ALSOS-60

ALSOS INTELLIGENCE MISSION
UNITED STATES NAVY

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	18.0 %
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 pyroforic 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 $H\ NO_3$ and 90 Kg of $Na_2\ CO_3$ 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 kieselfuhr 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:

$$ThO_2 + 4HNO_3 \dashrightarrow Th(NO_3)_4 + 2H_2O$$

$$MgO + 2HNO_3 \dashrightarrow Mg(NO_3)_2 + H_2O$$

$$Co + 2HNO_3 \dashrightarrow Co(NO_3)_2 + H_2$$

In the second tank is put 10% strength sodium carbonate and up to 1000 liters of distrilled 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:

$$Co(NO_3)_2 + Na_2CO_3 - XH_2O \dashrightarrow Co(OH)_2 + CO_2 + 2NaNO_3 + (X-1)\ H_2O$$

$$Mg(NO_3)_2 + Na_2CO_3 \dashrightarrow MgCO_3 + 2NaNO_3$$

$$Th(NO_3)_4 + 2Na_2CO_3 \dashrightarrow Th(CO_3)_2 + 4NaNO_3$$

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 passgge 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:

$$Co(OH)_2 + H_2 \longrightarrow Co + 2H_2O \quad (70\%$$

$$Co(OH)_2 + 1/2\ H_2 \longrightarrow CoO + H_2O \quad (30\%$$

$$2Mg(CO_3) + 2H_2 \longrightarrow 2MgO + CO_2 + 2H_2O$$

$$Th(CO_3)_2 + 2H_2 \longrightarrow ThO_2 + 2CO_2 + 2H_3O$$

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:

$$Co + CoO + MgO + ThO_2 + MgSi + S + HNO_3 \longrightarrow$$
$$Co(NO_3)_2 + Mg(NO_3)_2 + Th(NO_3)_4 + Ca(NO_3)_2 + H_2SO_4$$

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:

$$Co(NO_3)_2 + Ca(NO_3)_2 + Th(NO_3)_4 + Mg(NO_3)_2 + XNa_2\ CO_3$$

$$\text{------}\ Co(NO_3)_2 + Ca(NO_3)_2 + Th(CO_3)_2 + MgCO_3 + XNa_2NO_3 +$$

Na_3SO_4 & traces of Fe (OH)

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:

$$Co(NO_3)_2 + Ca(NO_3)_2 + 2NaF + XH_2O \text{ -----}\!\!> Co(NO_3)_2 + CaF_2$$

$$+ 2NaNo_3 + XH_2O$$

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 $Fe_2(OH)_6$, $MgCO_3$, $Th(CO_3)_2$ 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, $Na_2SO_4 + SO_3ThO_2$ which is soluble. The iron and magnesium nitrates are converted to insoluble hydroxides. The double salt will not decompose at ambiant temperatures.

Filter press #4 removes the $Fe_2(OH)_6$ 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 $Th(OH)_4$ 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.

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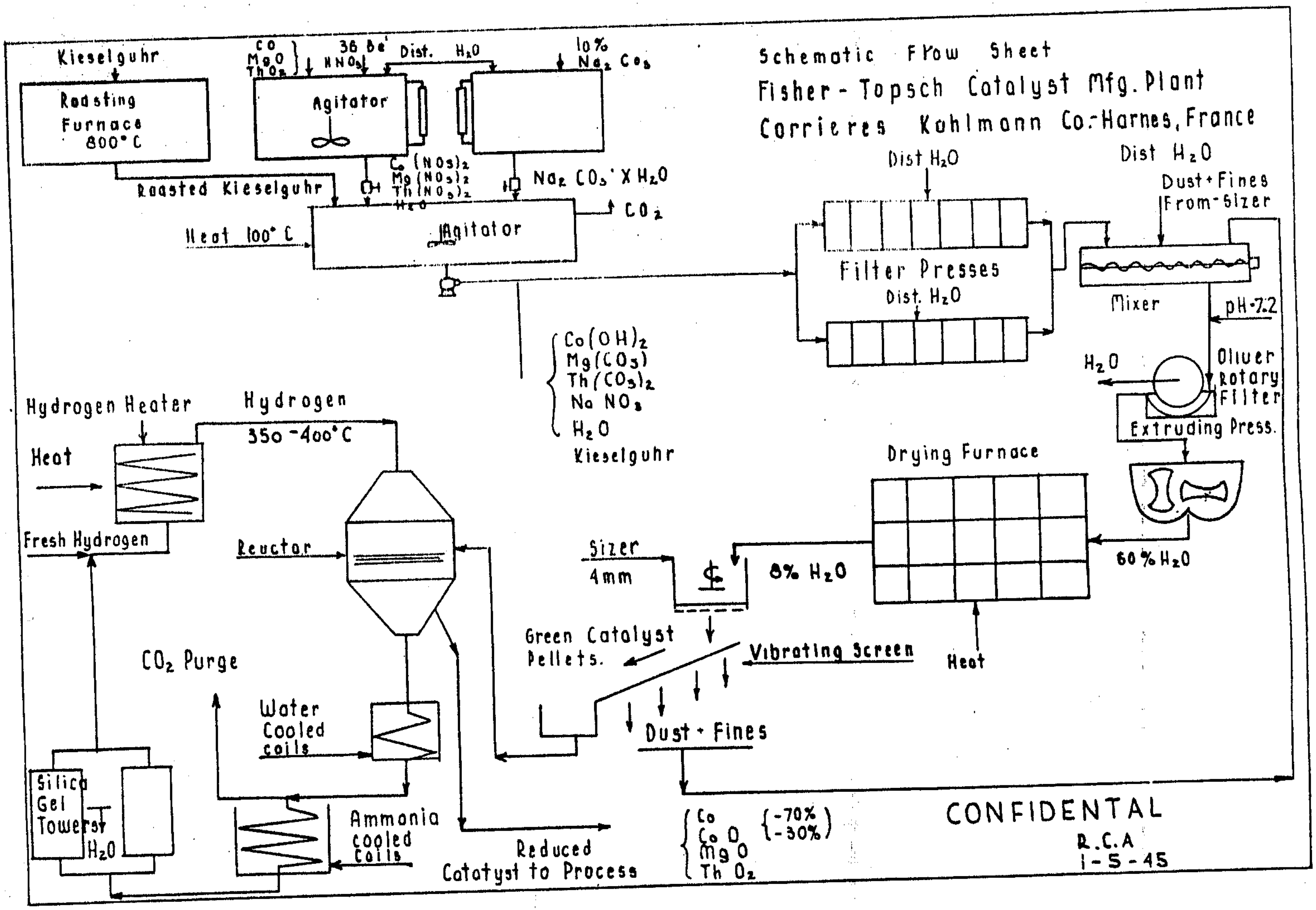
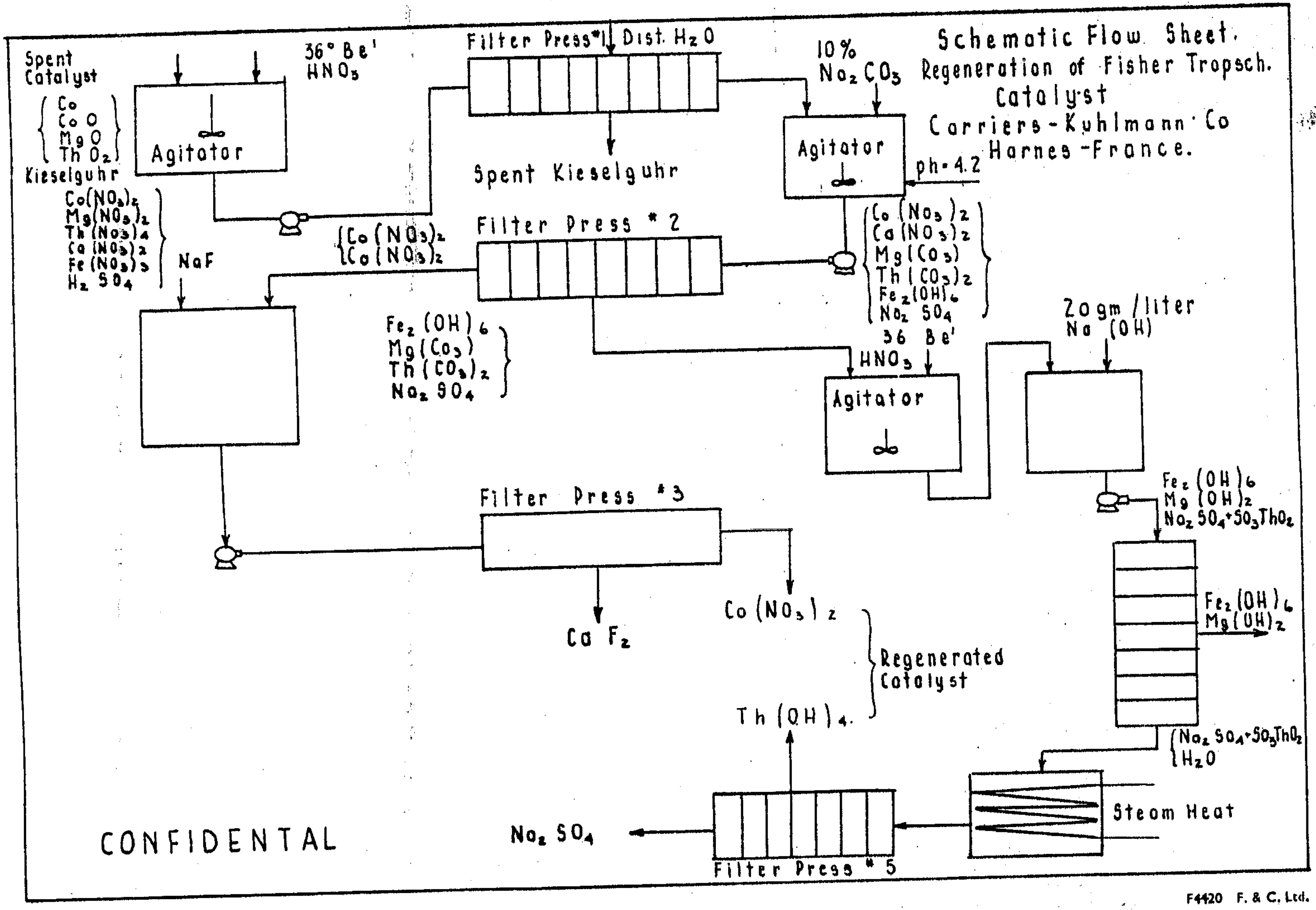


Schematic Flow Sheet
Fisher - Topsch Catalyst Mfg. Plant
Corrieres Kohlmann Co.-Harnes, France



Schematic Flow Sheet.
Regeneration of Fisher Tropsch. Catalyst
Carriers-Kuhlmann Co
Harnes-France.

F4420 F. & C. Ltd.