CATALYTIC ASPECTS OF INDUSTRIAL FISCHER–TROPSCH SYNTHESIS

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Summary

A brief description of the commercial Sasol process is given. Two types of reactors using two different iron-based catalysts are used, the one producing predominantly gasoline and the other waxes. The hydrocarbon product spectrum can be varied over wide ranges (*e.g.* CH_4 from *ca.* 1 to *ca.* 80%). The probability of chain-growth is influenced by the temperature, the catalyst type and its promoter level and the gas composition. It is not influenced by the type of reactor.

By subjecting the products to additional processes, *e.g.* oligomerisation of olefins or selective hydrocracking of the waxes, the final product slate can be further altered. Thus a 75% overall yield of either gasoline or diesel fuel can be achieved. A major advantage of the Fischer–Tropsch process over other processes which produce fuel from coal is that a very high quality diesel fuel is produced.

The exact nature of the chain-growth mechanism on the catalyst surface is still a disputed subject. It is probable that both 'oxygen-containing' and 'oxygen-free' hydrocarbon fragments participate in the surface reactions. Because of the likelihood that the bonds between the complexes and the catalyst are highly labile and consequently ill-defined, it is no simple task to assign 'clear-cut' structures to the intermediate complexes. The proposed reaction scheme accounts for the many different products obtained from $CO + H_2$ mixtures over various types of catalysts.

Brief history of the Sasol operations

South Africa has no petroleum oil deposits but does have vast coal fields which can be mined at low cost. The first Fischer–Tropsch plant came on line in 1955 at Sasolburg. After the Middle East oil crisis of 1973 the profitability of the process improved markedly, and in 1975 it was decided to construct a much larger plant. Sasol Two came on stream in 1980; in 1979 construction of a third plant commenced. The Sasol Two and Three plants are virtually identical and both are situated at Secunda.

Fischer–Tropsch reactors and catalysts

Two types of reactors are used by Sasol. The Synthol reactors are of the circulating fluidised bed (CFB) type (see Fig. 1). The Arge reactors are of the fixed bed tubular type (see Fig. 2). The Arge catalyst is loaded into 5 cm ID tubes which are surrounded by boiling water.
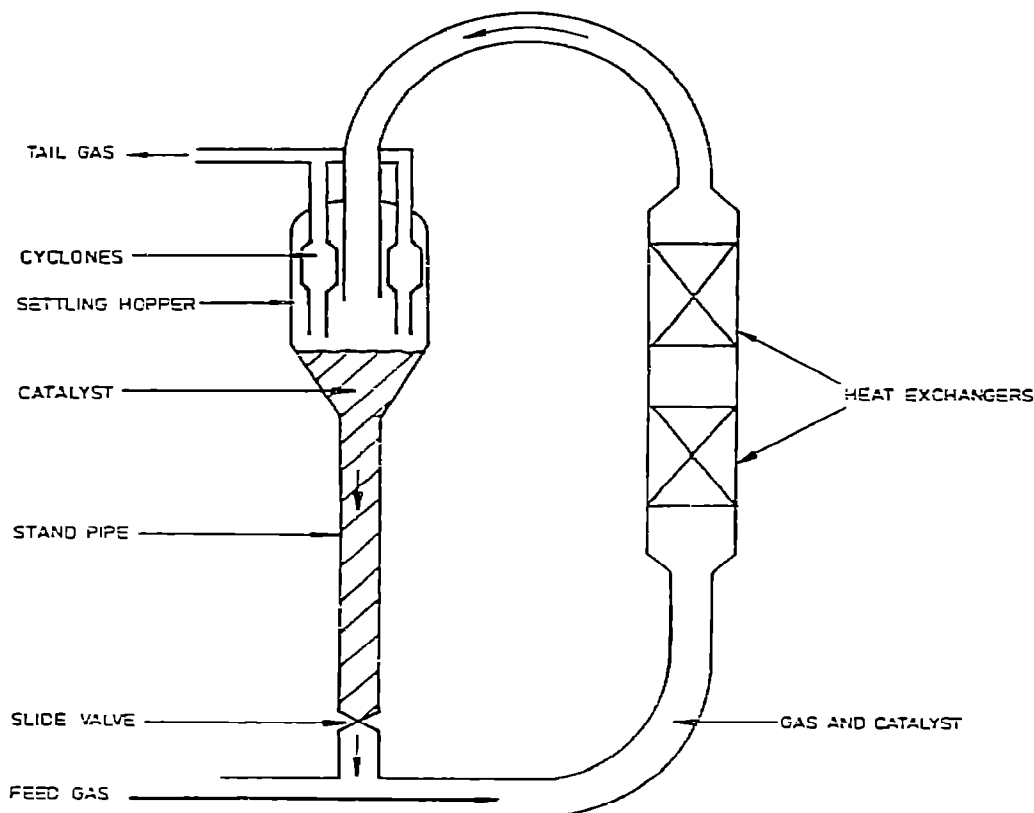

Fig. 1. The transported fluidised bed Synthol reactor.

To date, only iron catalysts have been used. Not only are they cheaper than cobalt or ruthenium, but they have the advantage that even at high synthesis gas conversions the C_2 to C_6 fractions are highly olefinic. The Synthol catalyst is manufactured by fusing iron oxides, together with the required promoters. The ingots are crushed to the desired size and the powder reduced. The catalyst is then charged to the Synthol reactors and under synthesis conditions the metallic iron is converted to Hägg carbide (Fe_5C_2) and also partly re-oxidised to Fe_3O_4. The catalyst used in the fixed bed reactors is prepared by coprecipitating iron and copper with an alkaline solution. The washed precipitate is mixed with the support and promoter materials, and then extruded and dried.
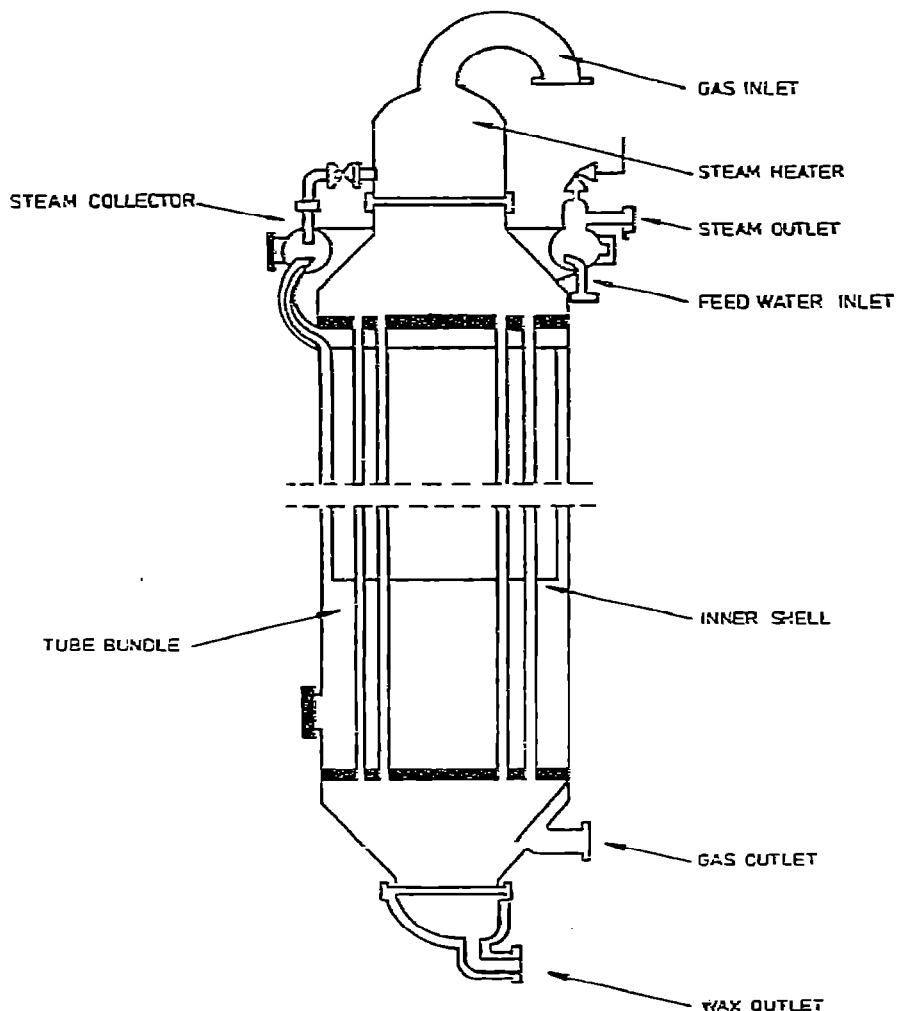
Fig. 2. The Arge fixed bed reactor. Only a few of the catalyst tubes are illustrated.

A more detailed description of the commercial reactors, of the preparation of the catalysts and of the physical and chemical properties of the catalysts is given in a recent review [1].

In addition to the two types of reactors already mentioned, Sasol operates both fixed fluidised bed (FFB) and slurry phase reactors on pilot plant scale. Studies have shown that the product spectrum is not dependent on the type of reactor but rather on the catalyst and the synthesis conditions. Thus, if the same powdered fused-type catalyst is operated in the CFB, FFB or slurry phase mode the product spectra are all the same. Similarly, if the precipitated catalyst is used in the fixed bed or the slurry bed, the hydrocarbon selectivities are similar [1].

Process schemes

Figure 3 depicts a generalised process flow scheme for a Fischer–Tropsch complex. At the Sasol One plant both Synthol and Arge reactors are used. Typical product spectra obtained under current operating condi-
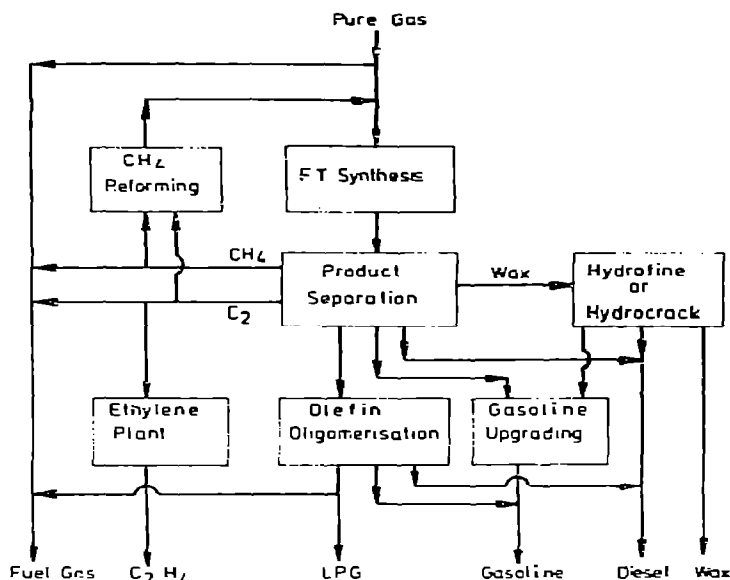

Fig. 3. Generalised process flow scheme for a Fischer–Tropsch plant and the work-up of the products.

TABLE 1

Selectivities of Sasol commercial operations (C atom basis %)

Product	Fixed bed 220 °C	Synthol 325 °C
CH_4	2.0	19
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 chemicals	3.2	6

tions are given in Table 1. The Arge reactors produce mainly long-chain hydrocarbons, with diesel fuel and waxes constituting 66% of the total. The Synthol reactors produce mainly gasoline and lighter olefins.

At the Sasol One plant the C_3 and C_4 olefins are catalytically oligomerised to gasoline. There the Synthol process yields a gasoline to diesel ratio of ca. 9. At the Sasol Two and Three plants only Synthol units are used and the light olefins are oligomerised to yield predominantly diesel fuel. The overall gasoline to diesel ratio currently obtained there is ca. 1.5. By maximising the oligomerisation and also adjusting the cut points, it is possible to obtain a gasoline to diesel ratio of ca. 0.75 from the Synthol process. The fact that the Synthol process produces a large amount of light olefins accounts for the high degree of flexibility obtained.

If higher diesel yields are required, the recommended process is to maximise wax production (using either fixed or slurry bed reactors) and then to hydrocrack the wax catalytically. Extensive pilot plant investigations at Sasol have demonstrated that the wax can be cracked to extinction under relatively mild process conditions. The overall gasoline to diesel ratio obtainable is ca. 0.3 (combining the straight-run Fischer–Tropsch products with those obtained by oligomerisation and hydrocracking).

The gasoline produced by oligomerisation has a high octane rating, but the straight run Fischer–Tropsch gasoline requires upgrading. At Sasol One it is catalytically isomerised while at Sasol Two it is catalytically reformed.

Since the hydrocarbons produced in the Fischer–Tropsch process are predominantly straight-chained, the diesel fuel produced is of high quality. The overall diesel produced via the Fischer–Tropsch and wax hydrocracking process has a cetane number above 65. Furthermore this diesel fuel contains no aromatics and thus makes a highly desirable fuel, bearing in mind that there is strong public demand for low noxious engine exhaust emissions. The Fischer–Tropsch process thus has a marked advantage over the other processes which can convert coal to motor fuels, namely, that it can produce a high yield of high quality diesel fuel.

As can be seen from Fig. 3, the CH_4 present in the product gases is either reformed back to $CO + H_2$ and recycled to the Fischer–Tropsch reactors, or it is sold as fuel gas.

Product selectivity control

It is well known [2] that in the Fischer–Tropsch process the product selectivity can be varied over a wide range. At Sasol this aspect has been fully investigated for many differently prepared iron-based catalysts [1]. CH_4 selectivity has been varied from ca. 1% to ca. 80%. At the other end of the spectrum the hard wax selectivity (that fraction having a boiling point above 500 °C) can be varied from zero to above 50%. There are, however, clearly established interrelationships between the different carbon number products (C_n) as is evidenced by the fact that plots of log C_n/n against n produce

straight lines [2, 3]. These interrelations have been mathematically inter-preted in terms of the Schulz–Flory polymerisation theory [3, 4].

It appears that in general the probability of chain growth is indepen-dent of chain length. (Notable exceptions usually observed are the C_1 and/or C_2 products. This aspect has been discussed elsewhere [1]). Figure 4 illus-trates the relationship between the CH_4 and a few other hydrocarbon prod-ucts in the case of fused iron catalysts in a fluidised bed reactor at Sasol [1].
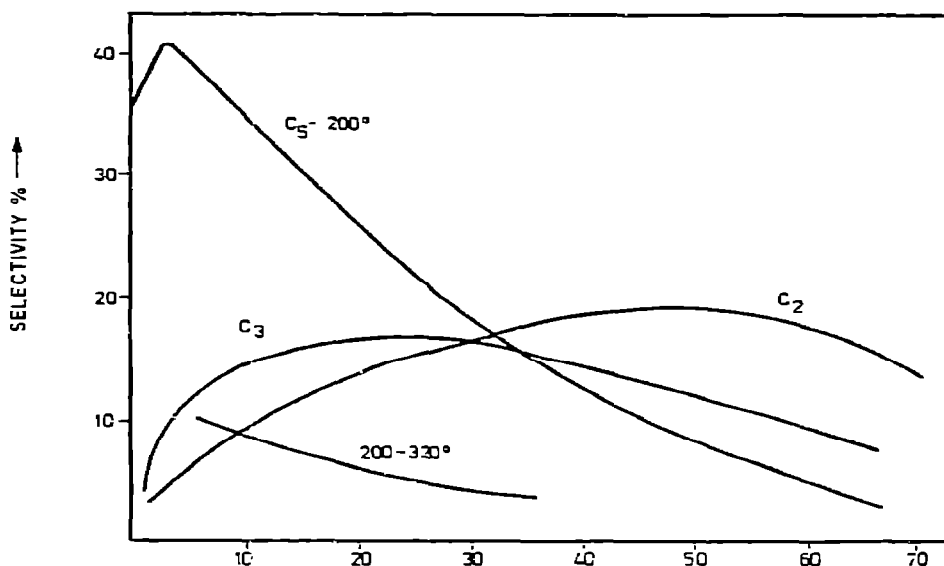

Fig. 4. The relation between the selectivity of various product cuts and the CH_4 selec-tivity (C atom basis).

The data points used to plot these curves were taken from many experi-ments in which different process parameters were varied (*e.g.* catalyst promoter content, temperature, gas composition, pressure *etc.*). The results indicate that irrespective of how the probability of chain growth is altered, the fixed interrelationship between the different hydrocarbon products remains valid.

Temperature

As the temperature is increased the selectivity shifts towards the lighter hydrocarbon products. The rate of the Fischer–Tropsch reaction also in-creases, but so does the tendency to lay down carbon on the catalyst and hence a balance must be struck.

Catalyst basicity

For iron catalysts this is a key parameter. The basicity is not only dependent on the amount and type of the alkali added but also on the inter-action of the alkali with other promoters or impurities. The most commonly

used alkali promoter is K_2O, which reacts with any silica present to form the less basic silicate. In such a case the amount of alkali must be increased to achieve the desired basicity. The presence of 'acidic' component such as Al_2O_3 or TiO_2 also depresses 'basicity' and therefore alumina is not a satisfactory support for iron catalysts. The higher the basicity of an iron catalyst, the higher the average molecular weight of the products.

Catalyst structure

Experience to date has indicated that only iron catalysts with a large number of narrow pores are effective for producing high wax yields. This implies that the primary products (e.g. olefins) should have a long residence time within the catalyst particles, so that they can readsorb on the catalyst and further chain growth can occur. These catalysts have areas of above 300 m^2 g^{-1} and the majority of the pores have diameters below 5 nm. The reduced fused catalysts used in the fluidised bed reactors for producing gasoline and lighter products have areas of ca. 10 m^2 g^{-1} with an average pore size of ca. 30 nm.

Gas composition and reaction pressure

For iron catalysts it has been found that there is a correlation between the selectivity spectrum and the value of the ratio a $p_{H_2}{}^w/(b$ $p_{CO}{}^x + c$ $p_{CO_2}{}^y + d$ $p_{H_2O}{}^z)$. p_{H_2}, p_{CO} etc. are the partial pressures of H_2 and CO etc. The values of the constants depend on the process conditions. For the fixed bed reactor charged with extruded iron catalyst and operating at a low temperature, the simple ratio p_{H_2}/p_{CO} adequately reflects the selectivity. This is illustrated in Fig. 5. The wax selectivity is apparently not affected by the partial pressure of CO_2 nor by the value of the total pressure [1]. For the fluidised bed catalyst operating at a high temperature, the selectivity is, however, also
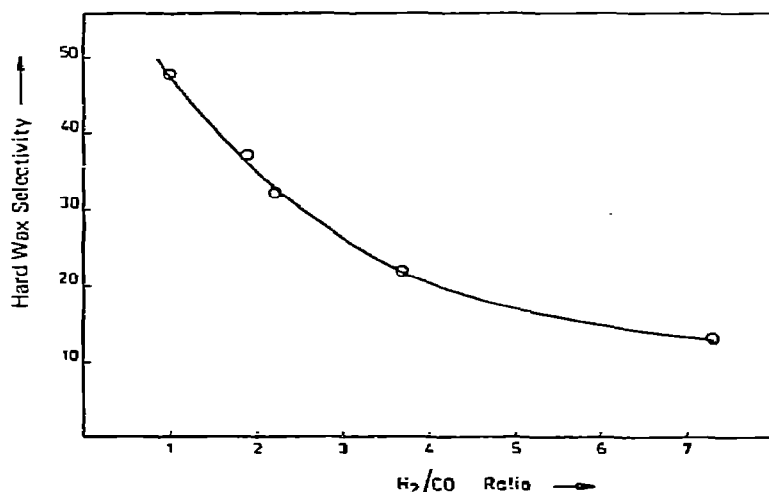

Fig. 5. The relation between the H_2/CO ratio at the reactor entrance and the hard wax selectivity (C atom basis) for low temperature fixed bed operation.

influenced by the partial pressure of CO_2 as well as by the total pressure [1]. To account for these observations a more complex relation is required. Figure 6 shows that there is a reasonable relation between CH_4 selectivity and the value of the ratio $p_{H_2}^{0.5}/(p_{CO} + p_{CO_2})$ at the entrance of the reactor. More recent studies carried out in a stirred tank reactor (Berty type) have shown that the CH_4 selectivity did not change as the degree of conversion changed. Table 2 illustrates a typical example. As the percent conversion increased, the ratio $p_{H_2}^{0.5}/(p_{CO} + p_{CO_2})$ increased. The value of the ratio $p_{H_2}^{0.5}/(p_{CO} + p_{CO_2} + p_{H_2O})$, however, remains constant and this latter ratio thus appears to be the more correct correlating factor. At the entrance of an integral reactor the partial pressure of H_2O is usually very low, and so the numerical value of the above two ratios are the same; hence the relation depicted in Fig. 6 remains valid. Further research work is being carried out at Sasol to refine the above correlation factors.

TABLE 2

Influence of gas partial pressures on selectivity

% CO conversion	CH_4 selectivity	$\dfrac{p_{H_2}^{0.5}}{p_{CO} + p_{CO_2}}$	$\dfrac{p_{H_2}^{0.5}}{p_{CO} + p_{CO_2} + p_{H_2O}}$
30	9	1.3	1.0
39	9	1.4	1.0
46	8	1.5	1.0
64	9	2.1	1.0
75	10	2.8	0.9

Reaction mechanism

Arguments about the mechanism are as old as the Fischer–Tropsch synthesis itself. One point of contention is whether the chemisorbed CO molecule participates as such in the chain growth or whether it first dissociates to C and O atoms. In the latter case, the C atom is hydrogenated to a CH_2-type species which participates as such in the chain growth. Already in 1926 Fischer [5] assumed a carbide was involved in the Fischer–Tropsch reaction. The 'carbide' theory was later refined by Craxford [6]. To account for the large amounts of oxygen-containing products, the concept of intermediate CHOH species was later widely supported [2, 7]. This meant that the bond between the C and O atoms was not ruptured. Pichler [8] assumed that the chemisorbed CO remained intact, and that chain growth occurred by CO insertion. The wheel has now turned full circle and in the past decade many refined experiments have been carried out, the results of which apparently support the concept that CO first dissociates [3].

It must be strongly emphasised that in the actual Fischer–Tropsch synthesis a considerable quantity of oxygen-containing products (e.g. alco-
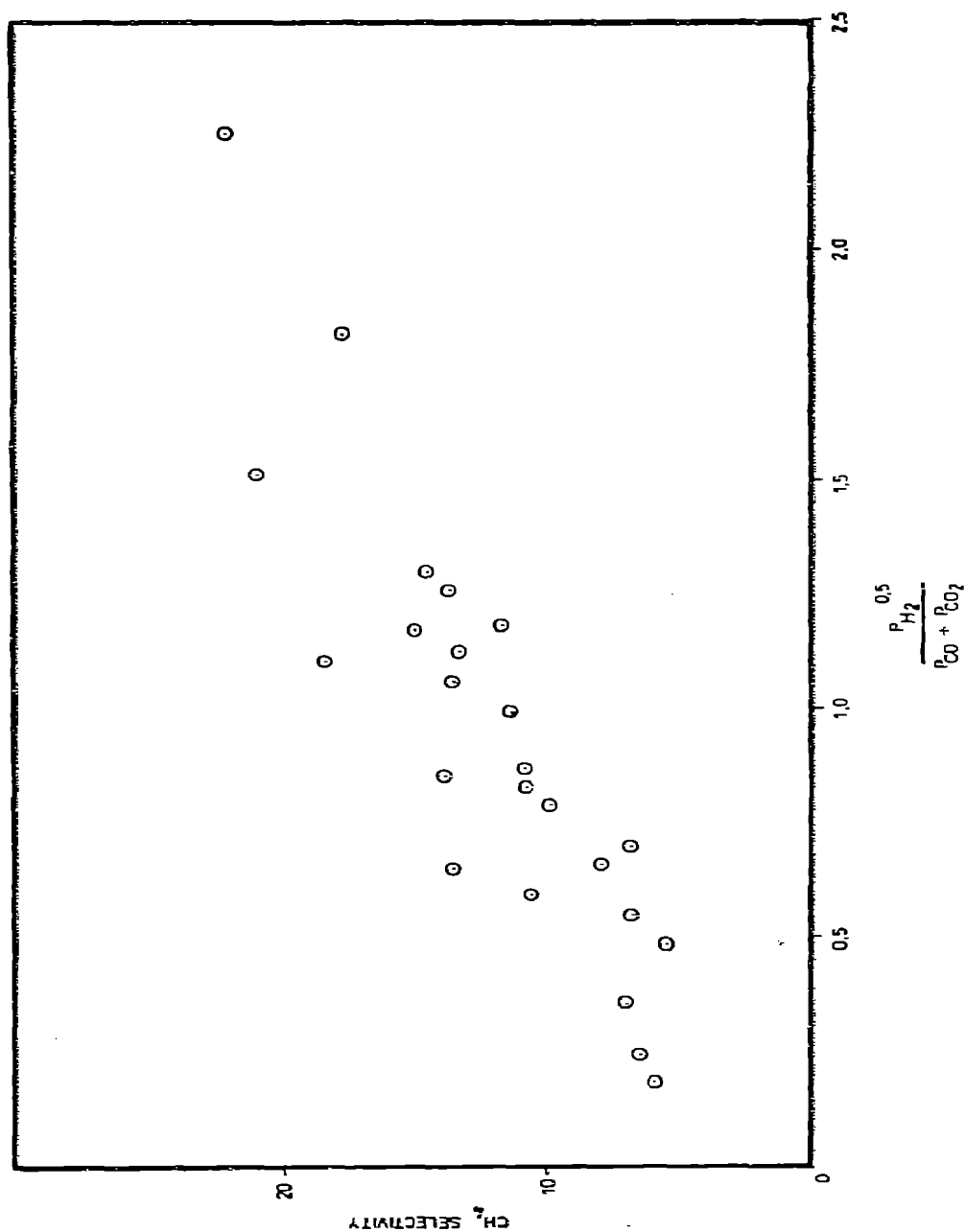
Fig. 6. The relation between the CH$_4$ selectivity and the parameter $p_{H_2}^{0.5}/(p_{CO} + p_{CO_2})$ at the reactor entrance for high temperature fluidised bed operation.

hols, ketones, aldehydes *etc.*) are formed, and that by the adjustment of process conditions (high alkali promotion, low H_2/CO ratio gas, high pressure and low temperatures) these oxygenated compounds become the dominant product [1]. The formation of oxygenates is not unique to iron catalysts, as cobalt and ruthenium can also form significant amounts. It has been suggested [3] that oxygenates are formed by the insertion of CO (or an oxymethylene group) into a growing chain, and that this insertion in fact blocks further chain growth. This, however, would not explain the formation of methanol which is a one-carbon species. Insertion of CO into a chemisorbed hydrogen atom would of course be an acceptable mechanism for methanol formation.

Let us consider the broader field of catalysed $H_2 + CO$ reactions, ranging from methanol synthesis over *e.g.* zinc oxide catalysts, the normal Fischer–Tropsch synthesis to the formation of glycol and glycerine over rhodium. Also bear in mind that in the methanol synthesis some higher carbon-number alcohols are also formed, the formation of which is enhanced by alkali promotion (just as for iron Fischer–Tropsch catalysts). In the formation of methanol from $CO + 2H_2$, no H_2O or CO_2 is formed and there is no need to rupture the C—O bond of the chemisorbed CO molecule. In the formation of glycerine every C atom ends up being attached to an O atom, and here also no C—O bond rupture need be envisaged. If CO insertion is assumed to occur in the formation of glycol and glycerine [1] then this step cannot be chain terminating. By implication it need not be chain terminating either in normal Fischer–Tropsch synthesis.

For the formation of: (a) methanol, (b) glycerine and (c) oxygenated products in the Fischer–Tropsch reaction, the involvement of undissociated CO or of a HCOH-type complex is therefore apparently an essential feature. The formation of oxygen-free products (paraffins and olefins) are readily accounted for in the proposed schemes of Anderson [2, 7], Pichler [8] and Dry [1]. The question then arises as to whether there is any real need for insisting that C—O dissociation is an essential step in the Fischer–Tropsch reaction. However, the studies of Biloen *et al.* [9] do strongly imply this. ^{13}C was pre-deposited on a Ni catalyst and the Fischer–Tropsch reaction then carried out. Not only was $^{13}CH_4$ formed, but also a significant portion of the C_2 to C_4 product molecules contained more than one ^{13}C atom.

As discussed elsewhere [1, 10], the author does not feel it is necessary to choose between the 'undissociated' and 'completely dissociated' CO theories, since the distinction between the two on a working catalyst surface could be very vague, and the possibility of some 'hybrid' being the 'active' species seems quite acceptable. All catalysts active in $CO + H_2$ reactions have a chemical affinity for both C and O atoms, and on CO chemisorption some sort of bond between the adsorption sites and both the C and O atoms can be expected. Consider the four possible 'adsorbed species' depicted in Fig. 7. All four could co-exist, their abundance depending on the relative strengths of the S—C, S—O and C—O bonds. The bond strengths could be affected by the type of catalyst, the promoters present and the process conditions.
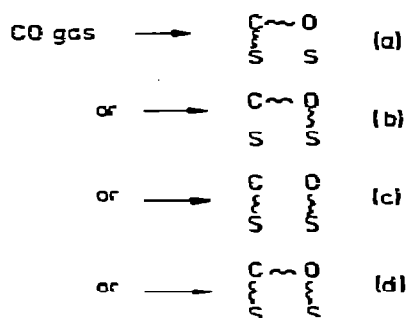
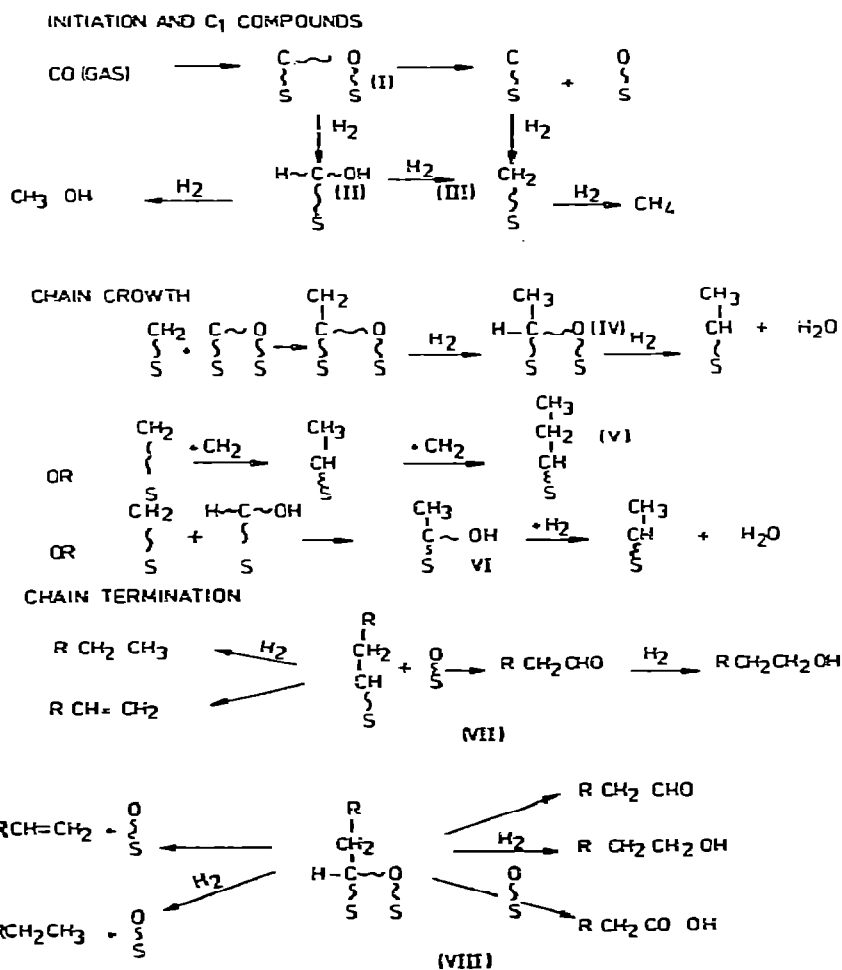Fig. 7. Possible configurations of activated chemisorbed CO. The symbol ⌇⌇ denotes a bond of indefinite order.

Fig. 8. General reaction scheme. The symbol ⌇⌇ denotes a bond of indefinite order.

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Since the role of a catalyst is specifically to weaken the bonds between the atoms of the reactants, the 'bonds' of the adsorbed active species, such as (d), could be so 'loose' and 'vague' that normal techniques such as infrared spectroscopy would not recognise them.

Figure 8 depicts a mechanism which could account for all the major products observed in the Fischer—Tropsch reaction. The basic 'building blocks' could be species I, II or III. The relative abundance of these species would depend on the strengths of the C—O, C—S and O—S bonds. Chain growth is depicted as insertion of either species I, II or III with surface 'alkyl' groups to produce intermediate species IV, V or VI. Chain termination can occur in various ways, as depicted. If the S—O and S—C bonds remain 'loose and vague' it will remain difficult to identify the intermediate species. If the C—O bond remains strong throughout, then oxygenated compounds will predominate. The formation of polyhydric alcohols and the mechanism of the hydroformylation reaction can be explained using the same general reaction scheme [1].

Although elucidation of the Fischer—Tropsch mechanism remains an intriguing research topic, the question that still begs an answer is how will such knowledge enable the industrialist to maximise the desired product cut?

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