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RUHR-CHEMIE A. G. STERKRADE HOLTEN

INTERROGATION OF DR. O. ROELEN

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RUHR-CHEMIE A.G. STERKRADE HOLTEN

Interrogation of Dr. O. Roelen at Wimbledon
November 15th and December 20th 1945

Reported by :

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Fuels and Lubricants

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A. Various Catalysts and Their Conditions of Use.

(1) Synthol

As early as 1923 it was shown by Fischer and Tropsch that a complicated mixture of alcohols, esters, ketones and other oxygen-containing compounds can be obtained from water-gas using alkalised iron at pressures of 100 atm. and above. This mixture is called Synthol.

(2) Ruthenium as a Catalyst.

Fischer and Pichler found that ruthenium is an excellent catalyst for the synthesis of high and very high molecular paraffin hydrocarbons. At 100 atm. pressure, for example, the use of ruthenium produced the biggest hydrocarbon molecule so far obtained, one having well over 100 carbon atoms in the molecule.

The work was confined to the initial laboratory experiments because of shortage of ruthenium.

(3) The Iso-Synthesis.

More recently, it was found by Fischer and Pichler that, under certain conditions, using thorium dioxide as catalyst, strongly branched chain or cyclic hydrocarbons can be obtained directly from carbon monoxide and hydrogen.

The working conditions that must be maintained are not simple; they are among others, high temperatures, e.g. 400 °C.; high pressure, e.g. 100 atm. and above, as well as complete absence of even traces of metals of the iron group, particularly iron itself.

These severe conditions supply the reason why the iso synthesis has so far been restricted to the laboratory scale, although the products are very interesting, e.g. high-octane benzine, naphthenes and aromatics.

During the war we tried to erect a semi-technical plant at Ruhrchemie for the iso synthesis, but could not obtain the necessary special steel high pressure equipment.

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(4) Nickel Catalysts.

In 1931 it was discovered by Fischer and Meyer that like cobalt and iron, Ni can bring about the formation of higher hydrocarbons than methane from carbon monoxide and hydrogen. This action also takes place at normal pressure. Nickel catalysts were perfected to such an extent as to produce more than 100 g. of liquid products per cubic meter of synthesis gas on passing the latter only once through the system.

Successful semi-large scale work has been done with such catalysts, but these have two great drawbacks which cannot be overcome :

  a. They produce mainly saturated hydrocarbons and only small amounts of olefines.

  b. More methane is formed than with cobalt or iron catalysts so that the same maximum yield cannot be obtained.

For these reasons all trials with nickel catalysts were given up and have not since been re-commenced.

B. Iron Catalysts.

(1) Historical Development.

The Fischer-Tropsch synthesis was first carried out using an iron-zinc oxide catalyst in 1925. From then on, research was continued for four years at the Kaiser Wilhelm Institut für Kohlenforschung at Mühlheim in the Ruhr, using chiefly iron catalysts, until it was discovered in 1929 that cobalt catalysts could be much more easily and rapidly developed to give the highest yields.

Only during the war, when cobalt became increasingly scarce, was iron again tried in the Fischer-Tropsch process. Work was based on the extensive experiments made during the development of the cobalt synthesis, above all when using the increased working pressures which had been introduced in the intervening period (medium pressure synthesis at 10 to 20 atm.). In a comparatively short time, considerable progress was made. Soon iron catalysts were known which gave yields equal or even surpassing those obtained with cobalt. However, owing to various factors, the development of iron catalysts was still in full swing at the end of the war and had to be broken off at a particularly interesting and promising stage.

When research with iron catalysts was renewed, the temperatures employed were at first about 300° to 250°C. Later iron catalysts were found for temperatures of about 230° to 250°C. A large scale plant for Italy (Arezzo) was based on this. **The problem arose** to replace cobalt by iron in the German plants already extant. The maximum temperature which could be reached in these installations was only 225°C. This necessitated the development of new and considerably more active iron catalysts effective below this maximum temperature. This, too, was substantially achieved, but <u>at first only for the medium pressure synthesis</u>.

Even this, however, came very recently to be regarded as insufficient and the aim was to fill the normal pressure synthesis reactors with iron catalyst. Usable iron catalysts fulfilling all the requirements of normal pressure synthesis are not yet known, although good progress has also been made in this direction. Although it is possible to obtain good yields with iron catalysts at normal pressure and below 225°C. there is one main difficulty (apart from the present unavoidable production of more low boiling products and methane). This is that CO_2 is formed and not water as with cobalt. This leads to a considerably larger volume of residual gas and consequently to quite different conditions in all the pipe lines, reactors, separators etc. after the first stage reactor.

At medium pressures (10 atm. and above) water formation can be successfully brought about at the present time with iron catalysts, at least to the degree necessary in the conversion of water gas with a CO : H_2 ratio of 1 : 1.25. Thus the position is now, that the known iron catalysts at working temperatures below 225°C. are quite suitable for medium pressure syntheses but not for those at normal pressure. Consequently all the following data on iron catalysts relates to working pressures of 10 to 20 atm.

(2) Peculiarities of the Iron Synthesis.

(a) Possible variations.

The chemistry of iron catalysis is considerably more complex than that with cobalt. On the one hand, this involves greater developmental difficulties but on the other hand, there are more varied possibilities. Even today, so many products can be obtained using iron catalysis, that it is only possible to cite merely a few as typical. Only examples for the limiting possibilities can be given, between which there can be produced all manner of intermediate stages. The details are as follows :

(b) **Hydrogenating power.**

The hydrogenating power of the 3 metals of the iron group diminishes strongly in the order Ni, Co, Fe. Thus nickel, when used as a Fischer-Tropsch catalyst, gives only saturated hydrocarbons together with quantities of methane, while iron yields most easily more olefines and less methane. Cobalt occupies an intermediate position.

In the case of iron, the hydrogenating power can be altered by the composition and mode of production of the catalyst, either to fall to a minimum or to increase, e.g. by small additions of copper or nickel. Since the degree of saturation of the products can be influenced by the $CO : H_2$ ratio as well as by the mode of working (once-through or circulating), it is possible when using iron catalysts to produce either predominantly saturated or highly olefinic hydrocarbons, e.g. in a range of 10 to 90% olefines.

Only mono-olefines are produced, mainly those with a terminal double bond.

(c) **Boiling range.**

The use of iron catalysts gives the greatest latitude in adjusting the boiling range of the products. Predominantly low boiling or predominantly high molecular or the highest molecular hydrocarbons can be produced with all kinds of intermediate stages. This is exemplified in the following compositions:

	Benzine (200°C.)	Heavy Oil 200-230°C.	Soft Wax 320-460°C.	Hard Wax over 460°C.
(i)	81%	13%	6%	
(ii)	59%	24%	14%	3%
(iii)	17%	16%	17%	50%

All the above figures are from semi-large scale trials.

(d) **Amount of branching.**

As yet, no exhaustive knowledge of the degree of branching with the higher hydrocarbons from the iron synthesis is available. For one thing, there are no sufficiently simple and reliable analytical methods for carrying out large numbers of serial estimations with these high molecular hydrocarbons.

Further, the so-called "branching numbers" obtained up to now, e.g. using antimony pentachloride, are not regarded as sufficiently trustworthy. None the less, there are several unobjectionable observations which show that more strongly branched products are obtained in the iron synthesis. Among other compounds, we produced a primary benzine (up to 200°C.) with the octane number 72, the careful fractionation of which revealed the unmistakable presence of the corresponding iso-hydrocarbons.

(e) The formation of oxygen-containing products.

Whereas with nickel or cobalt catalysts, oxygen-containing by-products are produced either not at all or only in quite small amounts, very variable quantities are formed with iron catalysts, according to conditions; indeed so much may occur that it may be regarded as a means for a direct synthesis of higher primary alcohols from water-gas. (That is under consideration here is a synthesis of mixtures of higher alcohols of the most varied molecular weights at medium pressures. This should not be confused with the synthesis of e.g. isobutanol with oxide catalysts at high pressures, circa 200 atm., developed from the methanol synthesis). Besides the alcohols, large amounts of esters are formed, but less aldehydes and acids. The ratio of these products to one another as well as their total quantity is strongly dependant on the composition and mode of preparation of the catalyst as well as on experimental conditions. For example, the proportion of oxygen compounds in the total product can vary from 5% through all proportions to about 70% and more.

All these oxygen compounds are saturated. So far, there is no reliable confirmation of the occurrence of compounds containing both oxygen groups and olefinic double bonds.

C. Cobalt Catalysts.

(1) State of Development.

In contrast to the iron catalysts, the development of cobalt catalysts reached a definite conclusion a long time ago. A certain cobalt catalyst was recognised as the best chemically and technically at that time and has been manufactured since then in large quantities, its composition and mode of preparation remaining unchanged.

The products obtained with this so-called "cobalt mixed catalyst" (100 Co : 5 ThO_2 : 10 MgO 200 Kieselguhr) can therefore be more precisely described as regards yield and properties.

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It must be added that a series of variations are also possible here, depending on the conditions of synthesis. Further variations in the liquid products are also made possible by reason of advances made recently in laboratory trials with catalysts, namely the development of types of cobalt catalyst which contain as an activator, either manganese (among other metals), or exclusively magnesium. The pure magnesium catalysts yield more low boiling hydrocarbons, while the cobalt catalysts containing manganese yield considerably more high molecular hydrocarbons.

We have also succeeded in preparing and testing successfully on the semi-technical scale, cobalt catalysts which not only convert the oxygen of the carbon monoxide exclusively into water, but also, to a considerable extent, into carbon dioxide. This represents a further possibility of processing carbon monoxide-rich gases with cobalt catalysts and obtaining correspondingly varied products.

All the following treatment refers solely to the normal Co - Th - Mg - Kgr mixed catalyst.

(2) The Relation of the Products to the Conditions of Synthesis.

(a) Working pressure.

The pressure at which the synthesis is carried out can have a considerable effect on the course of the reaction. An increase from atmospheric pressure to about 10 to 20 atm. (medium pressure) brings about a substantially increased formation of high and very high molecular hydrocarbons. In contrast to normal pressure synthesis, this does not involve clogging the catalyst with wax and so bringing conversion to a standstill. Thus medium pressure synthesis makes possible the continuous formation of high molecular solid hydrocarbons.

If the distribution of the molecular sizes of the hydrocarbons formed is altered, either by means of the catalyst or the conditions of synthesis, then the change does not generally occur regularly throughout all the molecular groupings. It is much more usual for the low boiling and highest molecular fractions to disappear or increase, while the quantity of the mean molecular weight compounds (heavy oil 200-320°) remains more or less unchanged (about 15 to 30%). For this reason no real diesel oil synthesis has been achieved so far, either with the normal pressure or the medium pressure process, although more benzine or hard wax may be preferentially produced.

(b) Working period.

Catalytic activity, as measured by gas conversion or from the yield, gradually decreases in the course of running. This can be counteracted to some extent by gradual temperature increase. After 4-6 months, however, this measure no longer succeeds and the catalyst must be renewed.

In order to keep down costs, or for other reasons, the catalyst may be used as long as possible. Or, in order to maintain unvarying conditions and maximum yield the catalyst may be changed after a certain life period, without using up its residual activity. Both methods, and variations of them, were used, according to the needs of the moment.

The working period influences not only the yield, but also the quality of the products. With increasing length of working, the hydrogenating power decreases (because of wax clogging, partial poisoning by unremoved sulphur in the gas etc.). This leads to an increase in elefine content. Similarly, the proportion of low boiling hydrocarbons rises (because of the higher working temperature, among other reasons).

(c) Reactor regeneration.

In the course of normal pressure synthesis, the high molecular wax which collects in the catalyst must be removed from time to time, e.g. by solvent extraction, by hydrogenation using hydrogen, by combining these two methods or by some other procedure. This regeneration varies greatly from works to works, depending on local conditions.

The frequency and thoroughness of the regeneration process in removing the reactor wax is reflected in the state of the catalyst filling and consequently, depending on circumstances, also in the quantity and quality of the product. In general, however, this influence is not very great.

(d) Mode of running.

Alteration of the running conditions can cause considerable changes in the relative proportions and constitution of the hydrocarbons formed. The process may be run either in one or two or more stages one following on the other. Between the separate steps, only condensible higher hydrocarbons and water may be separated, or the lighter hydrocarbons (benzine, gas-oil) now remaining in the vapour can also be removed. The gas can be passed once through the system or parts of it can be re-cycled to a greater or lesser extent. Re-cycling can be carried out with or without removal of the benzine or gas-oil.

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All these steps influence the course of the synthesis more or less strongly and not only as concerns the total amount of yield. It is above all, a matter of olefine behaviour. These can react further during a lengthy stay in the reaction zone and become either **hydrogenated or take part in the formation** of higher hydrocarbons. Thus all conditions tending to decrease the length of time spent by the reaction products in the reaction zone increase the proportion of low boiling and olefinic hydrocarbons.

(e) Gas composition.

With the Co.Th.Mg.Kgr. catalyst, higher hydrocarbons are formed fairly closely to the equation :

$$CO + 2H_2 \longrightarrow (CH_2)_x + H_2O.$$

Correspondingly, normal synthesis gas contains carbon monoxide and hydrogen in the ratio of 1 : 2. This is maintained as closely as possible in the synthesis plants, mainly in view of the yield, but also on chemical grounds. If, for example, excess hydrogen is present it accumulates in the final gas and causes increased formation of methane and light hydrocarbons as well as hydrogenation of the olefines. Conversely, the production of olefines and higher hydrocarbons is favoured by increasing the carbon monoxide content. This is hardly practicable with a simple through passage of the gas, since carbon separates from undiluted carbon monoxide rich gas and soon renders the catalyst inactive.

This trouble can be avoided in the medium pressure synthesis by re-cycling gases rich in carbon monoxide, i.e. using them diluted. For example, the process may be carried out in several stages, starting with ordinary water-gas having a CO : H$_2$ ratio of 1 : 1.25, circulating it and attaining the CO : H$_2$ ratio of 1 : 2 before the last stage of addition of hydrogen or hydrogen rich converter gas and then working up the residual gas. In this way conditions favourable to olefine formation are combined, namely, a larger CO content than corresponds to 1CO : 2H$_2$ and decreased time in the reaction zone. This method of working makes possible the manufacture of products containing a considerably higher proportion of olefines with even the normal Co.Th.Mg.Kgr. catalyst. Such olefines are extremely valuable for further chemical processing.

A medium pressure, water gas, circulating plant of this type was being built by Ruhrchemie at Oberhausen-Holten and was nearly complete, but never came into operation.

## (3) The Products of the Cobalt Synthesis.

(a) General characteristics.

The products of the cobalt synthesis contain no carbon ring compounds, i.e. no naphthenes or aromatics. Only very small amounts of oxygen containing compounds are formed as by-products and simple, effective, methods are available for their removal.

A continuous, uninterrupted series of aliphatic hydrocarbons is produced, from methane up to high molecular hydrocarbons with 100 and more carbon atoms in the molecule. The only exception is the two C_2 hydrocarbons, the quantity of which is vanishingly small (ethane and ethylene).

The hydrocarbons formed are partly olefinic, but mainly saturated. The olefines are always mono-olefines, those with a terminal double bond predominating. The content of olefines with the double bond elsewhere is greater, the longer they are submitted to the action of the catalyst.

As was shown in section 2, although the same catalyst may be used throughout, the boiling range and degree of saturation may undergo more or less big changes for the most varied reasons, depending on the working conditions. Naturally, this is very evident on comparing the products of different plants, but can also be observed at a single plant. This fact should be kept in mind when any numerical data are being weighed up.

The following curve represents the approximate distribution of molecular size that can occur with normal pressure synthesis :

1 2 3 4 5 6 7 8 9 → C ATOMS PER MOLECULE.
10.
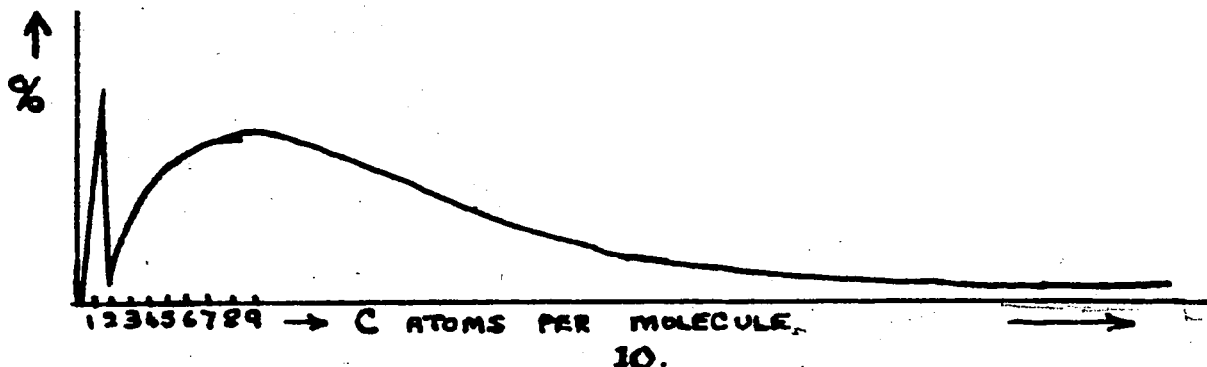
The greater part of the hydrocarbons are straight chain molecules. The amount of iso-compounds increases with the size of the molecule. Of course, there is no marked branching but probably, at the most, only methyl groups or short branch chains. The individual isomers have been isolated and identified up to about C_6.

(b) Gasol.

Under the name Gasol are grouped together those hydrocarbons which do not condense at normal pressure and temperature, i.e. mainly C_3 and C_4. They can be removed from the residual gas simultaneously with the light benzine, by using, for example, activated charcoal, and then separated by fractionation. Compressed in steel cylinders, they can be sold as auto-fuel. If desired, the olefinic portion may be removed beforehand for use in various chemical processes, e.g. polymerisation, etc.

(c) Benzine.

The benzine fraction boiling up to 200°C., e.g. 62% with about 30% of olefines, has only a low O.N., because of the chemical structure of these hydrocarbons, and cannot be used unprocessed as a fuel. There are many ways of overcoming this. Blending with higher knock-rating fuels from other sources may be resorted to, e.g. with benzol, polymerisation benzines etc. Certain fractions may be leaded with good results as can be seen from the following examples :

	O.N. of the fraction :		
	E.B.P. 125°	E.B.P. 150°	E.B.P. 180°
unleaded	62	57	47
+ 0.5 ml./lt. T.E.L.	76	73	67

The O.N. may also be increased by catalytic treatment of the benzine so as to displace the olefinic double bond. In the originally formed hydrocarbons the double bonds are almost completely terminal. This does not correspond, however, to the equilibrium of the various isomers. It is therefore possible catalytically to displace the double bond to the middle of the molecule, which brings about a marked improvement in O.N. (This is the so-called "hot refining" process (Heissraffination)).

(d) Diesel oil.

The chemical structure of synthetic heavy oils is such as to give outstanding combustion behaviour in diesel engines, e.g. maximum ease of ignition, clean exhaust even at overload, somewhat smaller consumption (because of the high hydrogen content), very smooth combustion etc. Synthetic diesel oils can therefore be very successfully blended with heavy oils from other sources which are unsuitable or unsatisfactory when used alone as diesel fuels. The greatest use was made of this possibility in Germany. It was found that the properties of the blending components were markedly improved as regards ease of ignition, pour point, viscosity, sulphur content etc. A well fractionated synthetic diesel fuel (200-320°C.) has usually a sufficiently low pour point so that no special de-waxing, e.g. by solvent extraction is necessary. The viscosity is usually too low (about 1.18°E.) so that it is convenient to add a small amount of lubricating oil if the unblended product is to be used. Sulphur is absent, as it is not contained in the source. The acid by-products are removed by washing with caustic solution.

The cetane number of the 200° - 320°C. fraction is above 70, that is considerably higher than with any commercial diesel fuel. It can therefore be used for testing the ease of ignition of other such fuels, and for this purpose Ruhrchemie prepared a standardised hydrocarbon fraction designated "RCH - Reference - Diesel Oil" which was delivered to the various centres carrying out engine tests for ignition quality.

"RCH Reference Diesel Oil" was also used in the analytical estimation of the asphaltic compounds separating from blends of oils from different sources. Its use here was based on the fact that this pure paraffinic oil gives the maximum precipitation of such compounds.

The cetane used for comparison purposes in the estimation of ease of ignition, was prepared from naturally occurring materials not obtainable in Germany. Ruhrchemie prepared a substitute called "RCH Cetane" which consisted of a closely cut hydrogenated fraction of synthetic hydrocarbons boiling near 300°C. and whose cetane number was continually tested so as to remain at 100. This "RCH Cetane" was eventually in general use throughout Germany.

The length of the C-atom chain in the 180°-320°C. fraction lies in the region of those fatty acids and fatty alcohols necessary for the manufacture of soaps and sulphonated washing media. By means of the Oxo synthesis, the heavy oil olefines mentioned can be converted to such fatty acids or

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alcohols with very good yields. Intensive tests showed that the synthetic soaps and washing media prepared in this way behaved excellently. Consequently, a large scale Oxo plant was under construction at Holten for the manufacture of fatty alcohols from the heavy oil olefines produced in the medium pressure, water gas re-cycling synthesis. This plant did not reach the operating stage, however.

(e) Hydrocarbons of high and extremely high molecular weight.

Hydrocarbons exceeding **Diesel** oil in molecular weight are also formed. They are obtained either as distillation residues from the products continually leaving the reaction chambers or, by extraction, from the catalyst filling. The lower members of these hydrocarbons are barely liquid or are even solid at ordinary temperatures. The highest members have more than 100 carbon atoms in the molecule with melting points above 100°C. They are processed according to the particular use in mind.

They can be changed to lower molecular olefines by cracking, more recently with only small gasification and considerable control of the molecule size required. The olefines so obtained have proved to be particularly valuable raw materials for further chemical treatment, e.g. in the manufacture of anti-knock benzine, synthetic lubricating oil, higher alcohols of the most diverse nature, plasticisers, solvents, washing media etc.

Large quantities of the 320°-460°C fraction were delivered as crude paraffin wax to the "Märkische Seifenindustrie" Witten - Ruhr, which produced fatty acids therefrom, by means of atmospheric oxidation, for soaps and cooking fats.

The higher molecular primary hydrocarbons can also be separated by physical means, e.g. by fractional distillation or melting etc., according to size of molecule and the products so obtained may be used as such. Fractions with a narrow melting point range, e.g. 50-52°C., are designated block wax and are at least equal in quality to commercial products from different sources known by the same name.

Still higher fractions form the various kinds of so-called hard wax. The different varieties vary according to mode of preparation and degree of refining, in melting point, colour, hardness etc. Special qualities may be developed by blending different fractions, e.g. plastic waxes from high and low melting point components.

The applications of these products were very numerous, especially since during the war substitutes had to be found for similar products from natural sources (the manufacture of candles; floor and shoe polishes; water proofed materials, such as paper; oxidation to high molecular acids for emulsifying agents, etc.). It was discovered, however, that the market for hard waxes is not without limit and that the quantities produced in the Fischer-Tropsch plants exceeded the amount wanted for processing in Germany.

There is no difference between products of this type from normal pressure and medium pressure synthesis, except in the relative quantities of molecules of different sizes.

D. Future Possibilities.

The development of the catalytic hydrogenation of carbon monoxide, especially that occurring in the Fischer-Tropsch process, has so far taken place almost exclusively in Germany. It has therefore been very greatly influenced by special conditions, e.g. by the requirements and scarcities of war. The technical level attained can not therefore be taken without comment as a measure even of the present potentialities of catalytic carbon monoxide hydrogenation in other and possibly more favourable circumstances.

It may be assumed that new plants will differ from those already extant, apart from general technical improvements; that in addition to fuel they will furnish increasing amounts of raw material for further chemical treatment. A pointer to this is the increased production of olefines and definite oxygen containing compounds of the most varied nature. Probably the catalytic hydrogenation of carbon monoxide will become the raw material basis for completely new branches of the chemical industry.

Wimbledon – London 10.12.45.

3. SYNTHETIC LUBRICANTS MADE BY RUHRCHEMIE A.G.

A. Olefine Polymerisation.

Experiments on the preparation of lubricating oils by olefine polymerisation were carried out by Dr. Clar. He has compiled an extensive report giving his results which is already in the hands of the Military Government, so that it is not necessary to say any more here.

The large scale plant in Holten was directed by Dr. Goethel.

B. Lubricants from Fatty Acids.

Small quantities of fatty acids are formed directly as by-products of the Fischer-Tropsch synthesis. They are removed as a crude solution in the course of the alkaline washing of the hydrocarbons. Besides the soaps in question, these crude solutions contain iron, hydrocarbons, very malodorous compounds etc.

The extraction and use of such fatty acids was dealt with in various ways at the synthesis plants. The main deciding factor was whether the crude solution was from the crude condensate or from the hydrocarbon fraction after distillation. In the first case a mixture of lower and higher fatty acids results, which it is necessary to separate. The second case is simpler. For example, the diesel oil fraction even gives fatty acids in the crude alkaline solution whose molecular size lies substantially in the saponaceous fatty acid range.

The fatty acids removed from the diesel oil fraction in this way were sent originally, in the crude solution, to the firm of Th. Goldschmidt, Essen. Goldschmidt made a drawing grease from them, using a DRP method, which grease was then sent to wire works etc. Later, Ruhrchemie itself undertook the processing of the diesel oil crude lye. We made tablet soap from it, which was given to the works personnel, who were very pleased with its quality.

At other plants, greases for industrial purposes were prepared from these fatty acids.

C. Lubricants from 'OXO' Products.

(1) Lubricating Oil Carboxylic Acids.

By means of the "OXO" synthesis it is quite easy to prepare aldehydes from the olefinic lubricating oils derived from the $AlCl_3$ olefine polymerisation. These aldehydes are always one carbon atom higher than the original hydrocarbon and can be converted into the corresponding carboxylic acids by atmospheric oxidation. Such compounds are completely new, containing on the one hand a carboxylic group, and on the other hand, a hydrocarbon stem which has itself the properties of a high quality lubricant. Experimental trials with these substances were just commencing, so that only laboratory results are so far available.

(a) Esterification.

The lubricating oil carboxylic acids can be esterified with lower alcohols, as with ordinary fatty acids. In this way, lubricants can be obtained combining the advantages of both synthetic lubricant and ester oil structure. This is especially so when branched chain "OXO" alcohols are used for esterification. The lubricating oil carboxylic acids can be esterified with lubricating oil alcohols, produced by the hydrogenation of the corresponding aldehydes. This yields very high molecular ester oils.

(b) Lubricating oil carboxylic acid soaps.

Analogous to the fatty acids, the lubricating oil carboxylic acids form salts, with characteristic properties, soluble in mineral oil. These can be used both as additives in the usual way, and in grease manufacture. The soaps of sodium, calcium, lead etc., are among those so utilised. Special mention may be made of the jelly-like aluminium soap which can be drawn out into extraordinarily fine threads.

A blend of synthetic oil with lubricating oil carboxylic acid soaps when tested in the test gear at Rheinmetall, Düsseldorf, proved to be an excellent gear oil.

(2) Lubricating Greases and Boring Oils from 'OXO' Fatty Acids.

(a) The "OXO" synthesis renders it easy to prepare from olefinic hydrocarbons, fatty acids with one more carbon atom. This is a simple way of making the various soaps, e.g. of sodium, calcium etc., which are used in the normal way for grease manufacture.

(b) The production of synthetic boring oils via the "OXO" synthesis is particularly simple. The starting material is the olefine containing heavy oil fractions which can be obtained both directly from the Fischer-Tropsch synthesis and also by cracking the high molecular hydrocarbons. Probably olefinic mineral oil fractions can also be used.

Water-gas is condensed with these olefines by means of the "OXO" synthesis. The crude aldehydic product plus the calculated quantity of lime is stirred, while air is blown in. On warming, the calcium soap is formed and immediately dissolves in the unchanged saturated hydrocarbons. After completion of the reaction, the mixture of calcium soap and mineral oil can either be used as such, or water may be added, whereby stable emulsions are readily formed. Practical results with cutting and boring oils of this type were excellent.

(3) Ester Oils.

By means of the "OXO" synthesis, the corresponding carboxylic acids and alcohols are prepared from olefinic hydrocarbons of the appropriate molecular dimensions. The two are utilised to form esters with one another in the normal way and then freed from unchanged hydrocarbons by distillation. Excellent ester lubricating oils are obtained in this manner.

For example, cracking olefines yielded ester oils which besides having a good pole-height etc., possessed pour points of -70° and below. Such low pour points are a consequence of the nature of the ester oils prepared as described, since they consist of blends of countless different isomers.

(4) Hydraulic Liquids and Similar Compounds.

(a) Ester oils.

If correspondingly low molecular olefines are used, then ester oils may be obtained (as described under 3) which are suitable for use as hydraulic fluids etc.

(b) "Isols".

An additional method for the production of hydraulic and similar fluids is provided by the possibility of preparing a large number of mixes of isomeric, branched primary alcohols and their derivatives (e.g. esters). This can be done by condensing the aldehydes obtained in the "OXO" synthesis, by the action of alkali or some other means, to give aldols. On hydrogenation, the latter form branched chain alcohols. Such

mixtures of branched primary alcohols are termed "Isols" and have already been prepared in considerable numbers and in quantities up to semi-large scale production. Their low vapour pressure and pour point are among their distinguishing features.

(c) The large number of possible combinations permits of the preparation of the greatest variety of hydraulic fluids, brake oils, buffer oils, recoil oils etc., all based on the "OXO" process. The physical properties of such oils can, within very wide limits, be adjusted as required so that, to a large extent, an oil can be made to suit any particular requirements.

London - Wimbledon, 11.12.45.

(signed) Roelen.

4. TOWN GAS AND METHANISED GAS FOR AUTOMOTIVE PROPULSION
BY DR. OTTO ROELEN.

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A. Untreated Town Gas and Coking Gas.

        In 1935 the first long distance journey with a
gas driven omnibus supplied from steel cylinders was under-
taken by Director Dr. Traenker of Ruhrgas A.G., Essen.
The gas supply for the whole journey from Essen to Koenigsberg
(East Prussia) was contained in steel cylinders stored in a
trailer.   There were no difficulties.   This run proved that
the use of town gas for automotive propulsion was a practical
proposition.

        Further development was concerned primarily with the
building up of a filling station network.   This was done in
conjunction with the already existing filling station organisa-
tions for liquid fuels, such as that of the Benzol Verband,
Bochum.   These installed the gas filling stations for public
supply, which were fed among other methods, by long distance
gas pipe lines, e.g. from the Ruhrgas A.G.

        In addition, the larger cities and industrial plants
had their own gas filling stations for car parks.

(2) Technical Installations.

Only a comparatively small number of vehicles depended on gas supply at normal pressure, e.g. in "balloons". The great majority carried the gas at high pressure in steel cylinders or, more recently, in spherical steel containers of various designs.

The high pressure gas filling stations had compressors (Demag, Duisburg) working to a maximum of 300 atm. Large supply reservoirs were filled at this pressure. The output was 180 c.m./hr. per unit or a multiple of the same.

Besides the gas cylinders, reduction valves and mixing apparatus were built into vehicles running on gas fuel. Latterly such equipment became very simple in design.

(3) Uses.

The chief use of compressed town gas was in lorries and, secondly, in private cars. It was not used in military vehicles. The gas was also used for running-in engines. It was planned in 1944 to use compressed and methanised town gas on a large scale for running in tank engines.

(4) Operational Results.

Town gas and coking gas contain a series of impurities which proved capable of causing considerable trouble.

Part of these impurities have a more or less strong corrosive action, e.g. on the walls of the steel cylinders. Hydrocyanic acid (HCN) was particularly dangerous in this respect. There were two ways of combating these difficulties. Firstly, by storage in large reservoirs for at least several hours after compression. During this time the water drops containing the corrosive agents in solution had a chance to settle. Because of the big demands made on the gas filling stations, this precaution could not always be properly carried out. Secondly, the gas was subjected to intensive cooling after leaving the compressor and before entering the storage vessels so as to separate water and all condensable constituents as far as possible.

Another part of the impurities caused deposits, gum formation, incrustations etc. This lead to valve trouble in automotive engines and piston ring sticking in the compressors. This latter was particularly unpleasant and was a definite disadvantage. The compressor repairs which became necessary continually put the gas filling stations out of action after more or less short running periods.

B. Methanisation.

(1) Historical Development.

There are a series of drawbacks to the use of compressed but otherwise unaltered town gas for automotive fuel. They are partly technical and partly fundamental in origin and led to the consideration of the possibility of catalytically converting the carbon monoxide and hydrogen content to methane. The grounds for such a methanisation were as follows :

(a) The calorific value of the gas per unit volume is much increased. Consequently the same volume of gas gives a greater radius of action and refueling is less frequent or for the same distance the dead weight of the containers is less.

(b) The same filling station can supply more fuel with unchanged compressor performance.

(c) The careful gas purification prevents corrosion and compressor disturbances.

These advantages were the reason for a questionnaire directed to German industry in 1941 as to whether filling station methanisation appeared possible with the technical resources then available. The unanimous reply from the industries in question was negative, for the following reasons:

(a) No practical method of sufficient simplicity was known for the purification of town gas in small filling stations, with intermittent running, to the extent necessary for catalytic hydrogenation of carbon monoxide.

(b) No sufficiently active catalyst was known which could produce methane at sufficient speed at a low enough temperature in small simple reaction vessels using water as coolant.

(c) It was thought impossible to interrupt the synthesis at will, without upsetting the gas composition and without tiresome supervision.

When Ruhrchemie A.G., (Oberhausen) was asked, I said that the problem could probably be solved. Work was immediately commenced, in autumn 1941. By June 1942 the first plant in Altenessen was put into operation and worked satisfactorily until destroyed by air attack in autumn 1944.

Based on this experience, Ruhrgas-Essen and Ruhrchemie Oberhausen undertook jointly, the practical application of the process, whereby Ruhrchemie supplied the catalysts and Ruhrgas looked after the building and operation of the plants. The first mass-produced type of plant was installed at Opel-Ruesselsheim and gave trouble free operation until it too was destroyed by air attack.

Further plants did not pass the constructional stage.

(2) Technical Details.

(a) Gas purification.

The chief difficulty in developing the process lay in purification of the gas. None of the large number of methods already proposed and described could simply be taken over. The method used for water gas, that of attaining a high degree of purity by using ferric oxide alkaline carbonate (Roelen and Feisst) is not suitable for distillation gases such as town gas. Catalytic decomposition of the organic sulphur compounds has been known for a long time and has already been used technically. But the catalytic action, flow rate and life period were insufficient for filling station methanisation.

At first we achieved satisfactory results with a catalyst containing finely divided copper. Later we discovered a simple solution by using the spent nickel catalyst from the methane synthesis. The spent catalyst was submitted to a comparatively simple after treatment for this purpose, but complete regeneration was not necessary.

The gas stream after passing through 1.5 liter of this catalyst at 425° with a velocity of 1 c.m./hr., is then cooled and freed from hydrogen sulphide with an ordinary gas purifying filling.

The degree of purity attained was sufficient with a catalyst life period of about 1500 working hours. A vessel containing activated charcoal was coupled on and could be regenerated with steam in the usual way.

(b) Methane synthesis.

We were soon able, with our experience of the Fischer-Tropsch synthesis, to evolve a new nickel catalyst with maximum activity for methane synthesis. This catalyst, which has given very satisfactory results, contains magnesium as activator and is precipitated on kieselguhr by means of soda. The flow velocity is 1 c.m./hr. through 1.2 to 1.5 litres of catalyst, whose life period may safely be reckoned at 500 uninterrupted working hours.

The very low reaction temperature is also noteworthy. Earlier methane syntheses required temperatures or 300° and above, with a minimum of 250. According to Fischer and Tropsch, higher hydrocarbons are formed below temperatures suitable for methane synthesis. Thus Fischer and Meyer prepared higher hydrocarbons with nickel catalysts at 185°. It follows, that to produce methane the lowest possible temperatures are 200° and above. Our new synthesis worked, however, at 170°-190°, and without forming even a trace of the objectionable higher hydrocarbons, a proof of the extraordinary activity of the new RCH nickel catalyst.

The synthesis can also be carried out at the increased pressure present in the long distance gas pipe lines, e.g. the Altenessen plant worked at 6 atm.

(c) The methanisation of gases rich in carbon monoxide.

Gases of town gas quality contain a proportion of hydrogen varying inversely with the carbon monoxide content. Thus as the latter increases, the proportion of hydrogen decreases. The methane synthesis, however, works best with the greatest possible excess of hydrogen. Consequently, coking gas, which besides 5-8% of CO contains more than 50% of H_2 can be methanised without further treatment. Town gas containing more than 10% CO (10-18% CO) on the other hand, must have this percentage brought below 10% to avoid trouble from carbon separation, carbonyl formation etc.

The conversion takes place in the same temperature range as the catalytic decomposition of the organic sulphur compounds and brings about such decomposition itself, to a certain extent. This allows both processes to be combined in one step, without enlarging the total catalyst space. It is merely necessary to lead the CO rich gas (carrying the corresponding quantity of steam) first over the conversion catalyst and then, at the same temperature, over the decomposition catalyst. For conversion, one of the known commercial catalysts can be employed. It is used to replace the first half of the decomposition catalyst. The remaining procedure is unchanged.

(d) Catalyst Equipment.

There is only an insignificant heat change during the partial conversion of town gas as described above. The catalytic decomposition of the organic sulphur compounds takes place with absolutely no measurable heat change. Consequently, simple cylindrical containers without any special arrangements for cooling may be used. All that is required is the heating up of the gas, for which heat exchangers may be used and the maintenance of a fixed temperature by means of automatic regulators.

On the other hand, the methane synthesis itself with its great heat of reaction necessitates, like the Fischer-Tropsch synthesis, careful leading away of the heat evolved and temperature regulation within very narrow limits. This did not represent much of a problem for us; we had only to take over the catalyst equipment developed for the Fischer-Tropsch synthesis and modify it to comply with the special requirements of filling station methanisation. The latter applies especially to additional equipment making it possible to stop or start the process at any time as desired, without causing any trouble or change in gas composition.

We used water tube boilers, the nickel catalyst being inside the tubes. The water cycle was heated from outside during shut down periods and cooled during running. Both processes were automatically controlled so that the temperature remained constant, within 1°–2°. The advantage of being able to use comparatively simple catalyst vessels cooled by water under pressure is a consequence of the low working temperature (below 200°) of our nickel catalyst.

(3) Operational Results.

(a) Methanisation Plant.

This can be set up besides existing gas tanking equipment in a comparatively small space. No further personnel are required for its maintenance than the filling station staff already available. Skilled labour is necessary only for changing the chemical fillings. Such labour can naturally deal with a large number of similar plants in turn, one after the other.

Supervision of the process involves merely readings of temperature and pressure and adjustment of a temperature regulator where necessary, as well as control of the water of reaction which runs away. The quantity of the latter immediately gives the output.

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The life period given above was far surpassed in practice, indeed it was almost doubled. There was no trouble during a running time of several years, not even when sulphur occasionally came through from the coking plants. The Altenessen plant was one of the few sources of fuel during the heavy air-raids on Essen, when it was working uninterruptedly.

(b) Gas composition.

A coking gas with about 6% CO content was delivered to the Altenessen plant. After methanisation the $CO + CO_2$ content was certainly less than 1%. Carbon dioxide was thus likewise converted into methane. Sulphur hydrocyanic acid, oxides of nitrogen or other impurities could no longer be detected.

The calorific value rose from 4200 K.cal./c.m. to about 6000 K.cal./c.m.

(c) Compressors and vehicles.

Whereas compressors working with unchanged town gas were always put out of action by piston trouble after short running periods, such stoppages were completely absent with methanised gas. The process was a complete success.

Damage due to corrosion was also no longer met with.

The mixing devices in the vehicles had to be altered to suit the higher C.V. gas. When this was done, complete satisfaction was expressed by all users.

(d) Summary.

The advantages expected from the introduction of filling station methanisation were all realised in practice It was therefore decided in 1944 to provide 120 gas filling stations with the equipment. Immediately a contract was placed for 40 plants, but it was not carried out.

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