

SECRET

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 con-
tinuously 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 Morroco 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 : $mCO \div (2M \div 1) H_2 \rightarrow C_m H_{2m} \div 2 \div mH_2O$. 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 :

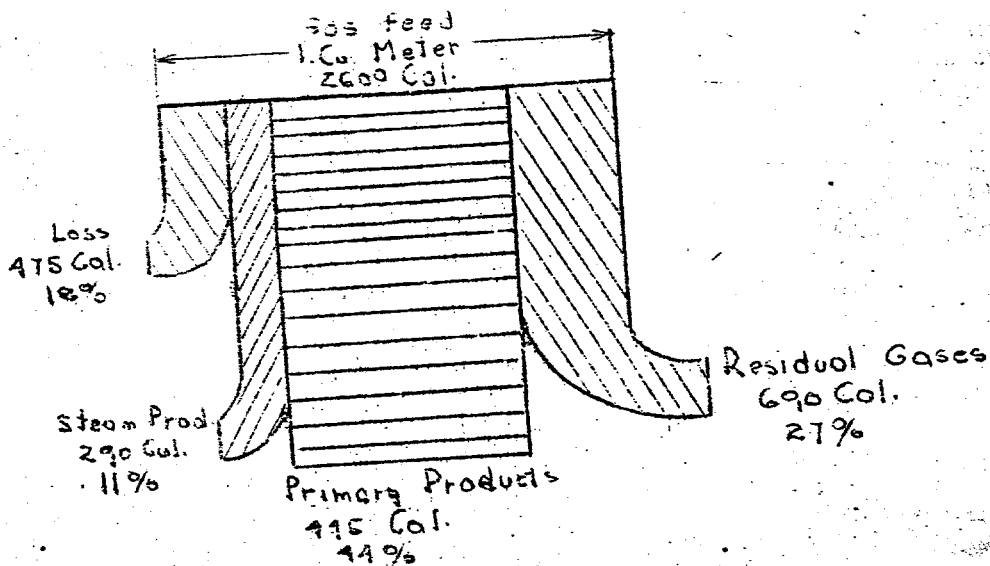
CO	-	27 %
H ₂	-	54 %
CO ₂	-	14 %
N ₂)	-	5 %
CH ₄)		

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 $200-300^\circ\text{C}$. 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 %	<u>23 BPD</u>
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 production 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.