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Item 29

Report on a Meeting to Exchange Information on the Operation of Fischer-Tropsch-Synthesis-Plants

Preliminary Purification of the Synthesis Gas (H₂S-removal)

Krupp-plant:

A box which was filled with a mixture consisting of Lux-mass, bog iron ore and partly enriched Lux-mass showed an increase in the pressure loss at a sulfur content of 30-35% making it necessary to shut down the box. The pressure loss was due to the slowly dried mass. It was attempted to use the box again by carefully moistening the mass. The procedure was as follows: Water was introduced into the top layer for such a period of time that the lowest layer was also thoroughly moistened. In order to secure a uniform moistening, a wooden grate was applied for the distribution of the water. The box was now put in operation. After a preliminary resistance of 100 mm water column, this dropped very quickly to 50 mm water column and increased slowly to 250 mm water column near the end of the record run. It was possible to enrich the sulfur-content to 53-55%, calculated on the dry mass. The discharged mass had a water content of 8-12%. The described procedure to moisten a dry mass succeeded very well.

It was further stated that the Bischoff distribution pipes which are placed between the single layers secure an especially uniform enrichment of the mass over the entire cross sectional area of an removal box. The investigation of 16 samples which had been drawn from one and the same layer showed differences of but 4-5% of the total sulfur content. It was mentioned that the addition of 2-3% saw-dust has a favorable effect.

Essener Stein Kohle Plant

When a purifier was recently discharged, the sulfur content of the mass was as low as 30-35%. Due to the high pressure drop, the box had to be shut down. The difficulties encountered were due to the utilization of a mixture consisting of Lux-mass and bog iron ore, which, before being fed to the box, had been subjected to the influence of the weather for a considerable period of time. Due to the muddy properties of the mass its pressure drop was very high. It was further mentioned that the Kloenne-towers had an insufficient gas distribution system. The application of an eight-or-four-fold distribution resulted in a higher efficiency of the H₂S-removal plant.

Schwarzheide-plant

Due to an unequal gas distribution the sulfur content of the mass was unsatisfactory. The high air addition of 2-3% to the gas before it is fed to the purifier resulted in a much shorter final-regeneration-period. The high dust content of the gas is responsible for the short runs of the boxes. But after a careful mixing of the discharged mass it can be returned to the purifier without deteriorating its efficiency. Mixtures of Lux-mass and bog iron ore, especially if they are very moist, showed unsatisfactory results.

Rheinpreussion-plant

With the coke oven gas now split separately, a higher enrichment of the mass has been observed. While formerly the sulfur content of the mass was as low as 35%, a 50% fouling is now possible.

Hoesch-plant

No unequal fouling of the mass has been observed. Due to too high a pressure drop resulting from the formation of mud, a purifier had to be shut down. With a sulfur content as high as 47% --based on dry mass-- a moisture content of 30% was determined. The mass consisted of a mixture of Lux-mass and bog iron ore with an addition of raw dust. The mud-formation cannot be traced to too high a water content of the recirculated gases when the shift reaction is put in operation. However it is possible that the gas contains water mist as it was equally observed at the Rheinpreussen-Essener Steinkohle, and Schwarzheide-plants respectively. It was mentioned that the most favorable gas temperature, especially during cold days, is 30-35°C. In order to prevent any condensation inside the purifiers. When spent mass originating from the final purification was added to the mass of the preliminary purification, a considerably high pressure drop was observed. The mass had become very crusty. It was further reported on the effect of addition of spent mass from the final purification system and of the dust of fresh mass to be used for the final purification to Lux-mass. Differences in the efficiency were experienced, but the sulfur contents at the end of the first runs were almost the same.

Wintershall-plant

At the Wintershall plant the H_2S is extracted by employing the Alkaid process. The H_2S is extracted from 20 g/m³ to 0.1 g/m³. Since no iron ore boxes are installed, 10 g H_2S per 100 m³ gas are fed to the final purification. The liquor consumption is normal. Heavy corrosion has been observed in the beginning of the operation due to the application of improper construction material. With a couple of alterations now completed the difficulties have been eliminated.

Final sulfur extraction (organic sulfur)

Schwarzheide plant

The final sulfur removal system is working satisfactorily. It was experienced that an inefficient sulfur removal is closely connected with the condensate content of the synthesis gas. The condensate content depends on operating temperatures of the gasification systems.

Experiments to remove such condensates by means of active charcoal have now been under way for one year. Operating with a normal output and a total sulfur content of less than 0.08 g/100 cu. m. was obtained whereby temperatures as low as 240°C, had to be applied. A 10% fouling may be expected while under commercial conditions in the presence of condensates such a high fouling of the mass is impossible to obtain.

Essener Steinkohle plant

From the beginning of the operation until June 1939 no difficulties were observed but since the end of June the efficiency decreased continuously despite the commonly used methods such as an increase of the temperature, variation of the output and oxygen admixture have been tried. The low efficiency of the final purification resulted already is a decrease of the activity of the catalysts of the 1. stage. Condensates as high as 0.5 ccm. per cu. m. which contained thiophene were found before and after the final purification. At first by adding refilled boxes to the primary purification it was believed to obtain the former conditions, but no improvement could be observed. It may be possible that the increased volume of condensate is due to an altered operating procedure of the carbonization and gasification system.

Formerly before the final purification system, the sulfur content of of the gas was 20 g per cu. m. against 12 g per cu. m. at present. It is worth mentioning that with an insufficient system in operation the first tower will extract the sulfur to 1 g per 100 cu. m. whereas the following tower does not extract any more sulfur. The efficiency of the single towers was determined as follows:

Total Sulfur Content in g/100 cu. m.

Plant	Before final purification	After tower 1	After tower 2	After tower 3
Schwarzheide	2-3	0.4	0.2-0.3	
Ruhrbenzin	13-15	2-8	0.1-0.2	
Rheinpreussen	6-8	0.5-5.0	0.5	below 0.2
Rauxel	15-20	2-6	0.5	0.1-0.2
Krupp	15-20	2-6	0.2-0.3	
Ess. Steinkohle	12-14	1.0-2.5	0.4	
Hoesch	13-14	1-3	0.1-0.2	

Krupp-plant

Since the end of June a decrease in the efficiency of the final purification system was observed without being able to give any explanations.

Wintershall-plant

The plant is suffering from condensates present in the gas. From 20-30 g organic sulfur which are present in the gas before the final purification 90% are extracted by the 1. tower, whereas the 2nd tower removes but a very small amount and the 3rd tower is without any effect.

Hoesch-plant

A decrease of the efficiency of the final purification system was recently observed which is very clearly indicated by the sulfur content of spent masses. The discharged mass of the 1st system contained 7% sulfur, the 2nd 4.5-5% whereas the 3rd and last system contained but 3.5% sulfur.

Rauxel and Rheinpreussen-plant which formerly performed the splitting of the coke oven gas in the producer itself but are now operating a separate splitting system in addition to the water-gas-produces reported as follows:

Rauxel

Even with the operation of a separate splitting system for coke oven gas condensate is still present in the gas but it cannot be stated whether the condensate influences the efficiency of the final purification system. Almost no change in the efficiency of the final purification has been observed since the application of a separate splitting system.

Rheinpreussen

When the coke oven gas was split in the producer itself the sulfur content of the spent mass was never higher than 5-7% despite the fact that temperatures as high as 420°C. had to be employed. The sulfur content of the synthesis gas was always unsatisfactory. With a separate coke oven gas splitting system in operation it was easy to obtain a sulfur content of 9-11% of the spent mass applying a maximum temperature of 340°C. But a considerable improvement of the sulfur content of the gas after the final purification system could not be obtained.

Not before a 3rd system had been installed was any improvement obtained. It was emphasized that even with a separate splitting system in operation condensate is still present in the gas.

Krupp Plant

It was experienced that a mass which had been subjected to elevated temperatures due to secondary reactions does not obtain its full efficiency even after discharging and screening. But it was believed that by an air-and steam treatment a regeneration of the mass could be possible.

Synthesis

a) Quality of the catalyst:

Essener Steinkohle plant

Unequal properties of the catalyst are especially troublesome if sets of 4 furnaces must be operated. It has been observed that a catalyst which contained 850 kg cobalt had a better efficiency than another the cobalt content of which was as high as 1,100 kg. Up to now magnesium catalysts are similar to the mixed catalysts but not better. Their high initial activity causes difficulties when the 1st stage is put in operation. But after refreshing by extraction or hydrogen treatment the catalysts begin to act at lower temperatures than the normally used mixed catalysts.

Krupp plant

Recently obtained catalysts varied in their activity causing considerable trouble during the starting period due to contractions varying between 42 and 68% at 164°C. The content of unproduced granule was often very high especially when a reactor operated unsatisfactorily.

Rheinpreussen

Now and before the activity of the catalysts is varying. The differences can be easily observed by comparing the gas volumes which can be led over equally prepared catalysts. The volume of the synthesis gas can vary between 5,500,000 and 2,100,000 cu. m. In the average the total capacity is between 3,800,000 and 4,200,000 m³. None of the magnesium catalysts was as efficient as the cobalt catalysts. 2 catalysts of such type showed an output of synthesis gas of 2,800,000 cu. m. The operating procedure was as follows: The catalysts are put in operation in the 2nd stage and allowed to remain in that position for 6-8 days. No difficulties have been observed but differences with respect to their capacity were to be perceived. While efficient catalysts can be started with an output of 1,800-2,000 cu. m. of gas, catalysts of inferior quality permit an output of but 1,500 cu. m.

Ruhrbenzin-plant

Differences of the activity of the catalysts have been observed.

Rauxel-plant

Rauxel objects to the quality of the recently furnished magnesium catalysts which are inferior to the former ones. A further acceptance of pure magnesium catalysts is not contemplated.

Krupp-plant

The Krupp plant does not intend to use magnesium catalysts in the future, because no advantages seem to be obtainable. It was found that by hydrogenation a refreshing effect of the pure magnesium catalysts can be obtained.

Hoesch-plant

It was observed that single batches of catalysts but not complete cargoes showed the above mentioned differences.

Wintershall

The properties of the catalysts varied widely. It was observed that sometimes the containers in which the catalyst was furnished, showed vacuum; the catalyst was even red hot or the so called inert gas which was to protect the catalyst from oxidation contained 10% and more oxygen.

Ruhrchemie, catalyst factory

The catalyst factory is anxious to obtain detailed reports from the single plants about the varying properties of the catalysts because such differences cannot be explained due to an unsatisfactory operation of the catalyst factory. It was mentioned that successful investigation can only be carried out if any objections to the quality of the catalyst are reported in full detail as soon as possible. The improper reduced particles as observed by the Krupp-people are not due to failures during the reducing procedure. The bright particles were investigated whereby a satisfactory activity was observed but their reduction value is lower than that of the dark particles.

With respect to the complaints of Wintershall it must be stated that, in compliance with numerous experiments, such an amount of solid carbon dioxide is added before shipping the catalyst that a proper delivery should be secured. Delayed transportation seems to be the only explanation of the observed deficiencies.

Questions concerning the particle size and the size distribution of the screened material were discussed. It was mentioned that 1-2 mm particles are superior to the 2-3 mm ones. But due to pressure conditions the small particle size can generally not be used.

Schwarzhoide plant

It was mentioned, that using catalysts with a particle size of 1-3 mm almost dust free catalysts can be furnished which are uniform with respect to their activity. More and more mixed catalysts are employed because they can be manufactured more easily. The mixed catalysts have a better solubility, the thorium losses are lower because less dust is formed during the manufacturing process. Nothing is known about the effect of various thorium-magnesium ratios but a mixture of 2.5% thorium will guarantee almost the same quality as shown by a catalyst which contains 5% thorium. An alteration of the composition of the mixed catalysts can be only made by the catalyst factory itself. The question arose how far can be the removal costs be reduced by a preceding paraffin removal.

The following table shows very clearly that with an extended delivery of almost paraffin-free catalysts the extraction costs can be considerably reduced.

1939	Regeneration-costs up to dissolution	
	Based on delivered mass	Based on Cobalt
1st quarter	RM 101/ton	RM 400/ton
2nd quarter	RM 93/ton	RM 390/ton
3rd quarter	RM 58/ton	RM 230/ton

The still remaining costs can be lowered only if uniform tendencies towards moistening can be achieved thus eliminating the preceding steaming before the dissolution procedure. It was proposed to perform further oxidation tests in the reactors themselves because such oxidized catalysts can be more easily regenerated. A reduction of the regeneration costs however cannot be expected by the application of th

proposed method because the reduced output of the plant during the oxidation period must be taken into account.

b) Removal and Hydrogenation Rheinpreussen-plant

The interim regeneration is carried out by means of removal. The favorable effect of that procedure could be observed when caused by an enlargement of the volume of the fed in gas the interim regeneration could not be carried out in the usually applied intervals thus extending the operating period of the catalyst. The total yield decreased from 126 to 118 g/m³ synthesis gas. Catalysts which were operated during this period of time without interim regeneration showed an increased gas production after eight weeks operation. No decrease of the yields could be observed against the interim regeneration by means of hydrogen. Even with higher temperatures employed the CO₂-formation was reduced. During an extraction period 20 m³ heavy gasoline (b.p. 160-190°C.) are sprayed upon the surface of the catalyst bed by means of 20 Schlick-jets which are permanently fixed to the cover of the furnace (furnace temperature 160°C.) The injected gasoline volume is approximately 2 cu. m. per hour. The resulting paraffin wax content of the catalyst is as low as 1%. A couple of recently constructed reactors are equipped with pipes, which can be inserted into the reactor.

Schwarzheide-plant

A fraction boiling from 140-180°C. is employed for the paraffin-wax extraction at reactor temperatures of 140°C. But this interim regeneration procedure is but seldom applied. According to the obtained results no difference could be perceived between extraction or hydrogenation. Resulting from the extraction procedure which is carried out in a cycle but small oil losses occur caused by the oil which remains in the catalyst after the distillation has been finished. The output of the plant is 2-3 m³/hr. Four reactors are simultaneously regenerated during a period of 8-10 hours. While operating without recycling the oil consumption was as high as 1,300-1,400 tons per month, it could be lowered to 200-400 tons per month. The final product of the described procedure is an oil-paraffin wax mixture which contains approx. 80% high melting paraffin waxes. According to the obtained results approx. 1-1.5 tons of paraffin-waxes are extracted from one reactor.

Essener-Steinkohle-plant

Some interim regenerations were performed by means of extraction. An oil-condensate was employed with a small percentage boiling above 300°C. The extraction temperature was 140°C. A short hydrogenation followed the extraction. The combined procedure showed equal results as were obtained by the hydrogenation alone.

Essener Steinkohle, Krupp and Rheinpreussen plants

Apply interim regeneration to the second stage too, but in longer intervals than is employed for the 1st stage.

Essener Steinkohle plant

The described regeneration procedure was of considerable success, although no formation of methane could be observed during the hydrogenation process. Large amounts of paraffin-waxes were extracted from the catalyst bed.

Schwarzheide plant

This plant was not able to confirm the above mentioned observations. No interim regeneration was carried out in the 2nd stage. An interim regeneration of the 2nd stage is necessary and accompanied by success only if the 2nd stage shows a high CO-transformation.

6) Corrosion problems

Corrosion troubles occurred only in such pipes carrying the exhaust gas of the synthesis, where condensation took place.

Ruhrbenzin plant

On the occasion of a shut-down the pipe carrying the exhaust gases leaving the reactor was inspected. No corrosion could be observed even if the pipe is not insulated and condensation is supposed to take place.

Raxol plant

Nothing but the expansion pieces showed any corrosion.

Rheinpreussen plant

The insulated pipes are in good shape.

Krupp plant

Only at such locations where the pipe is not inclined, corrosion has been observed.

Schwarzheide plant

The discharge pipe had to be partly removed which despite a proper insulation and a gas temperature of 155°C. was considerably corroded. As shown by the presented pictures corrosion takes place at such locations only where liquid gas-condensate is to be found. The corrosion is up to 5 mm. deep, but irregularly developed. A length of about 20 meters of the discharge pipe had to be replaced. It is possible that the observed corrosions, which are contrary to the experience gained at the other plants, are due to unsatisfactory properties of the material used in the pipes. In order to prevent further corrosion of the endangered parts of the pipe heating devices have been provided.

The pipes of the cooling water cycle of the condensing system, in spite of the utilization of 99.5% aluminum (treated by the Eloxal-process), were corroded at such locations where it had been subjected to considerable stress during machining. Microscopical inspections showed that flaws were present in the Eloxal-coating outgoing from which a pinhole-corrosion developed. Some tests have been made to coat the pipes with I.C. wax and paraffin wax. So far as can be now observed the coating proved satisfactory.

Ruhrbenzin plant

The pipes which feed the cooling water to the cooling tower are coated with "Heika" just at their outlet. The coating proved satisfactory.

Krupp plant

It was experienced that the "Heika" coating was slowly loosened from the pipes.