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THE FISCHER-TROPSCH PROCESS

Schade, Foran & Heinrich

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COMBINED INTELLIGENCE OBJECTIVES
SUB COMMITTEE

~~SECRET~~

THE FISCHER-TROPSCH PROCESS

REPORTS BY

**Capt. H.A.SCHADE, USN
Lt.Col. E.FORAN, USA
Lt. R.C.ALDRICH, USNR**

[1944]

CIOS Black List Item - 30

Fuels and Lubricants

**COMBINED INTELLIGENCE OBJECTIVES SUB-COMMITTEE
G-2 Division, SHAEF (Rear) APO 413**

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8 p.

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REPORT I: INSPECTION OF FISCHER-TROPSCH PLANT,
HARNES (LILLE) FRANCE

Date of Trip : Sept. 26, 27, 1944.

Officers Making Trip: Capt. H.A. Schade, USN.
Lt. Col. E. Foran, USA.
Lt. R.C. Aldrich, USNR.

Location of Plant: Village of Harnes, about 10 Km. South of Lille.

Object of Trip: To study the Fischer-Tropsch plant at this factory and to determine if any or all of it can be used by the Navy in the U.S., primarily for the production of high octane Diesel fuel.

Conclusions: This plant is too big for pilot plant work. It is also playing an important role in present French fuel supply. It is recommended that the plant not be moved and that its Diesel oil production be taken by the U.S. Navy.

History: This plant was originally built in 1936-1937. Its owners and operators, Courrieres-Kuhlmann, are manufacturers of fuel and chemical products. The original license allowed them to manufacture up to 40,000 tons of liquid product per year but the plant was only built up to 20,000 tons/year. It has operated continuously since 1937 except for a brief period in 1942 when it was shut down due to bomb damage. It is today only making 36 tons/day instead of 48 tons/day due to cobalt shortage. 36 tons is equivalent to 288 U.S. barrels.

Cobalt, for Catalyst manufacture, originally came from the Belgian Congo. When the war cut off this supply, another source was found in Morocco of slightly inferior quality. Since June, this supply has also been cut off. Kieselguhr, the second important ingredient in the Catalyst, originally came from Germany. A French source has been found which is probably suitable. The third ingredient, thorium, offers no problem. Due to the present shortage, 6 of the 24 reactors are not operating.

The products of this plant are in great demand at this time here in France due to the present fuel shortage and distribution problem. The gasoline product is sold directly to the public and is the one upon which most emphasis is placed. Its octane number is not high - around 50. The Diesel fuel which amounts to about 25% of

the total product is of extremely high quality, having a probable cetane number of 90 or above. It is used in France to blend with inferior low temperature carbonization coal tar. The diesel fuel is used in farm tractors and heavy trucks. The heavy wax is taken by various chemical industries for paints, varnishes and polish. Butane gas is also made and is compressed into bottles at 300 p.s.i. for gas driven automobiles.

From time to time, during the war, the Kuhlmann Co. have varied the above output to make special chemical products, lubricating oil, grease, etc. The extremely paraffinic nature of the liquid product makes it a very valuable base for further developments of this kind.

Description of Process: The basic raw material is coke from high temperature carbonization of French coal. After crushing the coke is taken by skip hoist to the water gas generators. These are of conventional design and are automatically controlled. The resulting water gas has an analysis as follows :

CO	-	40 %
H ₂	-	50 %
CO ₂	-	5 %
N ₂	}	5 %
CH ₄		

The basic Fischer-Tropsch reaction is : $mCO \div (2M \div 1) H_2 \rightarrow C_mH_{2m+2} \div mH_2O$. Although the theoretical requirements call for a H₂ to CO ratio of 1.5 to 1, the actual requirements are 2 to 1, due to mass action, hence the above analyses is too low. Accordingly, 1/3 of the gas produced is passed over a catalyst of FeO at 500° C with steam, resulting in a product rich in H₂ and CO₂. Considerable heat exchange is also done in this step. The final blend of this gas with the original is :

CO	-	27 %
H ₂	-	54 %
CO ₂	-	14 %
N ₂	}	5 %
CH ₄		

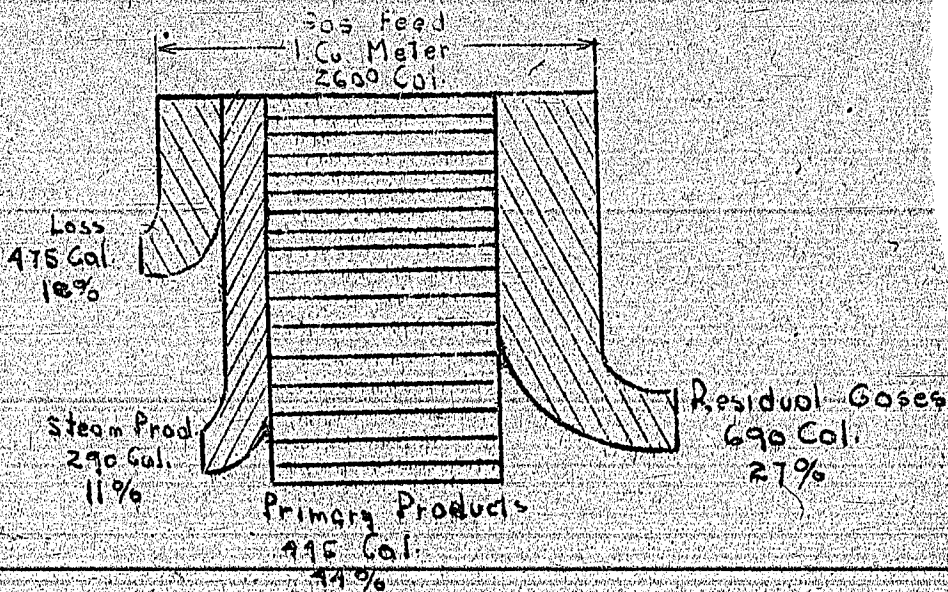
To remove sulfur, three separate steps are taken.

This is most important, as the Fischer-Tropsch catalyst is very sensitive to sulfur poisoning. The first step is a countercurrent wash with ammonia water to remove the H₂S. This is done in two towers, 10' in diameter and 20' high, filled with ceramic Raschig rings, 4" x 4". The ammonia water is regenerated in an open tank by violent air blowing from the bottom. The second step

consists of passing the gas through boxes containing trays of Fe_3O_4 and sawdust, the typical old fashioned method used by city gas works. The final step is the removal of organic sulfur compounds in two towers filled with a catalyst of FeO and Na_2CO_3 at $200\text{--}300^\circ\text{C}$. The catalyst is in 8 beds, 1 meter thick. Both towers are in series. The catalyst lasts 2-3 months.

The gas is now ready for the syntheses step. It is compressed to 3 p.s.i. prior to entering the reactors in order to overcome the pressure drop through the same. The 24 reactors are all cooled by a hot water-steam system, so arranged that each pair of reactors shares a common header and control valve.

The synthesis reaction is extremely exothermic. Approximately 7000 BTU results from the production of 1 lb. mol of liquid product. At the Kuhlmann Plant, the total energy balance is as follows (in metric units)



The cooling system of the reactors is one of the most important details of the installation. It is the one feature of the process which has caused more discussion in the U.S. than any other phase of the design. Its importance is twofold. One, the reaction must occur at a definite temperature range (in this case $200^{\circ}\text{C} \pm 30$) because if the temperature is lower, no reaction will occur, and if higher the products disintegrate into methane. Two, the catalyst itself is an extremely poor conductor of heat. As a result, the mean path of heat travel from any catalyst particle to the cooling surface is kept below 2 mm. This presents a hot spot from occurring in the catalyst bed. To obtain such cooling capacity entails a very complicated design. The reactors are essentially a square box consisting of 600 thin baffles pierced by 600 tubes filled with hot water. The water temperature is maintained by controlling the steam pressure on the system by an automatic relief valve. Each reactor has a total surface of 5,000 sq. meters and weighs 50 metric tons. The resulting density of the reactor is approximately 60 % that of solid steel. The catalyst fills the voids between baffles and tubes. To remove the catalyst for regeneration, a compressed air jet is used.

Of the 24 reactors, 16 are normally used for the 1st pass. The effluent from these is cooled and condensed, and the resulting heavy product removed. The gases are next sent to the remaining 8 reactors for its second pass which produces a lighter product than the first. As before, the products are condensed and separated. The remaining gas contains considerable gasoline and butane. These are collected in an activated charcoal system and later steam stripped. Propane and butane are sold separately. The latter is used for automotive work here in France.

The final product yield is as follows :

<u>Present Production</u>	
Gasoline - 60 % Vol%	171 BPD
Diesel Fuel - 22 %	66 BPD
Solid Wax - 10 %	28 BPD
Gaseous products - 8 %	23 BPD
100 %	288 BPD

A product analysis is not available at this time. However, it is known that the gasoline has a low octane number - 54 and is water white. The Diesel oil is of very good quality - cetane number about 100 and also water white. The wax is reported to have a fusion point of $200(?)$ at 1000°C .

This plant also had a T.V.P. cracking plant built prior to the war which was never put in operation. The stabilizer from the same is now used on the gasoline from the Fischer-Tropsch process.

No detailed information is available on catalyst regeneration except that it is difficult and requires careful handling. The lack of cobalt has already been discussed.

Miscellaneous: Some of the operating personnel from this plant have visited Germany as late as 1942. They report that the Germans have been working on a double concentric tubular reactor with cooling water in the inner tube and outside surface while the catalyst is in the middle annulus.. No other details are available.

They also report hearing of a new catalyst product in branched chain paraffins but are not able to discuss the same. On the question of cooling the catalyst bed by evaporating a cooling medium, they report that all experiments to this end have failed in Germany.

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REPORT II. THE FISCHER TROPSCH PROCESS WITH SPECIAL
CONSIDERATION OF THE LÜTZKENDORF PLANT OF THE WINTERSHALL
CO. BY PRISONER OF WAR ERNST NAGELSTEIN.

TRANSLATED BY LIEUT. R. C. ALDRICH, USNR.

Introduction : The Choice of Feedstock.

Since Germany has never had a sufficiency of natural, coke-oven or cracking gas, the gasification of Braunkohle becomes the cheapest and almost inexhaustible source of supply for its synthesis feed gas. Neglecting the economic side of the question, it becomes the most important source of raw material for synthesis work.

Main Report : Fischer-Tropsch Process.

A: Selecting the site for a Fischer-Tropsch plant.

Three factors must be considered before constructing a new synthesis plant. The first two are concerned with the feedstock and the third with the water supply. Should the site be chosen near the Braunkohle fields or near an insured water supply of good quality where used water can also be discharged? It is much easier to transport coal (by railroad) than water. This fact can be proven by the poor operation and failure to meet expected yields of the Lützkendorf plant of the Wintershall Co. The Leuna plant of I.G. Farben, on the other hand, has a good water supply and operates well despite the fact that it is some distance from the coal fields. The quality of the water is also important, as hard water clogs up Raschig ring packing, either completely or almost so.

B: Technical description of the Process.

I. Braunkohle - coal drying - gasification.

An exact knowledge of the possible variations of coal composition must be known. If large variations are expected, the coal of lowest quality must be used as the basis for selecting the gasification and purification systems to be used. The Lützkendorf plant is a good example of extremely faulty planning. Only twenty tons of the coal intended for use was run (and that through another plant) as a basis for the design. It was discovered too late that the content of sulfur, sand and other impurities were much higher than that anticipated. (Sulfur up to 6%, sand up to 4%). It is therefore not strange that 3 years after the plant was put into operation, the yield of liquid products was below 100 grams per cu. meter of feed gas, while that of neighbouring

plants, running out on the same coal, was as much as 160 grams per cu.ft. of gas feed.

Other important questions in the gasification process are the yield of benzol and the relative weights of heavy metals required. These will be referred to later.

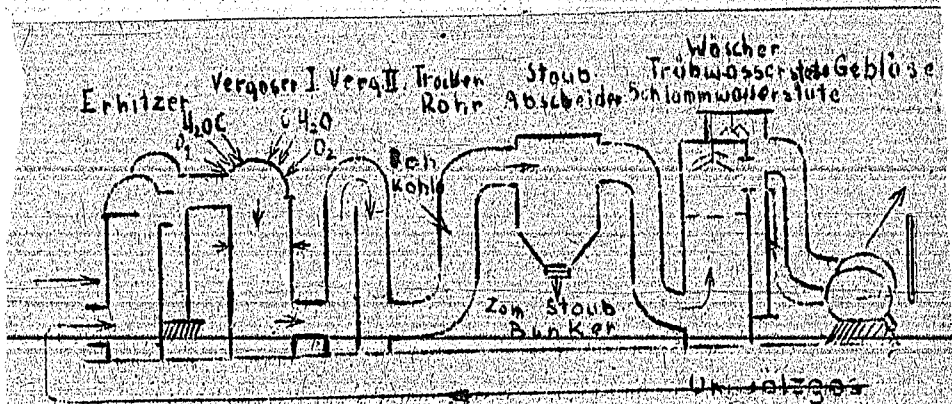
Two methods of gasification are today in use:

1. The Schmalfeldt-Wintershall Process.
2. The Winkler Process.

Both operate on different principles from one another. Their relative advantages and disadvantages will be briefly described. The method of coal drying will be included with the gasification.

Schmalfeldt, combines gasification and drying, in which the necessary cooling of the newly produced synthesis gas is accomplished by passing through the raw coal. In this way the damp coal is both dried and partly gasified. However, this ingenious idea cannot be technically carried out at this time without difficulty. Nevertheless, there is no doubt that the Schmalfeldt Process can ultimately accomplish this and become economically competitive (with Winkler).

The flow plan of the Schmalfeldt is as follows :



Heizgas - Hot gas
Erhitzer - Pre-heater
Vergaser - Gasifier
Trockenrohr - Dry pipe
Staub-Abscheider - Dust catcher
Geblase - Blowers
Wascher - Scrubber
Sygas - Synthesis feed gas
Umwalzgas - Pre-circulated gas
Rohkohle - Raw coal

Coal dust is gasified in the down flowing stream. The amount of gasification must be kept down to 50% here, as higher gasification will produce an ash melting, and resulting operating difficulties. The operating temperature at the top of the dome of the first gasifier is approximately 1450°C. The continuity of gasification is maintained by a re-cycling process. Part of the synthesis gas produced is re-cycled and part withdrawn. The circulating gas is brought up to temperature in two heaters, operating alternately in cycles of 11 minutes each. For four gasification units, each producing approx. 20,000 cu. meters per hour, 5 hot gas heaters are required of almost the same capacity. To the gas produced in these, is added the tail gas of the synthesis process. The subsequent increase in gas production (by raising the oxygen content in the first gas producer) entails an increase in gas velocity (normally 4 m/sec.). The time given to the gas in the gas chamber was consequently insufficient and resulted in the failure to obtain the exact H₂/CO ratio required. As a solution to this difficulty, a second gas producer was inserted - a simple pipe lined with firebrick and having a vertical baffle. After producer II, the gas with a temperature of about 1200°C. (I 1000°C) enters the drying pipe. Here it is cooled to about 850°C. This item has caused considerable discussion among the technical economists (as for example the Koppers Co.), as it is the reason for many disadvantages. These people feel that the gas at 1200°C. should be passed through an exchanger, thereby producing high pressure steam by giving up its heat to water. From the point of view of heat technique, it is impossible to draw a fair comparison between the dry pipe and the exchanger. Considerable corrosion in the exchanger entails considerable material costs which is not the case with the dry pipe. As opposed to that, there is another serious disadvantage to the dry pipe; namely, that the purity of the gas is definitely reduced. Especially is the content of organic sulfur compounds raised, which are difficult to remove.

The dust gasification at lower rates, from this author's viewpoint, results in a very important phenomenon - namely, that under certain conditions, the synthesis gas contains large quantities of benzol (up to 5% of the final gasoline). It appears to be the result of a catalytic formation of benzol from acetylene when in contact with hot iron-carbon particles. It is also to be noted that the formation of thiophenes from H_2S and acetylene can be prevented accordingly.

The gas passes into the dust remover after leaving the dry pipe. The dust falls into a collector and then to bunkers before re-entry into the gas cycle. The gas is next passed through a two-stage washer. This washer is packed with glazed Raschig rings, as the use of unglazed Raschig rings leads to severe operating difficulties as the result of stoppages.

After washing, the gas stream is divided, part being re-circulated, and part leaving as synthesis feed stock in separate blowers.

The coal dust which drops out in the dry pipe (as opposed to that which drops out in the dust remover) is of no further use in the gasification process as it requires very large drying towers with inordinate quantities of heat.

At the same time excess coal dust must be obtained from other plants, because the synthesis only produces a fraction of the required heating materials. Finally, the coal consumption of the energy (steam, etc.) requirements is over half of the total coal requirements.

The following are the conclusions about the Wintershall-Schmalfeldt Process :

- a) The dry pipe should in the future be placed in the hot gas producer as it will reduce the contamination of the gas.
- b) The cooling of the freshly produced synthesis gas can best be accomplished in an exchanger.
- c) The yield of benzol should be raised as high as possible. It will not be reduced by the elimination of the dry pipe.
- d) The oxygen fed into the gas producer (producer I) should not be exaggerated. Control equipment to maintain the proper amount must be installed.

The process used by the I.G. Farben, the Winkler Process, in Leuna and Brueggs, operates on a different principle. The

Winkler gas production is by oxygen under pressure. The gas production per unit is much smaller than with the Schmalfeldt process; hence more units are required. This has one great and generally unnoticed advantage:

With the Schmalfeldt process, the analysis of the collected gas is never constant as it varies from the start to the finish of the 11 minute period. By using many small units, this variation is eliminated. It is definitely known that catalytic processes in general work much better with constant analysis of feed stock and operating conditions. The maintaining of constant feed stock analysis is particularly important with the Fischer Tropsh Process.

The rate of gasification of the Winkler Process is maintained so high that the ashes fuze. The gasification occurs in the upflowing stream; hence the length of contact time with the incandescent coal is increased. Hence the ash particles bring about the desired H_2/CO ratio. The resulting gas is also leaner in organic sulfur compounds (than the Schmalfeldt process), which are so difficult to remove. It is, however, richer in CO_2 than the latter.

The higher CO_2 content (up to 28% CO_2) acts only as an inert ballast, which though it raises the total gas quantity 10% has no effect on the synthesis process or the yield of gasoline.

In conclusion, the Winkler Process is a well worked out gas producing process which is definitely superior to the Schmalfeldt Process from the point of view of technical completeness. A properly designed Schmalfeldt unit would definitely be superior to the Winkler from an economic point of view. Up to now, the Winkler Process is superior from the standpoint of gas purity and operating security.

II. Gas Purification - Benzol Recovery.

The synthesis gas upon leaving the producer, has the following composition:

H_2	47%
CO	23
CO_2	21
CH_4 + UNSATS.	6
H_2S	1
O_2 must be less than	0.3
N_2	remainder

Organic sulfur compounds	300 mg/100 litres
(SOC, Thiophthen, etc.)	300 g/m ³ sy-gas
H ₂ S	about 1000 mg/100 litres

The purpose of the gas purification step is to remove the organic and inorganic sulfur compounds which so easily poison the cobalt catalyst.

The use of an oil wash to remove organic sulfur compounds produces the unexpected result of increasing the yield of benzol, which in applying a definite gasification process remains apparently constant.

The synthesis gas passes next into the circulating scrubber in which the dust is completely removed. The exact quantity of the dust is an extremely difficult problem in the analysis.

It follows then into the alkazid unit where the largest part of the H₂S (85%) is removed.

The H₂S is next stripped out of the alkazid caustic and converted into elemental sulfur by a Claus unit. (Reaction between SO₂, burning H₂S and Hydrogen Sulphide.

The removal of organic sulfur compounds is accomplished in several units.

(a) The coarse purification occurs in 3 channeled pots, each having 12 gangs of 50 cu.m. surface, with iron-oxide (Lauta-material). Here as in (c) the fine purification, the organic sulfur is burnt to SO₂ (with a small quantity of oxygen) then to be converted to basic iron oxide.

*(b) The oil wash. This unit has been recently enlarged and will now operate as the corresponding unit on the coke oven. By this benzol is recovered and thiophthenes removed. The wash oil is a low viscosity oil with nonemulsifying properties.

(c) The fine purification unit. Here the last traces of organic sulfur are removed. The unit operates as the coarse purification unit (alkalized iron oxide), between 240 - 280°C.

(d) Of late, the synthesis gas has also been purified by activated charcoal, hence passing through

another "finest purification". This is done in order to use the hot dry gas as a drying agent to remove the steam used in stripping the primary product of the synthesis step (1st stage).

The sulfur deposited on the charcoal by the gasoline is very much lower than the allowable upper limit of sulfur content in the gas.

III. Synthesis - Catalyst.

If the previous purification step is accomplished well, then the proper synthesis will occur without difficulty. It has been possible in a modern synthesis plant to produce 168 gm. of primary product per cu.m. of synthesis gas, and also to obtain approximately 94% of the theoretical yield (180 gms.)

At Lützkendorf, a constant purity of synthesis gas was not obtained. Often traces of H_2S would reach the catalyst chambers and instead of the 2mg. of allowable organic sulfur, the quantity would exceed 10 or more gms/100 liters of synthesis gas. Frequently, the organic sulfur would reach the activated charcoal.

As a result, the catalyst and activated charcoal had a much shorter life cycle. A synthesis catalyst should reach 200 hours but often fell far below this figure. Other synthesis plants have given 8 times this life.

The synthesis occurs at $180^{\circ}C$. The temperature of the reaction is controlled by the steam pressure (within the exchanger). Local overheating is not uncommon and spent catalyst often gives proof (through carbon esters) of poor operation.

The synthesis usually takes place in 2 stages. In the first, over old catalyst, a contraction of only 15-33% is usual at Lützkendorf. This is increased in the second step, over new catalyst, up to 50%. The total contraction ranges from 65-70%.

The catalyst is quickly covered with a coating of hard wax, which often requires an extraction, generally with gas oil, lately with gas oil and gasoline, though this latter without good results. The removal of wax, however, is not as difficult as problem as the poisoning of sulfur bearing compounds.

The rebuilding of large synthesis plants and the difficulty of obtaining cobalt for the catalyst were the main causes for the researches undertaken to discover other easily obtainable metals for catalyst. The use of iron was unsuccessful because of the fact that this

metal only becomes active at higher pressures - at least 5 atmospheres. Among all of the synthesis units, many had to be converted as they operated at low pressure.

An attempt was also made to reduce the cobalt content in the catalyst. This was successful in a reduction of from 36 to 30%. But since the regeneration loss did not drop to 20% at the same time this saving was not of great value. In general the standard catalyst was used. It is made by a substitution reaction in thorium nitrate, magnesium nitrate and cobalt nitrate in a boiling solution of sodium carbonate. Great care must be taken during the cooking and washing step (as with all catalysts). The completed catalyst contains approximately 36% cobalt, 2% thorium, 4% magnesium and the rest sintered kieselguhr. The reduction of the catalyst must take place at from 400-470°C. The hydrogen used for this must be absolutely dry. Traces of moisture are removed by passing the hydrogen over magnesium nitride. After hydrogenation, the hydrogen is displaced by CO₂ in order to prevent contact with oxygen. The catalyst size is somewhat smaller than "peas".

IV. Activated charcoal unit.

The residual gas from the catalyst chambers is passed over activated charcoal in an adsorber - Lurgi type - for removal from other products. This adsorption, stripping by low pressure steam, and drying occur in sequence. The time required for one complete cycle is between 20 and 40 minutes, determined by operating tests.

Through use and poisoning, the activated charcoal becomes used up or made inactive, and must be rapidly washed or at least dried with high pressure steam. The size of the total unit must therefore not be made too small.

After the activated charcoal unit, the tail gas enters the deep cooling unit to recover the gas oil.

V. Further Processing.

Complete separation of the final products is important. Sulfur removal is not necessary. In a special stabilizing unit the desired vapor pressure can be obtained, by injecting a definite quantity of gas oil.

The octane number is obtained by the customary purification test, either by the USA Standard Method or the I.G. Motor method.

The liquid, boiling above the gasoline range, is taken to the high pressure hydrogenation unit and to the lubricating oil plant, in which it is converted to valuable lubes by either propane dewaxing or phenol extraction after the customary American practice. Concurrently, the same liquid is often taken to the Neuhausen Petroleum Distillation Refinery for other processing.

C: Possible Developments for the Process.

Fischer Tropsch Synthesis

Iso-Synthesis

Oxo-Synthesis

The first phase of developments in the synthesis, was always toward higher yields of gasoline. This was most important for war prosecution. With these improved yields, which are now only slightly below the theoretical, this solution has had a satisfactory solution.

The second problem has been to find catalysts for the Fischer Tropsch low pressure process which are not of cobalt. In this respect, no good solution has been found, to date.

For the last four years an entirely new phase of synthesis research has been under way. In this respect it has not concerned itself with the purely practical or yield viewpoint, but with a much bigger problem - namely - that "by-products" have impressed economists with the possibility of producing materials of much greater value through a total synthesis. This development is still under way.

For example, the following combinations are possible:

Through a simple, one-stage synthesis, produce gasoline. Then apply the synthesis to use iron catalyst at medium pressure. This stage can be used with circulation, resulting in both saturated and olefine compounds. The latter can be used in the oxo-synthesis. Ruhrchemie has been developing the work of D.F. Smith (J.Amer.Chem. Soc., 52.322 (1930) and also of Roelen. This work consists in combining olefines, hydrogen and carbon monoxide to form oxo-products, (aldehydes, ketones, etc.) which can later be transformed into fatty alcohols by hydrogenation. If the olefines are not used for oxo-synthesis, there are many applications for their uses in producing paraffines. These are both cracking processes and catalytic processes.

To increase the production of fuels, the direct synthesis of valuable materials must be used. Till now the use of subsequent isomerization has been of value to increase octane rating. New processes of Fischer, Pichler and Ziesecke, developed since 1941, have produced by direct synthesis large quantities of iso-paraffines (branched chains). Ruthenium and cerium appear to be the active metals used.

For a long time it has been known that small quantities of fatty acids exist in the Fischer synthesis. Future research should indicate the mechanism by which the direct production of fatty acids from CO and H₂ will be possible. This problem was investigated by the author and the Sunlight Co.

As far as benzol yields are concerned, that is a problem of the gasification process. Hence a truer evaluation of the yields is important.

One of the most important problems is to find new catalysts which are less sensitive to sulfur. In this respect sulfide compounds may be of value.

For the iso-synthesis much more porous catalysts must be found which will reduce the present high pressure and temperature requirements of this process.

The development of the Fischer Process will be economically possible after the war and will cease to be an "Ersatz" problem. Such products as lube oils, fatty acids, iso-gasoline, fatty alcohol and Diesel oils will become of great importance.

**D: Industrial and Scientific Concerns interested
in the development of Synthesis.**

<u>Field</u>	<u>Names</u>
Medium pressure synthesis	Wintershall Co. (ROSTERG) Hoesch
Iso-synthesis	Fischer, Pichler, Ziesecke
Oxo-synthesis	Natta, Roelen, Fischer Ruhrchemie, Henkel, I.G. Far- ben, Sunlight (Nagelstein)
Lubricants	Wintershall (Toennis, Billig)
Benzol yield	Wintershall (Toennis)
Olefining	Hoesch
Apparatus construction	Lurgi (general) Koppers & Didier (gasific- ation) Toennis (Wintershall)
Other processes	Pott

E: New books

1. Maximilian MARDER: Motor fuels
Springer. 1942. 2 vols.
2. KADMER: Lubricants and their research
1942.

SEPARATION METHODS

Deep cooling

1. Ethylene separated from coke and crack gases:

Work done by VAN NUYS, WILKINSON and SCHLITT for the AIR REDUCTION Co.

Work done by SAKMIN (about 8 to 10 years ago). See: J. Compressed liquid gases.

2. Purification of Acetylene:

Hexan washes at about -80°C .

Azeotropie

Seperation of Formic Acid and Acetic Acid through the addition of Thiophthene.

(Acetic acid remains in the column)

VULCAN COPPER

Crystalization

Benzol purification through crystalization

Methods of LINDE'S BISMASCHINEN A.G.

Adsorption

LURGI Programme

THE MANUFACTURE AND REGENERATION OF FISCHER-TROPSCH CATALYST CARRIERES-KULHMAN PLANT, HARNES, FRANCE.

Introduction.

The manufacture of catalyst is one of the most difficult and important features of the Fischer-Tropsch process. Except for sulphur removal in the feed gas, it is the operation which has the greatest effect on good plant operation. Along with this step, goes the regeneration of spent catalyst which is equally important.

All modern Fischer-Tropsch units have a special department for manufacturing and regenerating catalyst. This department is staffed with well trained chemists who have at their disposal the most modern control equipment. For this reason, the investment and operating costs of the catalyst department form a sizeable part of the total plant installation.

At the Carrieres-Kuhlmann plant at Harnes, the Fischer-Tropsch unit employs 120 men as operating personnel. This plant should be able to produce 350 bbls. of total liquid daily. Of the 120 men, 40 are employed in the catalyst manufacture and regeneration. There are also 80 men, not included in the 120 total, doing full time maintenance.

Description of Raw Materials.

The raw materials used at Harnes are pure cobalt metal, magnesium oxide, thorium oxide, and kieselguhr. These produce new catalyst as opposed to the regeneration of old catalyst which is a separate operation. Their percentage by weight of the finished catalyst (in the non-hydrogenated form) is as follows:

Co	13.0 %
MgO	1.8
ThO ₂	0.9
Kieselguhr	79.3

100.0 %

It must be stressed that the above analysis is in the unreduced form prior to hydrogenation, as after the catalyst is hydrogenated it is extremely pyrophoric and can not be analyzed.

Other chemical agents used are nitric acid (36 Be) and sodium carbonate (10% strength). The exact quantities of these used can not be definitely stated, but is approximately 40-50 Kg of HNO_3 and 90 Kg of Na_2CO_3 to produce 100 Kg of finished catalyst.

Purity of Raw Materials.

The raw materials used must be extremely pure. Small traces of impurities will poison the catalyst, e.g. CaO & Fe .

The cobalt must be at least 99% pure. The remaining 1% is either copper or nickel. Before the war the Kuhlmann Co. obtained their cobalt from the Belgian Congo. This ore, in its natural form is known as Katanga. Since the war, this supply has been cut off and another source in North Africa was used. The latter was not as pure as the Katanga and had to be concentrated by a process similar to the Parks process. The ore is dissolved in nitric acid and passed over a bed of pure cobalt. The pure cobalt displaces the copper and nickel in the nitrate solution. The two latter elements settle to the bottom while the cobalt nitrate is removed from the top.

The thorium oxide can not contain traces of lead or phosphorus. The calcium oxide content must be less than 0.2% by weight.

The kieselguhr used must be of a certain type. It must not contain iron or lime. The SiO_2 content must exceed 92%. The sand content can not exceed but a few percent. All organic matter must be removed by roasting at 800°C . but this temperature must not be greatly exceeded, as the structure of the particles will be destroyed.

The German kieselguhr from Kieselguhr Industrie- Hannover, No.120, is one of the best. It contains some impurities but has excellent size properties.

The Johns-Manville "Filtracel" will work well. Its chemical composition is purer than the German, but its size is not as accurately controlled.

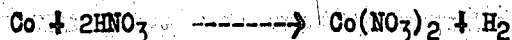
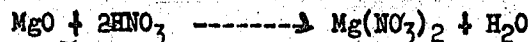
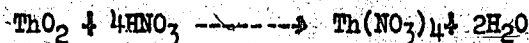
The French are currently getting their kieselguhr from the central part of France - (Murat). It is not as good as either of the above but will work reasonably well. The greatest difficulty is apparently in air blowing the material in such a way as to remove the sand and not incur great losses.

Finally, the nitric acid used must be made from distilled water in order to avoid all traces of CaO .

Description of the Catalyst Manufacture.

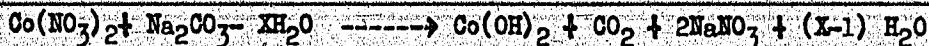
All of the raw materials, except the kieselguhr, are placed in one of three mixing tanks. These tanks are so arranged that two of them can quickly and simultaneously dump their contents into the third. Along with the raw materials in the first tank is put the required quantity of (36 Be strength) nitric acid. Mechanical agitation is used to assist the reaction. Distilled water, up to 1000 liters, is also added. The acid quantity is 20% in excess of that required theoretically to nitrate the magnesium and thorium oxides, and the cobalt.

The reactions in this operation are:



In the second tank is put 10% strength sodium carbonate and up to 1000 liters of distilled water. The contents of this tank and the nitrated products of the first, are now quickly and simultaneously dumped into a third larger tank. This tank has mechanical agitation and is heated up to 100°C. The pH of the resulting mixture is 7.2, slightly on the alkaline side.

This is most important, as under no circumstances must the formation of bicarbonates occur. The boiling temperature also aids in releasing CO_2 (especially with the cobalt salt) so that the final reactions are:



The kieselguhr, meanwhile, has been heated carefully to 800°C. to remove all organic material. It is now added to the mixture in the third tank and thoroughly stirred and agitated. The presence of any bicarbonates would tend to destroy the efficiency of the kieselguhr as a supporting medium, and for that reason all the latter must be removed before the kieselguhr enters the third tank.

The slurry is now sent through a series of washes with distilled water. The first is through a plate type filter press. It is most important that this filtration be done very quickly. At Harnes there are two of these in parallel. Next, the slurry enters a horizontal mixing tank with a screw type agitator. More distilled water is added here. After suitable stirring, the slurry is fed into an Oliver rotary type filter where the extraneous water is removed. Following this, the slurry enters an extruding type press (called "Strangpresse" by the Germans). Here the water content is reduced to 60%. It then passes through a dryer where the water content is reduced to 6-8%. The dryer is steam heated and maintained at a temperature of 120°C. The catalyst rests on moving belts in the dryer. The time of passage is 2 hours.

The catalyst is now ready for sizing. The optimum size is that of a pea. It is put into a unit with a screen bottom, 4 mm. mesh size, and a sweeping broom device which forces the catalyst through the mesh. It falls onto a vibrating inclined screen which removes the dust and fines. These are collected and returned to the horizontal mixing drum for reprocessing. The sized catalyst particles are now ready for reduction by hydrogenation.

The pellets are placed in a special type of container, having conical ends piped up to a closed hydrogen circuit. The pellets rest on a screen tray and can hence be easily exposed to the hot gas. The hydrogen is heated up in a furnace to 350°C (in Germany 400°C.) before entering the container. Since the reduction of the oxides and carbonates produces water, the exit gas must be dried. This is done by passing successively through water cooled coils, ammonia cooled coils and finally silica gel, returning to the hydrogen heater for recirculation. This step takes approximately 1/4 hour.

The reactions here are:

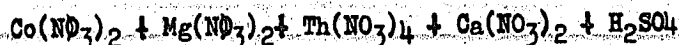
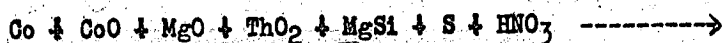


When the reaction is complete, the reactor is cooled and filled with CO_2 . The contents are transferred to a closed bucket container and placed in the reactor, still in a CO_2 atmosphere. If air comes in contact with the reduced catalyst, a violent fire will occur as the material is extremely pyroforic. The CO_2 is purged from the system as soon as the hydrocarbon feed enters the reactor.

Regeneration of Spent Catalyst.

The spent catalyst, containing cobalt, cobalt oxide, magnesium oxide, thorium oxide, and kieselguhr, is dumped into a tank with (36 Be strength) nitric acid. A small quantity of sulphur will also have accumulated from impure feed gas.

The reaction is approximately as follows:

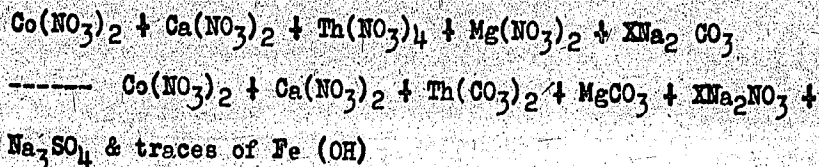


This equation is not exactly balanced. Further, the quantities of magnesium and calcium silicate and sulphur are very small, resulting from the decomposition of the kieselguhr, but are very important and must be removed. The quantity of nitric acid required is that which will completely nitrate all the oxides and silicate. It is found by experimental procedure. As a test, the nitrate material when roasted must appear gray and not black. Otherwise the cobalt oxide has not been completely converted to cobalt nitrate. Mechanical agitation aids the reaction.

The slurry is pumped through a plate type filter press, #1, where the bulk of the spent kieselguhr is removed. This is not recovered. The cake is washed by distilled water to remove all valuable nitrates.

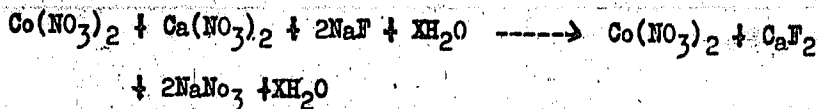
This solution, after leaving filter press #1, enters another tank with mechanical agitation. Enough sodium carbonate is added to result in a pH of 4.2.

The reaction is approximately as follows:



It should be noted that the cobalt and calcium nitrates are untouched as long as the pH remains 4.2. This allows for their separation from the insoluble carbonates.

The resulting slurry now enters a plate type filter press #2, where the magnesium and thorium carbonates and the sodium sulphate is removed as spent cake. The solution of cobalt and calcium nitrate then goes to a settling tank into which is pumped a solution of sodium fluoride and distilled water with the resulting reaction:



The resulting slurry goes to a final plate type filter press #3 where the calcium fluoride is removed and discarded. The purified cobalt nitrate is now ready to use again as part of the regenerated catalyst.

The spent cake from filter press #2, consisting of $\text{Fe}_2(\text{OH})_6$, MgCO_3 , $\text{Th(CO}_3)_2$ and Na_2SO_4 , now goes to a tank with agitator and is nitrated with 36 Be HNO_3 . From here, the slurry goes to another tank where a controlled quantity of sodium hydroxide, 20 grams/liter, is added. In so doing a double thorium salt is formed, $\text{Na}_2\text{SO}_4 + \text{SO}_3\text{ThO}_2$ which is soluble. The iron and magnesium nitrates are converted to insoluble hydroxides. The double salt will not decompose at ambient temperatures.

Filter press #4 removes the $\text{Fe}_2(\text{OH})_6$ and Mg(OH)_2 . The solution of the double salt now goes to a steam heated tank where its

temperature is raised above 80° C. This causes the double salt to decompose into $\text{Th}(\text{OH})_4$ and Na_2SO_4 . The former is removed as spent cake and in filter press #5 and is ready to use again as part of the regenerated catalyst. The sodium sulphate solution is discarded.

No attempt is made to recover the magnesium hydroxide as its value is not sufficiently great to warrant the effort.

10th January 1945

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