CONFIDENTIAL

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

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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.

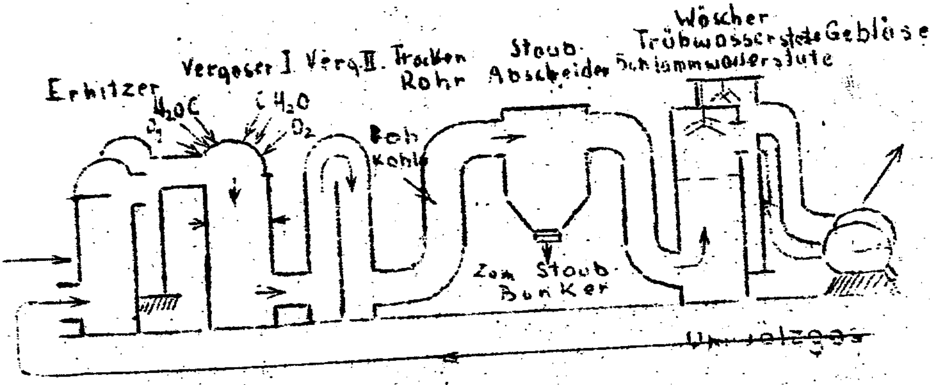
Two methods of gasification are today in use:

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 H_2/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 thiophthenes 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 Tropsch 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 (SOC, Thiophthen, etc.)	300 mg/100 litres 300 g/m^3 sy-gas
H_2S	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 H_2S (85%) is removed.

The H_2S is next stripped out of the alkazid caustic and converted into elemental sulfur by a Claus unit. (Reaction between SO_2, burning H_2S 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 SO_2 (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°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 Lutzkendorf. 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 CO_2 in order to prevent contact with oxygen. The catalyst size is somewhat smaller than "peas".

IV. Acitivated 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 seperation 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 Neuhagen 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 yeild 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 producting 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 H_2 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.

Field	Names
Medium pressure synthesis	Wintershall Co. (ROSTERG) Hoesch
Iso-synthesis	Fischer, Pichler, Ziesecke
Oxo-synthesis	Natta, Roelen, Fischer Ruhrchemie, Henkel, I.G.Farben, Sunlight (Nagelstein)
Lubricants	Wintershall (Toennis, Billig)
Benzol yield	Wintershall (Toennis)
Olefining	Hoesch
Apparatus construction	Lurgi (general) Koppers & Didier(gasification)
	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.
Azeotropic	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 EISMASCHINEN A.G.
Adsorption	LURGI Programme