

with the excess of chlorosulfonic acid.

3) A Synol-material freed from esters (250-350°) was tested in the laboratory. It was fractionated into sharp cuts. The physical constants were determined in order to find the distribution of the alcohols. A start was made with the sulfonation of various cuts of the alcohol-olefin-paraffin mixture with chlorosulfonic acid. When it has been established which cuts are suitable for the production of effective solvents, these alcohols will be sulfonated on a larger scale in Me 244.

4) A beginning was made to convert the sulfonated material, obtained from hydrocarbon alcohol mixtures, into ammonium salts. It will be tried to separate the hydrocarbons from this material.

5) In view of the experiments in Me 244 the stability of alcohol sulfates in acid solutions was tested. It was established that the alcohol sulfates are quite stable at low temperatures even in acid solution. Hydrolysis begins only above 70°.

B) Preparation of Pure Petroleum Alcohols via Boric Esters

Larger quantities (about 100 kg.) of alcohols were prepared from the dilute alcohol mixture which results on the Oxo-treatment and hydrogenation of cracked Roumanian middle oil in Me 458a. The esterification with boric acid was done in the apparatus of Dr. Reisinger in 225. Then the esters were saponified after distilling off the hydrocarbons. When the total yield of Oxo-material (containing all high boiling material) was used, without distillation, alcohols were obtained which contained considerable quantities (12-15%) of components not convertible by sulfonation. These result from non-sulfonated components of the

heavy oil and cannot be separated from the esters by distillation in the apparatus in Me 225. When using for the esterification Oxo-products, freed from high boiling materials, then the alcohols contained only 3-5% of material not convertible by sulfonation. The alcohols obtained via the boric acids were distilled and will be sulfonated in 244.

C) Experiments in Cooperation with Dr. Asinger

1) Isomerization Experiments

Complementing previous experiments, it was established that also with olefins with centrally located double bonds, that these double bonds tend to migrate toward the end groups at higher temperatures in the presence of cobalt carbonyl. Olefins with centrally located double bonds were prepared from ketones distilled off from fatty acids. These ketones were hydrogenated at 190°C. over a Ruhrchemie catalyst and were converted into secondary alcohols, which then were esterified with fatty acids. By thermal decomposition of the esters, the olefins with centrally located double bonds were prepared. The position of the double bond was proved by ozonization.

In order to establish the conditions of the Oxo-conversion for the preparation of bifunctional compounds, the migration of the double bond was investigated in an undecylenic acid with end double bond by treating over carbonyl at 170°C. Contrary to the expectation, the double bond did not migrate so far that conjugation was reached with the double bond of oxygen in the carboxyl group. Partial migration of the double bond occurred; the extent must still be determined.

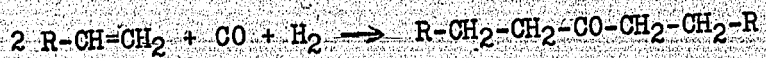
2) Production of Chloroformic Esters of P₃

For the preparation of plasticizers, a few experiments were done in order to obtain the chloroformic esters of P₃. These would have to be reacted further with alcohols and phenols. The reaction with phosgene was done both by admitting P₃ into phosgene and also by leading phosgene into a suspension of P₃ in tetra- or acetic ester. Both ways led to a partial formation of solid substances which were no more soluble in the solvent. The experiments were discontinued.

I) Investigation of the High Boiling Residue of the Oxo-Reaction (Dr. Meusel)

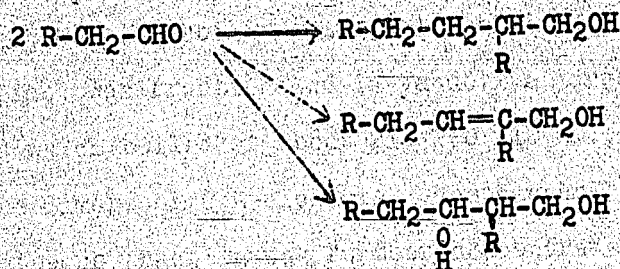
When distilling crude Oxo-alcohols from a sharp olefin cut, there always remained a high boiling residue, which amounted to up to 20% of the total material. It had a considerable OH-number and, thus, contained high molecular alcohols.

The problem arose to investigate if this high boiling residue consists of secondary alcohols. These secondary alcohols could have been formed because two olefin molecules reacted with one CO and one H₂ molecule, thus forming a ketone which subsequently was reduced to a secondary alcohol.



The second possibility is, that an aldol condensation of two monomeric aldehyde molecules occurred. In this case, diol molecules with a primary and a secondary OH-group would have been formed; the secondary OH, however, should split off easily, as was already found by v. Braun (B. 67, 1696), who on hydrogenating aldehydes obtained following compounds as byprod-

ucts:



To get an analytic estimate of primary and secondary OH-groups, a method had to be worked out for the determination of higher primary alcohols in presence of secondary alcohols.

Stephan (J. prakt. Chem. (2) 60, 248) found, that at lower temperatures, at which primary alcohols still form esters with phthalic anhydride, secondary alcohols do no more react. A method based on this observation was tried out with various primary and secondary alcohols. (Procedure may be obtained from me).

Analysis:

Substance	Calculated		Found	
	OH-number primary	OH-number secondary + primary	OH-number with phthalic anhydride	OH-number with acetic anhydride
Propyl-lauryl-carbinol	0	231	6	219
C ₁₃ -Oxo-alcohols technical	280	0	259	263
Diisopropyl-carbinol technical	0	483	0	428
Mixture of C ₁₃ -Oxo-alcohols + diisopropyl-carbinol	186*	310*	194	304

* Calculated from the OH-numbers found for the components.

The high boiling material, obtained on Oxo-treating C₈-C₁₀ olefins, was fractionated in vacuo. A larger fraction was obtained which boiled at about 210-250°/10 mm., corresponding to about the dimers of C₁₀-alcohols. The alcohol content of this rather viscous fraction was further concentrated via the boric esters. Then an analysis was made. The results obtained were:

OH-number estimated with acetic anhydride : 310 (prim. + sec. OH)

OH-number estimated with phthalic anhydride: 185 (primary OH)

OH-number (acetic minus phthalic) : 125 (secondary OH)

The theoretical OH-number for a C₁₉-alcohol is 197; for a C₂₀-diol it is: 356.

The results, thus, showed that a diol was formed with one primary and one secondary group. This excludes the possibility that at least part of the high boiling residue was formed by way of an aldol condensation. One should note, though, that of the high boiling residue only the fraction 210-250°/10 mm., and of this fraction only what could be combined with boric acid, was investigated; this amounted to roughly only 8% of the total residue.

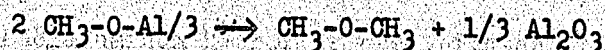
II. Preparation of Higher Ether

Other ethers were further prepared by heating alcohols together with aluminum alcoholates in autoclaves during 12 hours at 320°. The following were prepared:

diiso-hexyl ether (yield 57%)
diiso-tridecyl ether (yield 20%)
diphenyl ether (yield 50%)

Tischtschenko found that dimethyl ether can be obtained

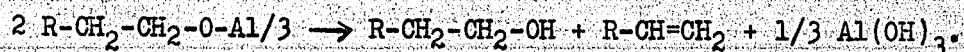
by thermal decomposition of aluminum ethylate (methylate ?) with a yield of 97%.



Since with the higher ethers the yield of 50% is not or but little exceeded, and since one might believe that here also the alcoholate molecules react only with each other, and that the following reaction might not occur:



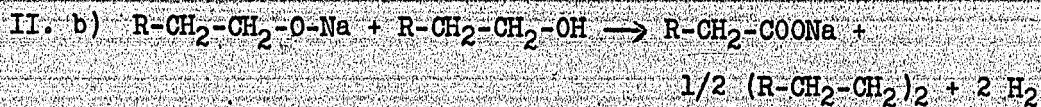
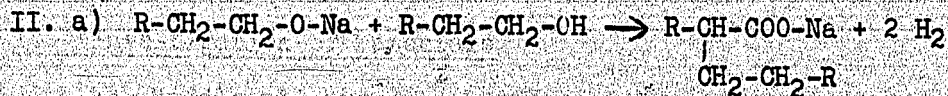
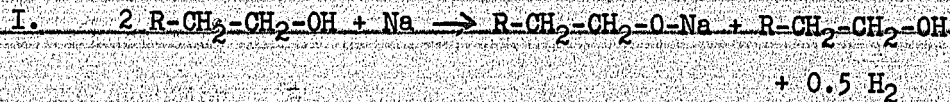
pr (? - illegible)-aluminum alcoholate was heated by itself. No ether was formed, but only alcohol and olefin, probably according to the following equation:



The exact situation will be investigated further.

A further experiment was done, in which instead of aluminum 1 mole Na was reacted with 2 mole C₉-alcohol. The alcoholate was formed first, then on further heating, however, C₉-acid was mainly formed, and also an acid and a hydrocarbon with probably the double number of carbon atoms and in toto 2.5 mole hydrogen.

One might assume that these compounds could be formed according to the following equations:



It was further tried to react a OH group of glycerine with aluminum alcoholates, which however did not succeed. The compounds formed at ordinary temperature are rather polyglycerines (?) and aluminum hydroxide precipitates. The glycerine was made anhydrous by distilling two times before the experiment.

III. Rose Essence from Dimethyl Hexadiene ("Rose-alcohol")

"Rose-alcohol" was purified still another time via the boric ester, and then was carefully fractionated. The OH-number was determined. The molecular weight was determined by means of the acetate. These constants were compared with the theoretical constants and the literature data for n-C₉-alcohol and n-C₁₀-alcohol:

<u>Substance</u>	<u>Boiling Point</u>	<u>OH-number</u>	<u>Mol. wt.</u>
"Rose-alcohol"	220-223	368	152
n-C ₉ -alcohol	213	390	144
n-C ₁₀ -alcohol	230	355	158

Although the OH-number is indicative of an impure C₉-alcohol, the more reliable boiling point determination indicates the presence of a C₁₀-alcohol. This alcohol must have been formed in this way that first a C₁₀-diol was formed and then a selective hydrogenation took place. It must be noted that purified C₁₀-diol is not hydrogenated to a monol under the same conditions.

Information was asked from Wolfen as to the highest price paid for rose-alcohol in time of peace. Since the price level must stay under RM 2.--, production in peace time is out of the question.

IV. Investigation of Materials

a.) Middle oil from the hydrogenation plant was subjected

to an Oxo-treatment in order to obtain alcohols. It contains about 30% phenols, which were first eliminated. The phenol free product contained 28% olefins according to the iodine number, but only 14% of the material could be converted by an Oxo-treatment.

b) Oxo-treatment of Dimethallyl Sulfide and Dimethallyl Ether

Dimethallyl sulfide and dimethallyl ether, prepared by Dr. Striegler, was investigated and subjected to an Oxo-treatment. It was expected that a higher yield of diol would be formed, since the sulfur atom or the oxygen atom prevents the double bond to migrate and to form a conjugated system. Both substances, however, react, when dissolved in cyclohexane and under the usual Oxo-conditions, in an understandable way.

The boiling point of the reaction products increased gradually from 100 up to 400° and each fraction had only a very small OH-number.

V. Production of Olefins

When Mepasin is heated with sulfur to about 200°, then H₂S is formed. After heating 1 kg. Mepasin (260-280°) with 30 g. sulfur during 50 hours, about 70% of the sulfur were transformed into H₂S. The oil was distilled, but gave no iodine number.

One time 100 g. Mepasin were heated with 3 g. sulfur for only one hour. At that time an iodine number of 16 was found. Thus, it seems that the time of heating must be shortened. The experiment will be repeated in such a way that the material is slowly led through a furnace and thus it will remain in the hot zone for only a short period.

VI. Hydrogenation of Esters

In view of the experiences obtained with the hydrogenation of the esters in Synol-products, at first some trial runs were done with C₁₄-ester dissolved in Mepasin in order to find out more about the behavior of catalysts.

Quite a number of catalysts were tested. Initially, they catalyzed the hydrogenation of 80-95% of the esters to alcohols at temperatures between 200 and 300°, but with most the activity markedly decreased after a short time. For instance, the BBE catalyst behaved in this way. With the catalyst No. 1930, used for the after hydrogenation of methanol, a yield of about 92% could be obtained during a longer period at 250° and with normal feed velocity. The run was discontinued after 8 days, but the catalyst was not spent at that time.

VII. The Clarifying of Synol Residues

Synol residues, which had been bleached with Tonsil and freed from iron by Dr. Reisinger, were cautiously hydrogenated in an autoclave with a Ba-Cu-Cr catalyst; quite clear products were obtained. The determination of the alcohol content still presents difficulties. Dr. Eckart had said himself to be willing to work out a reliable procedure.

Plasticizers (Dr. Ballaus)

Chlorocarbonic Esters (I)

When trying to prepare chlorocarbonic esters from higher alcohols, widely varying yields of I were obtained besides larger quantities of dialkyl carbonates. The reaction velocity was too small at lower temperatures. The addition of pyridine

or carbonates and dehydrating agents, according to DRP 251,805, did not yield the desired result. When using activated charcoal, the preparation with C_7 - C_8 -alcohols succeeded by increasing the reaction speed at lower temperatures. It is planned to protect the method after extending the experiments to higher alcohols. Chlorocarbonic esters from C_7 - C_9 -alcohols were forwarded to Dr. Falkenberg for the preparation of plasticizers.

Dicarboxyl-Esters and -Half Esters

The preparation of oxalic half ester chlorides with higher alkyl rest did not succeed because of the instability of these compounds. The following compounds were prepared: oxalic-decyl-phenyl-ester, decyl-ethyl-ester (as intermediate product); they were forwarded to Dr. Falkenberg together with oxalic-di-octyl-ester and also the chloride from adipic-mono-butyl-ester (iso). The mixture of light soluble dicarboxyl acids from the adipic acid plant was tested and mainly malonic acid, succinic acid and glutaric acid and adipic acid were detected up to the present.

Furthermore, precooler oil was reacted with C_{10} -chloroformic ester, corresponding to an OH-number of 40-50, and the product was forwarded to Dr. Falkenberg for testing as plasticizer.

~~Experiments on the Addition of Cyanic Acid to olefins were~~ started, but only traces of nitriles were obtained up to the present; the major part of the cyanic acid polymerized. It is planned to avoid the polymerization by using acid catalysts.

Oxo-Range

Gasoline from the Michael-Synthesis (100-200°) was tested. Boiling starts at 70°, and about 50% distills over below 120°. The material boiling in this range contains about 75% of the alcohols and the carbonyl compounds; the olefins are uniformly distributed over the boiling range. The product contains about 40% C₈ olefins. Approximately 90% of the olefins are Oxo-convertible.

Middle Oil from the Michael-Synthesis, 200-300°

About 55% distill over below 290°, and 90% roughly of the alcohols are in this fraction. The ester numbers increase with increasing boiling point and the iodine numbers decrease gradually. The product contains about 25% C₁₃ olefins, and of these 90% are Oxo-convertible. During the hydrogenation under the usual conditions, the ester number increased to 40 regardless of the high hydrogenation temperature of 9.5 mV. Thus, it was tried to hydrogenate the esters to alcohols catalytically. A Ba-Cu-Cr catalyst gave yields of 90%, but had a short life. Dr. Meusel obtained similar yields with more stable catalysts and will continue the experiments of hydrogenating esters.

The Texas Company

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Assignment: 813

Subject: The Effect Of Carbon Monoxide And Hydrogen On The Olefins (Oxo - Reaction)

In Charge: Gemassmer, Berg, Meusel

Situation As Of April 1, 1942

I. Study Of The Process

a.) Work With Fixed Catalyst

To save copper, alloy catalysts of iron/cobalt basis were tried out and their general suitability was established.

Experiments with gaseous olefins in the small reactor were continued but no new discoveries of importance were made.

Distillation

The crude product distillation plant was put at the disposal of Dr. Welz for the distillation of benzines during the period covered by this report.

As far as alcohols are concerned, the conversion products of the cracked olefin component C_{11}/C_{12} were distilled for the first time; separation was successful also with these components.

Study Of The Products

During the period covered by this report approximately 5 m³ of neutral component resulting from the preparation of carboxylic acid in the plant Me 458 were processed. The processed neutral component is to be amalgamated in the carboxylic acid plant.

Elimination Of CO From The H₂ Circulation System By Methanization

A new methanization reactor, built from N₈ materials, was installed. The reactor is provided with a preheater*. As catalyst, cobalt catalyst was used again for the time being. This catalyst was no longer very active and started operating only after the CO concentration had reached several per cent. The temperature within the reactor reached about 900°C. and the thermo-sleeve** was crushed. After this distressing experience, the reactor was filled with iron catalyst WK 17. It was found that this iron-catalyst effects complete methanization of the CO at no more than 200 to 250°. The catalyst also proved to be very stable during temporary periods of overheating.

During methanization, water is formed. This water has a considerable inhibiting effect upon the filtration when it comes into contact with the filter together with the mash; it must therefore be separated and removed. This removal of water from the gas in the H₂ circulation system was accomplished by installing a cut-off next to the condenser.

In order to prevent the undetected accumulation of a higher CO-level in the hydrogenation-H₂, the plant management

*Spitzenverheizer

**Thermohülse

installed a CO-recorder* for small amounts of CO (0-3%). This device operates on the reaction heat principle (methanization) and has given very satisfactory results. Despite prolonged periods of operation and high through put of CO, it was always possible to operate the methanization reactor within the desired temperature limits. At through puts of 2-3 m³ CO/hours, the CO was converted entirely into methane and in the issuing gas of the methanization reactor no more than .01-.06% CO could be measured. At higher through puts of CO, such as occur at injection rates of 180 liters and low molecular weights of the olefins, the reactor no longer converts the entire CO; the CO residue amounts to .1-.5%. Even this small quantity of CO is sufficient to greatly hinder the hydrogenation.

Gas Solubility And Gas Pressure Release

Since in the product-gas measurements discrepancies always occurred, measurements for the determination of the solubility of H₂, CO, N₂ and CH₄ under high pressure and at different temperatures were taken. It was found that the solubility per mole of hydrocarbon is constant; therefore one can calculate the gas solubility equilibria if the relation between gas-solubility and temperature is known. Recalculation of the oxo-circuit and the hydrogenation circuit showed that gas pressure release would not be necessary in either of the circuits. The degree of concentration of inert gases in the circulation system was calculated and in subsequent continuous experiments

* CO Schreiber

these results were proved correct by Pellux density-balances and by gas analyses. The concentration of CO dissolved in the gas release product of the oxo-reactor was calculated, and it was found to be equivalent to the methanization water separated in the H₂ circulation system.

Removal Of Sulfur From The Gas

In order to secure the system against a possible break-through of sulfur, a heated tower with Pattenhausen granular-coke was installed in the gas inlet main of the O-water gas. The purification was at first satisfactory until one day a slow increase in the sulfur values occurred, reaching a maximum of about 40 mg H₂S and 25 mg organic sulfur per m³ of gas, whereas before the refining tower only 1-2 mg sulfur were present. The explanation of this occurrence lies in the high CO₂ content, ab. 5%, of the water gas. Below 210 atm., this corresponds to a CO₂ partial pressure of about 10 atm. and thereby a portion of the sulfides in the coke are decomposed and H₂S is liberated; this H₂S in part reacts further with the CO in the presence of the Grude and COS is formed. Purification tests showed that granular coke washed with acid prevents this reaction without the coke losing its de-sulfurizing effect. The refining tower was therefore filled with granulated coke washed in H₂SO₄.

Formation Of Iron Carbonyl From The Iron Parts Of The Apparatus

It was found that the water gas in the circulation system had an Fe content of 200-300 mg Fe per m³ in the form of iron carbonyl. In order to prevent addition of iron carbonyl

from the watergas (supply) system, an active charcoal tower was inserted. Behind the A-coal tower, the gas is free of iron carbonyl. Nevertheless, the iron carbonyl content of the gas continues to vary within the same limits as before. In other words, this shows that despite the oil layer which may be supposed to be present in all the tubes, iron carbonyl formation continues to take place. The mash issuing from the oxo-stage contains, besides cobalt carbonyl, also iron carbonyl; the latter is reduced in the hydrogenation stage and precipitates into the catalyst. Examination of the catalyst revealed that the iron content of the catalyst had risen after several days of operation from hardly 1% to 3%. Precautions and measures against the formation of iron carbonyl are now being studied and experiments are in progress.

Life Of The Catalyst

The life of the catalyst is still as unsatisfactory as ever. Especially the hydrogenation effect drops rapidly. The factors causing this failure of the catalyst may be listed as follows at this stage of our experiments:

- 1.) Insufficient purity of the gas (S-content).
- 2.) Precipitation of the iron formed by reduction of the iron carbonyl onto the catalyst.
- 3.) Appreciable cobalt carbonyl losses resulting from the simultaneous release of the cobalt carbonyl with the water gas.
- 4.) Insufficient purity of the product (S-content).

Factors 1) and 4) should not be of much importance with the product used so far, whereas 3) seems to be the most important factor next to 2) with which one has to deal. It was found that

upon release of hot mash from the oxo reactor the released gas may contain 5-20 g. of cobalt/m³. By cooling of the mash this value decreases down to about 1 g/m³. Catalyst studies showed that the cobalt content of about 33% in the fresh catalyst had dropped to about 20-25% in the used catalyst which was no longer active enough. In order to eliminate these losses, it is planned to lead all release-gases containing cobalt carbonyl through a washing column in which the gas is to be washed with fresh olefins.

Further Processing Of The Oxo-Products (Dr. Berg)

1. Dehydrogenating Alkali Amalgam

a.) In Me 333 an installation capable of handling the amalgamation of larger amounts (20 kg) was started. It was found that a portion of the alcohols were converted into olefin. This side reaction, which is due to over-heating, is to be eliminated by rebuilding the heating arrangement which so far had consisted of electric heating elements. The heating is now to be accomplished by means of diphenyl vapor. Further difficulties were encountered when it was discovered that it would be impossible to empty the amalgam container into another container which is furnished with uneven blades* and which stands in a vacuum. The latter container was to be used for the vacuum distillation of the last residues of the neutral oil. The elimination of neutral oil is to be facilitated by covering the uneven blades* with thin films of melted soap. By improved heating of the circuit leading from the amalgamation vessel to the container provided with the uneven blades*, these difficulties are to be removed.

*Schikanenblech

b.) Amalgamation Of The Synol Alcohols

In order to study the properties of the soaps obtained from the synol-fatty acids, experiments were begun in which the alcohols are subjected to the alkali amalgamation process according to their C number. Results obtained in these tests should show from what C-number on, the synol fatty acids give odorless soaps.

2.) Conversion Of Oxo-Aldehydes Into Alcohols By Hydrogenation

In regard to the hydrogenation difficulties encountered in Me 458a it was attempted to rehydrogenate incompletely hydrogenated aldehydes obtained from there with Ni-catalyst (134). The experiments were performed in the small reactor with one- and two-fold charge rate, at different temperatures and at different hydrogen pressures. The aldehyde still present was thus converted under all the experimental conditions chosen, into alcohol. At 120°C., the OH-numbers were somewhat lower. This may possibly be due - since the carbonyl number was = 0, to non-hydrogenation of aldehyde polymers.

3.) Preparation Of Alpha Methyl Branched Acid

As has already been mentioned in the previous report, the fatty acids obtained from the oxo-alcohols are partly methyl branched. One has to deal here with a branch at the α -carbon atom. Now, in order to afford a comparison with the oxo-fatty acids, an α -methyl branched C₁₂ fatty acid was prepared. This preparation was made as follows: from the malonic acid diethyl-ester, over the methyl malonic diethyl ester and methyl-nonyl-

malonic acid diethyl-ester, methyl-nonyl malonic acid was obtained; by splitting of CO₂, the α -methyl branched C₁₂ fatty acid was obtained. This fatty acid and the soap prepared from it were of unpleasant odor; the melting point of the acid was 18.2°C.

4. Clarification Of The Constitution Of The Oxo- And Synol-Alcohols (With Dr. Asinger)

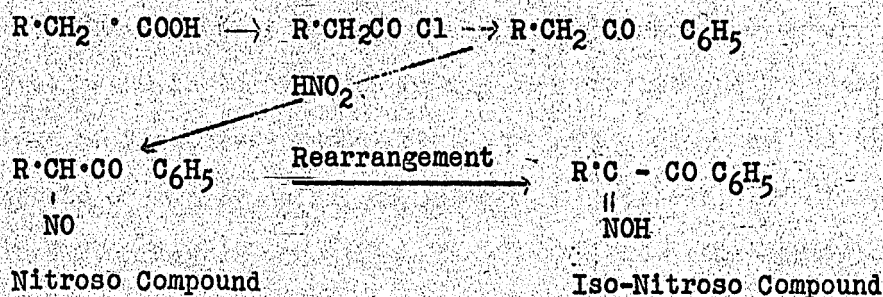
a.) Migration Of The Double Bonds In Olefins With Terminal Double Bond

The experiments, which were performed in the autoclave showed that in a dodecylene with terminal double bond, in the presence of Ruhrchemie catalyst at 200 atm. nitrogen and one-hour operating period at 200° no shift of the double bond occurred. However, at 300° such a double bond shift actually took place. If, on the other hand, 100 atm CO pressure was used instead of the nitrogen, an appreciable double bond shift occurred already at 150°C. The possibility is thus established that during the oxo-reaction a double bond migration may take place with consequent formation of α -alkyl-branched aldehydes.

b.) Clarification Of The Constitution Of Synol Alcohol

From a C₁₃ synol alcohol the olefin was prepared through the fatty acid ester. Analysis of the olefin revealed that the alcohol was to a great extent of the straight-chain type. This is in harmony with the higher melting points of the fatty acids obtained from the synol-alcohols.

c.) Experiments were continued for arriving at the degree of branching of the oxo-fatty acids by the following steps.



With an α -alkyl branched acid the rearrangement of the nitroso-compound could not take place. The straight-chain acid content is to be determined by measuring the amount of hydrogen of the OH-group in the iso-nitroso-compound.

5.) Preparation Of Fatty Acid According To Patent A. pl. H 1/9 371 IVd

The attempts for the preparation of acids from alcohols and water in the presence of a simultaneously dehydrogenating and hydrating catalytic agent are being continued; higher molecular alcohols (C₁₃ oxo-alcohol) are now being used. The experiments were carried out at ordinary pressure in small reactors at different temperatures. So far, it has not been possible to prepare fatty acids by this method. Generally, the reaction only went as far as the aldehyde formation. At higher temperatures, dehydration of the alcohol took place.

The Application Of The Oxo-Reaction To The Diolefins (Summarizing Report) (Dr. Meusel)

During the first experiments with the oxo-reaction, no solvent was used and strong resin formation due to polymerization of the dimethyl-hexadiene took place. Afterwards, in all the experiments which followed, operations were performed with solutions, the most generally used solvent being cyclohexane.

For instance, 20 parts of dimethyl-hexadiene were dissolved in 80 parts of cyclo-hexane and approximately 5 parts by volume of Fischer-synthesis catalyst were added; the catalyst is composed of 60% by weight Kieselguhr, 35% cobalt, 2.5% thorium oxide and 2.5% magnesium oxide. At 130°, 300-400 atm water gas were applied for one hour; then the water gas was released and pure hydrogen was applied under pressure and the hydrogenation was carried out with the same catalyst at 190°. After filtration, the solvent was evaporated and the oxo-product was fractionally distilled in a vacuum. Thereby two main fractions were obtained at 5 mm Hg at 70-75°C. and at 148-153°C., respectively (corresponding to about 210° and to 310° at ordinary atmospheric pressure). These fractions accounted for 54% and for 36% of the theoretical value, respectively. The remaining 10% consisted mainly of a high boiling residue. The two main fractions were purified by the boric acid ester method. According to the OH-number, the higher boiling fraction was a pure decane-diol, whereas the lower boiling fraction is a nonyl-alcohol.

The oxo-reaction therefore occurred only in a small part of the diene at both double bonds, while in a greater portion water gas combined only on one side, the other double bond being simply hydrogenated. The nonyl alcohol thus formed is entirely saturated and has an agreeable odor similar to that of citronellal, a substance to which it is structurally very near. The decane-diol is a colorless, odorless, thick liquid whose boric acid ester is stable even at 200°.

The problem is now to prevent the formation of the C₉ monol, or rather to repress it as much as possible. For this purpose, the carbon monoxide content of the water gas was increased to 90% in order to repress the hydrogenation. For the same reason, the oxo-reaction was carried out at the lowest possible temperature. However, the diol yield was not improved by these measures. Furthermore, other catalysts, similar to the Fischer catalyst were used for the oxo-reaction, and which experience had shown to be non-hydrogenating. Subsequently, the aldehyde groups formed were hydrogenated to alcohols with a different catalyst. Even this did not increase the yield beyond 35% of the theoretical. A further attempt to prevent the hydrogenation by using paraformaldehyde instead of watergas failed: no reaction occurred.

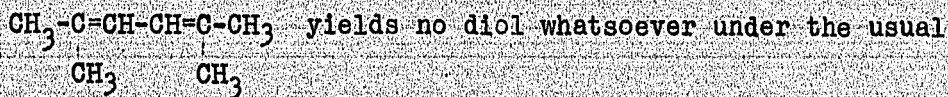
In order to avoid the splitting away of water gas once it had combined, it was attempted to fix the aldehyde at the instant of its formation by converting it into acetal; methanol was used as solvent, but no increase in the diol-yield was thereby achieved. Unsuccessful experiments also were performed, with the purpose of modifying the oxo-reaction by using, instead of water gas, carbon monoxide and water or carbon monoxide and alcohol on the diene, in the hope of obtaining a good yield of dimethyl-suberic acid or of its ester respectively.

It is remarkable that the dimethyl-hexadiene is hydrogenated already at very low temperatures with the Fischer catalyst. Once, when dimethyl hexadiene was heated with Ruhrchemie catalyst

and hydrogen in the autoclave, gas absorption began already at 85° but the rate of absorption was considerably slower than the rate of the oxo-reaction. This observation led to the assumption that hydrogenation and oxo-reaction are two simultaneous competing reactions, the first of which takes place at lower temperatures but proceeds more slowly than the oxo-reaction.

Therefore, dimethyl hexadiene was now heated, without gas and in the presence of the catalyst, to 130°; and only then water gas was added under pressure to avoid the heating up period during which supposedly the hydrogenation already begins without the oxo-reaction being activated as yet. For the same reason, the product in trickle phase* was once led over a fixed catalyst in the high pressure reactor under continuous operating conditions. However, neither with the first nor with the second method a better diol yield was achieved. Since a simple olefin may also be hydrogenated with hydrogen alone at temperatures below the oxo-temperature (with Fischer catalyst) and since nevertheless with water gas and subsequent reduction an almost 100% alcohol yield is obtained, this theory (of the two competing reactions) had to be dropped. Rather, it must be assumed that, by the presence of carbon monoxide, the hydrogenation is normally repressed.

The surprising observation was now made that 1,1,4,4-tetramethyl-butadiene (=2,5-dimethyl-hexadiene-2,4)



* Rieselphase

conditions, but that an almost theoretical yield of C₉ monol was obtained instead. An explanation for this outstanding fact may be the following: it is to be assumed that conjugated double bonds are very easily hydrogenated even in the presence of carbon monoxide at the terminal positions of the conjugated system, so that only the newly formed intermediate double bond is able to give an oxo-type reaction. It is furthermore very probable that this double bond will shift to a certain extent, so that no definite alcohol is formed. In order to verify this assumption tetramethyl-butadiene in cyclo-hexane solution was heated with Fischer-catalyst and water gas to 100°C., that is to a temperature at which no oxo-reaction takes place yet. A mol of hydrogen was actually absorbed, while the resulting mono-olefin, as has already been pointed out above, is not further hydrogenated due to the presence of carbon monoxide. The hydrogenation to mono-olefin occurs only within a very small temperature range because at only slightly higher temperatures the oxo-reaction sets in.

Maybe the reason why the oxo-reaction of dimethyl-hexadiene yields only 40% of the expected diol is that a certain amount of conjugated systems is present or that they are formed before the oxo-reaction sets in. Therefore, the initial diene was analyzed as to its possible content of conjugated systems.

The Diels-Alder Diene synthesis could not be used here because tetramethyl butadiene does not react with maleic acid anhydride, probably due to steric hindrance. The molecular refraction method was therefore used in the analysis since the degree of oxidation

is definitely higher in a conjugated system than in a compound containing two isolated double bonds. The measured values for dimethyl-hexadiene and tetramethyl-butadiene were definitely different and coincided exactly with the values calculated from the atomic refractions, increments and excitation values; therefore one can assume that the initial diolefin does not contain conjugated double bonds. The above conclusions may easily be checked by the physical characteristics of the two compounds: tetramethyl-butadiene boils at 134°, while dimethyl hexadiene distills over already at 113°; tetramethyl-butadiene solidifies at +16°, dimethyl-hexadiene is still liquid at -80°. For reasons which are not yet quite clear, tetramethyl-butadiene gives a bromine number (by the Klein method) which is only about one half of that of dimethyl-hexadiene.

Even dimethyl-hexadiene which had been heated for two hours with Fischer-catalyst without watergas at 130° was found to be free of conjugated systems when analyzed by the above methods. However, when the compound was heated to 220°, large scale isomerization actually occurred with formation of tetramethyl-butadiene. If one therefore assumes that at the instant of the oxo-reaction the temperature may "in jumps" attain considerable higher values than the 130° indicated by the thermometer, an explanation for the low diol yield is found. But if it were so, addition of a very large amount of solvent to the oxo-reaction should have given better results; this was not the case.

Heating of dimethyl-hexadiene to 220° without catalyst causes only limited isomerization; it was now to be determined

which catalyst component effects an easy isomerization. Since sillicic acid catalyzes such isomerizations, the Kieselguhr carrier was replaced by aluminum oxide, beryllium oxide and ethers, but the same 35% diol yield was obtained.

If, at 130°, no re-arrangement occurs without watergas and if, during the oxo-reaction, such re-arrangement does occur, there is still the possibility that the small amounts of carbonyl formed during the oxo-reaction make the re-arrangement feasible at low temperatures. Therefore, dimethyl-hexadiene was to be heated to 130° with Fischer catalyst and carbon monoxide alone. These studies are not completed and are being continued.

Resume

The conversion of dimethyl-hexadiene into dimethyl-octane-diol by means of the oxo-reaction gives only a 35% yield. Modification of the reaction conditions on the basis of many experimental hypotheses have thus far been unsuccessful.

Signed:

/GEMASSMER/ /BERG/ /MEUSEL/

The Texas Company

TOM REEL 55, BAG 2523, DOCUMENT 80

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Assignment: 813

Subject: The Effect Of Carbon Monoxide And Hydrogen On Olefins (Oxo - Reaction)

In Charge: Gemassmer, Berg, Meusel

Situation As Of December 1, 1941

1. Study Of The Processing Method

a. Work With Fixed Catalysts In A Flow System*

It was found that the porous copper cobalt sintered catalysts are very stable mechanically and that their life is very long. Such catalysts were run for four weeks in the small reactor and no appreciable activity drop was observed. However, the yields obtained with these catalytic agents rarely exceed 60% and no increase has so far been achieved by varying the injection and the temperature. The through put could be raised as high as 1:1 without noticeable effect on the yield. Experiments for the purpose of increasing the yield by a substantial increase of the catalyst layer length are now being prepared.

b. Study Of The Product

In order to extend the olefin basis for the semi plant scale oxo-installation at the Leuna Works, the first runnings (oil

*Festangeordneter Kontakt im strömenden System

of the isobutyl-oil distillation, which contain olefins, were examined. The study of these first runnings is still underway.

Work In The Semi Plant Scale Installation Me 458a

1. High Pressure

a. Continuous Operation Of The Oxo Reaction

A reactor was built to the specifications of a continuous operating process. The mash is injected into the reactor from above. A certain level is maintained in the reactor and the converted mash is removed from below and led into the hydrogenation chamber. The water gas is led through the mash in a counter stream through the reactor. This procedure has been found to be technically sound after the initial difficulties had been ironed out. However, despite an average contact time of 2 hours, the yield amounted to only 75%. In order to achieve a more uniform contact time to raise the yield it is planned to divide the reactor into several reaction zones located one behind the other. Removal of the reaction heat when operating under continuous conditions presents no difficulties with an 80% C₁₁ olefin. Lower boiling olefins have so far not been used. In the recycle gas system a certain level of cobalt carbonyl appeared; this caused trouble upon cooling, by obstructing the gas conduits.

b. Increase Of The Cooling Surface In The Discontinuous Oxo-Reactor

A cooling tube system was installed in the high pressure reactor. It was thus attempted to prevent the spontaneous heat of reaction and the consequent increase in temperature which occurs in a discontinuous operating process. The cooling surface

was increased by 70%, namely from 210 cm² per liter of reactor content to 356 cm² per liter of reactor content. Yet, not even this increase led to the desired success and the temperature continued to increase, after the start of the reaction, by 50-60°C. within a few minutes. Here, the cooling system was connected with the heating jacket; heat was to be obtained by evaporation of the water in the tubes. After this, the connections were changed and the cooling system was attached to the cooling water circuit. After the reaction had started, cold water was led through the cooling tubes and a sharp temperature increase was thus prevented. It may be recommended, when a discontinuous operating process is used, that the heating surface (for the starting of the reaction) and the cooling surface be entirely separate systems, so that cooling may take place at high temperature difference.

Hydrogenation

In order to achieve current removal of the hydrogenation inhibiting CO in the H₂ cycle, a reactor with fixed Fischer catalyst was installed in the hydrogen circulation system. The reactor is to convert, at temperatures ranging from 190 to 250°C., the hydrogen and the carbon monoxide into methane. This reactor has already given good results and the hydrogenation was successful during a long experimental period. The temperature in the methanization reactor was between 220 and 260°. When this reactor was "switched off", the hydrogenation failed entirely, only to resume again upon "switching on". Nothing can be reported as yet

on the life of the cobalt catalysts used in this methanization reactor. It is, furthermore, questionable whether the removal of the carbon monoxide present in the hydrogen cycle will constitute a definite solution of the hydrogenation problem; especially in view of frequent observations which have shown that despite complete cutting off* of the hydrogenation reactor and of the gas cycle, the hydrogenation still turned out to be unsuccessful.

Filtration

It has been observed that when the filtration is completed, the filtrate immediately becomes turbid when nitrogen comes through. It was assumed that this nitrogen passing through the filter carries with it catalyst particles and deposits them deep into the filter candle mass, thus causing obstruction of the filter. In order to prevent the filtering through of N_2 a trap was placed in the filtrate solution, which closes as soon as the first nitrogen comes through, thus automatically terminating the filtration. Furthermore, the nitrogen pressure on the filter was put on very slowly in order to give the catalyst enough time to form a filtration layer.

With these two precautions a considerable increase in filtration efficiency was achieved. After 50 filtration batches, no appreciable increase in filtration time has yet been noticed, and the filtrate is clear and free of catalyst throughout the whole filtration process.

*Entspannen

It was further noticed that the filtration takes longer with new candles than with used ones; and that a filter which has been in disuse for a prolonged period of time gives considerably poorer results than it did just before being used for the last time. The explanation of these phenomena may be sought in the highly hygroscopic properties of the ceramic filter mass. It is therefore advisable that the filters be kept under oil when not being used. As yet it is impossible to tell whether due consideration of these facts and proper precautionary measures against their occurrence will constitute a final solution of the filtration problem; or whether they simply delay the eventual obstruction of the filtration zone.

Further Processing Of The Oxo Products

a. Dehydrogenating Amalgam

1. Alkali Amalgam Of The Heavy Oil

From the high boiling residue which is obtained after the distillation of a C₁₃ oxo-alcohol in Me 458a, a fatty acid mixture was prepared after amalgamation with alkali (See previous report). After conversion into methyl esters, the amalgam was split into 20° fractions. Two main components were obtained; the first contained the fatty acids which had formed from the C₁₃ alcohol still left in the residue, and other fatty acids formed by the splitting of the molecules of the high molecular secondary alcohols during the alkali amalgamation (for the behaviour of alcohols during amalgamation with alkali, see previous report); the second component contained high molecular fatty acids formed

from the high molecular primary alcohols (which in turn were produced by adolization and hydrogenation) by the action of the dehydrogenating amalgam.

2. Alkali Amalgam Of Dehydrated And Oxo-Converted "Neutral Component Resulting From Carboxylic Acid Preparation"

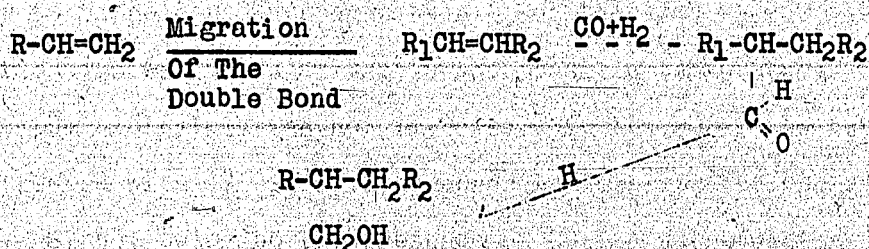
The phenol and phenol homologue content (mentioned in the previous report) of the fatty acids obtained by alkali amalgamation is due to the presence of phenol and of its homologues in the starting product (as high as 3%). No further study on this subject has been made.

3. Alkali Amalgam Of Diols

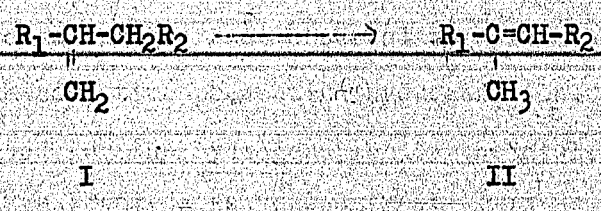
In view of the fact that diols may be prepared by the oxo reaction from olefins it was attempted to prepare dicarboxylic acid from adipol and methyl adipol through alkali amalgamation. This amalgamation could not be carried out in a stirring apparatus at ordinary pressure because the formation of a hard mass (alcoholate) even at high temperature, prevented proper stirring. The process was therefore carried out in a rotating autoclave and in order to achieve thorough mixing, hydrocarbons were added. For working up the product, the sodium salt of the dicarboxylic acid obtained in the process was dissolved in water, separated from the hydrocarbons and acidified with hydrochloric acid. The adipic acid was filtered off. The solution containing the hydrochloric acid was evaporated and by extraction of the residue with acetic ester the adipic acid still present in the solution was removed. The adipic acid yield amounted to 80%. Amalgamation of methyl-adipol gave a yield of only 33% di-carboxylic acid.

Study Of The Constitution Of The Oxo-Alcohols (With Dr. Asigner)

By the splitting of the ozonides, a fatty acid mixture was obtained (the ozonides had been prepared from the olefins which in turn had been obtained by thermal splitting of the esters of higher fatty acids with oxo-alcohols). This fatty acid mixture contained the acids C₆-C₁₂ when a C₁₃ oxo-alcohol was used as initial product (the alcohol was prepared from a dodecylene with a terminal double bond). Lower acids could not be isolated because of their solubility in water. The appearance of a fatty acid mixture may at this point be explained only if one assumes that during the oxo reaction a shift of the double bond occurs. Thus, despite use of olefins with a terminal double bond, formation of δ -alkyl branched alcohols takes place



Upon thermal splitting of the fatty acid ester, they yield olefin I which may then rearrange itself into form II.



The products of the ozonide splitting of these two olefins may vary. This rearrangement and the shift of the double bond render a quantitative determination of the composition of the isomeric mixture in the oxo-alcohol rather difficult. The ketone mixture obtained by the ozonide splitting with the fatty acid mixture gave carbonyl values which were too low.

Application Of The Oxo Reaction To New Compounds And Further Processing Of The Oxo-Products (Meusel)

a. Dimethyl-Hexadiene

The experimental conditions of the oxo reaction were varied, with the purpose of obtaining a shift in the ratio of C₉ alcohol to C₁₀ diol; this ratio has so far been of the order 60:40 and is to be shifted in favor of the C₁₀ diol. With this end in mind, the CO content of the water gas was increased to 90% in order to repress the hydrogenation. For the same reason, the oxo reaction was performed at the lowest possible temperature. However, the diol yield was not improved. Furthermore, the catalyst was treated with CS₂ in such a manner as to allow the oxo reaction only. Since, owing to the presence of CS₂, a subsequent hydrogenation to the diol is not possible, and since the dialdehyde polymerizes to a great extent during distillation, a catalyst (prepared by Dr. Hula) similar to the Ruhrchemie type was used; this catalyst had been observed to allow the oxo reaction while at the same time preventing hydrogenation. A different catalyst was used for the hydrogenation to the diol. With this method only about 40% of the theoretical yield of desired diol was obtained.

With CO only, no reaction takes place. Neither is there a reaction when paraformaldehyde is used instead of water gas.

It is a striking fact that the same ratio of monol to diol is always obtained. This indicates the possibility that the dimethyl-hexadiene may not be a homogeneous substance at the beginning of the reaction; rather, that it may contain two components - perhaps in equilibrium with each other - of which one leads to the monol, the other to the diol.

These phenomena will be further clarified.

b. Oxidation Of Dimethyl-Octane-Diol To Dimethyl-Suberic Acid

By oxidation of the dimethyl octane-diol with potassium permanganate in alkaline solution and at normal temperature, essentially only lower carboxylic acids are obtained. Even when the oxidation is carried out with 30% nitric acid at 80°C. only 6%*(?) of the desired dimethyl-suberic acid was obtained.

If adipol be oxidized in a similar manner, an adipic acid yield exceeding 90% is obtained whereas methyl-adipol yields only 30% methyl-adipic acid. The further oxidation may therefore be assumed to occur on the methyl branch. In order to stop the oxidation in time, the process was carried out by the continuous method in which the diol and the nitric acid are poured drop by drop into a centrifugal mixer and then led through a heated duct in which the reaction occurs; the mixture was then immediately cooled. The excess nitric acid was distilled off in a vacuum. With this method, the methyl-adipol yield was successfully increased to 40% of the theoretical.

*Illegible

c. Olefin Ethers

Instead of using a mixture of high percentage olefin and pure alcohol, a synol fraction (boiling pt. 100-160°C.) was placed into the autoclave for the direct preparation of the olefin ether. The synol fraction 100-160° contains the olefin C₈-C₁₀ and the alcohols C₄-C₆. Olefin ethers of chainlength C₁₃-C₁₇ were therefore expected (this is the region of the detergents). In many experiments however, only a maximum of 20% of the olefin ether (expected on the basis of the bromine number of the synol fraction) was obtained; addition of a large excess alcohol did not improve the result. The rest consisted of a high boiling residue.

Washing tests with the sulfonation product of an olefin ether obtained from C₁₂ aldehyde and C₁₇ alcohol showed that in detergent, lathering and wetting properties it is far below Mesapon. For this reason, the preparation of olefin ethers has been suspended for the time being.

Conversion Of Aldehydes Into Esters

The Wacker Company* manufactures acetic ester from acetaldehyde by using an aluminum ethylate catalyst containing additional ZnCl₂ and AlCl₃ (Germ. Pat. No. 579,566 and application I.G. No. 2316). This catalyst was to be studied for possible use for the conversion of higher aldehydes into esters. For the preparation of the catalyst, acetic ester was used as solvent.

To a catalyst prepared from 17 grams of aluminum and dissolved in acetic ester, 3 kg. of 50% C₁₂ aldehyde were added

*Wacker Gesellschaft

drop by drop in one hour at +5°C.; the aldehyde was thus entirely converted into ester. However, an ester-radical shift* between the expected C₂₄ ester and the acetic ester took place, so that large amounts of C₁₄ ester resulted. The C₂₄ ester is to be used as solvent in future experiments.

The further following attempt was made: by use of the aluminum ethylate catalyst in the oxo reaction, the aldehyde was to be converted into ester at the instant of its formation. Only poor yields resulted.

Signed:

/GEMASSMER/ /BERG/

/MEUSEL/

*Umesterung

The Texas Company

TOM REEL 55, BAG 2523, DOCUMENT 81

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Assignment: 813

Subject: The Effect Of Carbon Monoxide And Hydrogen On Olefins (Oxo - Reaction)

In Charge: Dr. Gemassmer, Dr. Berg, Dr. Meusel

Situation As Of October 1, 1941

1. Study Of The Processing Method

a. Work With Fixed Catalyst In A Flow System*

The experiments with metallic catalysts consisting of copper and cobalt, were continued. The alloy metal-shaving structure was abandoned; instead, pellets obtained from the oxides were used. In this form, the catalyst is characterized by increased yield and longer life. Research in this field is being continued.

b. Study Of The Products

The "neutral component" from the carboxylic acid plant was examined more closely and its suitability as eventual starting product for the oxo-reaction was studied. The "neutral component" was first of all dehydrated and then split into fractions. Use of the individual fractions and of the entire wide boiling-range component resulted in an alcohol yield of about 50%. After

*Festangeordneter Kontakt im strömenden System

separation, these alcohols have an appearance and an odor which indicate their suitability for re-use.

Work In The Semi Plant Scale Installation Me 458a

1. Distillation

Besides distilling cracked olefins, two batches of alcohols were distilled, namely the alcohols C₁₃ and C₁₆. The distillations were successful throughout and the alcohols were to a great extent pure. However, the first runnings still contained appreciable amounts of alcohols. A more careful fractionation should correct this error. A decomposition of the alcohols during the distillation could so far not be observed, despite the fact that the distillation temperature was 250°C.

2. High Pressure

a. Operation Of The Oxo Reaction

In order to obtain an improved heat control of the reaction, the injection of the mash into the high pressure reactor was carried out with a gas stream, so that already during the injection an appreciable part of the conversion occurs. This operating procedure permits extensive technical heat control and the reaction temperature during the entire process may be kept constant within 15-20°C. Preparations for a continuous operation of this reaction have already been made. Installation of a cooling tube system into the high pressure reactor should render it possible to obtain rapid heat removal even with the low molecular weight olefins.

b. Operation Of The Hydrogenation

Despite extensive purification of the gases by means of insertion of Grude towers, the hydrogenation often failed entirely. It was found that CO in the H₂ gas hinders the hydrogenation considerably, despite the fact that with a prolonged reaction period the CO disappears entirely from the hydrogen. By raising the gas flow through the hydrogenation reactor, the frequency of badly hydrogenated batches could be materially reduced. It may be stated at this point that the hydrogenation is much more sensitive than the oxo reaction; catalyst experiments were therefore begun with the purpose of increasing the hydrogenation effect.

c. Filtration Of The Catalyst

The filtration still presented severe difficulties, and remains the bottleneck of the process.

By heating the filters, the filtration time was reduced with reaction products of higher chainlength. Installation of improved stirring devices rendered possible the rinsing off of the catalyst from the candles. However, it was found that the pores of the candles are obstructed and this results in an increase of the filtration time exceeding four hours. Experiments to clear the obstruction of the candles by reflux rinsing have so far met with failure. Further methods for the clarification and elimination of these phenomena are being taken.

Further Processing Of The Oxo-Products (Dr. Berg)

Examination Of The Heavy Oil (High Boiling Component Of The Oxo Reaction)

The high boiling components which are obtained by the

fractionation of a larger amount of C₁₃ oxo alcohol in Me 458a were distilled into 20° fractions under a high vacuum; each fraction was then examined and its characteristic numbers were established. After separation of the first runnings, which amounted to 15% and which still consisted mainly of C₁₃ alcohol, fractions were obtained (boiling pt. 380-440°C.) whose molecular weights were about twice as high as that of the C₁₃ alcohol. The OH* numbers corresponded to about one half of the C₁₃ alcohol. The saponification-, carbonyl- and iodine numbers were low. In the last fraction, the iodine number had a higher value. The residue amounted to about 10%.

Dehydrogenating Amalgam

Alkali Amalgam Of The Heavy Oil

To complete the study of the heavy oil, the latter was amalgamated with alkali. By using a large excess alkali (100%), a fatty acid mixture yield of 60-75% of the initial product was obtained. Removal of the non-miscible oil by steam distillation was unsatisfactory owing to the high boiling point of the heavy oil. The latter had to be removed by extraction. The process turned out to be very difficult because of the presence of high molecular weight fatty acids. Removal of the neutral oil could be effected only down to about 3-4%. An examination of the fatty acid mixture, by distillation of the esters and by subsequent determination of the saponification number of the fractions, is now in progress.

*Illegible

2. Alkali Amalgam Of The Secondary Alcohols

Since in the high boiling component of the oxo-reaction products secondary alcohols may be present, the behaviour of such alcohols in alkali amalgam was studied: (the alcohols had been obtained from first run fatty acids formed by the oxidation of paraffins over their ketone). It was found that they too could be converted partly into fatty acid. In this reaction a molecular split occurs at the link at which the OH-group is located. When a C₁₇ alcohol (secondary) was used whose OH-group was in the center, C₈ and C₉ fatty acid was obtained. 20% of the initial product was converted into fatty acid. The main portion of the initial product is converted into olefins.

3. Alkali Amalgam Of The Dehydrated And Oxo-converted "Neutral Component Resulting From Carboxylic Acid Preparation"

50% of the initial product was converted into fatty acid. However, phenols and their homologues seem to be still present. Studies on this subject are being continued.

c.) Clarification Of The Constitution Of The Oxo-Products

In conjunction with Dr. Asinger, work was begun with the purpose of determining the amount of branched alcohols contained in the oxo-alcohols. Over the stearic ester of the oxo-alcohol, and by thermal splitting, the olefin whose constitution was to be studied, was obtained. The preparation of the ester was carried out as follows: 1) By heating of stearic acid and alcohol, and 2) by heating of fatty acid chloride with alcohol. The difficulty consists in obtaining as complete an esterification

and ester split as possible: this is to prevent an increase of the splitting product resulting from the straight or branched chain alcohols. The experiments are being continued.

Application Of The Oxo Reaction To New Compounds And Further Processing Of The Oxo Products (Dr. Meusel)

a.) Dimethyl-hexadiene

Dimethyl-hexadiene was dissolved in about 4 times its volume of cyclohexane and subjected to the oxo reaction, with the usual Ruhrchemie catalyst; it was then hydrogenated. According to the OH-number, the crude product freed from cyclohexane contained about 60% of the theoretical amount of the expected dimethyl-octane-diol. By distillation, the crude product could be separated into two approximately equal fractions whose boiling points are 200-220°C. and 300-320°C. respectively. The OH-number of the lower fractions corresponds to about 40% of the expected dimethyl-octane-diol content. That of the higher fraction, to 88%. Both products were purified by the boric acid ester method. The lower boiling component seemed to be the C₉ alcohol, whose formation can only be explained by assuming hydrogenation of the double bond of the dimethyl-hexadiene. Owing to the possibility that C₁₀ diol, already formed, may have been further hydrogenated, research on this subject is being continued.

The refined higher boiling fraction, a viscous colorless and somewhat water soluble liquid, gave an OH-number corresponding to a 94% dimethyl-octane-diol content.

It is to be noted that the boric acid ester of the dimethyl-octane-diol is stable. The cause of this is probably

to be sought in the fact that both acid and alcohol are multi-functional so that reticulation* with consequent formation of high molecular compounds may take place. Therefore, it will be difficult to remove by distillation the neutral oils from the boric acid ester which is still stable at 300°C.

The yield of pure dimethyl-octane-diol amounted to 35% of the theoretical. It now remains to be tried to inhibit the side reaction by varying both the gas concentration and the catalyst.

b.) Experiments For The Preparation Of Pure Higher Aldehydes

1. It was attempted to purify by distillation the C₁₂ aldehyde obtained from the oxo treatment of the olefin. Although the pure aldehyde boiled at 50° higher than the initial olefin fraction, it was not possible to obtain a high percentage aldehyde. Rather, over a wide temperature range, from 220-280°C., a 75-80% pure aldehyde distilled while at the same time 45% of higher boiling compounds were formed.

2. It was attempted to purify the aldehyde as the 2/3 acetal of trimethyl-ethane by distillative separation of the non-aldehydic components from the high boiling acetal, and by subsequent re-saponification of the acetal. However, no acetalization occurred with NaHSO₄ as catalyst whereas with p-toluol sulfonic acid (a much stronger catalyst) complete polymerization of the aldehyde occurred.

3. Since pure alcohols are easily obtained by distillation, it was attempted to arrive at pure aldehydes by catalytic dehydro-

*Vernetzung = probably means "association" in this case (Transl.)

generation of the alcohols in the liquid phase. A large number of different Cu, Ni and Cr catalysts were tried out. A copper chromite catalyst reduced at 220° caused only a feeble evolution of H₂ at 180°C. and within a period of 18 hours, 79% of the theoretical amount of H₂ could be split from the initial compound. However, 60% of the aldehyde was polymerized. Other catalysts of strong dehydrogenating effect, and capable of operating at lower temperatures and within shortest possible reaction times, are to be tried out.

c.) The Preparation Of Olefin Ethers

Since in the acetalization generally one half of the product consists of aldehyde polymerization products, a catalyst was sought which might catalyze the acetalization while at the same time not polymerizing the aldehyde. For this purpose, distilled C₁₂ aldehyde was first of all heated for three hours with 1% of all the catalysts in question. The following results were obtained:

Without catalyst	:	14%	high boiling
With NaHSO ₄	:	17%	" "
With HCl	:	47%	" "
With p-toluol-sulf.ac.	:	56%	" "

NaHSO₄ was therefore used in the acetalization. It was further found that better results are achieved in the acetalization if, rather than separating the reaction water at high temperature in a water condenser, the water is removed at ordinary temperature by CaCl₂, in the presence of NaHSO₄, with Na₂SO₄. However, even with this method the olefin ether yield was only 38% (based on the initial aldehyde). Since now the aldehyde must be prepared

with a 45% loss from the olefin, the yield as based on the initial olefin used is actually lower than the yield obtained by direct acetalization in the autoclave. So far, the best possible yield, namely 32% of the theoretical calculated on the basis of initial olefin, is obtained by oxo reacting and acetalizing the olefin directly in the autoclave in the presence of a three-fold excess of alcohol and CaCl_2 . The low bromine number mentioned in the previous report has in the meantime found the following explanation.

The p-toluol-sulfonic acid used for the splitting of the acetal had not acted long enough so that during the distillation of the olefin ether further splitting was taking place. Thus, at the distillation temperature of the olefin ether, also alcohols and even unchanged acetals distilled over, with the result that the real molecular weight turned out to be fictitious. When a second distillation with p-toluol-sulfonic acid was made, at first the same copious amounts of alcohols distilled over and a 92% pure olefin ether was obtained. The method for the determination of the hydrogenation number with PtO_2 as a catalyst developed and perfected in the meantime, gave the same values.

d.) Sulfonation Of The Olefin Ethers

Whereas olefinsulfonate readily with sulfuric acid alone, the olefin ethers sulfonated only to a small extent, amounting to a few per cent. In this case, one has to use acetyl-sulfuric acid (1 mol acetic acid anhydride and 1 mol of H_2SO_4).

- 10 -

The sulfonation product is white; it was freed of salts by extraction with isopropyl alcohol. Detergent tests are to be made with this product.

Signed:

/GEMASSMER/ /MEUSEL/ /BERG/

The Texas Company

TOM REEL 55, BAG 2523, DOCUMENT 83

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Assignment: 813

Subject: The Effect Of Carbon Monoxide And Hydrogen On The Olefins (Oxo - Reaction)

In Charge: Gemassmer, Berg

Situation As Of June 1, 1941

1. Study Of The Processing Method

a.) Catalyst Experiments

The studies and experiments on catalysts have been temporarily discontinued.

b.) Kilo Reactor Experiments In Me 333a

The installation for the continuous operation of the oxo-reaction in Me 333a was put at Dr. Wintzer's disposal during the major part of the period covered by the present report; Dr. Wintzer is studying the Michael synthesis. Furthermore, besides cracked-olefin fractions of wide boiling point ranges, experiments were performed with wide-range boiling fractions of synol product. The conversion of synol product was satisfactory. The esters contained in the synol product are hydrogenated only to a small extent.

c.) Study Of The Products

1. Synol Product

Various synol fractions were converted in the autoclave

in an attempt to hydrogenate the esters of the synol product by increasing the hydrogenation temperature. It was found that, even at hydrogenation temperatures as high as 300°C., only a small amount of esters is hydrogenated to alcohols.

2. Allyl Alcohol

It was attempted to subject allyl alcohol to the oxo-reaction in order to obtain butane-diol. It was found that allyl alcohol reacts with CO and H₂ under the usual conditions; however, it has not yet been possible to prove unequivocally the presence of butane-diol in the reaction product.

3. 1-Butenyl-Chloride

Experiments for the conversion of iso-butenyl-chloride with CO and H₂ have thus far been unsuccessful. During the process in the autoclave no decrease in pressure occurred which points to the conclusion that a reaction does not occur on any noticeable scale. The treated product consisted partly of unchanged iso-butenyl chloride and partly of a black resinous mass.

d.) Investigation And Survey Of The Methods Used In The Determination Of Olefins

Various different methods for the determination of olefins were examined and it was found that the bromine number method developed by Dr. Klein (Oppau) gave reliable olefin values ~~provided certain precautionary measures and certain improvements~~ for cracked olefins and synol products are used.

Experiments with the hydrogenation number are now in progress.

e.) The Determination Of Small Quantities Of Neutral Oil In Alcohols

Two methods were followed in the determination of small amounts of neutral oil in alcohols:

1. Sulfonation of the alcohol and extraction of the alcohol sulfates.
2. Oxo-ethylenization of the alcohol and extraction of the neutral oil from the resulting product.

Neither method has been developed to the point where it can be used for analysis. The experiments are being continued.

f.) Work In The Semi Plant Scale Installation Me 458a

1. Distillation

Both distillation columns were washed with methanol and put under pressure. The large column was put in operation. The initial operating difficulties could be removed almost entirely; but since the high pressure steam necessary for the plant operation was not yet available, only the olefins up to C₁₂ could be distilled.

2. High Pressure

The major part of the high pressure system was put under pressure and also the gas cycle pumps were put on a trial run. A number of faults and errors were eliminated.

3. Filtration And Mixing Of The Catalyst

~~The catalyst filter was examined thoroughly.~~ Pumping of fresh oil through the filters when rinsing them was found to be harmful because a turbid initial filtrate is invariably formed. Furthermore, the filtration time is strongly affected when the filter is not rinsed after each filtration. The porolith filter candles "Ultra" and "ff" were found to be very suitable filter materials.

2. Separation And Further Processing Of The Oxo Products (Dr. Berg)

a.) Separation

Experiments for the separation of the aldehydes from the hydrocarbons by bisulfite formation were undertaken. This was tried at first with dilute bisulfite solutions. It was expected that this procedure would allow the separation of the bisulfite compound from the hydrocarbons, the former being soluble in dilute bisulfite solution. It turned out that the addition compound is only very sparingly soluble. It was therefore attempted to carry out the separation as follows: the bisulfite compound which, with the hydrocarbons, forms a thick pasty mass still containing appreciable amounts of bisulfite solution, is repeatedly treated with solvents in a stirring apparatus; first the aqueous solution and then the hydrocarbons were thus to be separated. This method was tried with methyl-, ethyl-, and isopropyl alcohol. The separation was found to be very difficult owing to the difficulties arising in the filtration of the bisulfite compound. The addition compound, after treatment with warm dilute sulfuric acid, yielded the aldehyde. Because of polymerization, these aldehydes showed very variable carbonyl numbers. According to the carbonyl number, increase in aldehyde ~~from 40 to 60% was achieved.~~

b.) Further Processing

1. Preparation of Olefin Ethers

From aldehyde - hydrocarbon mixtures and iso-heptyl alcohol with hydrochloric acid and calcium chloride, olefin ethers

were prepared in the usual manner through acetal formation. By subsequent sulfonation, the sulfonates were prepared. Oxidation experiments with oxygen and manganese stearate as catalyst showed the olefin ethers to be very resistant. An olefin ether from iso-hexyl aldehyde and iso-heptyl alcohol showed, after a six hour oxygen treatment at 70°C., a saponification number of 115. The experiments are being continued: the olefin ethers are to be prepared by direct action of alcohol, CO and H₂ on the olefins. Studies on the olefin-ether sulfonates from the textile chemical point of view are now in progress.

2. Alkali Amalgam

The amalgamation was carried out at normal pressure with high percentage oxo-alcohols and a yield of 85% distilled fatty acids was obtained. The amalgamation of synol products was carried on. Alkali amalgamation of synol products subjected to the oxo-reaction and re-hydrogenated, was begun. The process of alkali amalgamation of fatty alcohol - hydrocarbon mixtures with low initial boiling temperature (which cannot be amalgamated at ordinary pressure) was carried out at a constant pressure of 40 atmospheres. This was done by regulating the pressure on the amount of the hydrogen given off at 40 atm. gauge pressure. The component of unsaponifiable fatty acids was reduced to 1% by steam distillation (for the removal of the neutral oil, or at least of its major portion), followed by another steam distillation at 30-50 mm Hg.

Signed:

/GEMASSMER/ /BERG/

The Texas Company

TOM REEL 55, BAG 2523, DOCUMENT 84

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Assignment: 813

Subject: Effect Of Carbon Monoxide And Hydrogen On The Olefins (Oxo - Reaction)

In Charge: Gemassmer, Berg

Situation As Of April 1, 1941

1.) Study Of The Process

a.) Catalyst Experiments

In experiments which had been performed with Ruhrchemie cobalt catalyst, this catalyst from one container showed no oxo-reaction whatsoever; yet, hydrogenation of the olefins to paraffin hydrocarbons took place. The catalyst showed good activity and under oxo-reaction conditions the cobalt carbonyl formed, but without aldehyde formation. However, after treatment with hydrogen under normal reaction conditions the catalyst gave a normal oxo reaction.

The reason for this behavior of the Ruhrchemie catalyst, observed here for the first time, has not yet been found.

b.) Catalyst Reduction

The apparatus for the reduction of catalyst dust in Me-333a was improved by the installation of a filter candle in

the gas chamber so that not even the minutest traces of catalyst can be carried off. This improvement allows a smooth, easy reduction of the catalyst. The problem of the reduction of catalyst dust may therefore be considered as solved.

c.) The Regeneration Of Used Ruhrchemie Catalyst

It has been found that treatment of used catalyst by washing with light gasoline* and methanol, followed by desiccation and reduction, does not restore enough of the catalyst to its original activity. This regeneration method has so far been used three times and no activity decrease has been noted.

d.) Kilo Reactor Experiments In Me 333a

In order to study further the continuous oxo reaction for the preparation of alcohols, all cracked olefin fractions from C₈-C₁₇, and also fractions of wide boiling point range, were put through the process. Throughout, the yields varied between 80 and 90%. The alcohol yields varied within the same limits. Only in the conversion of the high-boiling fraction C₁₇-C₁₈ a yield exceeding 50% has not yet been obtained.

e.) Study Of The Products

It was attempted to subject 2,5-dimethyl hexadiene 1,6 to the oxo-reaction with the purpose of obtaining 3,3'-dimethyl-suberic acid through the dialdehyde or the glycol. Both the alcohol process and the aldehyde process showed that only one double bond reacts or that at least the dialdehydes resulting from the primary reaction quickly react again since components

*Leichtbenzin

of much higher boiling point were formed. The low boiling components have a pleasant odor similar to that of citronellal. The desired synthesis of 3,3'-dimethyl-suberic acid does not seem to be feasible, by this method.

Furthermore, research of a wider scope and dealing with the products of the $\text{CO} + \text{H}_2$ synthesis and with the synol products, were begun.

f.) Detergents and Wetting Agents Obtainable From Alcohols

In order to gain an insight into the various possible uses of the oxo alcohols, a systematic conversion of all alcohols into alcohol sulfates and into oxy-ethylation products with variable amounts of ethylene oxide, was begun.

2.) Separation And Further Processing (Berg)

I. Separation

a.) By The Acetal Stage

Experiments were carried out for the conversion of aldehydes into acetals and for the separation of the latter from the hydrocarbons by distillation. The acetals were prepared from ethyl alcohol. After fractional vacuum distillation and after separation of the hydrocarbons, high boiling residues of great stability when treated with dilute sulfuric acid, were obtained. Even prolonged heating with sulfuric acid gave as only result that the determination of the carbonyl number showed an aldehyde content differing only slightly from that of the initial product.

b.) By The Aldehyde Ammonia

In these experiments, ammonia was led into the aldehyde-

neutral oil mixture. The ammonia combines and heat is given off. The hydrocarbons were distilled by fractional distillation in a vacuum with addition of small amounts of ammonia (to prevent the decomposition of the ammonium aldehyde). By treating the high boiling residue with dilute sulfuric acid only very incomplete re-formation of aldehydes was achieved. This may be explained by the fact that the unstable ammonia-aldehyde compounds are easily polymerized or condensed. The same results were obtained in experiments in which the separation of the neutral oil by steam distillation from the chloride salt of the aldehyde-ammonia complex had been carried out. Here too, the high boiling residue was treated with dilute sulfuric acid at higher temperature and the resulting carbonyl numbers were far below those of the initial product.

c.) By The Oxime

A re-formation of the aldehyde from the oxime by treatment with sulfuric acid was not successful with the oxo-aldehydes. The oxime was absolutely stable.

II. Further Processing

a.) Alkali Fusion

Experiments for the preparation of fatty acids by means of the dehydrogenating amalgam of alkali were carried on. Fatty alcohol - hydrocarbon mixtures were amalgamated. The process was carried out at normal pressure and at different temperatures. It was found that, especially at higher temperatures, dehydrogenation is accompanied by dehydration. The crude

soaps obtained at higher temperatures are of very dark color. The distillation residues resulting from the breakdown of the fatty acids were greater when the amalgamation was done at elevated temperatures. Experiments are being carried on with the purpose of finding a method of carrying out the amalgamation under the mildest possible conditions.

Fatty alcohol - hydrocarbon mixtures containing C_{13} -C (illegible) alcohols were amalgamated with alkali with the purpose of obtaining, after distillation, fatty acid mixtures suitable for the preparation of soaps. Furthermore, experiments were begun for the removal of synol products from the amalgam. These experiments are now being continued.

b.) The Preparation of Acetals From High Molecular Alcohols

It is the aim of these experiments to obtain fatty acids or esters by oxidation (with air or oxygen) of olefin ethers. The olefin ethers are formed by splitting of the alcohol from the acetal. Experiments designed to obtain acetals directly from the oxo-reaction in the autoclave in the presence of high molecular alcohols gave no clear picture when the reaction products were analyzed by distillation. This may possibly be explained as follows: CO and H_2 further react upon the acetal which is formed (hydrogenation, oxo-reaction of the olefin ethers resulting from the splitting away of the alcohols). Therefore, acetalization experiments with HCl as catalyst were begun and are now in course.

The Texas Company

TOM REEL 55, BAG 2523, DOCUMENT 85

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Assignment: 813

Subject: The Effect Of Carbon Monoxide And Hydrogen On Olefins (Oxo - Reaction)

In Charge: Gemassmer, Berg, Meusel

Situation As Of February 1, 1941

a.) Catalyst Experiments

Further small scale catalytic experiments were carried out with the purpose of poisoning the catalysts in such a manner as would still allow them to produce the oxo-reaction but which would at the same time prevent the subsequent hydrogenation of the primary aldehydes to alcohols. It was found that such a result may be achieved by adding to the catalyst mixture a small amount of organic sulfur compound (carbon disulfide); the hydrogenation inhibiting effect of the sulfur is sharp indeed: a pure cobalt catalyst may be poisoned so that upon re-hydrogenation the cobalt carbonyl will be reduced, without the appearance of alcohol formation.

Experiments to poison the catalysts by addition of exactly measured amounts of hydrogen sulfide at precipitation, have thus far been unsuccessful. It has not been determined

whether the added sulfur is lost during the reduction or if it is actually necessary to poison the active centers formed during the reduction, by subsequent addition of sulfur. The experiments are being continued. When an experiment was performed in which bismuth was the poisoning agent, it was found that this metal exerts no poisoning action whatsoever on the hydrogenation; on the contrary, it strongly increases the hydrogenation of the olefins.

b.) Reduction of the Catalysts

For the reduction of catalysts, a good sized installation was set up in Me 333a and operations have already begun. The apparatus is supposed to permit the reduction of the catalyst dust while it is in suspension; the purpose is the achievement of a more uniform reduction. The initial difficulties have been almost entirely ironed out but it is yet too early to judge the performance of the installation and to critically examine the results obtained.

c.) Experiments With The Ascending Tube Reactor*

Experiments in this reactor showed without exception that the hydrogenation of the oxo-aldehydes is faster rather than slower than the oxo reaction itself. A hydrogenation period of 15 minutes was found to be sufficient. Experiments are now in progress, with the purpose of finding out whether an increase of the hydrogenation period or of the hydrogenation temperature will result in the reduction of the alcohols to hydrocarbons.

*Steigrohrofen = ascending tube reactor

d.) Kilo-Reactor Experiments In Me 333a*

Several experiments were carried out with a copper-cobalt catalyst for the obtaining of aldehydes. The yields varied between 50-70% because of faulty catalyst reduction, and no significant new points were discovered.

In order to study the synthesis of alcohols under the continuous operating procedure, experiments with Ruhrchemie catalyst were performed; at the first passage through the reactor, at 120°C., the addition of CO and H₂ took place at the second passage, at higher temperature, the hydrogenation of the oxo-products was carried out. For these experiments, a low boiling, olefin-rich fraction (140-160°C., 70% olefin content) was used. It was found that in this case the removal of the heat of reaction by means of an oil bath was insufficient since the temperature in the individual reaction tubes rose up to 170-180°C. During the hydrogenation which followed it was not possible to heat the reactor above 160°, so that only after repeated passage through the reactor a complete hydrogenation of the alcohol could be achieved. In order to eliminate this disturbing factor, an additional electric heater was installed in the oil circulation system.

Thus, a yield of 87% was obtained. The products consist of approximately 70% alcohols and 30% high boiling components whose nature has not yet been determined.

*Kilo-Ofen = Kilo reactor Probably a larger reactor of semi-plant scale (Transl.)

Further Processing And Separation

a.) Oxidation Experiments (Berg)

Since the oxidation of the aldehyde - neutral oil mixture had only been incomplete, it was attempted to remove the oxidation inhibiting components from the neutral oil. This was to be accomplished by fractional distillation; but the only result achieved by this method was an increase in the aldehyde content. Determination of the iodine numbers revealed the presence of unsaturated compounds. The oxidation of these illegible.....aldehydes was also incomplete.

..... Next eight lines illegible.....(note of translator).

b.) Dehydrogenation Alkali-Fusion*

The preparation of fatty acids by passing through the soap stage gave only very poor fatty acid yields with the oxo-aldehydes. The amalgam was passed through a V2A blower without pressure and the neutral oil was removed with super heated steam after termination of the reaction (i.e. after termination of H₂ formation). This method allowed easy removal of the hydrocarbons containing one less C-atom in the form of their corresponding aldehydes; however, it was not possible to remove either the high molecular components formed by aldolization nor the high molecular compounds (ketones) formed during the side reaction which occurs during the oxo-reaction. Breakdown of the soaps (obtained from

*Dehydrierende Alkali-schmelze

the amalgam) by means of acidification with mineral acid and by subsequent distillation of the fatty acids thus obtained yielded a residue of 45-50% by weight when a C₁₆ aldehyde was used as starting product.

It was also attempted to remove the aldehydes from the alkali amalgam by exposure to air, i.e. by oxidation. This renders possible not only the conversion of the aldehydes present into soap, but also the conversion of the fatty alcohols into their respective fatty acids. Here, with an initial C₁₆ aldehyde, the residue of the fatty acid distillation amounted to 18-23% by weight.

c.) Extraction

For the isolation of the aldehydes contained in the neutral oil mixture, the experiments were continued with aqueous SO₂; the foaming which occurs during the boiling out of the SO₂ and the re-formation of the aldehyde was reduced by addition of methanol. The aldehydes thus obtained gave carbonyl numbers no higher than those of the initial product.

By extraction with acetonitrile, a richer aldehyde content was obtained. The experiments were carried out at different temperatures. At -20° and with 200% acetonitrile, a concentration of the C₁₆ aldehyde up to 80%, with very small yield, was achieved.

The Texas Company

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TOM REEL 55, BAG 2523, DOCUMENT 87

Assignment: 628

Subject: Synol work

In Charge: Reisinger, Breywisch, Geiseler.

Situation as of 1 December 1942

Work in research laboratory Me 245 (Dr. Reisinger)

I. Studies of the product

Research on the decomposition of synol alcohols on various surfaces (surfaces with which one has to deal in the synthesis or in the processing of the alcohols) has not been continued. Although a number of problems have not yet been solved, these studies had to be abandoned for lack of experienced personnel.

II. Experiments for the utilization of synol.

1) Studies on the utilization and on the properties of the distillation residues of primary synol product (h.r.).*

Experiments for the brightening of "h.r."

In the previous report (1 October 1942) it was pointed out that a decisive factor for the brightening of the high boiling synol residues is the adsorptive treatment of such residues while they are being formed or in their pre-treatment.

Two different residues were examined more closely and it was especially attempted to get a clear picture as to their iron content and the form in which this iron is present.

h.r. II: collected residue above 400°C from column Me 776

May be brightened very satisfactorily with bleaching earth

H.R. is an abbreviation of "Hochsiedender Rückstand" = high boiling residue (Transl.)

h.r. III: distillation residue above 350° from the large size column Me 458, completely de-esterified.

Brightens very little when treated with bleaching earth.

Both residues were treated with bleaching agent under the same conditions. 20 Kg of h.r. (=A) were dissolved in 35 liters of Decalin*; the solution was then treated with 4 kg of tonsil clay while being stirred and kept at 110-126°C. for a period of three hours; the solution was then filtered. Each 1 Kg of the filtered clay was then extracted for 14 hours in a Soxhlet with the following solvents:

Initial weight: — A = 20 Kg of h.r. III

Obtained: 5700 g adsorbent + adsorbate

		Iron content	O ₂ -content
Decalin	1180 g = 5.90% of A	.79 g = .00395% of A	2.96%
Acetone	325 g = 1.63% "	.22 g = .00110% "	10.20%
Acetic ester	57.0 g = .29% "	.05 g = .00025% "	4.30%
Chloroform	51.3 g = .26% "	.10 g = .0005% "	3.92%
n-Butanol	22.8 g = .11% "	.00 g = .00% "	
<hr/>			
	1636.1 = 8.19%		

Extracted amount of silica clay:	3960 g	141 g	Total iron in h.r. III
Total extract:	<u>1636 g</u>		<u>.1308%</u>
Loss	104 g		
4 kg initial silica clay		116 g	
Adsorbed iron		25 g = .125% of A	

*Decalin = deca-hydro naphthalene (Transl.)

Initial weight: A = 20 Kg of h.r. II

Obtained: 5600 g adsorbent + adsorbate

Solvent		Iron content	O ₂ -content
Decalin	1300 g = 6.50% of A	6.00 g = .030% of A	%
Acetone	172 g = .86% "	1.48 g = .0074% "	4.97%
Acetic ester	86 g = .43% "	2.73 g = .0142% "	7.15%
Chloroform	43 g = .22% "	1.17 g = .00585% "	
<hr/>			
Total extract	601 g = 8.01%		
Extracted amount of silica clay:	3960 g	157.3 g	
	5561		
Loss	39 g		
4 kg of initial silica clay		134.0 g	
Adsorbed iron		23.3 g = .117% of A	
Total iron in h.r. II:		.1745%	

The two examples of the examination of high boiling distillation residues cited above revealed the following facts:

I. High boiling distillation residues of synol synthesis products may be very different in their behavior when bleached by means of adsorptive substances, especially as far as the brightening of such residues is concerned.

II. Distillation residues obtained from various different experiments may also differ to a great extent in their composition.

a) H.R. II contains a much greater amount of iron compounds soluble in organic solvents than does h.r. III.

b) The components adsorbed by clay from h.r. III and then extracted by stages with various organic solvents are all

liquid at room temperature as far as the oxygen compounds are concerned. The corresponding products obtained from h.r. II are all solid.

III. A common property of both products is their content of oil-soluble organic iron-complexes and the high oxygen content of the products. For instance, the oxygen content of the component extracted from the clay by means of chloroform in h.r. III is 3.92%; should one use this figure as basis for an alcohol of C-number C₃₅, this would correspond to an alcohol content of 86%.

IV. The far reaching importance of the chemical composition of the solvent used for the dissolution of the h.r. for the bleaching process with bleaching earth is shown by the following experiment:

Equal amounts (1 gram) of acetone extract obtained from the clay after the bleaching are dissolved in 200 g decalin, 200 g triisobutane and 200 g triisobutylene. Three equally colored red-brown and absolutely clear solutions are obtained; these solutions, when treated under the same conditions with the same amount of clay, give the following results:

Brightest	=	triisobutane
Somewhat darker	=	decalin
Darkest	=	triisobutylene

V. Experiments for the reactivation of used tonsil clay have so far yielded the following results:

1.) Used clays may be reactivated up to 50% of their original activity if they are thoroughly washed with liquids of hydrocarbon-like nature and then exhaustively extracted with oxygenated organic solvents; after this, they have to be treated at temperatures

around 100°C with aqueous acids, especially with 50% sulfuric acid.

2.) Similar reactivation effects may be obtained without previous extraction, by oxidation with strongly oxidizing inorganic acids at their boiling point (HOKO-acid $H_2SO_4 + Br_2$).

3.) Oxidation of the organic components adsorbed on the used adsorptive agents in the presence of air by means of calcination at higher temperatures (above 500°C) leads to extensive inactivation, as is also the case with fresh and highly active adsorbents.

2) Studies for the utilization of the synol components boiling between 100 and 200°C.

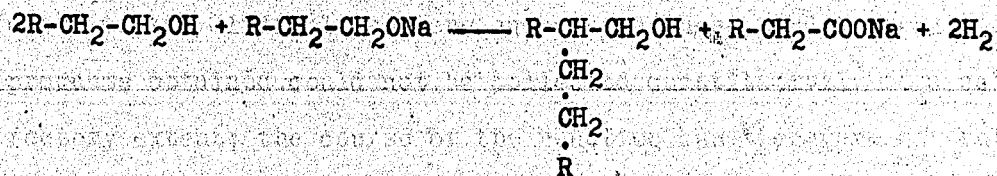
The experiments performed were merely concerned with the extraction of these fractions by means of methanol. This study has been in course for an extended period of time with some interruptions but a final comprehensive report cannot yet be given. So far, fractions 100-120°, 120-140°, 140-150° and 150-170° have been subjected to the extraction; the extraction was performed by mixing two parts of 50-75% aqueous methanol to one part of oil in the turbo-mixer until the extraction equilibrium was reached. The percentage of the methanol was increased with increasing boiling points of the fractions treated. It can already be reported that it is possible to extract at least 85% alcohols from the oils; the residual oils have an alcohol content varying from 3 to 8%. This is the case for the boiling range 150-170°C. In the lower boiling ranges, these ratios are still more favorable; for instance, an almost 100% butyl alcohol may be extracted from the 100-120° fractions by means of a 50% aqueous methanol solution.

3) A number of samples were prepared and were sent to various I.G.

Farben branches for the utilization of synol products (Cf. enclosed correspondence).

4. Dimeric alcohols. In the endeavor of extending the field of the chemistry of alcohols with the aim of gaining a more comprehensive view as to their utilization, the study of a new reaction was begun. This reaction may best be termed an alcohol alkylation; it was described (for propyl and butyl alcohol) by Guerbet in the Comptes Rendus, vol. 133 (1901), page 1220.

According to this author's observations, alcohols may be alkylated by themselves; the following process takes place:



This reaction occurs when mixtures of alcohols and sodium alcoholates in proportionate amounts are heated to temperatures of 180-250°C.

The experiment cited above was checked and repeated with a C₆-synol alcohol; the results were in accordance with the findings reported in the literature; however, both the quantitative and the qualitative course of the reaction are very variable; the reaction is as yet very difficult to control. Not only the alkyl alcohols of the above reaction scheme are formed: -propyl-propyl alcohol, -butyl-butyl alcohol, -amyl-amyl alcohol, etc., but also, to a lesser extent, the dialkyl-ethers, besides olefins and -substituted carboxylic acids derived from the -alkylated alcohols. As far as the alkyl-alcohols are concerned, Dr. Asinger was able

to prove the correctness of the above given constitutional formula with hexyl-hexyl alcohol. We had no interest in the formation of fatty acids, and therefore a working hypothesis was assumed to the effect that the formation of fatty acids is not a result of the primary reaction, but rather of a secondary reaction which occurs with the formation of water; and that, should the formation of water take place under different circumstances, the reaction equilibrium could be shifted in favor of the alkyl alcohol.

The first series of experiments was therefore devoted to the study of the role played by the sodium concentration. Great experimental difficulties were encountered here, and the reaction products obtained could not be collected quantitatively to a satisfactory extent; the course of the reaction has therefore not yet been cleared up as far as its quantitative aspects are concerned.

Experiments for the confirmation of our hypothesis are still being continued.

Catalyst examinations in Me 245 (Dr. Geiseler).

Previous experiments have shown that iron precipitate catalysts with small additions of arsenic or antimony gave excellent results. Therefore, further experiments along this line were carried out with such catalysts; the catalysts contained about 0.1% As or Sb respectively; partly they were in pelleted form, and partly they were used in non-pelleted form.

1. Catalyst 4305 (96.2% Fe_2O_3 , 3.5% Al_2O_3 , 0.3% K)

Synth. temp. 200° , finished catalyst: 0.25% K (determined by spectro-analysis).

Fraction	Weight %	% Olefins	% Alcohol	Ester Number
33-200°	46.0	38.4	39.6	
200-230°	3.8	33.1	38.0	
230-350°	24.0	17.7	57.6	14.2
300-400°	7.0	10.9	47.2	
Above 400°	18.8	-	-	

2. Catalyst 4305/1 (96.2% Fe₂O₃, 3.5% Al₂O₃, 0.3% K, in 4 mm pellets)

Synth. temp. 206°

Fraction	Weight %	% Olefins	% Alcohol	Ester Number
26-200°	59.8	45.3	40.3	
200-230°	3.3	28.4	31.9	
230-350°	19.0	19.5	40.8	0.0
350-400°	5.3	13.9	24.2	
Above 400°	10.0	-	-	

3. Catalyst 4303 (71.1% Fe₂O₃, 3.5% Al₂O₃, 0.3% K, 0.1% As₂O₅)

Synth. temp. 195°, finished catalyst: 0.24% K (det. by spectro-analysis)

Fraction	Weight %	% Olefins	% Alcohol	Ester Number
27-200°	53.1	36.6	43.8	0.0
200-230°	3.9	19.1	42.8	0.0
230-350°	23.6	14.1	55.7	2.6
350-400°	6.2	11.7	30.0	-
Above 400°	11.4	-	-	-

4. Catalyst 4339 (96% Fe₂O₃, 3.5% Al₂O₃, 0.3% K, 0.1% Sb₂O₃)

Finished catalyst: 0.1% K (det. by spectro-analysis)

The experiment was discontinued owing to excessive synthesis temperature (203°C and still increasing).

5. Catalyst 4304 (96% Fe₂O₃, 3.5% Al₂O₃, 0.3% K, 0.1% Sb₂O₃)

Synthesis temperature 202°, finished catalyst: 0.22% K (det. by spectro-analysis)

Fraction	Weight %	% Olefins	% Alcohol	Ester Number
44-300°	57.3	29.5	46.3	
200-230°	2.5	18.0	42.2	
230-350°	21.2	14.0	50.4	12.7
350-400°	6.6	13.6	27.9	
Above 400°	10.9	-	-	

These results show that the effect of the arsenic or the antimony respectively is not very considerable. Again, the alkali content seems to play the decisive role here; the question whether the increase in ester formation is due to the arsenic or the antimony content is therefore not cleared up. Further experiments are to be carried out.

Experiments in Me 776

Since September, throughput tests have been run; it was to be determined how the yield, the composition of the product and the life of the catalyst vary when, under otherwise equal conditions, such as conversion rate (1:150) and synthesis pressure (= 24 atm. gauge), the entrance load is varied. The catalyst used was WK 17, grain size 1-2 mm, reduced in H₂ current at throughput of 1:3000.

1. Composition of the product as related to throughput.

a) Throughput 1:250; reactor 14/8

Fraction	Weight %	Alcohol %	Olefin %
Below 200°	57.4	44.7	34.0
- 230°	3.02	33.5	34.0
- 350°	18.1	47.8	26.2
- 400°	5.81	31.4	17.2
Above 400°	15.3		

b) Throughput 1:350; reactor 9/3

Fraction	Weight %	Alcohol %	Olefin %
Below 200°	54.9	40.2	35.5
- 230°	2.3	39.0	33.0
- 350°	18.0	54.3	23.5
- 400°	5.7	45.3	25.2
Above 400°	18.9	-	-

c) Throughput 1:400; reactor 9/9

Fraction	Weight %	Alcohol %	Olefin %
Below 200°	53.8	40.6	35.4
230°	1.5	35.2	39.8
350°	18.1	51.6	28.7
400°	5.8	38.9	25.8
Above 400°	20.1		

d) Throughput 1:500; reactor 13/5

Fraction	Weight %	Alcohol %	Olefin %
Below 200°	57.9	37.2	33.2
230°	2.6	34.2	35.3
350°	17.6	54.2	26.1
400°	5.4	41.1	24.2
Above 400°	16.6		

2. Product yield

Reactor	8/9	8/9	9/9	9/9	13/5	13/5	14/8	14/8
Throughput	1:350	1:400	1:350	1:400	1:350	1:500	1:350	1:250
CO ₂	15%	16%	15%	16%	15%	12.5%	15%	32%
Catalyst	30%	27%	31%	30%	27%	23%	28%	40%
Synth.Temp.	194°	200°	194°	199°	195°	204°	196°	207°
Spec.Yield	64 g	61 g	63 g	63 g	63 g	46 g	65 g	105 g
Space Yield	450 g	525 g	410 g	525 g	400 g	475 g	430 g	450 g
Conversion-Yield	145 g	150 g	140 g	145 g	150 g	145 g	160 g	145 g

These figures show that the alcohol yield shifts, with increasing throughput, in favor of the higher boiling fractions whereas apparently the olefin content does not change. In contrast to this, the specific yield very definitely diminishes with increasing throughput; the relation being almost inversely proportional.

The throughput has no noticeable effect on the life of the catalyst.

Questions concerning the processing of synol

Isolation of the alcohols by adsorption on silica gel (Me 245)

1. On the reactivation of the silica gel.

150 cm³ of silica gel B of grain size 1-2 mm were treated with a solution of 30 cm³ of synol product (fraction 260-265°, alcohol content = 37.5%) in 100 cm³ petroleum ether; another 50 cm³ of solvent were poured into the flask and then the extraction was carried out for 1/2 hour. Then the petroleum ether solution was separated and another half hour extraction with methanol was made. The two solutions thus obtained were evaporated in a water bath and then freed from the last residues of solvent in a vacuum; then the products were examined and their OH- and iodine numbers respectively were determined. The desiccation of the silica gel was carried out very carefully in an electric furnace with nitrogen current. A series of experiments thus performed showed that after more than 40 experiments the gel had shown no visible "tiring."

2. Acetone as diluting agent.

In a second series of experiments, acetone was used as extraction solvent instead of methanol. The results were in no way different from the ones cited above, despite the fact that the polarity of acetone is below that of methanol.

3. Heat of adsorption.

In order to gain a comprehensive view of how strongly the adsorption of the low molecular alcohols differs from that of the long chain alcohols, a calorimeter was built for the purpose of measuring the adsorption heats of the primary straight chain alcohols and possibly also those of other strongly polar substances. These experiments have just begun.

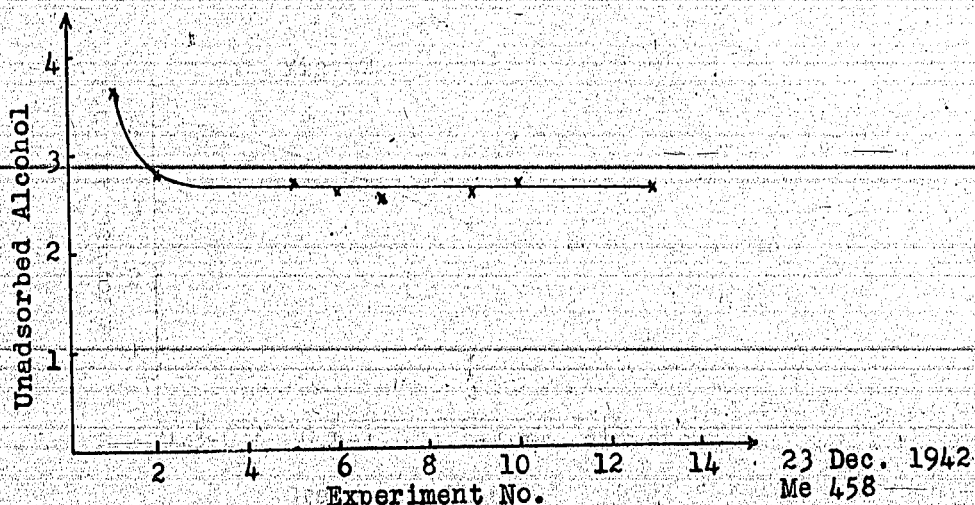
B) Semi plant scale experiments.

1. Loading of the silica gel

In order to determine the extent to which the gel may be loaded, experiments were carried out in the apparatus described in our report of 1 October; under otherwise constant conditions, the initial amount of product and the concentration of the product were varied. The results show that the capacity of the gel is independent of the amount and of the concentration of the product within the variable ranges selected for our tests.

Exp. No.	Amt. of product used	Adsorbed alcohol		% alcohol in the petroleum ether extract
		liters	% alcohol in the methanol extract	
9	(10 liters	2.58	101.6	44.1
13	57.3% alcohol (5 "	2.60	99.1	18.3
15	(4.5 "	2.47	96.8	11.4

Pure gel fresh from the factory usually shows the highest degree of adsorptive activity; after the first reactivation, this activity is somewhat reduced but assumes a constant value after the second or third reactivation.



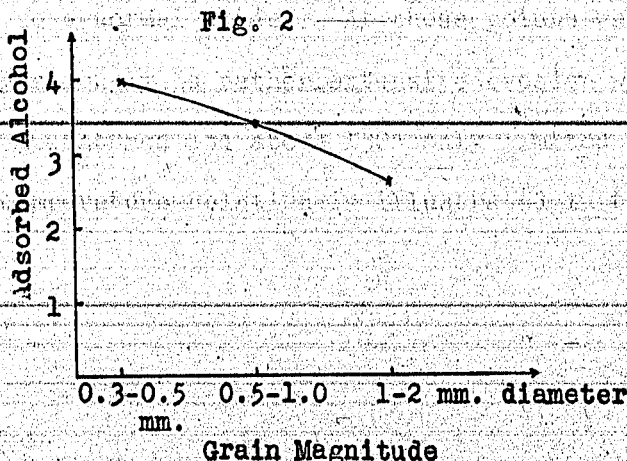
On the rate of adsorption

Experiments for the determination of the rate of adsorption have shown that the adsorption occurs with extraordinary rapidity, i.e. that it is instantaneous.

Loading capacity and grain size

The dependence of the maximum loading capacity is illustrated in Table 2 and Figure 2. From these data it appears that the adsorption takes place only on the surface and that the inner nucleus of the gel apparently does not contain capillaries.

Exp. No.	Grain magnitude of the gel	Amt. of product used (in liters)	Adsorbed alcohol (liters)	lit.alc. / lit.gel .100
6	1-2 mm	10	2.59	5.2
7	"	10	2.54	
9	"	10	2.58	
10	"	10	2.64	
13	"	5	2.60	
15	"	4.5	2.47	
19	0.3-1 mm (sic)	10	3.42	7.0
20	"	10	3.38	
21	"	10	3.57	
23	"	11	3.40	
24	"	10	3.68	
26	0.3-0.5 mm	11	4.10	8.1
27	"	11	4.00	



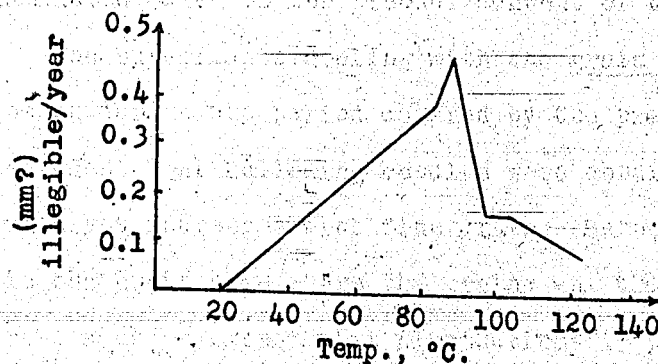
Experimental plant Me 458 (Dr. Breywisch)

Reactor 2 was used as our first larger-size reactor; after 182 days operation its contents were removed. Reactor 2 is a tubular reactor with 1400 tubes of 14 mm diameter. With a catalyst content of $1/2 \text{ m}^3$, the bed depth amounted to 2.30 m. After release, the gas was displaced by N_2 and then the catalyst was freed from the collected paraffin by treatment with $1 \cdot \text{m}^3$ of synthesis product (boiling between $140-200^\circ$). With the reactor temperature at $120-130^\circ$, the oil went through the tubes within approximately one half hour. After this treatment, the catalyst was found to be both free of paraffins and dry. The tubes had to be discharged by the same method used for the smaller tubular reactors in Me 776, i.e. they had to be drilled through. However, the removal was somewhat simpler in our case than was to be expected from previous observations in Me 776: two men did the work in 45 hours, which corresponds to 90 hours per m^3 of catalyst.

The corrosion tests mentioned in the previous report were concluded. Details of the findings and of the study of the materials are available. According to these, ordinary iron is attacked only to a normal extent. At those points where the product moves very strongly, a rather extensive erosion was observed.

At ordinary temperatures and above 130° only limited corrosion occurs. The temperature relation is illustrated in the graph below.

Relation Between Corrosion and Temperature



In order to avoid corrosion, the separation part of a 500 l tubular reactor was built in in such a manner that the product/gas mixture is introduced at 130° by immersion into a soda solution, which in turn is led into the cycle over the hot separator. Details may be gotten by looking at the enclosed sketch. The apparatus is almost completed and operations will begin in January. As far as the product processing is concerned, no particular difficulties or irregularities are expected with this method, because the synthesis products have to be neutralized anyway for the distillation which follows, and emulsions are not formed owing to the high alcohol content of the product water.

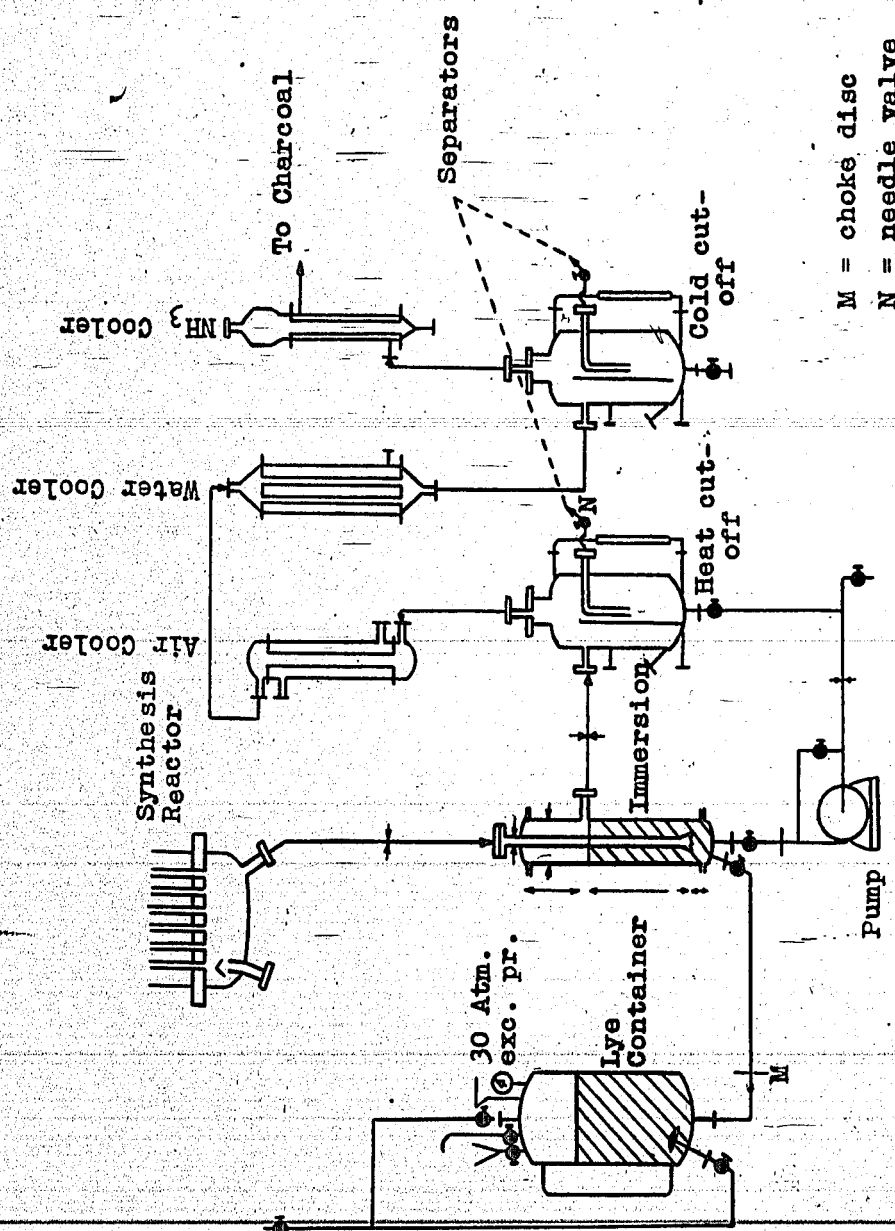
The de-esterification of the primary product before the distillation could be successfully accomplished in the 30 m³ still (which has a recycle arrangement) with a solution of NaOH in the product water. Owing to the solubility-increasing effect of the lower alcohols present, the de-esterification occurred more rapidly than usual. Upon rewashing with the product water, the emulsions

which so far had rendered impossible the washing out of the last remnants of alkali from the product containing the entire residue, were eliminated owing to the alcohol content of the product water.

The experiments dealing with the grain size of the catalyst, begun during the period covered by the previous report, have been concluded. The following results were obtained: the activity of the catalyst increases with fine grain. Here, the limiting factor is the grain size where the grains and the paraffins stick together to such an extent that fluctuations in the gas passage occur. Optimum results were obtained with a grain magnitude of 0.3-0.5 mm (as compared to 1-2 mm in the experiments carried out so far). At equal conversion rate (1:150), the synthesis can be made at a temperature level 10° lower than the usual (188° with 0.3-0.5 mm catalyst as compared to 198° with 1-2 mm catalyst on the twentieth day of operation). The ratio $\text{CO}_2:\text{H}_2\text{O}$ in the final gas shifts in favor of the water. Since the CO_2 must be washed out before the next synthesis stage as inert gas, a further advantage is thereby achieved. In Me 776, Dr. Geiseler has begun some experiments on larger scale.

Signed

/REISINGER/ /BREYWISCH/ /GEISELER/



M = choke disc
 N = needle valve

4 Jan. 1943
 Me 458

TOM Reel 55
 Bag 2523
 Doc. 87