditions are suitable⁸: if this happens, then the migrating metal will remain active and will affect carbon formation. Examination of the deposits from the stainless-steel sample (Fig. 10) by electron probe microanalysis indicates that metal migration could be responsible for this anomalous result, in that significant amounts of iron had migrated to the surface of the carbon.

It would thus appear that the surface of the reactor can have a significant effect on the product spectrum obtained from pyrolytic reactions. Although the relative effects of different surfaces has been established, the absolute effect of a carbon surface requires further study.

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