

Liquid Fuels from Coal

DEVELOPMENTS IN THE USE OF RUTHENIUM CATALYSTS FOR THE FISCHER-TROPSCH REACTION

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It is now possible by selecting appropriate reaction conditions to use ruthenium on alumina catalysts to produce economically viable ranges of gasoline and diesel fractions from the synthesis gas produced by coal gasification. Recent work has shown that simultaneous use of ruthenium with an intermediate pore zeolite produces high octane gasoline. The activity and selectivity achievable with ruthenium are compared and contrasted with results from systems based on iron and cobalt catalysts which have already achieved commercial significance.

Natural mineral oil is an essential commodity in the world economy and although known reserves are still very substantial there will eventually be an increased demand for synthetic oils which cover the boiling point ranges of refined natural oils. Since coal is present in far greater quantities than oil in the Earth's crust and its occurrence is more wide-spread, thoughts have turned increasingly to the possibilities of converting coal into oil.

Research in connection with synthesis of liquid hydrocarbons from coal has increased enormously over the last decade. Most of these investigations have been based either upon a direct coal liquefaction or the gasification/Fischer-Tropsch route.

The direct liquefaction processes presently developed originate from the work done by Bergius (1) and all methods essentially use pulverised coal dispersed in a liquid medium, under hydrogen at high pressures and moderate temperatures, in the presence of a catalyst. Under these conditions the reactive component of coal reacts with hydrogen and dissolves to produce a wide spectrum of products ranging from gases to high molecular weight oils,

leaving behind the unreacted solids. Processes for the removal of these unreacted solids from the so-called syncrude and for the refining of the latter to liquid motor fuels, both gasoline (C_5 to C_{12}) and diesel (C_{13} to C_{30}), still need to be developed to an economic scale in order to make the overall process industrially more attractive. Also, because of the complex heterogeneous reactions occurring between certain components of the coal and hydrogen, the grade of the coal can determine the success of the process. There is little doubt that high grade coals are the most desirable. The thermal efficiency of this potentially viable process can be as high as 60 per cent relative to motor fuel. It should however be noted that pretreatment of especially low grade coals, such as de-ashing, could well make the process adaptable to many grades of coal.

This article is however principally concerned with the alternative route to liquid hydrocarbons from coal, which involves initial gasification of the coal followed by chemical interaction on a catalyst surface between the carbon monoxide and hydrogen so produced to give liquid hydrocarbon products. This so called

Possible Stoichiometric Equations for Reactions between Carbon Monoxide and Hydrogen

Methanation	$3\text{H}_2 + \text{CO} \rightarrow \text{CH}_4 + \text{H}_2\text{O}$ $2\text{CO} + 2\text{H}_2 \rightarrow \text{CH}_4 + \text{CO}_2$
Alkanes ($n > 1$)	$(2n+1)\text{H}_2 + n\text{CO} \rightarrow \text{C}_n\text{H}_{2n+2} + n\text{H}_2\text{O}$ $2n\text{CO} + (n+1)\text{H}_2 \rightarrow \text{C}_n\text{H}_{2n+2} + n\text{CO}_2$ $(3n+1)\text{CO} + (n+1)\text{H}_2\text{O} \rightarrow \text{C}_n\text{H}_{2n+2} + (2n+1)\text{CO}_2$
Olefins ($n > 1$)	$n\text{CO} + 2n\text{H}_2 \rightarrow \text{C}_n\text{H}_{2n} + n\text{H}_2\text{O}$ $2n\text{CO} + n\text{H}_2 \rightarrow \text{C}_n\text{H}_{2n} + n\text{CO}_2$ $3n\text{CO} + n\text{H}_2\text{O} \rightarrow \text{C}_n\text{H}_{2n} + 2n\text{CO}_2$
Methanol	$2\text{H}_2 + \text{CO} \rightarrow \text{CH}_3\text{OH}$
Alcohols ($n > 1$)	$n\text{CO} + 2n\text{H}_2 \rightarrow \text{C}_n\text{H}_{2n+1}\text{OH} + (n-1)\text{H}_2\text{O}$ $(2n-1)\text{CO} + (n+1)\text{H}_2 \rightarrow \text{C}_n\text{H}_{2n+1}\text{OH} + (n-1)\text{CO}_2$ $3n\text{CO} + (n+1)\text{H}_2\text{O} \rightarrow \text{C}_n\text{H}_{2n+1}\text{OH} + 2n\text{CO}_2$
Water Gas Shift	$\text{CO} + \text{H}_2\text{O} \rightarrow \text{CO}_2 + \text{H}_2$
Boudouard Reaction	$2\text{CO} \rightarrow \text{C} + \text{CO}_2$
Coke deposition	$\text{H}_2 + \text{CO} \rightarrow \text{C} + \text{H}_2\text{O}$
Carbide formation	$x\text{M} + \text{C} \rightarrow \text{M}_x\text{C}$

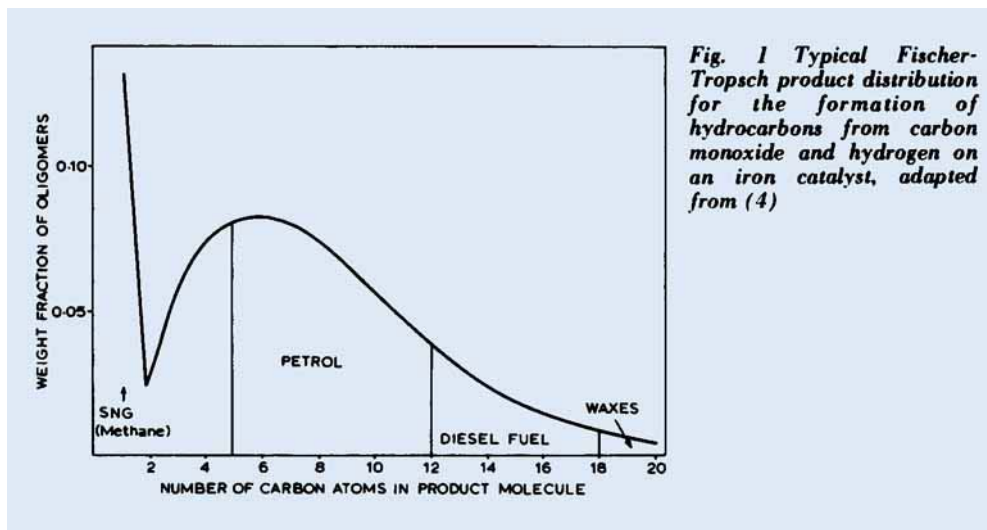
Fischer-Tropsch route can operate on a very low grade coal (containing up to 34 per cent ash). Coal is disintegrated to mainly carbon monoxide, hydrogen and carbon dioxide by direct gasification with oxygen and steam and the so-called syngas (carbon monoxide and hydrogen), produced after purification of the gasifier product, reacted in the presence of an appropriate catalyst to produce liquid hydrocarbons.

Production Developments

The first developments towards a commercial Fischer-Tropsch process were based on cobalt. These took place in Germany, Japan and elsewhere in the 1930s and 1940s and by 1945, for example, nine cobalt based plants were in operation in Germany with a total annual capacity of 740,000 tonnes, (2). The next major commercial development was based on iron catalysts and in the mid 1950s SASOL (South Africa) was operating its first iron-potassium catalyst based plant, SASOL I. The experience gained in operating this plant and the growing uncertainties in oil supplies in the 1970s have led to the decision to construct two further and much larger plants; SASOL II and SASOL III

which will be in full operation during the early 1980s. In spite of the highly capital intensive nature of the gasification of coal the cost of this route is beginning to look more feasible as the price of oil continues to rise. A very important contributing factor in the success of SASOL to date is the local source of readily available coal. However, specific commercial plans are also now being made for Fischer-Tropsch operations in other parts of the world, notably in the U.S.A.

This commercial success, together with the potential increased demand for synthetic fuels, has led to increased research activity in many centres throughout the world during the last ten years. The hydrocarbon growth reaction was first studied in the early 1920s. Fischer and Tropsch showed that a range of liquid hydrocarbons and oxygenated products could be produced from carbon monoxide and hydrogen, by a growth reaction over iron and cobalt catalysts at 200 to 250°C and atmospheric pressure. This discovery was an extension of Sabatier's work, in 1902, in which it was shown that nickel catalysts may be used to prepare methane from synthesis gas. Nickel catalysts are used for the production of methane – substitute natural gas – from synthesis gas, but ruthenium is now



also being actively considered (3). Starting with syngas, methane is in fact the only member of the hydrocarbon series which can be formed as the only product.

The presence of chemical and structural promoters in the catalysts has significant effects, as have the procedures used for catalyst manufacture, the surface conditions (including metal area), the degree of reduction, and other factors. The Fischer-Tropsch synthesis involves an oligomerisation growth mechanism and a typical product range is shown in Figure 1, (4). Cobalt and iron catalyst systems have achieved the most commercial significance so far, but ruthenium could be important in the future. Recent research work (5, 6) on product distribution has shown that ruthenium on alumina catalyst systems can be used to give higher proportions of petrol and diesel fractions than either equivalent iron- or cobalt-based catalysts. Consequently the yields of both gaseous products (methane and carbon dioxide) and waxes were lower with ruthenium, and a high conversion run at 30 atm yielded 85 per cent liquid hydrocarbons.

With further study on relationships between conditions and product distribution, ruthenium seems likely to prove the most desirable Fischer-Tropsch catalyst for producing a commercially acceptable range of hydrocarbons.

Other metals such as nickel and rhodium are also active Fischer-Tropsch catalysts but use of these metals has not been significant industrially.

Reaction Mechanism

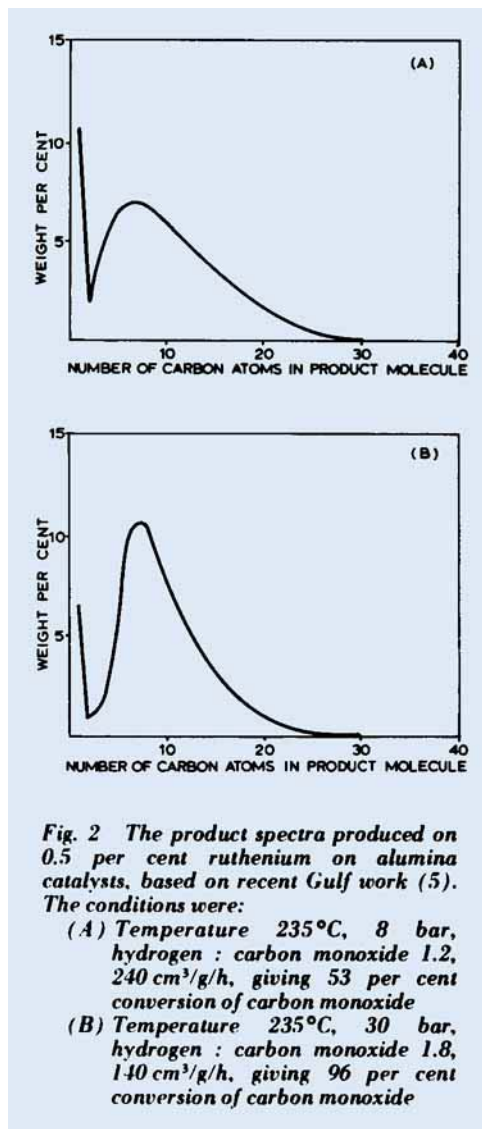
A very complex range of products can result from the reaction of carbon monoxide and hydrogen over a suitable catalyst as shown by the stoichiometric equations in the Table. In addition to aliphatic hydrocarbon formation, analogous reactions can result in the production of alcohols, aromatics, aldehydes, ketones and cyclic compounds (7). When it is borne in mind that isomerisation can also occur, it can be seen that a very large variety and number of products can be produced. However, it is possible to control the reaction to give mainly linear hydrocarbons, and this reaction mechanism involving the growth of hydrocarbon molecules, C_nH_{2n+2} and C_nH_{2n} , on the catalyst surface is not yet fully understood although various theories have been advanced. From a practical point of view it is possible to control the carbon numbers of especially the alkanes and olefins in the final product by suitably adjusting the reaction conditions, such as temperature, pressure, feed composition and space velocity, to give the desired motor fuels. The basic aim is to increase the selectivity relative to the useful fuel

fractions, that is (C_5 to C_{12}) and (C_{12} to C_{18}). The less desirable products are the low molecular weight hydrocarbons and high molecular weight waxes, and operating conditions are selected to minimise the formation of these fractions.

The formation of all Fischer-Tropsch products is exothermic, and product formation becomes less probable, thermodynamically, as the reaction temperature is raised (8). Also the degree of unsaturation of the product increases with temperature; but since the yield per pass through the reactor would be small for compounds which have a positive free energy change for formation, alkynes are not produced under these reaction conditions. Methane is by far the most thermodynamically favoured hydrocarbon product but in chemical reactions the yields are controlled by kinetic considerations, so the types of products formed in practice and their molecular weight distributions are controlled by choice of reaction conditions, catalyst and reactor configuration.

Recent Work

Extensive comparative laboratory investigations involving the Group VIII metals iron, nickel, cobalt, ruthenium, rhodium, palladium, platinum and iridium on various supports such as alumina, silica and titania have recently been reported (6, 9). These catalysts (with crystallite sizes of the order of 10 to 100 Å) are more highly dispersed on the metal oxides and have lower metal loadings, when compared to those used commercially involving promoted fused iron catalysts. Vannice (6) ranked these metals for methanation activity and reported the following order, ruthenium-iron-nickel-cobalt-rhodium-palladium-platinum-iridium; for optimum yield of higher hydrocarbons at atmospheric pressure, ruthenium being the most favourable. Pichler however showed many years ago that ruthenium was capable of producing waxes at very high pressures and low temperatures, and some of these compounds had molecular weights of the order of 7,000 to 100,000 (2). On the other hand ruthenium also has a very high activity for methanation at high temperatures and low pressures, a characteristic



which is reflected in the fact that some twenty to thirty units for gas purification via methanation over supported ruthenium existed in the U.S. by 1974 (10). Ruthenium on titania and manganese oxide have also been used to increase the yield of light olefins under suitable reaction conditions. Work at the Universities of Natal and Potchefstroom (11) and at the Johnson Matthey Group Research Centre has indicated that under suitable conditions ruthenium may be used to give very useful ranges of liquid

hydrocarbon products. These results are consistent with very recent literature reports.

Perhaps the most significant recently published work is by a Gulf research team (5) which has highlighted the potential of ruthenium compared with iron and cobalt. For a 0.5 per cent ruthenium on alumina catalyst turnover numbers of 0.028 per second at 250°C were recorded, but this figure increases to 0.085 for freshly reduced 5 per cent ruthenium on alumina (6). The shape of the product distribution curve depends on the precise reaction conditions chosen, see Figure 2, for example use of higher hydrogen : carbon monoxide ratios gives decreased olefin content and a slight increase in the extent of chain branching. A high conversion run at 30 atmospheres yielded 85 per cent liquid hydrocarbons. Selectivity to gas was low due to low hydrogen partial pressure and the selectivity to waxes, C_{19+} , was also low.

Reaction rates and product distributions for cobalt, ruthenium and iron catalysts were measured under steady state conditions free of external heat and mass transfer effects, and the different product spectra obtained were compared. The potential advantages of ruthenium for producing useful ranges of petrol and diesel fuels are again apparent.

Research at Mobil has taken the development of ruthenium catalysts one stage further by combining use of this metal with an intermediate pore zeolite of the ZSM-5 type to produce a high octane gasoline in a single step (12). The system upgrades the small molecular weight intermediates into a mixture of products rich in aromatics and with a boiling point in the gasoline range. The Fischer-Tropsch reaction intermediates are converted in situ to aromatics and highly branched aliphatics by acid catalysed hydrogen transfer reactions. This bifunctional catalyst system converts at least 95 per cent of the synthesis gas to a product mixture that boils in the gasoline range and is rich enough in aromatics to give an octane number between 80 and 104. The initial products from the SASOL process are reformed to increase their octane numbers. Mobil workers

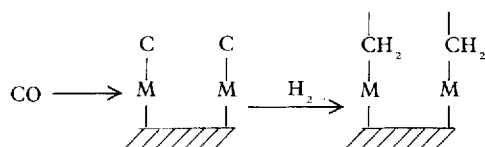
also found that methane production can be limited either by using low hydrogen : carbon monoxide ratios or by operating at higher pressure, lower temperatures, and for shorter times.

The use of metal clusters, also involving the Group VIII metals, for producing alcohols and alkanes from carbon monoxide and hydrogen dispersed in a liquid medium is receiving a lot of attention in some laboratories (13), but substantial conversion to hydrocarbons in the petrol range has still to be achieved. It is expected that more research in this field will be undertaken to produce suitable clusters for synthesis of exclusively higher hydrocarbons.

Detailed Mechanism

Ever since the reaction was first discovered more than 50 years ago, the nature of the surface species and the detailed mechanistic sequence by which the Fischer-Tropsch reaction proceeds has been the subject of much study and discussion and this debate is still continuing (14).

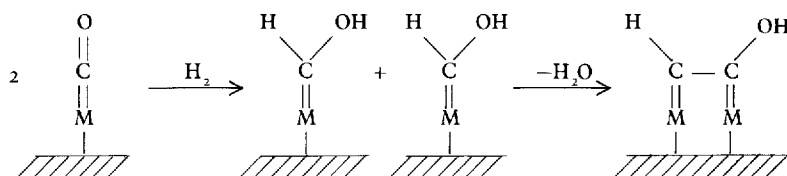
A common feature of all the mechanistic proposals is that of oligomerisation initiated by a C_1 species on the surface, with the product distribution being determined by relative rates of chain propagation and termination. This will be affected by a number of factors including the nature of the metal atom and the ease with which it forms and breaks metal-carbon and metal-hydrogen bonds under the reaction conditions. There are likely to be significant differences between cobalt, iron and ruthenium in this respect. Fischer and Tropsch themselves postulated initial reduction of the carbon monoxide to form a bulk metal carbide species (2). This theory was later modified to include surface rather than bulk metal carbide:



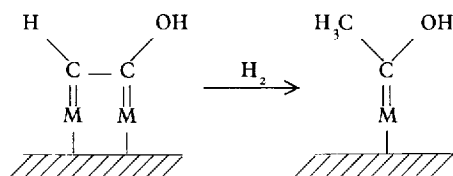
The metal carbides are reduced to methylene groups and chain growth is then accomplished

by linking adjacent methylene groups, followed by hydrogenolysis of the remaining metal-carbon bonds to give a range of predominantly straight chain hydrocarbons.

Another mechanistic theory, which achieved prominence in the 1950s, involves the formation of **oxygenated intermediates** on the surface. In this hypothesis adsorbed carbon monoxide is hydrogenated to an hydroxylated species and these then link by condensation with the elimination of water:

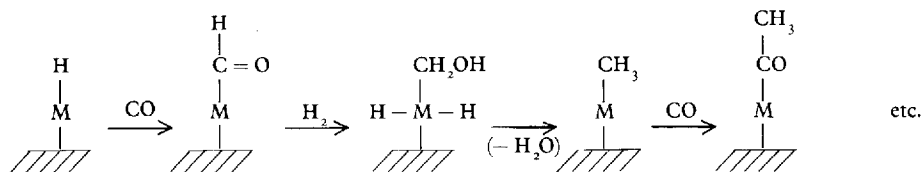


Partial hydrogenolysis then gives carbon chains attached to the metal surface, for example:

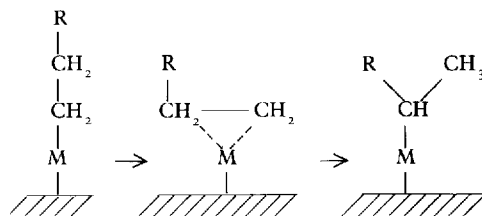


This mechanistic pathway involves associative adsorption of carbon monoxide rather than dissociative adsorption to give a carbene.

Yet another mechanistic postulate involves growth from a **single surface** site (4). This mechanism is related to those postulated in homogeneous catalysis, and it involves initial metal hydride formation. It is known that pre-reduction of ruthenium with hydrogen at temperatures of around 500°C produces good results and this may facilitate the initial formation of metal hydride. Carbon monoxide is then co-ordinated to the metal surface and inserted into the metal-hydrogen bond to initiate chain growth which then proceeds by successive reaction with hydrogen and carbon monoxide:



Hydrogen transfer of the following type could give some branching (15):



Reductive elimination of metal carbonyl species would give oxygenated products. In experiments with ruthenium at low temperatures and high pressures alkyl metal carbonyls have been isolated and shown to be intermediates in the synthesis of polymethylene (2). The chain growth within the alkyl metal carbonyl complex may indeed have proceeded by alternate reaction with carbon monoxide and hydrogen (via metal hydride).

From the vast amount of experimental evidence now available on Fischer-Tropsch it is difficult to conclude that one universal mechanism covers all situations, and elements of each of the above three types of reaction sequence may operate depending on procedures used for pretreatment of the catalyst and the reaction conditions used.

Conclusion

Some recent research results indicate that it is now possible to synthesise liquid hydrocarbons from synthesis gas over 0.5 per cent ruthenium on alumina with a better overall

product range than is obtained at present with iron catalysts on a commercial scale. Reaction conditions may be selected such that hydrocarbons above C₁₈ can be minimised to negligible quantities and hydrocarbons in the range C₁ to C₄ can be kept to manageable proportions. Cobalt-based catalysts were the first to be used commercially and these have been followed by iron-based systems. It now seems likely that ruthenium will find significant use in third generation systems. Ruthenium is intrinsically more expensive than cobalt and iron, however

it may be recovered from spent catalysts and recycled in the form of fresh catalyst, thus reducing the overall catalyst inventory. Ruthenium was not considered as a potential industrial Fischer-Tropsch catalyst in the early 1930s because of its cost; but with the currently available improved catalyst technology involving highly dispersed supported ruthenium the intrinsic high activity of this metal can be effectively utilised and its overall economic performance compared with iron now looks more favourable.

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Cogeneration of Nitric Acid and Electricity

PLATINUM ELECTRODES EMPLOYED IN HIGH-TEMPERATURE FUEL CELL

One of the most important industrial processes to utilise a platinum group metal catalyst is the production of nitric acid. In the process a mixture of ammonia and air is passed over a rhodium-platinum catalyst gauze at a temperature of 750 to 950°C, first producing nitric oxide and then nitrogen dioxide which is subsequently absorbed in water. The reaction is highly exothermic and in many modern high pressure plants the heat energy from the tail-gas is recovered as it passes through a turbine, thus contributing to the power required to compress the process gas.

For a long time the desirability of obtaining this energy as electricity, rather than as heat, has been appreciated. Now workers at the Massachusetts Institute of Technology have reported on an ammonia high temperature solid electrolyte fuel cell which appears to offer an

opportunity for producing nitric acid while recovering the exothermic energy as electricity, (R. D. Farr and C. G. Vayenas, *J. Electrochem. Soc.*, 1980, 127, (7), 1478-83).

Their fuel cell consists of an yttria-stabilised zirconia tube with electrodes of porous platinum, having an estimated thickness of 3 microns, deposited on both surfaces. The electrodes performed well over long periods of time, and scanning electron microscopy showed that extensive sintering and faceting had occurred on the anode, similar to that which is observed during the normal catalytic oxidation of ammonia over platinum. The fuel, ammonia diluted with helium, flows through the tube while the cathode is exposed to air. Nitric oxide is the primary electro-oxidation product, and under optimum operating conditions yields in excess of 60 per cent can be obtained.