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Commercial conversion of carbon monoxide to fuels and chemicals

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Abstract

The Fischer–Tropsch (FT) process has been applied on a commercial scale by Sasol in South Africa since 1955. The main chemicals produced are ethene, propene, high quality paraffinic waxes, alcohols and ketones. Both gasoline and diesel fuels are produced in large volume. Significant advances have been made in the technology of the FT reactors and also in the upgrading of the primary products.

The mechanism of the FT reaction involves stepwise chain growth and because of this, a wide range of products is inevitable. The probability of chain growth can, however, be controlled by adaptation of the catalyst formulation, synthesis gas composition, reactor temperature and pressure. The sequence of the elementary catalytic reactions and the nature of the main participating surface complexes have been controversial subjects for many years. The primary products are straight-chained paraffins, α-olefins, alcohols, and aldehydes and their formation can be accounted for by various modes of desorption of two interrelated surface complexes. Ketones, branched hydrocarbons and aromatics are formed in secondary reactions.

History and economics

In the Fischer–Tropsch (FT) process carbon monoxide is catalytically hydrogenated to yield a wide spectrum of hydrocarbons and oxygenated compounds, e.g.:

$$\text{olefins:}\quad 2nH_2 + nCO \rightarrow C_nH_{2n} + nH_2O$$
$$\text{alcohols:}\quad 2nH_2 + nCO \rightarrow C_nH_{2n+1}OH + (n-1)H_2O$$

Sabatier [1] reported in 1902 that methane was formed when a mixture of H_2 and CO was passed over Ni or Co catalysts. In 1913 the German firm BASF patented the production of liquid hydrocarbons using a cobalt catalyst [2] and in 1923 Fischer and Tropsch [3] published their classical work using alkalised iron as catalyst. By 1936 four Fischer–Tropsch production plants were operating in Germany using supported cobalt as catalyst.

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In the late 1940's it was thought that the world's petroleum reserves were limited and efforts continued to find improved ways of converting coal to liquid fuels. South Africa had no known reserves of petroleum but did have vast deposits of coal which was well suited for gasification to produce CO and H_2. The first Sasol FT production plant came on stream in 1955. By this time, however, the huge oil deposits in the Middle East had been discovered and consequently the expected rise in the price of crude oil did not materialise, thus making the construction of further FT plants uneconomic.

Whether synthesis gas (CO plus H_2) is made by the partial oxidation of methane or of coal, it remains an expensive part of the overall process. A capital cost break-down of a Sasol FT plant [4] is approximately as follows:

	Percentage of total
Coal mining; steam power and oxygen production	47
Synthesis gas production	23
FT synthesis and product refining	30

Since 70% of the cost involves the production of the required purified synthesis gas, it is self-evident that it is essential that the basic raw material, coal or CH_4, is available at a low price.

The Middle East oil crisis of 1973 resulted in a huge increase in the price of oil and hence the economics of the FT process in South Africa improved dramatically which lead to the construction of two new and much larger Sasol plants which came on stream in 1980 and 1982, respectively.

The Sasol process

A simplified process flow diagram of a typical plant is given in Fig. 1. Due to the fact that a wide range of products is formed in the FT synthesis, a complex system of product separations and upgrading is required. Since there is a limited local market for fuel gas, the bulk of the product methane is catalytically reformed to produce H_2 and CO which is then recycled back to the FT reactors. Ethene and propene are refined and used in the production of polyethylene and polypropylene. The remaining light olefins (C_3 to C_5) are oligomerised over "solid acid" catalysts to gasoline and diesel fuels. As there is also a limited market for heavy heating oils, these oils are selectively hydrocracked to gasoline and diesel fuels. The water produced in the FT synthesis contains dissolved alcohols, ketones and aldehydes which are extracted and refined.

Two types of FT reactor systems are used at Sasol. In the low temperature fixed bed reactors the iron catalyst is packed into long narrow tubes (see Fig. 2A). The gas enters at the top and liquid and gaseous products leave at the bottom. The heat of reaction is removed via water circulating on the outside of the tubes. The main objective of these reactors is the production of high molecular mass linear paraffinic waxes and the catalyst formulation and synthesis conditions are geared accordingly.

In the high temperature fluidised bed Synthol reactors the ion catalyst is present as a fine powder. There are two types of fluidised bed reactors. In the "circulating fluidised bed" (CFB) reactor the catalyst is transported by the gas up one side of the reactor and then falls back (as a denser phase) down the other side (see Fig. 2B). In the "fixed fluidised bed" (FFB) system the feed gas also fluidises the catalyst

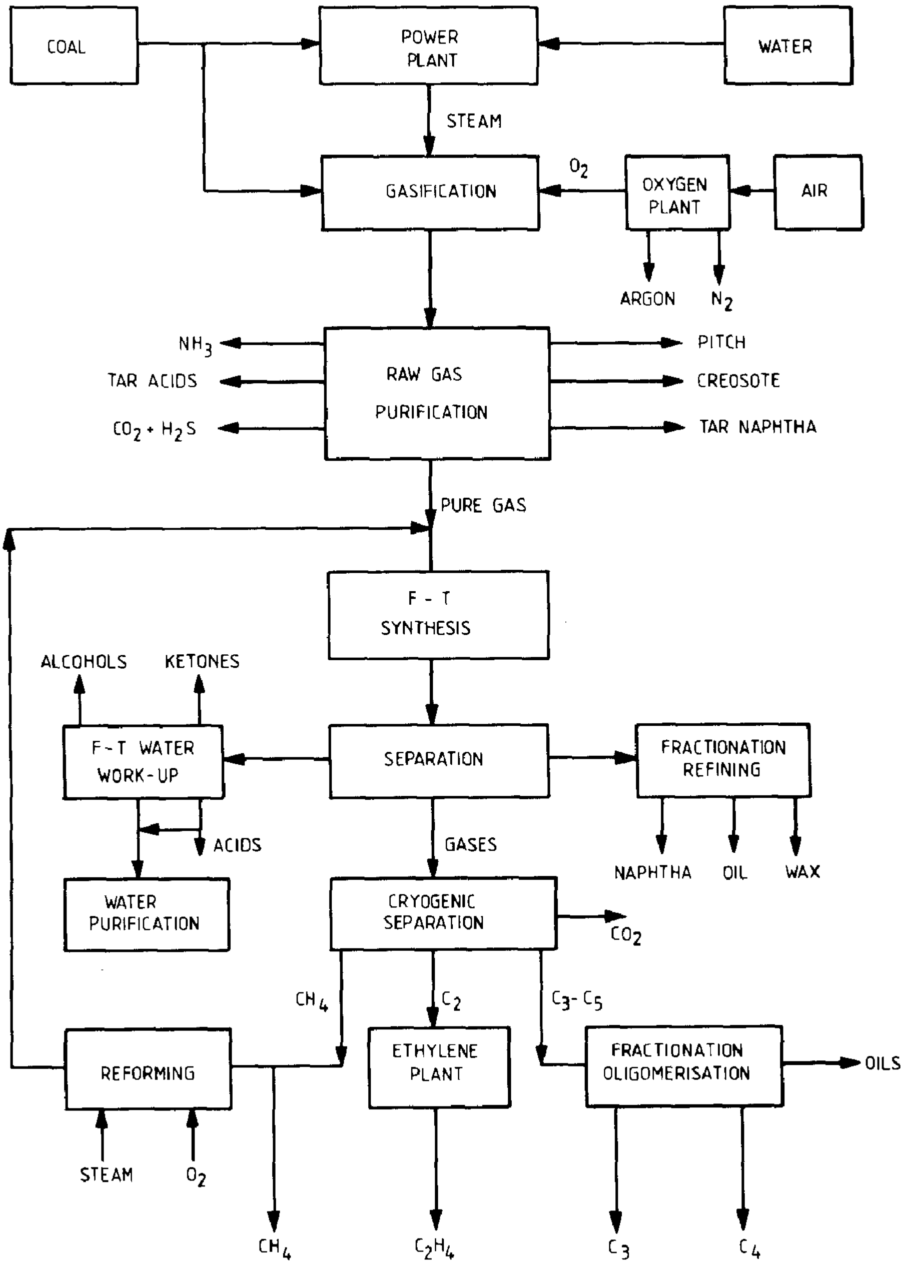


Fig. 1. Process flow scheme of a Sasol coal based Fischer–Tropsch plant.

powder but because the gas linear velocity is lower (than in the CFB reactor) the bed is not transported but ebulates in a "fixed" position (see Fig. 2C).

In fluidised bed reactors the objective is the production of lower molecular mass hydrocarbons, specifically C_2 to C_4 olefins and gasoline. The production of high molecular mass products must in fact be minimised as they would result in catalyst particle agglomeration and hence in defluidisation of the catalyst bed.

The FFB system is a new development and a single commercial unit has recently been built to evaluate its potential.

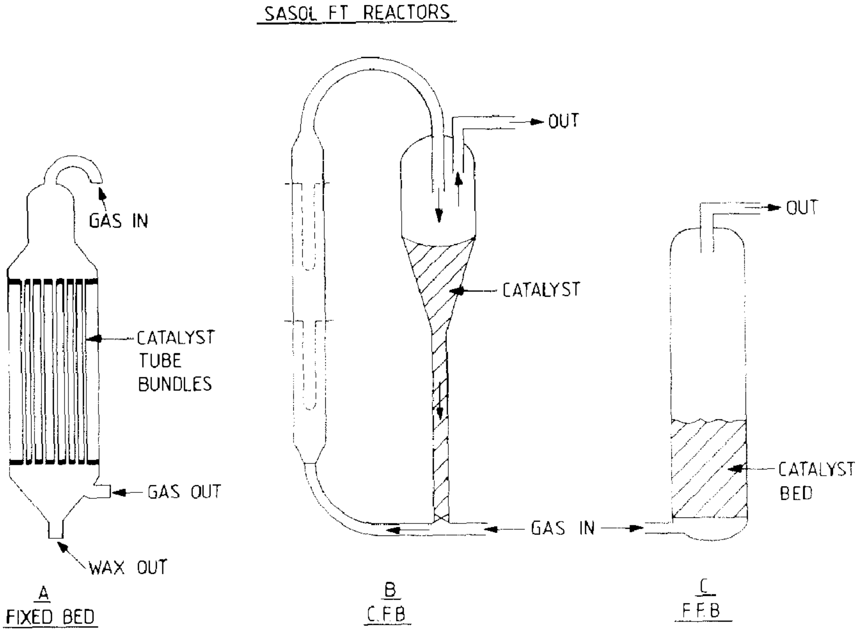


Fig. 2. Types of synthesis reactors used as Sasol. A is a fixed bed reactor, B is a circulating fluidised bed and C is a "fixed" fluidised bed reactor.

Kinetic studies and pilot plant tests showed that a reactor's production could be increased in direct proportion to the reactant partial pressures. The operating pressure of the CFB reactors at the new Sasol plants were consequently raised and recently a new higher pressure fixed bed reactor has been commissioned.

As an alternative to the fixed bed system for wax production, Sasol is currently investigating the "slurry bed" system. This system is similar to the FFB except that the powdered catalyst is suspended in a liquid medium (e.g. molten wax). There are thus three phases inside the reactor: gas, liquid and solid (catalyst). The main advantages of the slurry over the fixed bed reactor are lower capital and running costs.

Typical product spectra obtained in the fixed and fluidised bed reactors used at Sasol are shown in Table 1. Note that for Synthol (fluidised bed) the C_2 to C_4 olefins and gasoline cuts are 24 and 36% respectively while for Arge (fixed beds) the

Table 1

Selectivity (carbon atom basis) for Sasol FT processes

Product	low temperature fixed-bed	high temperature fluidised bed
CH_4	4	7
C_2 to C_4 olefins	4	24
C_2 to C_4 paraffins	4	6
Gasoline	18	36
Diesel fuel	19	12
Waxes	48	9
Water soluble oxygenates	3	6

wax accounts for 48% of the total hydrocarbons. Note also that the amount of diesel fuel produced in the two systems is relatively low. To increase the overall diesel production, it is necessary to apply additional downstream processes such as C_3 to C_6 olefin oligomerisation and selective wax hydrocracking. Both of these processes can yield 80% diesel fuel. This makes it possible to vary the final gasoline to diesel fuel ratio over a wide range to meet varying market demands.

More detailed reviews of the Sasol process can be found elsewhere [4–6].

The chemical nature of FT products

Over iron catalysts at low temperatures the primary products formed in the FT synthesis are linear 1-alkenes, alkanes, alcohols and aldehydes. At higher temperatures secondary reactions occur such as double bond isomerisation, chain branching, cyclisation (yielding naphthenes and aromatics) and the formation of ketones.

The waxes produced in the low temperature fixed bed process are thus straight chained and entirely free of aromatics. The latter property is very important for health regulation reasons and allows the waxes to be used for instance in the production of hand-creams and waxed paper used in the food industry. The waxes are also utilised in the production of a wide variety of products such as jellies, lubricants, printing inks and hot melt adhesives. Sasol FT wax is unique amongst industrial waxes since it has a high congealing point coupled with a low viscosity.

The C_9 to C_{15} olefins produced in the low temperature FT process, being straight chained, are ideal for the manufacture of biodegradable detergents. The hydrogenated C_{10} to C_{18} cut makes an ideal diesel fuel because the paraffins are straight chained (hence have a high cetane number) and there are no aromatics present (hence exhaust pollution is minimised).

In the higher temperature Synthol process the products are more branched and contain aromatics (both factors improve the octane rating of the gasoline). The formation of ketones also become more prominent. Table 2 compares the composition of low molecular mass oxygenated compounds and of the C_{12} to C_{18} cuts produced in the two Sasol FT processes.

Table 2

Comparison of some cuts from low and high temperature FT synthesis [a]

Product type	Compounds	Low temperature fixed-bed	High temperature fluidised bed
Water soluble oxygenated chemicals	CH_3OH	25	1
	C_2H_5OH	50	55
	C_3H_7OH	11	16
	Acetone	2	10
	Methyl ethyl ketone	<1	3
C_{12} to C_{18} oil	Olefins	26	73
	Paraffins	66	10
	Aromatics	0	10
	Oxygenates	8	7
	% straight chained products	93	60

[a] The numbers are mass % of the product type.

At the higher temperatures normal alcohols and aldehydes (e.g. ethanol and acetaldehyde) are in thermodynamic equilibrium, as are ketones and iso alcohols (e.g. acetone and isopropanol).

Selectivity correlations

As is apparent from the data in Table 1, the FT process produces a wide range of products. The Sasol pilot plant reactors have been deliberately operated with differently promoted iron catalysts, different reactor temperatures, feed gas compositions and pressures in order to study the influence of these parameters on the product selectivities. Perusal of the results indicated that there was a clear-cut interrelation between all the products. Figure 3 illustrates the results obtained with the fluidised bed reactors while Fig. 4 gives the results for the fixed bed reactors. These plots indicate that if, for instance the CH_4 selectivity is changed (irrespective of how this is achieved) then the selectivity of all the other products will change by predictable amounts.

This predictability indicates that the chain growth mechanism may be a relatively simple one. Although the detail of the mechanism of the FT synthesis is still a matter of controversy, there has always been agreement that chain growth is probably a step-wise process. The matter can therefore be treated mathematically without needing to know the chemical detail of the surface reactions. If one assumes a certain value for the probability of chain growth, one can calculate the entire selectivity spectrum. Repeating this for different probability values results in a set of curves as shown in Fig. 5. (Further detail of the calculations can be found in previous reviews [5,7]). It can be seen that the theory (Fig. 5) agrees with the practice (Fig. 3 and 4) in that while it is possible to obtain high yields of the

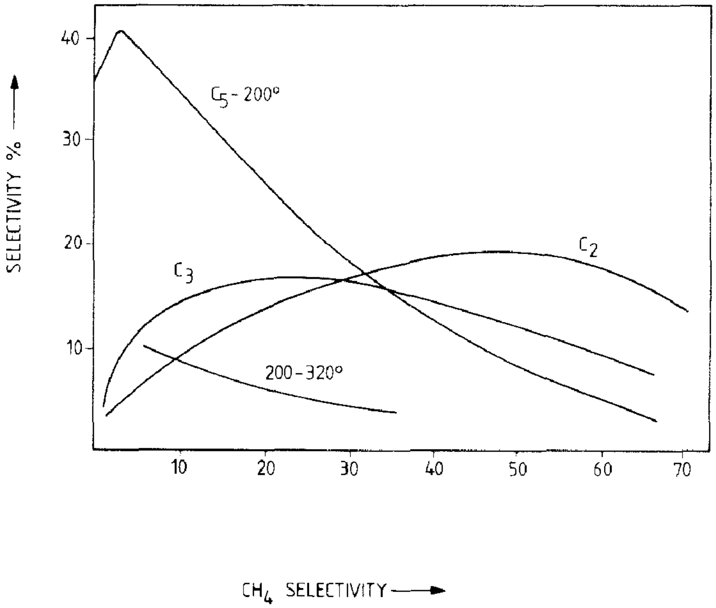


Fig. 3. Relationship between the CH_4 selectivity and the selectivity of a few selected other product cuts in the case of fluidised catalyst bed reactors. Boiling point ranges are in degrees centigrade.

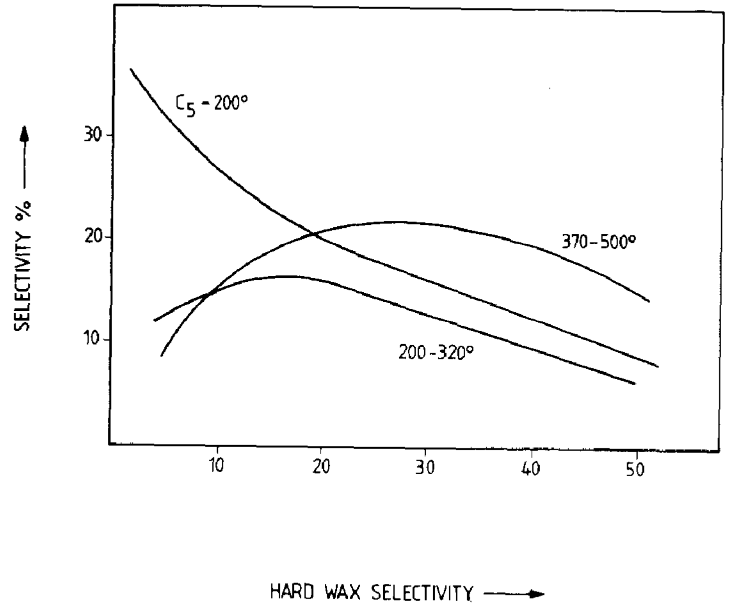


Fig. 4. Relationship between the hard wax selectivity (wax having a b.p. above 500 ° C) and the selectivity of the other product cuts (boiling point ranges in degrees centigrade).

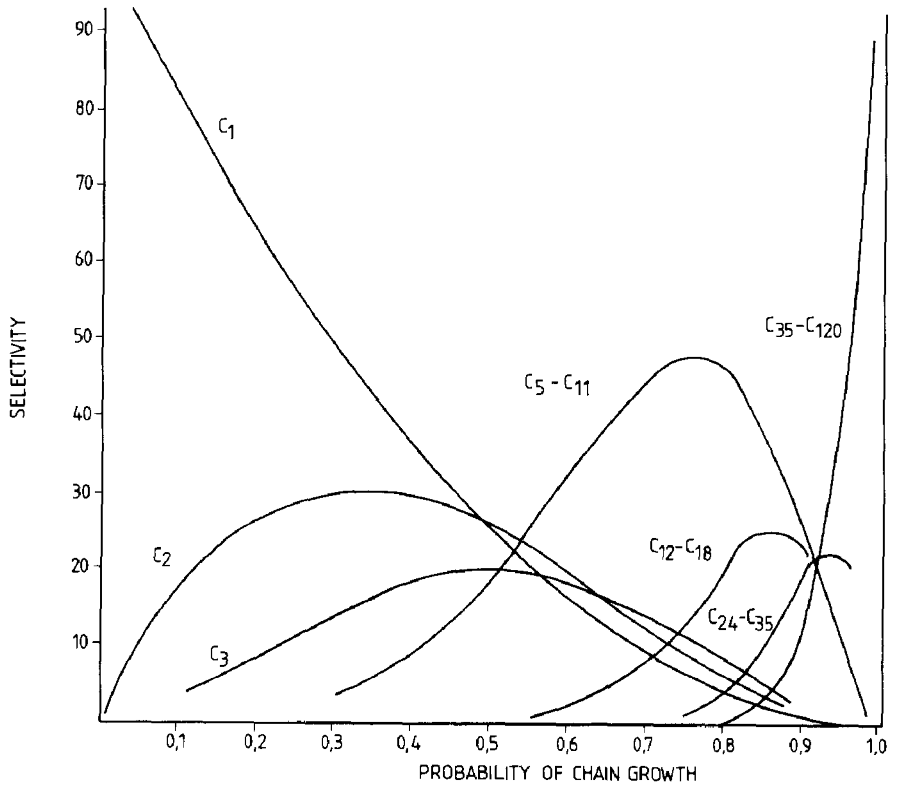


Fig. 5. Plots of the calculated selectivities of certain carbon number product cuts as a function of the probability of chain growth.

extremes (i.e. CH_4 and wax), all other products pass through different maxima. Thus it seems to be impossible to produce more than about 50% gasoline or 25% diesel fuel or about 20% propene.

Mechanism of the FT synthesis

Over the years various mechanisms have been proposed [5,7,8] and it is still a controversial subject. The proposals can be divided into three categories:

(a) The CO molecules dissociate completely after chemisorption on the catalyst surface and the carbon atoms are then hydrogenated to CH_2 entities which link up to form hydrocarbons.

$$CO \rightarrow C + O$$

$$C + H_2 \rightarrow CH_2$$

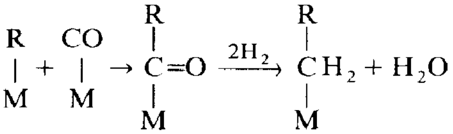
$$nCH_2 \rightarrow (CH_2)_n$$

(b) The chemisorbed CO molecules do not dissociate but are hydrogenated to hydroxy intermediates which link up by water elimination.

$$CO + H_2 \rightarrow HCOH$$

$$HCOH + HCOH \rightarrow HCCOH + H_2O$$

(c) The undissociated chemisorbed CO molecules insert into metal–hydrogen or metal–alkyl bonds and the oxygen is subsequently removed by hydrogenation.



$$\begin{array}{c}R\\|\\M\end{array} + \begin{array}{c}CO\\|\\M\end{array} \rightarrow \begin{array}{c}R\\|\\C{=}O\\|\\M\end{array} \xrightarrow{2H_2} \begin{array}{c}R\\|\\CH_2\\|\\M\end{array} + H_2O$$

The original "carbide" theory proposed by Fischer belongs to category (a) but because of its failure to explain the large amounts of oxygenated products that are formed under certain synthesis conditions theories (b) and (c) were introduced. The wheel has, however, turned full cycle and a considerable amount of experimental evidence now again favours the category (a) concept, i.e. CO dissociation followed by the formation of surface carbenes (CH_2). The formation of oxygenates are postulated to result from the insertion of CO into surface alkyls.

Figure 6 illustrates a possible reaction scheme which is essentially a combination of concepts (a) and (c) and which in a simple way shows how all of the observed primary FT products may be formed. The existence of both undissociated and completely dissociated CO is postulated, either of which can participate in further reactions. The relative abundance of the C_1 species will depend on the chemical state of the catalyst surface, which in turn will depend on the catalyst itself, the temperature and the gas composition.

While chain growth under normal FT synthesis conditions may be predominantly due to CH_2 insertion (to form type **A** surface species, see Fig. 6) it could also occur by insertion of activated undissociated CO to form type **B** species. The latter species may possibly be converted into type **A** by hydrogenation.

The simple desorption or hydrogenation of the two types of surface complexes accounts for the formation of alkenes, alkanes, aldehydes and alcohols which are the primary products of the FT synthesis. It is well established that for an iron catalyst

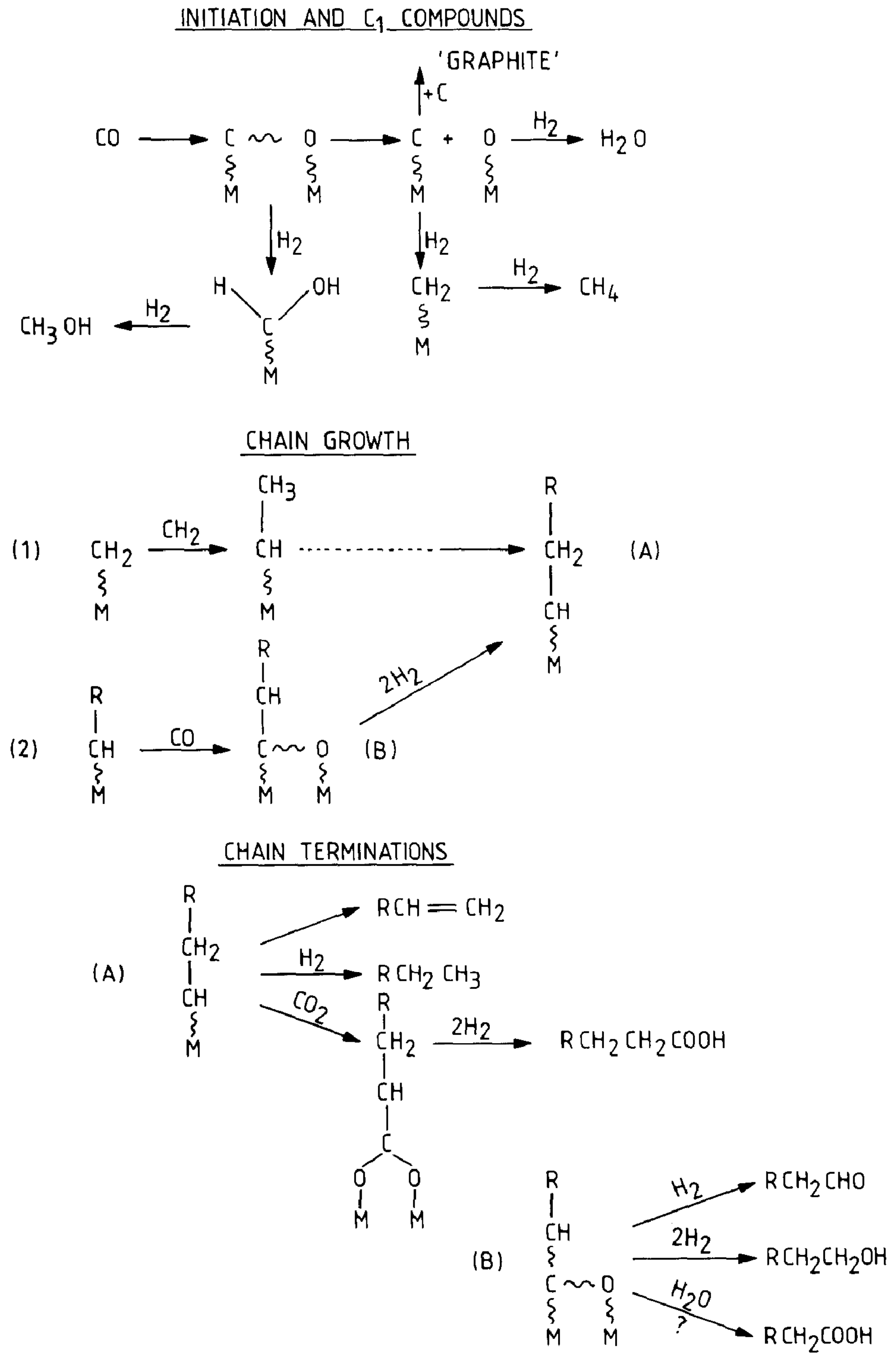


Fig. 6. Possible reaction scheme indicating initiation, chain growth and chain termination steps.

at a fixed temperature, the alcohol selectivity is directly proportional to the hydrogen partial pressure (ref. 5, page 241) as is the ratio of alkanes to alkenes produced. These observations fit the proposed chain termination steps.

The reason for the proposal that acids may be formed via CO_2 insertion, is that the acid selectivity correlates much better with the partial pressure of CO_2 than it does with the partial pressure of water vapour in the reactor.

Selectivity control and reaction mechanism

The main factors effecting the probability of chain growth (and hence the overall selectivity spectrum) are: (a) the partial pressures of the reactants and products inside the reactor; (b) the "basicity" of the catalysts; and (c) the reaction temperature.

(a) Gas partial pressures

In the low temperatures Sasol FT process it is found that the wax selectivity (and hence the overall spectrum as shown in Fig. 4) correlates well with the simple ratio P_{H_2}/P_{CO} inside the reactor [5]. For the high temperature fluidised bed operations the relationship is more complex and it is found that the CH_4 selectivity and hence the other products (see Fig. 3) correlate well with the ratio $P_{H_2}^{0.5}/(P_{CO}+P_{H_2O})$ inside the reactor. These two correlation factors are not as different as they may at first appear to be. It is well known that on iron surfaces both CO and H_2O are strongly chemisorbed while hydrogen is relatively weakly adsorbed. This means that under normal synthesis conditions the surface coveraged by chemisorbed hydrogen will be low compared to that by CO or H_2O. The coverage by hydrogen should be proportional to the hydrogen partial pressure and inversely proportional to the partial pressures of other gases (such as CO and H_2O) with which hydrogen has to compete for the vacant adsorption sites on the catalyst surface. If the coveraged by hydrogen is increased (by say increasing the hydrogen pressure) the probability that the individual CH_2 species will be hydrogenated to CH_4 will increase as well as the probability that other longer chained alkyl species will be hydrogenated to alkanes instead of reacting further with the CH_2 species. The overall effect will be that the probability of chain growth will decrease, i.e. the whole spectrum will shift towards lower molecular mass products. Inversely, if the CO (or H_2O) partial pressure is raised, the hydrogen coverage will be decreased resulting in an increase in the probability of chain growth. In view of the foregoing the practically observed correlations between selectivity and the H_2 and CO pressures are understandable.

The observed correlation of alcohol and acid selectivities with the partial pressures of hydrogen and CO_2 respectively are also understandable when considering the proposed chain termination steps.

(b) Catalyst "basicity"

It is well known that when iron catalysts are promoted with potassium salts the FT selectivity shifts towards the heavier products. The catalyst's "basicity" does not only depend on the amount of "K_2O" added but also on the amount and type of other promoters or impurities present [5]. Thus if silica is present, the "K_2O" will react with it to form a less basic silicate and this will mean that more "K_2O" has to be added to attain the required level of "basicity".

It has been established that when an iron surface is promoted with alkali the work function of the metal is lowered which indicates that electrons have been "donated" to the metal phase. It has also been established that when CO chemisorbs on iron, it "extracts" electrons from the iron. It thus follows that alkali promotion should enhance the chemisorption of CO on iron catalysts. This effect has in fact been repeatedly demonstrated [5]. By increasing the CO chemisorption, the chemisorption of hydrogen is diminished and this, as explained in the previous section, will result in an increase in the probability of chain growth. The higher concentration of chemisorbed CO should also increase the probability of CO insertions resulting in higher levels of oxygenated products being formed. This fits the experimental observation that alkali promotion increases the oxygenates selectivity [5].

(c) Temperature

Irrespective of whether the catalyst used is iron, cobalt, nickel or ruthenium based the probability of chain growth decreases as the reaction temperature is increased, i.e. more CH_4 is formed at higher temperatures. From a strictly thermodynamic point of view the final products of the FT process should be only CH_4 and graphite [5]. The formation route of these two compounds is shown in Fig. 6. The fact, however, that CH_4 and graphite are not major products under normal FT conditions shows that kinetic rather than thermodynamic factors are dominant. As the temperature, however, is increased, the thermodynamic driving forces start having an influence and more CH_4 and graphite is formed.

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