JOURNAL OF CATALYSIS **143**, 166–174 (1993)

Fischer–Tropsch Reaction Studies with Supported Ruthenium Catalysts

III. The Production of Alkenes and High Molecular Weight Hydrocarbons in a Fixed Bed Reactor

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Received December 16, 1992; revised March 23, 1993

An investigation was undertaken to examine the production of low molecular weight alkenes ($C_2^=$ to $C_4^=$) and high molecular weight hydrocarbons (C_5^+) from synthesis gas in a fixed bed reactor with supported ruthenium catalyst. The catalyst used consisted of 0.5% ruthenium on gamma–alumina with a 43% metal dispersion. An experimental reactor consisting of a single 12.5-mm-diameter stainless-steel tube with catalyst packings up to 1 m long, surrounded by an aluminium block with heating elements and an outer insulating ceramic block was used. The effect of temperature, synthesis gas composition (CO/H_2), weight hourly space velocity (WHSV), and bed length on carbon monoxide conversion and selectivity was examined and results are reported. The presence of secondary reactions consisting of hydrogenation and chain growth involving alkenes along the reactor bed was observed. These reactions favour the formation of alkanes and high molecular weight hydrocarbons. The alkene to alkane ratio in the product can be increased by restricting the hydrogenation reaction with the use of a synthesis gas mixture with a high carbon monoxide to hydrogen ratio.

INTRODUCTION

It is well known that any Fischer–Tropsch catalyst produces a broad spectrum of hydrocarbons which may include gases, liquids and waxes with yields described in most cases by the Schultz–Flory equation. However, different supported metal catalysts can produce varying amounts of mainly alkenes and alkanes and to a less extent other organic components over a wide range of molecular weights. A commercially viable Fischer–Tropsch process for the production of motor fuel, which includes petrol and diesel fractions, may involve upgrading of various suitable hydrocarbon fractions. Consequently, a catalyst in a suitable reactor which is capable of producing a spectrum of hydrocarbons consisting of low molecular weight alkenes ($C_2^=$ to $C_4^=$) suitable for oligomerization to liquid fuels, liquid hydrocarbons (C_5 to C_{18}) suitable for upgrading to petrol and diesel and low to medium molecular weight waxes suitable for cracking to liquid fuels could have commercial value. In recent years there has been interest in the study of catalysts capable of producing C_2 to C_4 alkenes as well as studies concerning secondary reactions involving alkenes (*1–11*). Most laboratory studies using microreactors with cobalt and iron catalysts on various supports or in solid solution with partially reduced oxide have shown that very good yields of alkenes relative to alkanes in the low molecular weight range can be obtained at low carbon monoxide conversion levels

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0021-9517/93 $5.00

and high space velocities (*1, 2*). Copperthwaite *et al.* (*2*) obtained a ratio of nearly 6 : 1 for propylene to propane at a conversion level of less than 10% for a Co/MnO catalyst at 350 kPa pressure and 190°C. The production of alkenes from synthesis gas over supported ruthenium catalysts have also been investigated in microreactors under different operating conditions and with different catalyst preparations (*3, 4, 12–14*). Kellner and Bell (*3*) and Smith and Everson (*4*) reported results on the effect of metal dispersion on the selectivity of alkenes and showed that an increase in the propylene to propane ratio was obtained with a decreasing metal dispersion. Kellner and Bell (*3*) however obtained much greater yields of alkenes relative to alkanes (as much as 10 : 1) at 100 kPa pressure and low yields of high molecular weight hydrocarbons.

Possible secondary reactions with alkenes occurring during a Fischer–Tropsch synthesis have been studied with iron, cobalt, and ruthenium catalysts. Novak *et al.* (*6*) considered secondary reactions in an analysis of a continuous stirred tank reactor and a plug flow reactor and reported results showing the effect of readsorption and further growth of primary alkenes on the overall Fischer–Tropsch product distribution. For a plug flow reactor they concluded that the product distribution deviated from the Schultz–Flory model under conditions when most of the readsorbed alkenes participate in growth. The extent of the growth relative to other secondary reactions depends entirely on the catalyst material and operating conditions. Jordan and Bell (*9–11*), Schultz *et al.* (*7*) and others as summarised by Jordan and Bell (*11*) examined the effect of alkene addition to the synthesis gas on the growth process producing high molecular weight hydrocarbons. The addition of ethylene and propylene to synthesis gas with cobalt, iron, and ruthenium catalysts increased the selectivity to liquid hydrocarbons. Jordan and Bell (*9–11*) investigated the relative effect of ethylene, propylene, and butylene addition over silica supported ruthenium catalysts and concluded that the efficiency of alkenes in producing monomers for chain growth decreases in the order ethylene, propylene, and butylene.

The Arge reactors at Sasol I in South Africa are probably the most important commercial fixed bed reactors for the Fischer–Tropsch conversion (*15*). These reactors are packed with promoted iron catalyst pellets and are used mainly for producing medium and high molecular weight hydrocarbons with low yields of low molecular weight alkenes; the propylene to propane ratio is of this order of 1.6 : 1 (*16*). Experimental results involving laboratory fixed bed reactors for the Fischer–Tropsch reaction has been reported by many investigators (*17–22*) many of whom also attempted to model the reactor. Darby and Kemball (*19*) studied the effect of bed length on product spectra with cobalt catalysts and observed some hydrogenation of alkenes with very little chain growth. Feimer *et al.* (*20*) carried out a similar study with copper–potassium promoted iron catalysts in a fixed bed and concluded that at high carbon monoxide conversions, side reactions involving alkene readsorption with hydrogenation and readsorption of carbon dioxide with reaction also participate in the reaction. King *et al.* (*22*) used a long fixed bed to examine exclusively the durability of supported catalyst under conditions producing liquid hydrocarbons with properties suitable for motor fuel.

Experimental results reported in the literature from differential and Berty-type reactors as well as shallow fixed beds (*23–26*) involving ruthenium catalysts have all demonstrated that ruthenium metal has a high intrinsic activity for the formation of all possible hydrocarbons. However, there are no results published following a thorough investigation involving a fixed-bed type reactor with supported ruthenium for liquid fuel production.

An investigation was undertaken in our laboratories, involving a fixed bed reactor

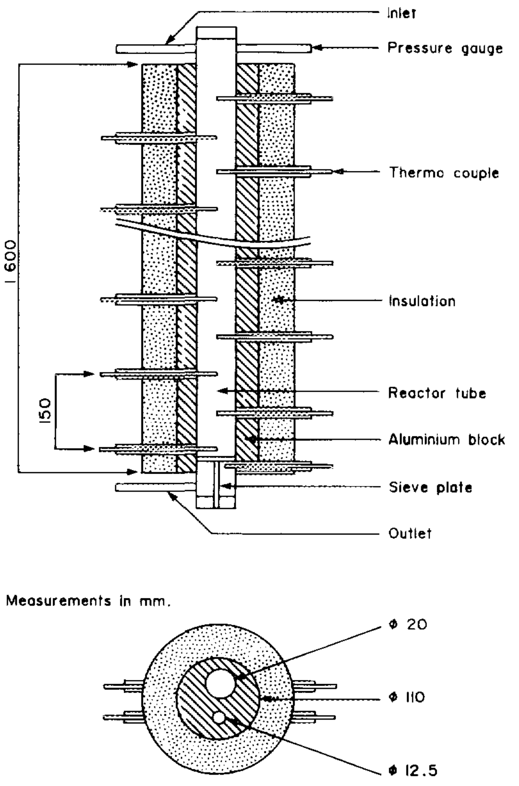

FIG. 1. Fixed bed reactor.

with a well characterized ruthenium on γ-alumina catalyst, in order to establish reaction conditions for producing a suitable range of hydrocarbons for motor fuel synthesis and to examine the production and effect of secondary reactions on the whole spectrum of products. This paper presents results showing the effect of feed temperature, feed composition, weight hourly space velocity (WHSV) and bed length on the relative yields of alkenes and high molecular weight hydrocarbons under conditions favouring a high yield of C_5^+ hydrocarbons.

EXPERIMENTAL

A sketch of the reactor used is shown in Fig. 1. Two stainless steel reactor tubes with diameters of 12.5 mm and 20 mm (not used) respectively are embedded in a cast aluminium block inside a tube with a diameter of 110 mm. Aluminium with a high thermal conductivity ensures that heat was evenly distributed along the length of the reactor thus establishing isothermal axial and radial temperature profiles for a wide range of operating conditions. All experiments were carried out by partially filling the reactor tubes with catalyst particles from the bottom upwards, thus providing a preheating section for the reacting mixture ahead of the catalyst packing for a down flowing gas. Thermocouples are inserted into the packing with the tips situated at the center of the tube and 150 mm apart along the length of the reactor. External heating is provided by means of three 3 kW electrical elements each wrapped around the aluminium block, and with the aid of temperature controllers a desired reactor temperature was maintained. The aluminium block is also surrounded with ceramic bricks in order to minimise loss of heat to the surroundings.

All gases used in this investigation were supplied from prepared high pressure gas bottles with the necessary flow measurement and pressure adjustment. The product stream was allowed to pass through a condensor, to remove high molecular weight hydrocarbons, and a sampling valve fitted inside a gas chromatograph. Analysis of the products was carried out with a Varian 3700 gas chromatograph equipped with TCD and FID detection and fitted with a SE30 capillary steel column and a 2 m Porapak Q stainless steel column for the gas and liquid analyses.

The catalyst used in this study was a commercial preparation of 0.5% (mass) ruthenium on γ-alumina obtained from Engelhardt Industries. The catalyst was in the form of approximately 3 × 3 mm cylindrical pellets with the ruthenium impregnated only on the outer shell of the pellet to a depth of approximately 150 μm. From chemisorption experiments it was established that the metal dispersion was approximately 43%.

The catalyst loading inside the reactor was reduced with pure hydrogen at 350°C

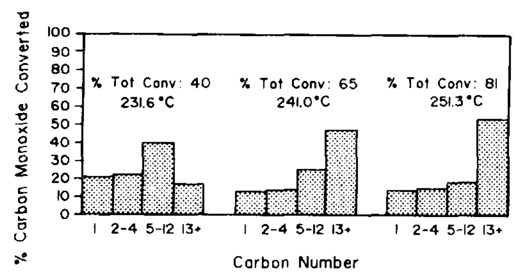

FIG. 2. Effect of temperature. Operating conditions: 2070 kPa pressure, vol% CO = 34.9, WHSV = 0.22/h, and bed length = 0.56 m.

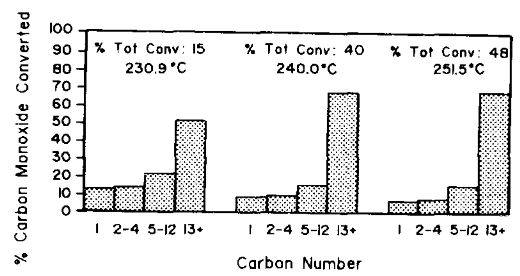

FIG. 3. Effect of temperature. Operating conditions: 2070 kPa pressure, vol% CO = 35.4, WHSV = 0.14/h, and bed length = 0.95 m.

and atmospheric pressure with a flowrate of 330 ml/min for 15 h. After this period synthesis gas at a desired pressure and temperature was introduced into the reactor and gas samples taken every 1.5 h. During the reaction period an initial unsteady-state behaviour (deactivation) was observed for about 12 h followed by a pseudo-steady-state operation as observed previously (*23*). Results reported in this paper are those taken during the later period only. Experiments were conducted for a total of 24 h and with the aid of the gas analysis and an analysis of the liquid collected over the pseudo-steady-state period a complete product spectrum was calculated.

RESULTS AND DISCUSSION

Effect of temperature. It was found that for a fixed set of operating conditions and for a fixed bed length an increase in temperature resulted in an increase in CO conversion with the product spectrum shifting towards the higher molecular weight hydrocarbons. Figures 2 and 3 show the effect of temperature on selectivity of the product for two bed lengths of 0.56 and 0.93 m, respectively. It is observed that the CO conversion increases with temperature which is consistent with results published by other investigators (*23–25*) but the shift to higher molecular weight hydrocarbons is contrary to that observed by the same investigators. It should however be noted that the temperature range in this investigation is within 20°C and that a long fixed bed was used. Also an increase in temperature lowered the ratio alkene to alkane as can be seen in Table 1 for the ratio ethylene to ethane. For a fixed bed length chain growth involving alkenes is enhanced at high temperatures, within the range 230 to 250°C, and this favours the formation of high molecular weight hydrocarbons. This is also accompanied by an increased CO conversion.

Effect of feed composition. The ratio of hydrogen to carbon monoxide (synthesis gas) in the feed stream also has a marked effect on the activity and selectivity of the reaction and is consistent with published results. A number of experiments were carried out with the temperature, pressure, bed length and feed flowrate kept constant. A constant feed flowrate was chosen instead of the WHSV because of the difference of densities of the different reaction mixtures. Table 2 shows the operating conditions and the results obtained. Results indicate that

TABLE 1

Effect of Temperature on Ethylene/Ethane Ratio

Bed length (m)	0.53			0.93		
Pressure (kPa)	2070			2080		
CO in feed (% vol)	34.9			35.4		
WHSV (h^{-1})	0.22			0.14		
Temperatures (°C)	231.6	241.0	251.3	230.9	240.0	251.5
Ethylene/ethane $C_2^=/C_2$	0.46	0.18	0.10	0.16	0.11	0.06

TABLE 2

Effect of Feed Composition on Alkene/Alkane Ratio

CO in feed (% vol)	26.6	35.0	49.6
Feed flow rate (ml/min)	443	446	449
Temperature (°C)	238	241	240
Pressure (kPa)	2100	2100	2100
Bed length (m)	0.56	0.56	0.56
CO conversion (%)	86	40	19
Alkene/alkane $C_2^=/C_2$	0.02	0.18	0.93
$C_3^=/C_3$	0.36	0.93	3.26
$C_4^=/C_4$	0.14	0.28	1.29
$C_{11}^=/C_{11}$	0.01	0.18	0.99
$C_{12}^=/C_{12}$	0.01	0.13	0.77

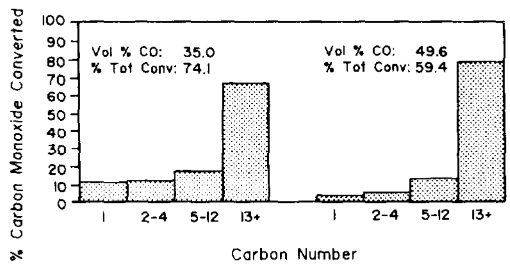

FIG. 5. Effect of feed composition. Operating conditions: 239.6°C, 2050 kPa pressure, and bed length = 0.93 m.

the total conversion of hydrogen and carbon monoxide decreased when the composition of CO in the feed stream was increased. This was accompanied by a shift in the product distribution towards higher molecular weight hydrocarbons as shown in Figs. 4 and 5, with the longest bed giving the most favourable result. Table 2 shows that the ratio of alkene to alkane increases with an increase in CO concentration. It is clear that by restricting hydrogenation with a feed with a high CO composition an improved yield of alkenes and high molecular weight hydrocarbons can be obtained, but unfortunately at a low CO conversion. Under these circumstances chain growth predominates with the maintenance of alkenes.

Effect of weight hourly space velocity. A space velocity (WHSV) defined as the mass of the gas fed per unit time divided by the mass of catalyst is used in this paper. Increasing the WHSV causes the very low molecular weight fraction to increase with a decrease in CO conversion mainly due to the shorter contact time in the reactor. The effect on the production of alkene is shown in Table 3, which indicates that low CO conversion is associated with a higher ratio of alkenes to alkanes. This result confirms that for long contact times secondary reactions occur with a decrease in alkene content and an increase in the formation of higher molecular weight hydrocarbons by chain growth.

Effect of bed length. A detailed analysis of the effect of bed length on activity and selectivity in a fixed bed reactor with ruthenium supported on alumina has not been

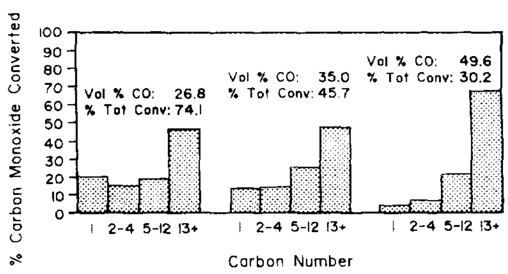

FIG. 4. Effect of feed composition. Operating conditions: 239.6°C, 2100 kPa pressure, and bed length = 0.56 m.

TABLE 3

Effect of WHSV on Alkene/Alkane Ratio

WHSV (h^{-1})	0.22	0.37
Temperature (°C)	251	251
Pressure (kPa)	2000	2060
CO in feed (% Vol)	35	35
Bed length	0.55	0.55
CO conversion (%)	48	30
Alkene/alkane $C_2^=/C_2$	0.10	0.22
$C_3^=/C_3$	1.10	1.47
$C_4^=/C_4$	0.53	0.76
$C_{11}^=/C_{11}$	0.13	0.24
$C_{12}^=/C_{12}$	0.09	0.17

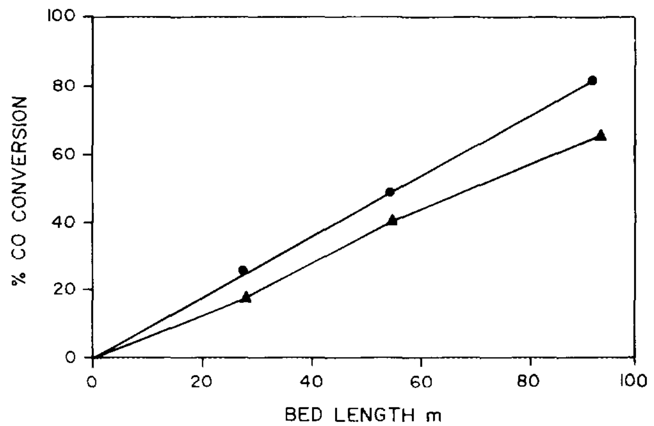

FIG. 6. Variation of carbon monoxide conversion with bed length. Operating conditions: (●) 252°C, 2070 kPa pressure, and WHSV = 0.14/h; (▲) 241°C, 2080 kPa pressure, and WHSV = 0.13/h.

reported in the literature. King *et al.* (*22*) used a fixed bed reactor 0.9 cm in diameter and 70 cm long in order to test the durability of the catalyst and operated at a CO conversion of 25%. In this investigation it was possible with the specially designed reactor described above, to obtain CO conversion greater than 90% under stable isothermal conditions throughout the bed. Figure 6 shows the CO conversion obtained at different levels in the fixed bed reactor for different operating conditions. The linear relationship is a result of two opposing effects, namely, an increased reaction time with length because of a decrease in the total number of moles and consequently a lowering of the linear velocity and a decrease in reaction rate as a consequence of decreasing reagent concentration.

The variation of the product spectrum at different positions in the fixed bed is shown in Figs. 7 and 8. All the results show that the longer the bed the lower the alkene fraction and the higher the high molecular weight hydrocarbons. There is a definite shift towards the higher molecular weight hydrocarbons. This result is different to that obtained by Darby and Kemball (*19*) and Feimer *et al.* (*20*), who used cobalt and iron catalysts respectively and found that there was no change in the width of the product spectrum with bed length. However, it was found with cobalt and iron catalysts that the ratio of alkene to alkane also decreased

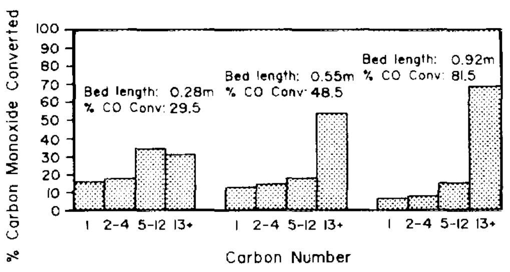

FIG. 7. Effect of position in bed on product spectrum. Operating conditions: 251.6°C, 2060 kPa pressure, and vol% CO = 35.4.

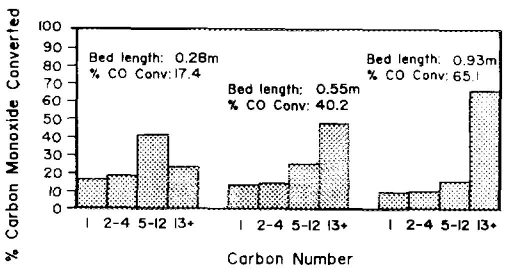

FIG. 8. Effect of position in bed on product spectrum. Operating conditions: 240.7°C, 2080 kPa pressure, and vol% CO = 35.0.

TABLE 4

Effect of Bed Length on Alkene/Alkane Ratio

Temperature (°C)	231		240		251		
Pressure (kPa)	2080		2090		2050		
CO in feed (%)	34.9		26.6		34.7		
WHSV (h^{-1})	0.14		0.18		0.20		
Bed length (m)	0.55	0.92	0.28	0.55	0.28	0.55	0.92
Alkene/alkane $C_2^=/C_2$	0.46	0.16	0.14	0.02	0.41	0.22	0.12
$C_3^=/C_3$	1.15	0.53	1.36	0.36	1.53	1.47	1.05

TABLE 6

Product Spectrum (% Mass)

C_1	Methane	7%
C_2 to C_4	Light gas fraction	8%
C_5 to C_{12}	Petrol fraction	16%
C_{13} to C_{18}	Diesel fraction	10%
C_{19}^+	Low molecular weight waxes	59%

with bed length which agrees with the results obtained in this investigation. Table 4 shows results obtained in this investigation.

The ratio of alkene to alkane decreased because the alkene formed at a section in the bed is readsorbed further down the bed and either undergoes hydrogenation to form alkanes or is polymerised to form higher molecular weight hydrocarbons. Further evidence of secondary reaction is shown in Table 5. In this table flow rates of ethylene are given at different positions in the bed and there is a definite decrease in the amount as it flows down the bed.

Product spectra. From the above results it is clear that ruthenium supported on alumina is not a good catalyst for the production of alkenes but rather favours alkanes. Alkenes, however, are present especially under conditions when the hydrogen partial pressure is low and the contact time small. Alkenes are produced over short fixed bed lengths corresponding to low CO conversions. The simultaneous production of significant amounts of alkenes (low molecular weight) and high molecular hydrocarbons with a high CO conversion is not possible over supported ruthenium. This catalyst, however, is most suitable for producing a useful spectrum of saturated hydrocarbons associated with a high CO conversion. A typical product spectrum found in this investigation comparable with that obtained with promoted iron in an industrial fixed bed, Arge reactor (*15*, *16*), is shown in Table 6. The operating conditions are 250°C, 2100 kPa pressure, WHSV of 0.14 h^{-1} with a synthesis gas containing 36% carbon monoxide. The bed length was 0.92 m, the CO conversion of the order of 81%, and the highest hydrocarbon detected was C_{50}.

Schultz–Flory distribution. The well known S–F equation was fitted to the data obtained in this investigation, namely,

$$M_p = (\ln^2 \alpha) p \alpha^p,$$

where α is the probability of chain growth and M_p is the weight fraction of a hydrocarbon of a certain degree of polymerisation p. It was found that the product distribution is such that no single value of α could describe

TABLE 5

Ethylene Flow Rates at Different Positions in Fixed Bed

Temperature (°C)	240		252		
Pressure (kPa)	2090		2070		
CO in feed (%)	26.6		35.0		
WHSV (h^{-1})	0.18		0.14		
Bed lengths (m)	0.28	0.55	0.28	0.55	0.92
Ethylene flowrate (10^{-7} mol/s)	0.5	0.2	0.7	0.6	0.4

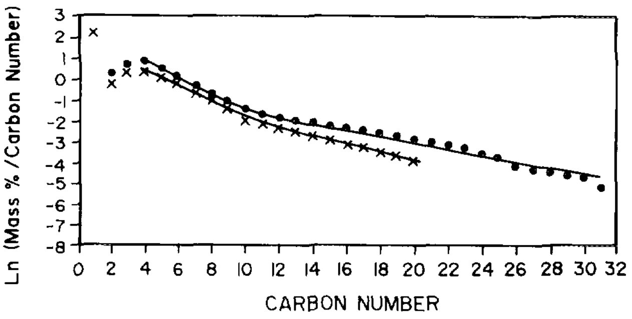

FIG. 9. Schultz–Flory distribution. Operating conditions: (●) 252 C, 2080 kPa pressure, vol% CO = 35.0; WHSV = 0.43/h, and bed length = 0.28 m., (×) 250.9°C, 1080 kPa pressure, vol% CO = 36.2; WHSV = 0.13/h, and bed length = 0.92 m.

the complete spectrum. Figure 9 shows Schultz–Flory fits for certain segments of the spectrum for two typical experiments.

CONCLUSIONS

Secondary reactions consisting of either hydrogenation of alkenes or chain growth by polymerisation of alkenes is important in fixed bed reactors in which the Fischer–Tropsch reaction on supported ruthenium occurs. These reactions which may occur simultaneously have a marked effect on the selectivity with regard to production of alkenes and high molecular weight hydrocarbons. It has been shown that supported ruthenium catalyst behaves differently to iron and cobalt catalyst in a fixed bed reactor of significant length. The effect of the presence of alkenes (low molecular weight) in feed streams (synthesis gas) which favours high molecular weight hydrocarbons formation as observed by previous investigators (*7, 9–11*) has been found to occur along the length of the fixed bed reactor. Long reactor beds favour a high CO conversion with a low production of low molecular weight alkenes and significant yields of high molecular weight saturated hydrocarbons. Reaction conditions were established for the production of a product spectrum consisting of a petrol fraction C_5 to C_{12}, a diesel fraction C_{13} to C_{18}, and a medium molecular weight wax C_{19}^+ fraction with a low yield of olefins at a CO conversion of 80%, comparable to that produced by an industrial reactor with promoted iron.

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