

TECHNICAL OIL MISSION; REEL 55,
BAG 2523, DOCUMENT 71

Project: 813

Problem: Reaction of Carbon Monoxide and Hydrogen on Olefins
(Oxo-Reaction).

Investigators: Gemassmer, Berg, Ballaus

Status on August 1, 1943.

Dimerization of Oxo-Aldehydes and Investigation of the High Boiling Residue (Dr. Ballaus).

The investigations of the high boiling residue (taken over by Dr. Gemassmer and Dr. Meusel) have shown up to the present, that it can be transformed only partially into alcohols with the same and with doubled chain length. A material, which was obtained by Dr. Gemassmer by saponification of the ester with NaOH, was sulfonated with chlorosulfonic acid and then it was tried to obtain the pure alcohols by hydrolysis of the alcohol sulfates. This was not successful because the alcohols thus formed were decomposed by the dilute sulfuric acid. When hydrolyzing the high boiling residue with dilute phosphoric acid, a product was obtained which had an increased OH-number, an increased carbonyl number and an increased saponification number. Thus, part of the high boiling residue apparently consists of polymeric aldehyde, acetals and similar products, which can be transformed into alcohols only with difficulty. Next it was tried in a trial run to obtain uniform condensations products with aldehydes of a different origin. It was found that at higher temperatures little aldol and little glycol monoester but much ester with double chain length was formed.

Dr. Meusel found with a condensation experiment, tried in the autoclave, that hydrogenation is already hindered appreciably with 0.2% sodium methylate present. Although methylate tends to promote condensation of aldehydes, appreciable quantities of aldehyde could be found in the reaction products. A C₈-aldehyde, which was obtained in this way, was condensed with solid NaOH at 30-40°C. and gave a 80% yield of the C₂₄-glycol monoester. Before the condensation experiments, however, are continued, it is necessary to accomplish the elimination of the cobalt carbonyls without decomposition of the aldehydes. Experiments about this point are in progress.

signed: Ballaus

Appendix to

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Investigator: Meusel

Status on August 1, 1943

Ester Hydrogenation

a) BBE-Catalyst

It appears to be important when working with the BBE-catalyst, with which the best results were obtained in Ludwigshafen, that no overheating occurs with the catalytic reduction (hydrogenation), which was accomplished by leading a stream of nitrogen over the catalyst at 180°C. while admixing but little hydrogen.

A pelargonic nonyl ester diluted with Mepasin was hydrogenated with this catalyst at 180°C. to alcohol to the extent of 70-75%, while the remainder was recovered unchanged as ester. At 250°C. about 80% is transformed into alcohol, 10% remains unchanged and 10% is decomposed. At still higher temperatures appreciably more is decomposed. When decreasing the temperature again to 180°C., the catalyst has become so inactive that the ester leaves the reactor completely unchanged.

In order to obtain good yields with the BBE-catalyst, it will be necessary to use appreciably longer contact lengths than 40 cm when working at 180-200°C.

b) Sulfur Resistant Ester Hydrogenation Catalysts.

All copper containing catalysts, as e.g. the BBE-catalyst, the catalyst for the after-hydrogenation of methanol, and

copper chromite catalysts, which catalysts are quite suitable for the ester hydrogenation, are strongly sensitive to sulfur. Since, furthermore, zinc and cobalt are fairly resistant to sulfur, it was advisable to replace copper by zinc or cobalt in the catalysts for ester hydrogenation in order to obtain sulfur resistant ester hydrogenation catalysts.

Using a zinc chromite according to Adkins, it was possible to transform at 300°C. 90% of sulfur free ester into alcohols, while the remainder was recovered as ester. When now adding (?)% carbon disulfide, then again only 10% ester remained unchanged, but the alcohol yield decreased to 80%. Thus, it is suspected that a new sulfur containing catalyst (ZnS) has been formed, which has a stronger hydrogenating action on the alcohols. No final conclusions can be drawn as yet, since the experiments are still in progress.

Addition of Sodium Methylate in the Oxo-Treatment of Dimethylhexadiene.

Since it was recognized that sodium methylate hinders hydrogenation, it was thought of adding this while Oxo-treating dimethylhexadiene. This was done expecting that it would hinder the hydrogenation of the one double bond and that only dialdehyde would be formed, or respectively only diol after eliminating the sodium-methylate by extraction and a second hydrogenation. No influence of the sodium methylate could be ascertained, since only 30% diol was formed as up to the present (see monthly report No. 813 of April 1, 1942).

signed: Meusel

TOM Reel 55, Document 71 (Continued)

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1) Product Studies on Laboratory Scale

Oxo-Alcohols from Primary Olefins from the "Ruhrchemie A. G."

The production of pure alcohols from the Oxo-reaction products from primary olefin fractions was carried further and finished by distillation in the laboratory. The alcohols were tested accurately and the physical properties were determined. The results and also the possible use of the so obtained alcohol sulfates will be presented and discussed in a special report. For the production of larger quantities of pure alcohols a start was made with working up the crude alcohols obtained in 458a by distillation in the technical laboratory. The experiments are still going on.

Cracked Gas Oil from Hungarian Petroleum

In connection with previous experiments a cracked gas oil from Hungarian petroleum was studied. The cracked gas oil was out in numerous sharp fractions by distillation, which fractions then were subjected to an extensive analytic investigation. The accurate determination of olefin content caused great difficulties also with this material. On the basis of the iodine number according to Hanus, one must assume an olefin content of about 35%.

About 50% is absorbable in phosphoric-sulfuric acid.

First, the total material was put in the autoclave for an Oxo-treatment. The Oxo-treatment was done at 185°C. and the hydrogenation at 200°C. In spite of a small sulfur content, the hydrogenation went smoothly. The reaction product, however, contained only 18% alcohols according to the OH-number. It seems that also in this case only part of the hydrocarbons, which are olefinic as determined by analysis, can be Oxo-treated. The experiments are being continued with the individual fractions.

Carbonization Gasolines from Brux and Light Oil from Deuben

Experiments were started about the possibility of using the Oxo-treatment as a refining process for carbonization products. The basic idea is to transform the easily gum forming olefins into alcohols and to obtain as a remaining oil a refined high grade gasoline. The aromatics originally present have been concentrated correspondingly.

According to the experiments done thus far, this problem involves appreciable difficulties. The Oxo-treatment occurs to a certain degree. The hydrogenation, however, occurs only incompletely. Thus, an after-hydrogenation over a sulfidic catalyst or over other sulfur resistant catalysts is necessary. The separation of the unchanged gasoline from the alcohols does not seem to succeed by a simple distillation. Nothing can be said as yet about the gasoline, since only small quantities were available until now. Since now larger quantities of raw material are available, the experiments are being pushed further on a larger scale.

Estonian Shale Oil from the Tunnel Furnace

Estonian shale oil from the tunnel furnace was fractionated by Dr. Barkow and the fractions - 100°, 100-200° and 200-300°C. were tested and Oxo-treated by us. Also with these materials, the determination of olefin content causes great difficulties and the estimates obtained by different methods show large discrepancies. While the olefin values are in the range of 30% to 60(?)%, the content that can be absorbed by phosphoric-sulphuric acid is in the neighborhood of 80%. Only a fraction of the olefins is affected by an Oxo-treatment. The fraction that can be Oxo-treated is appreciably lower than with the previously tested shale oil samples. The experiments are being continued.

Centrifuge Experiments with a Technical Centrifuge

In order to form a clear picture of the possibility of separating the catalyst in a technical centrifuge, experiments were carried out in Me 496 with a Krupp-separator. A separator size 7 was used with a drum volume of 25 liters and a sedimentation space of 10 liters. The centrifuge speed was 5000 rpm., which produces a centrifugal force of 3000 (?) times g. It was found that the centrifuge must be operated with a definite streaming velocity in order to keep the sedimentation space uniformly filled. When the streaming velocity is too small, then the lower part of the drum becomes settled too soon and a normal operating of the separator becomes impossible. When using the commonly employed finest catalyst powder one does not attain a complete clarification of the oil. Using the separator, when the process

is functioning normally, one should assume that the separator yields completely cleared oil.

Runs in Me 458a

In the report period 50 tons of diisobutylene were reacted in a continuous run (Expt. 44). Although the available apparatus was not very suitable for this purpose, because of the poor temperature control, a 77% reaction calculated on the basis of total input was obtained. The content of high boiling residue (heavy oil) amounted to 17% of the reacted material. 40% of the residue can be reacted to form monomeric alcohols by a simple hydrogenation (hydrogenation of polymeric aldehydes. The hydrogenation experiments were run in the small furnace in Me 225). This larger scale experiment about the Oxo-treatment of isobutylene made it possible to study difficulties with the apparatus and with the operating technique and to obtain valuable information for the (construction and the operation) of the new plant. The isononyl alcohol so produced was distilled and forwarded to the Organic Department (lubricating oil tests).

Fractionations in Me 458a

In the report period more than 50 m³ diisobutylene, crude and Oxo-treated, were fractionated. It was again found that the dephlegmators of the column are too small and spraying over of the light fractions can be hardly avoided when starting with evacuating. New and larger dephlegmators have been ordered quite some time ago and will be mounted shortly.

Trials to Improve the Sedimentation Stage

Sedimentation (Entschlammung) of the mash while relieving the pressure of 200 atm. to zero pressure was accomplished until now with high pressure valves with a "Widia"-seat and "Widia-gel". Although safety devices were installed, it happened that valves were smashed because of faulty manipulation. As Widia valves are very hard to get, it was tried to alter the sedimentation (clearing) process in such a way that ordinary valves could be used. By inserting a set of three nozzles with 1 mm bore in the sedimentation connection, the sedimentation was retarded so much that with the reducing valve wide open only 250-300 liter mash per hour could be sedimented. It was found that when sedimenting, intermittently an ordinary HD valve could be used and that when operated properly (either wide open or fully closed) no wearing was noticeable after 300 hours of operation. On account of these favorable experiences, a ball valve was ordered, which valve working with a membrane acted with compressed air would allow independent and intermittent sedimentation (clearing). Besides simple orifices with 1 mm bore, Widia-nozzles were found to be quite reliable sedimentation nozzles.

Enlarging the Oxo-Plant Me 458a for Auxiliary Production

Operation of the high pressure stages of the Oxo-plant was suspended on July 18, 1943 and dismantling of the reactors and piping was started in order to make space for the improved plant. This situation offered a good opportunity to inspect the interior of all ducts, tubing and units and to obtain an accurate

picture of the type and extent of corrosion, erosion and crustation. All findings were carefully noted down, samples of crust formation were taken for analysis and especially characteristic phenomena were photographed. The results were collected and discussed in a special report.

Status of the Construction of the Enlarged Oxo-Plant

The low pressure units with mash stage and swivel filters were made ready for operation. A trial run with one filter will be done in the next few days. All old tubing of the high pressure valve chamber was taken down. The flow plan for the high pressure part was decided upon in all details and is represented in the attached figure. Special care was taken to simplify the lay out of piping and ducts in order to be able to survey the flow plan with ease and to reduce the number of valves to a minimum. Instead of the use of ball divers, aluminum floats will be used for measuring liquid levels, as was worked out by DI. Weis for hydrogenations. These level indicators allow accurate measurements, but have only a narrow measuring range of 1 m.

The Oxo-stage is laid out in such a way that both furnaces are operated at almost maximum capacity and mash and gas are cooled in a separate cooler. In this way all clogging difficulties due to crystallized cobalt carbonyl should be eliminated. In addition, due to the combined cooling of mash and gas together, a good scrubbing of the carbonyl from the circulating gases by the mash itself should result. The gas circulating pumps are so arranged that they force gas uniformly into the furnaces, regardless of whether the mash level in the HD (high pressure) part

rises or falls. This makes it possible to carry out desludging (Entschlammung) intermittently without being troubled by a non-uniform flow of gases in the furnaces. With the arrangement of the flow system thought was given to the possibility of operating furnace 1 and furnace 3 alternately, in order to be able to dissolve, if necessary, the cobalt separated in furnace 3 (hydrogenation furnace) as carbonyl. The mash preheater before the hydrogenation furnace will be used only when alternating furnaces 1 and 3, since otherwise a clogging would result because of the decomposition of cobalt carbonyl.

Methyladipol

The production of methyladipol was interrupted during the report period, as both filters were used for the Oxo-treatment of diisobutylene, but will be started again as soon as possible.

(Three attached figures are partly illegible and are not suitable for reproduction.)