

CATALYSTS IN THE PRODUCTION OF SYNTHETIC FUELS FROM COAL

by S.B. Tatarskii, K.K. Papok and E.G. Semenido.

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The importance of the catalyst is exceptionally great in the production of synthetic fuels and oils.

A knowledge of catalysts and of the conditions for their use is like having a key to unlock production secrets of the synthetic fuel manufacture, which has been widely used in Germany.

It is difficult to hide from an observer's eye the 18 m converters, sizes of furnaces or the different equipment, which are integral parts of the synthetic plants, while when telling about catalysts secrets are easily kept, which makes it not impossible, that the information given us by the German specialists will contain some inaccuracies and omissions.

CATALYST FOR THE HYDROGENATION OF COALS AND
OF THE PRODUCTS OF THEIR THERMAL
TREATMENT.

The preparation of catalysts resistant to poisoning with sulfur, to be used in the hydrogenation of coal and of the products of their thermal decomposition, was the turning point in the development of synthetic fuel manufacture after which the development of industrial hydrogenation was quickly brought to conclusion. It has, however, been found necessary to forego the hydrogenation in one single step, because of the necessity of working with very low partial pressures of the material (and therefore also with small yields of the finished product) in order to avoid the poisoning of the catalyst with asphaltic products. This has caused the breaking up of the process into two steps, the liquid phase and vapor phase hydrogenation.

Heavy oil (init. b.p. 320 - 360°C) was hydrogenated in the liquid phase in the presence of powdered iron catalyst at 450°C and at pressures of 275 - 700 atm. Coal, in a paste form, was hydrogenated under similar conditions. The used-up iron catalyst was continuously removed from the cycle and replaced with fresh catalyst. The catalyst was not regenerated.

Middle oil, b.p. 200 - 350°C was hydrogenated in the vapor phase. The hydrogenation temperature was 420 - 450°C, with 300 atm. pressure and a fixed bed catalyst (tungsten sulfide).

Catalysts used in the hydrogenation were principally prepared in two main factories, which belonged to the I.G. Farbenindustrie A.G. One of these was located in Ludwigshafen, the other one in the town of Leuna near Merseburg (Leipsic).

These factories made new, and regenerated old catalysts returned by the hydrogenation plants in exchange for new. In addition to these two catalyst factories there were two others located near the plants in Pöhlitz and Schwarzheide. These latter two factories furnished catalysts only for their own plants.

Detailed study of the work in the factories at Leuna and in Pöhlitz was made difficult by the absence of the technical personnel and the accounting office.

A. Liquid Phase Catalysts.

"Catalyst I". Bog iron ore, or other material containing dispersed iron oxide, such as the lauts mass (a by-product of the Bayer's method of manufacture of alumina, containing about 35% iron oxide), the ash from Winkler gas producers working on powdered fuel, etc., were used as catalysts in the liquid phase hydrogenation. This was designated as Kontakt I and 9% of it by weight of coal used was added.

"Catalyst #10927, or "Kontakt II". When tar was hydrogenated, a carrier consisting of iron oxide saturated with hydrated ferric oxide was used as catalyst. Carriers were substances used as "Kontakt I". Saturation was done by wetting with a solution of ferrous sulfate and sodium hydroxide, taken in equivalent amounts, in a way to produce 5% precipitated hydrated oxide of iron (as metallic iron). Such a catalyst was listed as #10927, also known as "Kontakt II".

The fresh catalyst was introduced as a paste, in an amount of 0.2 - 0.5% of the weight of the tar. The total proportion of the catalyst paste and tar, used during hydrogenation, was considerably higher: 3 - 4 m³ of paste was used for 20 - 25 m³/hour of tar, the paste containing 30% of the dry catalyst powder.

Catalyst "Kontakt III". We have found indications in many plants that when low sulfur raw material was hydrogenated, "Kontakt III" was added, which contained sulfur either as sodium sulfide, or as elementary sulfur (about 0.1 - 0.3% of the raw material). An insufficient sulfur content in the raw material would cause a lowering of sulfur in the prehydrogenation catalyst, which would reduce its activity.

Catalyst 11002. Before the use of catalysts I and II (prior to the outbreak of the war) a few of the plants hydrogenating tar used a powdered molybdenum catalyst, listed as 11002. We have not succeeded in collecting information on its preparation, and we only know that its molybdenum content was low, 2 - 3%. Change from the molybdenum to the iron catalyst was caused by the difficulties of obtaining molybdenum during the war.

B. Catalysts for the Vapor Phase Hydrogenation.

The pre-hydrogenation catalyst #5058 was pure tungsten sulfide (WS_2). It replaced molybdenum sulfide because of its 4 times greater activity. The amount consumed was 0.09% of the hydrogenated middle oil.

One converter charge, weighing 19 - 20 te was sufficient for the production of 60,000 te of products. The life of the catalyst was 200 - 400 days. The cost of the catalyst was RM 33,890 per te.

Preparation of the Catalyst. A mother liquor of ammonium sulfide was prepared (from 14% solution of hydrogen sulfide and 12 - 13% ammonia water) for the solution of tungstic acid (called the yellow earth in the preparation directions). 350 - 400 kg "yellow earth" is used for 1100 li. ammonium sulfide solution. The mixture was stirred while heating to $70^{\circ}C$, and then settled for two hours. The solution was filtered, sent to the saturator and heated to $50^{\circ}C$. Hydrogen sulfide was next bubbled through. The yellow salt (ammonium sulfo-tungstate) began then to precipitate and the temperature was raised to 70° during one half hour. The saturator was next slowly cooled (4° per hour), while passing hydrogen sulfide continuously, the pressure of the hydrogen sulfide being kept 380 - 300 mm Hg. The yellow salt kept coming down continuously. The saturated solution was cooled to $15 - 20^{\circ}C$.

Should the solution leaving the saturator contain an insufficient amount of ammonia, more ammonia was added to the saturator, while cooling it with cold water to avoid overheating.

The solution must at all times contain 14% hydrogen sulfide and 12% ammonia. 400 kg "yellow earth" produces 500 kg yellow salt. The saturator was opened after the salt had crystallized and the solution with the precipitate was suction filtered. The salt remains on the filter cloth, the solution was collected. The salt was transferred from the filter cloth to a drier with a stirrer and dried for three hours at $130^{\circ}C$. The drier was heated with a steam jacket. The escaping gases (hydrogen sulfide, ammonia) were absorbed in recirculating water.

After drying the salt was dried to 20° (by water circulating through a cooling coil) and the drier emptied into a worm-driven

furnace. It took the salt two hours to pass the furnace. Water gas (5 - 6 m³) was passed through the furnace. The worm was operated at the same speed as with other catalysts: three 180 kg. drums in eight hours. The salt which left the furnace was yellowish black. As soon as the drum was filled with the salt, it was covered to prevent oxidation of the salt. When the powder was cold, it was sifted through a 1/2 mm screen and ground in an atmosphere of nitrogen. The ground powder was compressed into tablets and the catalyst was ready for use.

The preparation of the catalyst 8376 was begun during the war, because of the shortage of tungsten. Its composition was: 18% tungsten, 2% nickel, 80% alumina (carrier). Its consumption amounted to 0.03 kg/te hydrogenated middle oil. The catalyst charge in the converter is 6 - 7 te. The catalyst can hydrogenate up to 60,000 te middle oil. The cost of the catalyst was RM 17,432/te.

Preparation of the catalyst. 200 liters water was poured into a cooled container and 1500 kg aluminum sulfate added. The salt was stirred and heated to 60 - 70°C with live steam. After settling for two hours the solution was pumped over into another vat and from there into a mixer where ammonia was added while heating to 90°C. The hydrated alumina was filter-pressed, washed for 8 - 10 hours and transferred to driers where it was heated for 8 - 10 hours with high pressure steam. When dry, the product was ground and sifted through 6 mm screens. The sifted product was tabletted to a pressure resistance of 20 - 25 atm.

The tablets were ignited in a vertical electric furnace at 890 - 902°. They were next saturated with a solution of tungsten and nickel and dried at 80 - 90°. The saturation was done three times. The saturated tablets were reground and sifted through 3 mm screens. The powder then entered a worm driven furnace with three compartments. Two of them were heated from the outside, the third one was the cold zone of the furnace. The powder was kept in the furnace for 1 1/2 - 2 hours. Hydrogen sulfide and pure water gas were then introduced while the worms rotated uniformly and moved the powder downwards. The gases were scrubbed with sodium hydroxide to absorb the hydrogen sulfide. The waste liquor contained 6 - 8% hydrogen sulfide and up to 6% ammonia. About 5 m³ hydrogen sulfide was run through in one hour, and somewhat less water gas (3.5 - 4 m³).

The powder must be pure black when finished, and was then transferred from the furnace to the tablet press. The tabletted catalyst was once more ignited in an electrical vertical furnace at 920° C in a stream of hydrogen sulfide. The tablet machine operated under a pressure of 50 - 60 atm. Three drums of 180 kg each of the 8376 catalyst were made in 8 hours.

Hydrogen sulfide was produced in a special generator from sodium hydrosulfide and 75% sulfuric acid.

Benzination catalyst 6434. Its composition was 20% tungsten and 80% carrier (Bavarian activated earth, called "Terrana"). The catalyst may be used for up to 3.5 months. The amount consumed was 0.07 kg/te gasoline.

Method of preparation. 250 kg bleaching earth "Terrana" was added to a mixer, then 300 liters diluted hydrofluoric acid (160 kg acid to 1000 li. water). The mixture was mixed for 30 minutes and 600 liters of the mother liquor of ammonium sulfotungstate was added, while running the mixer and heating to 80 - 90°. The product was dried after 8 - 9 hours of such treatment, and then cooled to 20°. The product was next transferred to a mill, ground, and sifted through a 6 mm screen. It was next sent to a worm-driven furnace where it was heated in an atmosphere of hydrogen sulfide (6 m²) and water gas (5 m²) to a temperature of 920°C. The thermal treatment lasted for 2 hours. The product was ground upon leaving the furnace, mixed with a small amount of water and tabletted. The tablets were sifted, dried in a furnace for preliminary treatment (at 320 - 400°) for about 2 hours. They were then reheated in a vertical furnace to 1040 - 1080°C in an atmosphere of hydrogen sulfide (6 m²) and water gas (5 m²). This heat treatment also lasted two hours.

Catalysts for Hydrogenation Products.

The insufficiently high octane number of the hydrogenation gasoline, (70 - 72), which was the principal source of German aviation gasoline, has caused the German motor fuel industry to find means of raising that number. This was done in two ways: by means of catalytic aromatization (dehydrogenation) of the hydrogenation gasoline (the so-called DHD installations) and through the production of isobutane (polymerization of isobutylene and the alkylation of isobutane with butylene).

The principal features of both these methods were solved by the use of catalysts.

Catalyst 5633 was used for the catalytic aromatization of gasoline to raise the octane number of the hydrogenation gasoline. The catalyst was composed of 5% molybdenum oxide and 95% alumina (according to data obtained in Leuna, according to information from the town of Most, molybdenum oxide formed 9% of the catalyst).

Method of Manufacture. The technical grade of aluminum oxide was plasticized with water and nitric acid in a kneading machine, and shaped into cubes on a roller press. The cubes were dried and ignited at 450° C. The cubes were saturated with a solution of ammonium molybdate in such a way as to leave 5% molybdenum oxide in the finished product.

Catalyst 6448 was used for the dehydrogenation of butane into butylene. It was composed of 90% alumina, 2% potassium oxide and 8% chromium oxide.

Method of manufacture: 22.5 kg activated alumina (list number 5780) 2 kg of an other activated alumina (list number 5780-100), a calculated amount of potassium hydroxide, chromic anhydride, as well as 2 1/2 liters of 62% nitric acid and 7 - 9 liters of water were mixed for 40 minutes in a mixer, formed into balls, dried for 16 hours at 150° and ignited for 4 hours at 450° (to destroy the nitrates).

The polymerization of isobutylene into isooctylene was made with the help of catalyst 2730, consisting of activated carbon saturated with phosphoric acid, and consisting of 35% phosphoric acid, 60% carbon and 5% water.

Method of Preparation: 8 kg of activated carbon were mixed with 5.12 kg phosphoric acid and 4 liters of water. The mixture was permitted to stand until the carbon was soaked through, and dried at 80 - 100°.

Catalyst 4821 was used for the polymerization of isobutylene. The catalysts consisted of asbestos saturated with pyro-phosphoric acid, (25% asbestos, 75% pyrophosphoric acid). Orthophosphoric acid was concentrated at 260° for the conversion into pyrophosphoric acid; 16 liters of the pyrophosphoric acid were mixed with 8 kg. asbestos, the mixture shaped and dried for 60 hours at 150°.

Catalyst 3076 was used for the hydrogenation of isooctylene and isooctane. It was composed of 1 molecule of nickel sulfide and 1 molecule of tungsten sulfide.

Method of Preparation: 50 kg nickel were dissolved in 60% nitric acid and precipitated with soda (90 kg). The carbonate was filtered, washed, dried, ground and sifted.

50 kg tungstic acid (H₂WO₄) was added to 25 kg nickel carbonate and 25 kg of water. The mixture was stirred and evaporated to a thick paste, dried counter currently for 12 hours and ignited at 400°. The mixture was next ground, after having about 1% graphite added to it, compressed, reground and compressed into 10 mm tablets.

CATALYST FOR THE FISCHER TROPSCH GASOLINE PROCESS

The calculated composition of the catalyst: for every 100 g. metallic cobalt there was

	5 g thorium dioxide
	10 - 11 g. magnesium oxide
	200 g Kieselguhr

The raw materials were used in the form of nitrates. The solutions were kept in separate containers. A mixture of the three nitrates was prepared of the following composition:

Co(NO ₃) ₂	40 g	Co/li
Th(NO ₃) ₄	2.4 g	ThO ₂ /li
Mg(NO ₃) ₂	4.4 g	MgO/li

The mixture of the nitrates was mixed to 100° and poured rapidly into a solution of soda (104 g/li), also heated to 100°. The volumes mixed were 1.3-1.4 m³. The mixture was then vigorously stirred for 3-4 minutes. Kieselguhr was added next, and the mixture re-mixed. It was next filter-pressed, washed with distilled water until 100 ml wash water were neutralized with 4 ml(sic) 0.1 N sulfuric acid.

The filtered sludge was mixed with the dust residue of the catalyst obtained previously and pressed in a Wolf rotating press.

The pressed mass was dried in a drier (at 95 - 104°) to a water content of 4 - 5%, crushed and sifted into lumps 1 - 3 mm in size. The catalyst was next reduced at 400° for 50 minutes in a rapid stream of hydrogen.

W.M. Sternberg
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