Ruthenium Catalyst Systems for the Production of Hydrocarbons from Coal

RECENT STUDIES ON THE FISCHER-TROPSCH REACTION

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A new catalyst with a low metal loading has been developed for the Fischer-Tropsch synthesis, and has shown good activity, selectivity and durability in laboratory reactors, demonstrating that these catalyst systems could be used in future commercial processes.

Although in the short term crude oil is in plentiful supply, mainly as a consequence of decreased demand resulting from the worldwide recession, it should not be forgotten that, based on existing knowledge, the estimated reserves of oil are only sufficient to sustain supplies into the early decades of the next century. Currently, crude oil is the mainstay of the chemical economy and in the free market economy countries of the world it accounts for 98 per cent of the energy used in transportation and 85 per cent of the sources of chemical feedstocks. The remaining 15 per cent of chemical feedstock is natural gas and this can be expected to play an increasingly important role as the reserves of crude oil decrease. In addition, there are vast reserves of coal and many research workers have investigated the possibility of converting it into the liquid hydrocarbons currently produced from oil.

In general, coal is much more difficult to process than crude oil or natural gas and hence it is more expensive to convert into useful products. Attempts to synthesise liquid hydrocarbons have been based primarily upon either direct coal liquefaction or gasification to carbon monoxide and hydrogen (syngas) for use in the Fischer-Tropsch synthesis.

In the direct liquefaction of coal it is necessary to increase the hydrogen:carbon ratio in order to transform the coal into oil. This is achieved by the hydrogenation of pulverised coal in a suitable solvent in the presence of a catalyst and at high pressures. The liquid products resulting from the hydrogenation of coal are significantly different from those of naturally occurring petroleum. The middle distillates from the coal derived liquids are highly aromatic materials compared with the equivalent oil derived products. This high aromaticity is suitable for use as petrol but it makes the middle distillates of coal liquids unsuitable for the production of jet fuel and diesel oil.

The alternative processes for the production of liquid hydrocarbons are based on the gasification/Fischer-Tropsch route. Coal is reacted at elevated temperatures with oxygen and steam to produce carbon monoxide and hydrogen which, after purification, are then reacted together in the presence of a suitable catalyst to synthesise a range of hydrocarbons. This synthesis is known as the Fischer-Tropsch reaction and is the subject of this article, which includes a description of advances that have been made during research work carried out at the Johnson Matthey Technology Centre.

Process Developments

The history of the Fischer-Tropsch process goes back to 1902 when Sabatier and Senderens observed that methane could be formed by reacting carbon monoxide and hydrogen together in the presence of a nickel or cobalt

catalyst (1). The hydrocarbon growth mechanism was first studied in 1923 when Fischer and Tropsch discovered that a range of liquid hydrocarbons and oxygenated products could be produced from syngas over iron and cobalt catalysts (2).

$$CO + 2H_2 \longrightarrow (-CH_2-) + H_2O$$
$$\Delta H_R = -165.5 \text{ kJ}$$
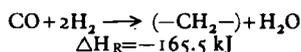
Further developments took place in Germany, Japan and elsewhere, and the first four commercial plants were commissioned in Germany in 1936. By 1944 nine cobalt based units were in operation in Germany with a total capacity of approximately 700,000 tons per year.

After the second world war several companies in the United States of America developed new reactors for the Fischer-Tropsch process. However, the next major commercial exploitation of the process did not occur until 1955. In that year an iron-potassium based plant was commissioned by the South African Coal, Gas and Oil Corporation (SASOL). Two types of reactor were used: a fixed bed tubular (Arge) reactor and a circulating fluidised bed (Synthol) reactor. This plant has operated successfully up to the present day.

Following the development in the 1950s of the large oil deposits in the Middle East, interest in the Fischer-Tropsch process declined. However, a resurgence occurred following the Middle East oil crisis in 1973 and this resulted in SASOL constructing two additional much larger plants: SASOL II and SASOL III. The first of these plants was commissioned in 1980 and both plants are in operation today employing an iron catalyst in Synthol reactors. Typical examples of the product spectrum produced by the SASOL reactors are given in Table I. Despite the recent fall in oil prices the SASOL plants still continue to be commercially viable, primarily due to the availability of vast reserves of coal.

Fischer-Tropsch Selectivity

So far the only metals to achieve commercial significance in catalysing Fischer-Tropsch processes have been cobalt and iron; however, other metals are active as catalysts, and ruthenium is perhaps intrinsically the most active for the hydrogenation of carbon monoxide (3, 4, 5). Ruthenium could be very

Table I
Product Selectivities of SASOL Commercial Reactors (12)

Product	Composition, percentage carbon atom	
	Fixed bed at 493 K	Synthol at 598 K
CH_4	2.0	10
C_2H_4	0.1	4
C_2H_6	1.8	4
C_3H_6	2.7	12
C_3H_8	1.7	2
C_4H_8	3.1	9
C_4H_{10}	1.9	2
C_5 to C_{11} (Gasoline)	18	40
C_{12} to C_{18} (Diesel)	14	7
C_{19} to C_{23}	7	
C_{24} to C_{35} (Medium wax)	20	4
$> C_{35}$ (Hard wax)	25	
Water soluble non-acid chemicals	3.0	5
Water soluble acid	0.2	1

important in the future because in addition to its high intrinsic activity it is selective for the formation of higher molecular weight products (5). These higher molecular weight straight-chain products are premium paraffinic materials, which are ideal for use as jet and diesel fuels. Thus it is not surprising that ruthenium continues to attract considerable research attention (6–10).

However, in the assessment of any potential Fischer-Tropsch catalyst it should be borne in mind that the reaction is essentially a polymerisation process and that the product spectrum can only be adjusted within certain limits. It has been found that for a given product distribution the quantity of one particular carbon number species is fixed, and that if the selectivity to this species is altered then the selectivities to all the other species will shift in a predictable ratio (11). This relationship has been shown to hold irrespective of the means by which the selectivity shift was brought about, that is whether resulting from a change in the process operating conditions or by a change in catalyst formulation (12). The selectiv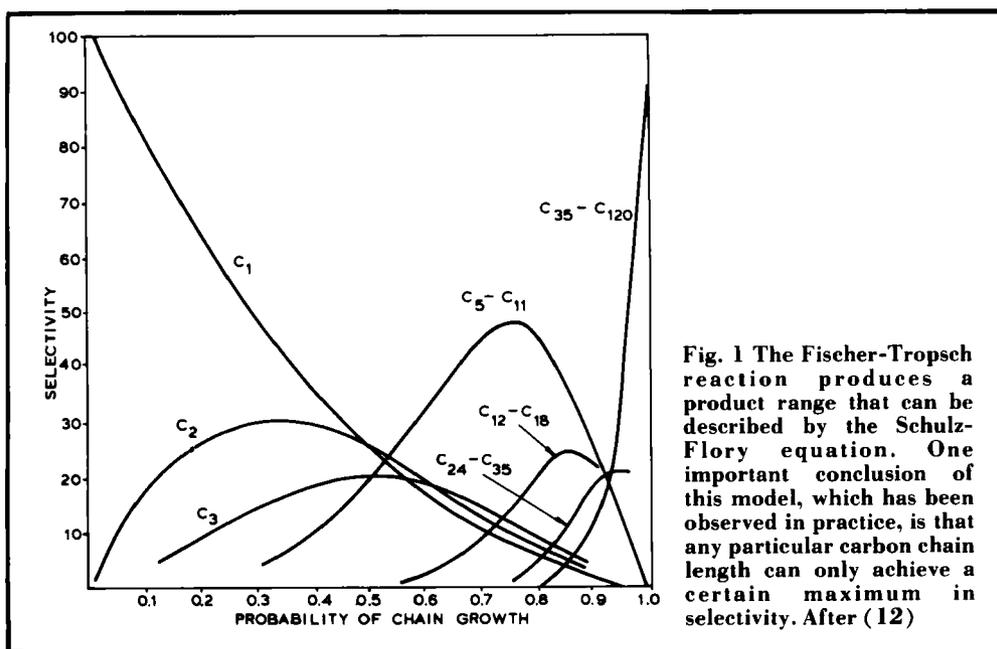ities of the products at either end of the spectrum, namely methane and hard wax, can attain very high values but all the intermediate products can only reach limited maximum values.

Although there are several proposed mechanisms for the Fischer-Tropsch synthesis (13) all assume the growth of carbon chains in a stepwise process. The product distribution is usually described by the Flory equation as modified by Schulz (14):

$$W_n = na^{n-1}(1-a)^2 \qquad (i)$$

where n represents the product carbon number, W_n the weight fraction of carbon number n, and a the chain growth probability factor. The chain length selectivity as predicted by the Schulz-Flory model is shown in Figure 1. The distribution curves for alcohols or alkenes are similar to those illustrated for the hydrocarbons. The model has its limitations and attempts have been made to improve the fit with experimental data by steadily increasing a between certain limits.

Thus, any catalyst used in the Fischer-Tropsch synthesis will produce a broad spectrum of hydrocarbon chain lengths, with

Fig. 1 The Fischer-Tropsch reaction produces a product range that can be described by the Schulz-Flory equation. One important conclusion of this model, which has been observed in practice, is that any particular carbon chain length can only achieve a certain maximum in selectivity. After (12)

yields described intrinsically by the Schulz-Flory equation. However, individual metals will also produce varying amounts of branched alkanes, alkenes and carbonyl compounds, and the yields of these products can also be described by the Schulz-Flory model. Ruthenium is potentially superior to iron and cobalt because it is intrinsically more active and produces significantly less of the undesirable materials. Furthermore the metal has little, if any, water gas shift activity and only very small amounts of carbon dioxide are produced.

Until very recently the desired activity for a ruthenium catalyst could only be achieved with relatively high metal loadings but now a catalyst has been developed which under laboratory conditions has shown good activity and selectivity at a ruthenium metal content low enough to allow significant commercial use.

Laboratory Reactors

The choice of laboratory reactors to investigate the catalytic behaviour of the low metal loading ruthenium catalyst system was, to a large extent, determined by the type of reactor most likely to be used in a commercial process. Supported catalysts do not normally have sufficient attrition resistance to cope with a fluidised bed environment, as created by a Synthol reactor. Therefore the use of ruthenium in a fluidised bed reactor would be inappropriate, since economics dictate that the metal has to be supported in order to maximise its effectiveness. Another drawback of the Synthol reactor is its inability to deal with high molecular weight products such as wax. Consequently the use of ruthenium is probably limited to fixed bed tubular reactors similar to the Arge system operated by SASOL, as shown in Figure 2.

Two types of reactor were chosen to simulate the behaviour of a catalyst in an Arge system, a Berty reactor and a fixed bed tubular reactor. The control equipment and pipework used with the Berty reactor were similar to those used for the fixed bed reactor (see Figure 3). The Berty reactor is an internal recycle reactor which can simulate the linear gas velocity experienced in

commercial processes. In effect the catalyst charge can be considered to be a small section through an Arge tube, and this reactor was used to determine the behaviour of the catalyst under a variety of operating conditions.

The tubular reactor used was of a conventional design and consisted of a 70 cm length of 0.9 cm internal diameter stainless steel tube; a schematic drawing of this equipment is shown in Figure 3. Since it was known that the tubular reactor was incapable of simulating the heat/mass transfer characteristics of a commercial reactor its use was restricted to durability studies.

Variation of Operating Conditions

The purpose of this work, carried out in the Berty reactor, was to determine the sensitivity of the process to various operating parameters in order to help identify the conditions which
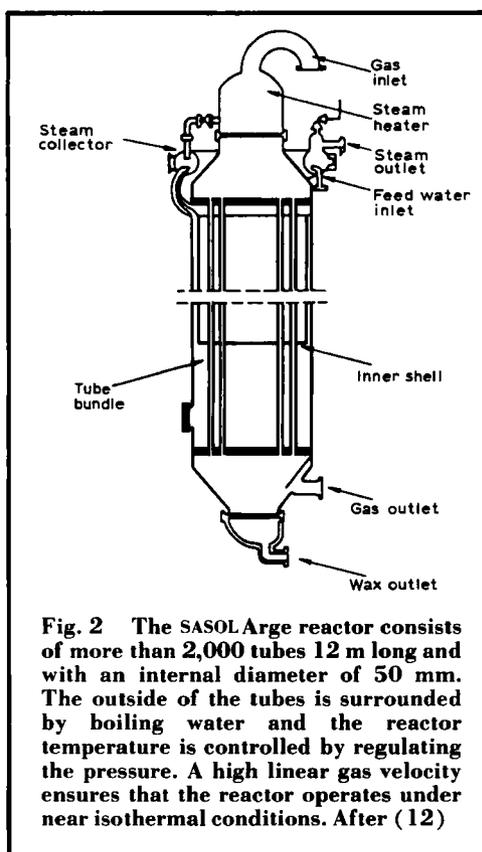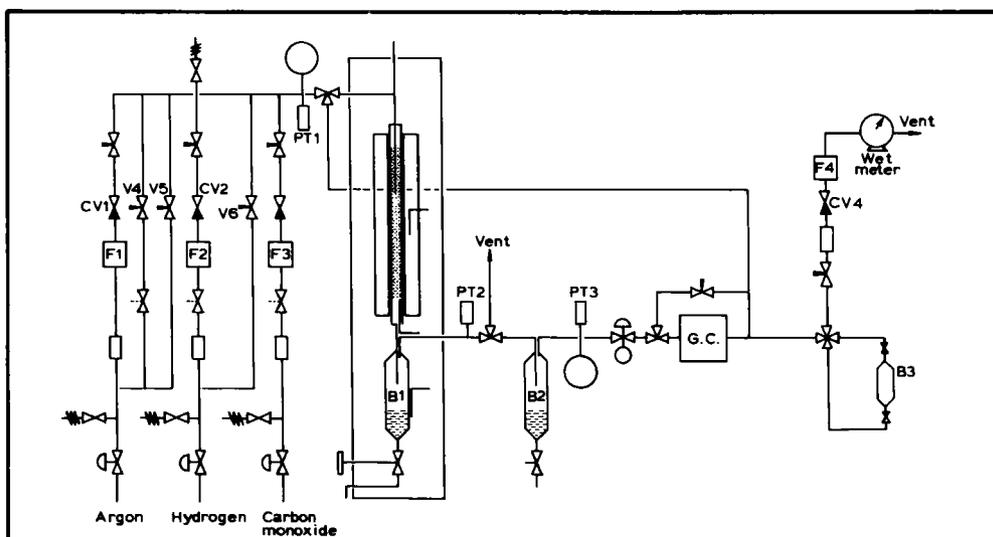

Fig. 2   The SASOL Arge reactor consists of more than 2,000 tubes 12 m long and with an internal diameter of 50 mm. The outside of the tubes is surrounded by boiling water and the reactor temperature is controlled by regulating the pressure. A high linear gas velocity ensures that the reactor operates under near isothermal conditions. After (12)

Fig. 3 The fixed bed reactor was designed to operate continuously over extended periods of time with the minimum of supervision. Gas flowrates, pressure and temperature were automatically controlled and gas and liquid hydrocarbon products were periodically removed from the collecting bottles. The exit gas was routinely monitored by on-line gas chromatography. This schematic gas diagram of the equipment shows the most important features of the reactor, namely:
F1 to F4 mass flow sensors,
PT1 to PT3 pressure transducers,
B1 to B3 product collection,
G.C. gas chromatograph

could be used in a future commercial reactor.

The effect of temperature on the performance of the low metal loading ruthenium catalyst at 22 bar is illustrated in Fig. 4. As the temperature increased the conversion increased and so also did the selectivity to methane. However, up to 250°C the selectivity to methane was still less than 5 per cent. Experimentally it was found necessary to operate the process below 250°C in order to minimise deactivation of the catalyst by coke formation.

Increasing the reactor pressure had a beneficial effect not only in increasing the reaction rate but also in significantly decreasing the selectivity to methane. The results obtained for a catalyst at 210°C are also illustrated in Figure 4. The experimental data obtained during this experiment were also used to confirm the Schulz-Flory model. An examination of Equation (i) shows that a plot of log (W_n/n) against n
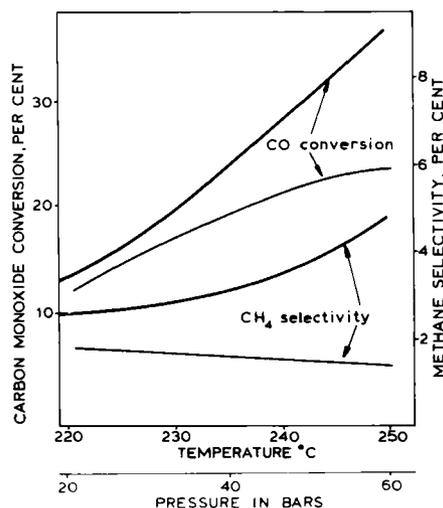
Fig. 4 The Fischer-Tropsch reaction gives rise to a very broad range of hydrocarbon products. Consequently the quantification of the entire product spectrum is a formidable task. The behaviour of the catalysts under various operating conditions has been assessed by comparing performance in terms of the conversion of carbon monoxide and the selectivity to methane.
Conditions 500 GHSV:H_2; CO= 2:1

should yield a straight line of slope log a. This has been confirmed in a number of the experiments and a reasonable fit to experimental data obtained. The entire product spectrum could then be described in terms of one number: the chain growth probability factor a.

Perhaps a more useful number which also uniquely describes the product distribution is the location of N_{max}, the carbon chain length with the highest weight frequency. If Equation (i) is differentiated with respect to n and rearranged it can be shown that N_{max} and a are related by Equation (ii):

$$N_{max} = \frac{-1}{\ln a} \qquad \text{(ii)}$$

This treatment was applied to the wax samples obtained during the pressure experiments, and Figure 5 shows the relationship obtained between N_{max} and pressure. This Figure confirms the published trend, that the average product chain length increases with increasing pressure.

The above treatment assumed that a constant value of a existed over the carbon number range examined, but there exist some interesting variations in the value of a which are dependent upon the reactor used and these are described later.

Table II	
Ruthenium Catalysed Fischer-Tropsch Synthesis with 0.3% Ru/Al₂O₃ Catalyst in a Berty Reactor*	
Conversion	24.6 per cent
Selectivity to wax	88.3 per cent
Selectivity to liquid hydrocarbons	9.6 per cent
Selectivity to methane	1.4 per cent

* Conditions: 210°C, 60 bar, 500 GHSV, H_2:CO=2:1

The effect of changes in the gas hourly space velocity (GHSV), that is the number of catalyst bed volumes of reactant which can be treated per hour, on the performance of a low metal loading catalyst has also been investigated. As the space velocity increased the conversion of carbon monoxide decreased and the selectivity to methane increased. The increase in methane selectivity can be explained in terms of a reduction in the residence time of the reactants on the catalyst surface.

The hydrogen to carbon monoxide ratio was varied and the effects on catalyst activity and selectivity at 210°C and 60 bar were established. Increasing the ratio of reactants caused a moderate increase in activity and a noticeable increase in methane selectivity. As might be expected, the alkane to alkene ratio in the liquid product also increases with an increase in the hydrogen to carbon monoxide ratio, but no effect on the selectivity to alcohols was observed.

A typical example of the kind of results that can be obtained with a low metal loading catalyst in the Berty reactor is given in Table II. The example chosen was not the most active catalyst but one on which an accurate mass balance had been carried out, that is there was a good correlation between the total amount of reactant and products. The selectivity to wax is very high and the selectivity to methane exceptionally low. If required the wax may be
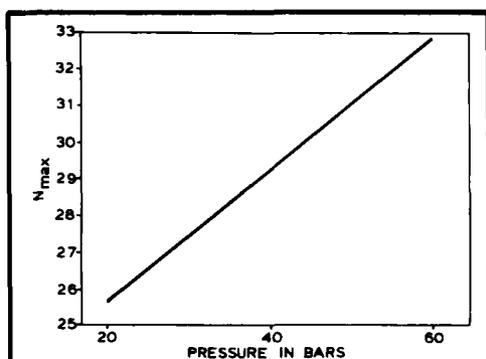

Fig. 5 The average product chain length obtained during the Fischer-Tropsch synthesis increases with increasing pressure. This property has been quantified by plotting the relationship between N_{max}, the carbon chain length with highest weight frequency, and the reactor pressure

Table III		
Characterisation of Diesel from Fixed Bed Reactor		
Test	Method	Results
Cetane Index[a]	I.P. 218[b]	78
Specific Gravity 60 to 60°F	I.P. 160	0.7555
API[c] Gravity at 60°F	Conversion	55.79
Cloud Point, °C	I.P. 219	−10

(a) Cetane Index is the percentage of cetane in a mixture of cetane and 1-methylnaphthalene that has the same ignition quality as the oil under test
(b) I.P. numbers correspond to standard Institute of Petroleum Test procedures   (c) American Petroleum Institute

hydrocracked back to maximise the diesel yield. The quality of wax was similar to that obtained in the durability trial.

Durability Trial

The most effective utilisation of a noble metal such as ruthenium is usually an essential prerequisite for its use in an industrial process. However, in general a prolonged operating time is preferable to a higher initial activity which decays rapidly. Consequently, having developed a very active low metal loading catalyst for the Fischer-Tropsch process it was necessary to determine how the catalyst would perform over a prolonged period of time. The trial was conducted in the fixed bed tubular reactor under conditions which were expected to produce reasonable quantities of wax and liquids. The catalyst was operated for more than 3,000 hours and its activity and selectivity to methane regularly monitored. The conversion observed levelled off at 25 per cent after 300 hours due to a wetting of the catalyst bed, and thereafter stayed virtually constant throughout the trial. Methane selectivity was relatively high compared with the Berty reactor but this was not surprising considering the nature of the tubular reactor. The wax was of excellent physical quality with a melting point in the range of 80 to 110°C. The characterisation of this wax confirmed it to be a very high quality product, comprising straight chain alkanes with negligible quantities of branched chains or alkenes. Fig. 6 shows a typical chromatographic analysis of the liquid hydrocarbon product.

Once again the material is a high quality, predominantly paraffinic product. Details of the characterisation of the liquid product which boils above 160°C are given in Tables III and IV. The very high cetane number of 78 (compared with commercial diesel of cetane number about 45) is very impressive.

Periodically, during the durability trial the product gas was analysed for carbon dioxide indicating that the selectivity to this product was never greater than 0.6 per cent.

The durability data demonstrate very satisfactorily that it is possible to operate the new low metal loading ruthenium catalyst to

Table IV	
Characterisation by Distillation According to I.P. 123	
	°C
First boiling point	161.0
10 per cent recovered at	176.0
20 per cent recovered at	188.0
30 per cent recovered at	199.0
40 per cent recovered at	210.0
50 per cent recovered at	221.5
60 per cent recovered at	233.0
70 per cent recovered at	246.5
80 per cent recovered at	262.0
90 per cent recovered at	282.5
Final boiling point	303.0
Recovery, volume per cent	97.5
Residue, volume per cent	2.5
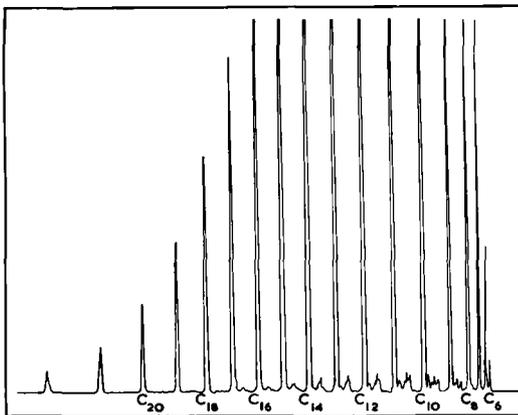
produce good quality products for very long periods of time.

Comparison of Berty and Fixed Bed Reactor Results

The exothermic nature of the Fischer-Tropsch reaction means that careful account must be taken of heat transfer phenomena when scaling up to plant size equipment. An important part of the temperature control of a reactor is the linear velocity of the gas molecules through the catalyst bed, and this should be above a minimum value. The small fixed bed reactor used in this work had a typical linear gas velocity of 10 cm/s which was well short of the minimum required. Consequently temperature control of the bed was poor and the use of the reactor was limited to durability studies. Furthermore the most active catalyst concepts could not be studied in this reactor due to thermal runaway. In comparison the linear gas velocity of the Berty reactor was well above the minimum value and the catalyst bed could be considered to be isothermal.

Although the Schulz-Flory plots for the wax products (obtained from the Berty and fixed bed reactors) yield reasonably straight lines, it was clear that both sets of data fitted curves. Consequently it was decided that rather than fit the data to a Schulz-Flory model, the a value would instead be calculated as a function of chain length. To achieve this the weight fraction versus molecular weight plot which was obtained from the Gel Permeation Chromatographic analysis of wax was converted to a number fraction versus carbon number plot. In order to calculate the a value as a function of carbon number it was necessary to calculate the number fraction at each carbon number. This was achieved by fitting a seventh order polynominal to the data using a matrix curve fitting program. The probability of chain

Fig. 7 During the course of the work described in this article an interesting dependence of a, the chain growth probability factor, upon reactor type was observed
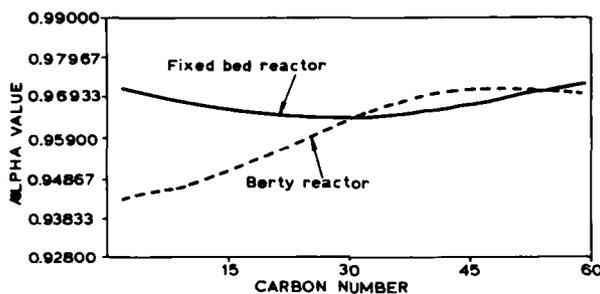
growth a was then calculated according to the formula:

$$a_n = \frac{F_{n+1}}{F_n}$$

where F is the number fraction. The variation of a with carbon number obtained with both reactors is illustrated in Fig. 7. The fixed bed sample a was virtually constant and had a value of approximately 0.969. In contrast the Berty sample had an a value which increased from 0.943 to a steady value of 0.969 at a carbon number of approximately 40. The dependence of a upon a reactor type has previously been predicted in the literature (15). One conclusion that can be drawn from these calculations is that on using a similar catalyst a fixed bed reactor will tend to produce more and harder wax than that obtained with a Berty reactor under similar conditions.

The Future Prospects

The worldwide introduction of the Fischer-Tropsch process will primarily depend upon the availability of oil and on its cost. The use of ruthenium in the process will depend upon the availability of low ruthenium loading catalysts with good activity and selectivity compared with the presently used iron-based systems. We have successfully demonstrated that a low metal loading catalyst can be very active and also have good selectivity. In addition the catalyst was durable enough to survive on an extended laboratory durability trial with little loss of performance. It is our belief that the use of new ruthenium catalyst systems as indicated in this article represents a substantial improvement on previously available ruthenium catalysts, and will achieve significant utilisation in commercial operations to produce premium products such as jet and diesel fuel and wax.

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An Organometallic Chemistry Monograph

Organometallic Chemistry of Rhodium and Iridium
BY RONALD S. DICKSON, Academic Press, London, 1983, 421 pages, £61

The latest monograph in a series on organometallic chemistry deals with rhodium and iridium in a comprehensive yet very readable way, and both the concepts and the structures are clarified with numerous illustrations. Following a general survey of the chemistry of rhodium and iridium, the author deals with specific topics: carbonyls in Chapter II, their complexes in III, pseudo carbonyls in IV (M—CS, M—PF₃, M—CNR, M—NO and M—N₂R), organo-rhodium and -iridium complexes in V, alkyne complexes in VI and finally in Chapter VII σ-alkyl, -aryl and related complexes.

The book is well supported by references to the literature which has been covered comprehensively up to the end of 1978, with some key references from 1979 included. Additionally, an addendum to the key references from the recent literature is given.