

Table I

Summary of the 2nd Trial Run

| Reaction less sum | Input | Vol.% Olefin | Reaction Temp. C | Conditions | | Amount of Poly- Naphtha Prod. l. | % Polymerization |
|----------------------|---------------------|-----------------|---------------------|----------------------|-----------------------|--|-------------------------------------|
| | | | | Pressure atm.abs. | l.liquid prod./hr. | | |
| 145 | gasol | 35-48 | 190-200 | 60 | 13-15 | 770 | 90-95% |
| 175 | C ₅ -KC* | 75 | 110-150 | 60 | 13-15 | 110 | 90 |
| 227 | C ₄ -KC | 77-92 | 130 | 60 | 12-14 | 510 | 90 |
| 267 | C ₄ -KC | 80-90 | 110-120 | 60 | 12-14 | 300 | 85 |
| 311 | C ₅ -KC | 90 | 130-140 | 60 | 12-14 | 425 | 90 |
| 322 | C ₄ -KC | 92 | 110 | 60 | 14/2 | 40 | over-polymeriza- tion at 2 l/hr. |
| sum 322 | | | | | | 2,455 l. | |

Since 6.7 kg. = 8.4 l. of catalyst were put in, the efficiency of the catalyst equals 367 l. of poly-naphtha per kg. of catalyst. The space-time yield equals 9,100 l./m³ catalyst/hr.

* catalytically cracked.

The Texas Company

T O M REEL 55

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Item 68

Nr. 2291/0

Deutsche Gold -und Silber-
Scheideanstalt vormals Roessler
Dep.: Research

Frankfurt o/Main July 7, 1941
Lab.: Org. Dr. Bay./Schbg.

Topic: Laboratory Report Nr. 2291/0
3rd report:
Experiments with alkaliied Zinc-Chromium - catalysts
Effect of different amounts of alkalies.

Investigator: Dr. Bayer

Catchword: Synthesis of Methanol

S u m m a r y

The formation of higher alcohols using alkaliied Zinc-Chromium - catalysts was investigated. Catalyst "Kul" yielded ample quantities of 1-butanol. Catalyst "Stal / RB" gave some n-propanol besides 1-butanol. Catalyst "Stal / Kac" produced principally substances boiling above 110 deg. C.

1) General observations and remarks

In carrying out the synthesis of methanol it is desirable to maintain constant and relatively low temperatures as far as possible over the entire extent of the catalyst (so for instance the "optimum temperature" resulting from the isothermes) or to lower at least at the end the temperature so that only in the midst a "peak" is formed. In producing higher alcohols as by-products on alkalinized catalysts on the contrary it is desired to apply higher temperatures. Therefore care must be taken in the first case (in methanol synthesis) to lead off the reaction's heat by appropriate means (single or double pipes within the catalyst, or by placing the catalyst within pipes) and to lead it to gas having a lower temperature so that this cool gas is warmed up completely to the temperature of the entrance layer of the catalyst. In the second case the reaction's heat is left in the gas whereby the temperature rises from the point of entrance to the point of exit, in some type of exponential curve. Thus in this case means for transferring the heat of reaction from the catalyst to the entering fresh gases are omitted; a simple cylindrical reaction's chamber (Wallraum-Ofen) can be used herein. It has been

proved in the first report (2286/0) that the effect of methanol catalysts decreases with increasing temperatures (above the optimum temperature) thus obviously the yield of such a "non-cooled" reaction's space must be less than that of a "cooled" one. But on the other hand the higher alcohols are obtained in a better yield.

Such an "increasing temperature characteristic" could comparatively easily be produced in the "V 2 A" autoclave, which was used for the experiments. I have already pointed out that as a result of no preliminary heating of the gas, the first layers of catalyst are chilled. Temperature conditions can therefore widely be varied by adequately adjusting the quantity of the filling material and the speed of the gas. Unfortunately temperature can only be measured at the end of the catalyst layer; thus the conditions cannot be exactly tested. Therefore the tests have a rather preparative character, (i.e. examination of the products). If necessary, the experiments should be repeated in an autoclave better suited for these tests - having means for regulating gas pre-heating and for measuring the temperature all over the length of the catalyst.

Because the progress of temperature within the catalyst is uncertain, an exact calculation of the space velocity is impossible; it is unknown which portion of the catalyst is too cold to be able to participate in this reaction. Moreover the gas consumption cannot be calculated as easily as in the methanol synthesis because the gas consumption increases with a higher percentage of higher alcohols produced. So for instance the theoretical gas consumption for one kg is as follows:

| | | |
|----------|---|--------|
| Methanol | 2.1 m ³ NTP (standard temp.) | 100% |
| Ethanol | 2.92 " | 139% |
| Propanol | 3.36 " | 160% |
| Butanol | 3.64 " | 173.5% |

Generally however the percentage of higher alcohols is 10% at a maximum. So the error is not too important.

The space velocity has to be computed therefore by determining the methanol content from the specific gravity of the product obtained in the operation (thus disregarding the higher alcohols) and calculating the gas consumption for this quantity.

Products were tested as before for their content of free acid, combined acid, aldehyde and acetone.

Higher alcohols were determined by careful fractionation of the condensate from several experiments, by salting-out the alcohol-water mixture with NaCl and drying. Three ways for drying were available:

- 1.) the azeotropic distillation wherein the higher alcohols (C₄ and higher) themselves remove the water
- 2.) an azeotropic distillation by adding benzene, carbon-tetrachloride, etc.
- 3.) drying with K₂CO₃, CaO, etc.

None of these methods was absolutely satisfactory however. A drying process with caustic lime brought great waste because the content of water of the azeotropic mixtures is relatively high. The boiling points of the pure substances being here in question and of the azeotropic mixtures will be reported later.

2) Experiments with a catalyst, containing potassium bichromate ("Kal")
Preparation of the Catalyst:

326 g Zinc Oxide (same brand as before)
 73.5 g potassium bichromate

Both substances were mixed to a stiff paste by adding some water, the paste was dried, pulverized and shaped in a press (6 mm diameter).

Result of the analysis:

| | |
|--------|--------------------|
| 19.9 % | CrO ₃ |
| 76.1 % | ZnO |
| 2.3 % | K ₂ O |
| 98.3 % | (Balance moisture) |

Results of a series of experiments with 100 cc catalyst at 250 atm (atmospheres excess pressure) are reported in Table 1 and in Fir. 1:

Table 1
 Kal (100 cm); 250 atm

| Nr. "Kal" | Temp. | RG* | D ₄ ¹⁵ | g CH ₃ OH /h/lit | g CH ₃ OH /m ³ residual gas | g CH ₃ OH /h |
|-----------|-------|------|------------------------------|--------------------------------|---|----------------------------|
| 1 | 375 | 5525 | 0.8231 | 416 | 82.2 | 41.6 |
| 2 | 400 | 5165 | 0.8366 | 250 | 49.5 | 25 |
| 3 | 425 | 5040 | 0.8592 | 191 | 41.2 | 19.1 |
| 4 | 450 | 4880 | 0.8999 | 114 | 24.6 | 11.4 |

* Space velocity

Condensates of experiments 1-4 were combined and had a specific gravity of 0.8479⁵ (81.0% CH₃OH)

Free acid..... 0.03%

Combined acid..... 0.5%

Aldehyde..... 0.1%

Acetone..... 0.8%

A distillation of 106 ml gave the following figures:

B.P..... 53 deg. C.

up to 64 deg. C..... 4.5 ml

64-66 deg. C..... 67.0 ml

over 66 deg. / loss 34.5 ml

Fraction over 66 deg. C. was salted out with NaCl and dried with K₂CO₃. 7.2 ml of an oil strongly smelling of isobutanol was obtained. The total yield of alcohols is therefore about:

4.5 + 67 + 7.2 ml = 74.5% by volume (78.7 ml)

First runnings were repeatedly mixed with water and distilled again.

0.7 ml of the oil mentioned above were obtained (0.65% by volume).

Results of the gas analyses are not reported since methane remained within the limit of 3-5%.

The quantities obtained in the single experiments were unfortunately so small that it was not possible to work them up. In a further experiment the filling material of the catalyst was still increased in order to obtain authentically a strongly ascending characteristic temperature curve. Here the alkali-free zinc chromium catalyst (already described previously) --"Stal"-- was filled in at the cold side and then only the alkali-containing catalyst "Kal", in an amount of 70 cc³ each. The results of experiments with this catalyst are reported in Table 2 and Figure 2.

Table 2
70 cm³ Stal / 70 cm³ Kal; 250 atm

| Nr. "Kal" | Temp. | RG | D ₄ ¹⁵ | g CH ₃ OH /h | g CH ₃ OH /n/lit | g CH ₃ OH /m ³ |
|-----------|-------|------|------------------------------|-------------------------|-----------------------------|--------------------------------------|
| 5 | 375 | 3900 | 0.8140 | 49.6 | 356 | 112 |
| 6 | 375 | 7500 | 0.8101 | 82.5 | 590 | 93 |
| 7 | 400 | 3330 | 0.8190 | 35.0 | 250 | 91.5 |
| 8 | 400 | 7750 | 0.8240 | 56.4 | 402 | 58.5 |
| 9 | 425 | 7500 | 0.8480 | 35.1 | 250 | 36.3 |

Figures interpolated for RG = 5000 are in good agreement with the figures of Table 1 and Figure 1 (for "Kal" without addition) in the order of magnitude. Methane content remained within the limits 2.5-3.8%, while CO₂ increased, however, up to 6%. Therefore it can be assumed that a minor reaction

CO / H₂O --- CO₂ / H₂ occurs at the cost of H₂O resulting from formation of higher alcohols.

An investigation of the combined condensates had the following results:

| | | |
|------------------------------------|--------|---------------------------------------|
| D ₄ ¹⁵ | 0.8248 | (according to the Table 89.6% by wt.) |
| Free acid..... | 0.1% | |
| Combined acid..... | 0.6% | |
| Aldehydes..... | 0.2% | |
| Acetones..... | 0.5% | |

In fractionating 355 ml the result was:

| | |
|---------------------|---------|
| 64-66 deg. C.... | 280 ml |
| 66-74 deg. C.... | 3.5 ml |
| water / higher alc. | 71.5 ml |

By salting out and drying 30 ml higher alcohols were obtained (8.5% of the volume of the raw material). After adding 25 ml carbon-tetrachloride the following figures resulted:

BP. 62 deg.C.
Up to 77 deg.C. 28 ml, 2 ml of them water
77-88 deg.C. 1 ml
88-104 deg.C. 0.5 ml
104-112 deg.C. 16.5 ml (isobutyl-fraction)
over 112 deg.C. 9.5 ml (higher than C₄)

The total quantity of alcohols amounted to:
 $280 + 16.5 + 9.5 = 297$ ml = 83.7% by vol.; isobutyl-fraction
4.6% by vol., the higher fraction 2.7% by vol.; together therefore
7.3% by vol. of the raw material.

In order to investigate more thoroughly the connection between
temperature and composition of the products some experiments were
carried out over a longer duration. Filling of the catalyst tube
remained unchanged. Detailed description might be too long, thus
only the principal data will be reported.

Experiment Kal 10

Experimental conditions: 400 deg. C. Velocity: about 1000 Lit./h
measured on the gasometer after expansion ("Rota" - meter 125 mm)

Condensate: 10 $\frac{1}{2}$ hours production 890.5 ml corresponding to 85 ml in
an hour average. (Minimum value: 75.5 ml; maximum value: 93.5 ml).
Fluctuations show no downward trend (corresponding to decreased ac-
tivity) but are connected with fluctuations in temperature and varia-
tions of the gas velocity.

Properties of the Condensate:

D₄¹⁵ 0.8215 (correspond. about
91% CH₃OH)
Free acid 0.09%
Combined acid 0.5%
Aldehyde 0.2%
Acetone 0.3%

In fractionating 830 ml the result was:
64-66 deg. C. 660 ml (?)
furthermore 78 9.4% by volume "Isobutyl oils" + 92 ml water. The
78 ml "Isobutyl oils" were worked up by adding 50 ml CCl₄. This
quantity was insufficient as appeared later on. The intermediate
fraction up to 100 deg. C. still disengaged some water and had to be
transferred back to the flask several times after separating the water.
The following figures were found:

fraction 100-112 deg. 50.5 ml (isobutyl)
over 112 deg. 13.5 ml (higher than C₄)

Total output of alcohols was:

| | | |
|---------------------------|-----------|-------------------------------|
| 64-66 deg. | 660 ml = | 79.5% by vol. (methanol) |
| 100-112 deg. ... | 50.5 ml = | 6.1% by vol. (isobutanol) |
| over 112 deg. .. | 13.5 ml = | 1.6% by vol. (higher than C4) |
| | Total.... | 87.2% by vol. |
| Plus water ab. 100 ml.... | | 12.1% by vol. |
| | Loss..... | 99.3% by vol. |
| | | 0.7% by vol. |

The portion containing C4 and higher was therefore 6.1 + 1.6 = 7.7% by vol. or 6.55 ml/h.

Ratio C4 to higher products is 3.8.

Experiment 11a

Experimental conditions: 425 deg. Velocity about 1500-1600 lit/h (200 mm Rotameter)

Condensate: in 5 hours 460.5 ml, corresponding to 92.1 ml/h average (minimum value 90.0 ml/h, maximum value 94.5 ml/h)

Properties:

| | |
|------------------------------------|---------------------------|
| D ₄ ¹⁵ | 0.8333 (correspond. |
| | 86.5% CH ₃ OH) |
| Free acid..... | 0.06% |
| Combined acid.... | 0.4% |
| Aldehydes..... | 0.2% |
| Acetones..... | 0.6% |

By fractionating 450 ml the result was:

| | |
|--------------------|--------|
| 64-66 deg. C. | 340 ml |
| 66-82 deg. C. | 1 ml |

Furthermore: 41.5 ml "Isobutyl oils" (9.2% by vol.) and about 58 ml water.

Isobutyl oils were mixed with 50 ml CCl₄, whereby still some water separated out. Result of the distillation:

| | |
|-----------------------|---------------------------|
| B.P. | 57.5 deg. C. |
| up to 78 deg. C. | 55 ml, 3 ml of them water |
| 78-90 deg. C. | 3 ml |
| 90-100 deg. C. | traces |
| 100-110 deg. C. | 21 ml isobutanol |
| over 110 deg. C. | 8.5 ml (over C4) |

Output of isobutanol is 4.7% by vol., of alcohols over C4: 1.9% by vol., therefore together 6.6% by vol. or 3.15 ml/h.
Ratio C4: higher products (than C4) is 2.5.

Experiment Kal 12

Experimental conditions: 450 deg., Velocity about 1900-2100 lit/h.
(Rota 260mm)

Condensate: In 5 hours 404.5 ml corresponding to 80.9 ml/h average.
(Minimum value 75 ml, maximum value 90.5 ml)

Properties:

| | | |
|------------------------------------|--------|--|
| D ₄ ¹⁵ | 0.8522 | (corresponding to 79.3% CH ₃ OH) |
| Free acid..... | 0.1% | |
| Combined acid..... | 0.5% | |
| Aldehyde..... | 0.2% | |
| Acetone..... | 0.9% | |

The result of fractionating 400 ml was:
 64-66 deg. C. 281.5 ml
 furthermore 38.5 ml isobutyl oils (9.6% by vol.) and about 71 ml water.
 Isobutyl oils were mixed with 50 ml CCl₄ and fractionated.
 B.P. 57 deg.C.
 up to 78 deg.C. 56 ml, 3 ml of them water
 78-82 deg.C. 4.5 ml (?)
 82-100 deg.C. 3 ml (?)
 100-110 deg.C. 17.5 ml (isobutanol)
 over 110 deg.C. 10 ml (higher than C₄)

Output on isobutanol is 4.4% by vol., on alcohols over C₄ 2.5% by vol., together therefore 6.9% by vol. or 5.58 ml/h. Ratio C₄ to "higher than C₄": 1.76.

These experiments are represented in Figure 3 and show unequivocally that at increased temperatures the amount of fractions over C₄ increases relatively to the fractions of C₄. That is not desirable. In opposition to the opinion generally found in literature references it is suggested to work also in these cases at a not too high temperature.

Under the same conditions as in Exp. Kal 11 an experiment of longer duration - 2 days - was carried out. The following result was obtained:

| | |
|--------------------|--------|
| Spec. Gravity..... | 0.8330 |
| Free acid..... | 0.04% |
| Combined acid..... | 0.4% |
| Aldehydes..... | 0.3% |
| Acetone..... | 0.1% |

4250 ml = 3540 g of the raw material were subjected to distillation.
 Boiling started already below 30 deg. C.: In the beginning heavy vapors developed which could not be condensed (methylated ether?).
 Up to 64 deg. C. 50 ml (D₄¹⁵ = 0.787) followed. This first running

smelled aldehyde-like. An aldehyde-content of about 1.6% by vol. (calculated as acetaldehyde) was determined by the hydroxylamine reaction. By diluting with water and distilling (boiling point at the start: 31 deg.C.) and by several times repeating this operation altogether 5.7 ml "oils" were separated. Furthermore now 35 ml distilled over at 64-66 deg. C. (pure methanol). Loss in these operations was therefore 9.3 ml.

The main fraction 64-66 deg. C., to which the quantities obtained in repeated distillations of the last runnings amounted to 3173 ml = 74.6% by vol. By adding to this sum the quantity obtained from the first runnings the total output was 3206.5 ml = 75.5% by vol. thus exactly the same as in Exp. 11a.

Remaining intermediate fractions were:

| | | |
|------------------|---------|--|
| 61-70 deg.C..... | 1 ml | |
| 70-74 deg.C..... | 28.5 ml | (D=0.8155) |
| 74-79 deg.C..... | 8 ml | |
| 80-84 deg.C..... | 12.5 ml | (D=0.8460) (Isopropyl water) azeotrope ? |
| Total | 50.0 ml | (about 1% by vol.) |
| | | (denoted as "intermediate fraction") |

407 ml "isobutyl oils" and 350 ml water remained as residue.

All together 4075 ml were recovered. The relatively big loss of 175 ml = 4.1% by vol. can partly be explained by the non-condensed portions, and partly simply by the fact that the Raschig - rings of the distilling column apparatus were first dried out while they remained at the end of the operation a certain amount of liquid.

358.5 ml of the Isobutyl oils were distilled without adding any other substance by using the isobutanol itself for the purpose of azeotropic dehydration with the following result:

| | | |
|-----------------|------------|---|
| B.P..... | 74 deg. C. | Probable Content |
| 74-79 deg..... | 0 ml | |
| 79-84 deg..... | 1 ml | (Isopropanol-water azeotrope and isopropanol) |
| 84-88 deg..... | 35 ml | (n- propanol-water azeotrope and propyl ?) |
| 88-102 deg..... | 24.5 ml | (isobutanol-water azeotrope) |
| further..... | 3.0 ml | water |

Residue (C₃ and higher); 285 ml (D₄¹⁵ = 0.8138)

This would correspond to 324 ml = 7.6% by vol. C₃ and higher when calculated on the whole amount. C₄ (isobutanol) was not separated here because the major part of the resulting product was obtained in this form.

In working up the fraction 64-66 deg. additional small quantities of oil settled out. Altogether about 31 ml = 0.7% by vol. of raw methanol were obtained; 21 ml of them were fractionated.

Boiling started at 51.2 deg.

| | |
|-----------------------|------------------------|
| 2 ml.... 56.0 deg. C. | 12 ml.... 68.8 deg. C. |
| 4 ml.... 58.2 | 14 ml.... 76.0 |
| 6 ml.... 59.5 | 16 ml.... 81.6 |
| 8 ml.... 63.0 | 18 ml.... 99.5 |
| 10 ml.... 67.0 | 19 ml.... 102.0 |

The residue over 102 deg. had a hydrocarbon-like smell. The density of the product was determined on another sample (collected from different experiments) with 0.7747.

The combined fractions up to 102 deg. C. (D = 0.8258) contained aldehydes. After removing them by a bisulfite-treatment a mixture resulted smelling from hydrocarbons the same.

Regarding the presence of C-3-alcohols (n-propanol and isopropanol) there is a possibility that fraction 80-84 deg. (12.5 ml = 0.3% by vol.) of the intermediate fractions might contain the azeotropic mixture isopropanol-water (80.4) respect. isopropanol (82.4 deg.). The fraction obtained by distilling isobutyl oils boiling at 84-88 deg. (35 ml = 0.8% by vol.) might contain the azeotropic mixture n-propanol-water (87.7 deg.); it smelled, however, definitely like isobutanol, although the azeotropic mixture of this alcohol with water is known to boil only at 89.8 deg. But ethanol is only perceptible in traces (very slightly positive Iodoform test).

It would be desirable to start experiments, giving a greater quantity of material.

3) Experiments with a catalyst, containing potassium ferricyanide (Stal 7 RB)

The catalyst which differed from catalyst "Stal" by addition of $K_3Fe(CN)_6$ only was prepared:

- 326 g ZnO
- 76 g Cr_2O_3
- 62.5 g CrO_3
- 30 g $K_3Fe(CN)_6$

Results are reported in Table-3.

Table 3
100 com Stal 7 RB; 250 atm

| Exp. Nr. Stal 7 RB | Temp. | RG | D_{74}^{15} | g CH_3OH /h | g CH_3OH /h/lit | g CH_3OH/m^3 |
|-----------------------|-------|-------|---------------|------------------|----------------------|----------------|
| 1 | 375 | 5770 | 0.8568 | 36.2 | 362 | 72.2 |
| 2 | 375 | 9910 | 0.8424 | 29.0 | 290 | 31.2 |
| 3 | 400 | 10300 | 0.8610 | 32.7 | 327 | 34 |
| 4 | 425 | 8980 | 0.8788 | 30.0 | 300 | 36 |
| 5 | 425 | 14410 | 0.8550 | 36.1 | 361 | 26.5 |

The products obtained were worked up with those of Exp. 6 in the first layer of 70 cc Stal and adjoining a 70 ccm Stal / RB were used.

In six hours during test at 425 deg., gas velocity about 1500 lit/h (Rota 180-200 mm) a quantity of 309.5 ml condensate altogether was obtained; this averages 51.6 ml/h.

Properties of the condensate:

Density..... 0.8601
Free acid..... 0.1%
Combined acid... 0.7%
Aldehyde..... 0.3%
Acetone..... 0.6%

In fractionating 514 ml, resulting from experiments 1-6, the following quantities were obtained:

64-66 deg..... 329 ml
66-70 deg..... 2.5 ml
70-80 deg..... 11.5 ml
60.0 ml oil
Residue 90.0 water
 493.0 ml
(Loss 21.0 ml)

The oils were first distilled without drying them and without adding CCl_4 . In this case, however, a great quantity of a fraction 77-88 deg. C. was obtained (38 ml, having a $D_{4}^{15} = 0.8702$), which obviously contained the azeotropic mixture n-propanol-water ($D = 0.880$). This fraction which could not be dehydrated as intended first was dried later on with K_2CO_3 and distilled again. Altogether the quantities obtained were:

up to 80 deg. C..... 4.0 ml
80-85 deg. C..... 3.2 ml (isopropanol)
85-90 deg. C..... 1.7 ml
90-95 deg. C..... 0.5 ml
95-100 deg. C..... 11.0 ml (n-propanol)
100-110 deg. C..... 9.5 ml (iso-butanol)
over 110 deg. C..... 23.0 ml
 42.9 ml

Fraction 80-85 deg. C. is probably isopropanol (0.6% by vol.) fraction 95-100 consists of n-propanol (2.1% by vol.), fraction 100-110 of isobutanol (1.85% by vol.), the remainder higher than C_4 (4.5% by vol.). Ratio C_3 / C_4 to "higher than C_4 " is: $(0.6 + 2.1 + 1.85) : 4.5 = \text{approx. } 1$, thus rather unsatisfactory.

The experiment was repeated (Exp. 7 and Exp. 8). The condensate showed the following properties:

Density..... 0.8517
 Free acid..... 0.09%
 Combined acid... 0.6%
 Aldehydes..... 0.3%
 Acetone..... 0.4%

Fractionate distillation of 1160 ml gave the following results:

up to 64 deg. C.... 24.5 ml
 64-66 deg. C..... 771.0 ml

Furthermore after salting-out and drying with K_2CO_3 : 88 ml "isobutyl oils" (7.6% by vol.).

By fractionating the oil (boiling started at 71 deg. C.) the following results were obtained:

| | Possible Constituents |
|------------------------------|--|
| up to 79 deg. C..... 6.0 ml | ethanol-water; ethanol iodoform-test slightly positive |
| 79-85 deg. C..... 3.0 ml | Isopropanol-water azeotr. 80.4 deg. |
| 85-91 deg. C..... 2.0 ml | Isopropanol 82.4 |
| 91-94 deg. C..... | n-Propanol-water azeotr. 87.7 |
| 94-102 deg. C..... 15.0 ml | isobutanol-water 89.8 |
| 100-105 deg. C..... 3.0 ml | n-butanol-water 92.3 |
| 105-110 deg. C..... 10.5 ml | n-propanol 97.0 |
| over 110 deg. C..... 43.0 ml | isobutanol 108.0 |
| | higher than C_4 |

The fraction, containing isopropanol, has still decreased (0.26 % by vol.), the fraction n-propanol amounts to 1.3% by vol., the fraction isobutanol to 0.9% by vol. while the fraction "higher than C_4 " is 3.7% by vol.

The experiment should be repeated at lower temperatures. However, it has to be considered as an interesting fact that this catalyst produces by far more n-propanol than the catalyst "KAl".

4) Experiments with a potassium acetate containing zinc-chromium catalyst: (Stal / Kac)

This catalyst was prepared according to the following formula:

326 g ZnO
 76 g Cr_2O_3
 62.5 g CrO_3

49 g acetate of potassium
 (Analysis: 67.4% ZnO, 3.7% CrO_3 , 17.8% Cr_2O_3 , 3.6% H_2O , balance acetic acid / water)

Results are reported in Table 4.

Table 4
100 ccm Stal / Kac; 250 atm

| Exp.Nr. Stal / Kac | Temp. | RG | D ₄ ¹⁵ | g CH ₃ OH /h | g CH ₃ OH /h/lit | g CH ₃ OH/m ³ |
|-----------------------|-------|------|------------------------------|----------------------------|--------------------------------|-------------------------------------|
| 1 | 375 | 5000 | 0.8860 | 13.8 | 138 | 29.5 |
| 2 | 400 | 5220 | 0.8508 | 19.0 | 190 | 39.5 |
| 3 | 400 | 9000 | 0.8549 | 19.3 | 193 | 22.5 |
| 4 | 425 | 5335 | 0.8670 | 18.35 | 183.5 | 38.5 |
| 5 | 450 | 4060 | 0.8810 | 15.4 | 154 | 41 |

By comparing these values with those of the catalyst Stal / RB (from which it differs only by the use of another acid) the figures related above are throughout lower as is shown in Table 5. This table gives a comparison of the following values (for approx. RG = 5000).

Table 5
RG approx. 5000; 250 atm

| g/h/lit at deg.C. | (for 100 ccm catalyst each) | |
|----------------------|-----------------------------|------------|
| | Stal / RB | Stal / Kac |
| 375 | 362 | 138 |
| 400 | 327 | 190 |
| 425 | 220 | 183.5 |
| | (interpolated) | |

Analysis of the combined condensates resulting from experiments 1-5 showed the following figures:

| | |
|------------------|--------|
| Density..... | 0.8678 |
| Free acid..... | 0.4% |
| Combined acid... | 0.3% |
| Aldehyde..... | 0.2% |
| Acetone..... | 0.4% |

Analysis by fractionated distillation did not yield a useful result because of the small quantities of the condensate. Only 32.5 ml oil remained (from 102 ml initial material) which still contained methanol. It should be mentioned that the residue in the flask solidified to a salve-like mass. The odor was plainly different from that observed in other experiments. (Ketones ?)

Also a series of experiments using in the first layer 70 ccm Stal and 70 ccm Stal / Kac brought not very interesting results. But

also in these cases the relatively high content of combined acid remained remarkable (1.5%).

In an experiment of longer duration (N deg. 12) at 400 deg. and approx. 1000 lit/h gas velocity, where the same arrangement of catalysts as mentioned just here above was used, the production of condensate was 595.5 ml in 11 hours thus average 54 ml/hour.

Properties:

| | |
|------------------------------------|--------|
| D ₄ ¹⁵ | 0.8323 |
| Free acid..... | 0.2% |
| Combined acid..... | 0.9% |
| Aldehyde..... | 0.3% |
| Acetone..... | 0.9% |

Fractionated distillation of 600 ml had the following result:

| | |
|------------------|---------------|
| 64-66 deg..... | 460 ml |
| 66-74 deg..... | 2.5 ml |
| over 74 deg..... | 54.0 ml oil |
| | 83.5 ml water |
| | 600.0 ml |

These 54 ml oil were worked up together with 16 ml coming from the experiment mentioned above (translator's note: not specified, probably the 32.5 ml oil mentioned in the lower part of the previous page). After drying with K₂CO₃, 58.0 ml remained. Fractionation gave the following figures:

| | |
|-------------------|---------------------------------|
| 72-82 deg..... | 1.3 ml |
| 82-88 deg..... | 3.5 ml |
| 88-104 deg..... | 3.0 ml |
| 104-112 deg..... | 13.0 ml (isobutanol) |
| 112-150 deg..... | 4.0 ml |
| over 150 deg..... | 32.7 ml (partially solidifying) |

The ratio of "higher than C₄" (32.7 / 4 = 8.175 ml) to C₄ (13 ml) is very unfavorable despite the relatively low temperature. Thus this catalyst is not very interesting.

In working with these three catalysts the CH₄-formation was so unimportant in all the experiments that the content on CH₄ rose only occasionally over 3% in spite of the working method by circulation (in cycles).

According to different references a gas mixture in the ratio CO : H₂ = 1:1 is said to be essential for forming higher alcohols, whereby half of the quantity of CO is converted into CO₂ using the water formed in the reaction. Regarding the relatively small percentage of higher alcohols - approximately 10% by vol. - obtained in these experiments formation of CO₂ did not occur and there was no difficulty in working with the usual gas mixture: one CO : two H₂.

(signature)

BAYER

The Texas Company

T O M REEL 55

Bag 2523

Item 69

Not to leave the research laboratory without permission of the laboratory director.

Problem: 813

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

Investigators: Gemassmer, Berg, Meusel

Status on December 1, 1943

Product Studies: (Gemassmer, Berg)

Oxo-Treatment of Coal Distillation Products from Blechhammer.

On the request of Dr. Wenzel three different coal distillation fractions were delivered to us by Blechhammer. These fractions were registered as samples OHW I, II and III. Samples I and II were clear, brown colored liquids, while sample III was a blackish brown fraction boiling above 200 deg. C. and with a density higher than 1.00. Samples I and II were Oxo-treated and hydrogenated without any pretreatment. The results are summarized in Table A.

Oxo-Treatment of Coal Carbonization Tar. (Blechhammer)

One can see from the figures that the content of materials which are subject to Oxo-treatment has the same order of magnitude with these carbonization products as is the case with the distillation products obtained from bituminous coal. One may expect that the same viewpoints can be developed for the technical treatment as with the bituminous coal carbonization oil.

Oxo-Treatment of Fractions from Hungarian Cracked Gasoil.

In order to obtain a better knowledge of the distribution of olefins in petroleum cracking products, part of the Hungarian cracking gasoil (Apollo, Preszburg) was fractionated and the individual fractions were investigated and Oxo-treated. The results of these investigations are given in Table B.

Oxo-Treatment of Fractions from Hungarian Cracked Gasoil.

The percentages in the one but last column in Table B give the distribution of the individual alcohols in terms of the maximum total alcohol content obtainable by Oxo-treatment. It is shown that also with the petroleum cracked products the content of short chain alcohols of the solvent range is disproportionately large with respect to the specially estimated alcohols from C₁₅ on.

Oxo-Treatment of SO₂ Refined Hungarian Cracked Gas Oil.

Hungarian cracked gas oil from the Apollo refinery in Pressburg (see also work reports of August first and October first, 1943) was refined by Dr. Rennhak with liquid SO₂ under varying conditions. The refined products were Oxo-treated by us. The results obtained this way are given in Table C.

Oxo-Treatment of SO₂ Raffinates.

One can see from the data given in Table C that the SO₂ refining removes also substantial amounts of the olefins that can be Oxo-treated and is not limited to removing aromatics.

Crude Tar from the Alkylation Plant at Leuna.

The investigations were continued and brought to completion within the report period. The neutral components were separated by neutralization and extraction with pentane and were then distilled and tested. About 10% of the crude tar consists of acidic components, the sodium salts of which form a water-soluble, foaming, brown powder. A sample of these sodium salts was handed to Dr. Richter for further testing.

The composition of the neutral fraction is given in Table D.

Since the product formed changed on standing with respect to composition, the table gives the averages of several tests. The iodine number was difficult to determine and therefore is not reliable. The residue was a black brittle resinous mass and was handed to Dr. van der Horst for further investigation. The fractions of the neutral material extracted from the acidic tar are hardly affected by an Oxo-treatment.

The Oxo-treatment of the undistilled neutral extract also yields products with low OH-number. The reaction product, however, has a lighter color and is clearer (red brown and free of turbidity) and possesses a higher viscosity. ~~Since the Oxo-reaction product, just as the neutral extract before treatment, has drying properties, both materials were handed to Dr. van der Horst.~~

After Hydrogenation of Oxo-Products.

The investigation of an after-hydrogenation of aldehyde containing Oxo-reaction products was continued. The best after-hydrogenation contact catalyst up to the present was found to be catalyst 3076. Taking into account the plans for the after-hydrogenation stage of the Oxo-plant Me 458a, where steam heating will be used, tests were run for determining if a hydrogen treatment at a higher temperature (400 deg. C.) is required for the activity of catalyst 3076. It was shown that such a pretreatment has no influence on the activity of the catalyst so far as hydrogenating aldehydes is concerned. Thus, one can place catalyst 3076 in the hydrogenation reactor without any pretreatment and start operating at the lower reaction temperatures of 150-220-deg. C.

Determination of Optimum Charge Velocity in Ka 1a in Me 333a.

After the first preliminary tests were run with an hourly space velocity of 1, then it was investigated how much the charge velocity can be increased while still retaining a practically complete hydrogenation. With the available apparatus it was possible to pass 65 liters of aldehyde containing Oxo-treatment products per hour through a 11 liter catalyst space. With this charge velocity the electric preheaters of the apparatus were insufficient. Thus, one might assume that otherwise the charge velocity could have been increased further.

An hourly space velocity of 5 was assumed for the layout of the after-hydrogenation chamber in Me 458a according to the above runs. Since the after-hydrogenation chamber in Me 458a must serve also with sulfur-containing materials, analogous runs were done in Me 333a with low temperature carbonization oils. Fundamentally identical results were obtained with the sulfur-containing materials.

Status of the Construction of the Oxo-Plant Me 458a.

The mounting of the Oxo-plant has been practically nearing completion during the report period. The high pressure section with injection pumps and the sediment elimination stage could be taken over by the production department. As some packing boxes of the high pressure section were not tight because of faulty construction, annoying delays resulted. It was still possible in this report period to make a run with pure oil under nitrogen pressure in the high pressure section. The initial difficulties with pumps and sedimentation valves caused by dirt present in the tubing and the chambers could be overcome. Everything was arranged for putting the plant in operation with mash as soon as possible.

For putting the plant in operation it is planned to use dehydrated neutral extract from the ester oil - and carboxylic acid plant. Three tank cars of this material have been put in reserve.

Preparation of Oxo-Aldehydes free from Cobalt Carbonyl Compounds.
(Meusel)

Dr. Ballaus found that cobalt carbonyl, which is dissolved in crude Oxo-aldehydes can be efficiently decomposed by heating with carbon dioxide. Probably because of a mix-up of samples on the way to the analytical department, doubt was expressed as to the validity of these observations. Dr. Ballaus decided to charge me with repeating these experiments.

I found that crude Oxo-aldehyde contains about 2500 mg. cobalt dissolved per liter, while the cobalt content decreased to at the most 100 mg. per liter after treating half an hour with 25 atm. carbon dioxide at 170 deg. C., the aldehyde content remaining unchanged. Therefore, the observation of Dr. Ballaus is confirmed. Further runs on the effect of carbon dioxide treatments are in progress.

Oxo-Treatment of Coal Carbonization Tar (Blechhammer)

| Sample | Boiling Point Ranges | D ₂₀ ⁴ | CO No. | OH No. | I No. | S.P.L. | Crude Oxo-Treatment Product % | Oxo-Treatment Product OH No. | % Oxo-Treated Calculated from Characteristic Nos. |
|---------|----------------------|------------------------------|--------|--------|-------|---------------------|-------------------------------|------------------------------|---|
| OHW I | 90-170 | 0.807 | 15.6 | 7 | 92 | 86 | 0.849 | 98 | 22% |
| OHW II | 110-210 | 0.814 | 30 | 63 | 78 | 82 | 0.859 | 162 | 30% |
| OHW III | 200-400 | 1.03 | | | | Not studied further | | | |

Oxo-Treatment of Fractions from Hungarian Cracked Cassil

| Boiling Point Range | Number of C-Atoms of the Olefins | Weight % of the Untreated Oil | % Alcohol after Oxo-Treatment | % Alcohols of Given Number of C-Atoms in terms of Total Alcohol | Total Alcohol Obtained by Oxo-Treatment | Number of C-Atoms of the Alcohols |
|---------------------|----------------------------------|-------------------------------|-------------------------------|---|---|-----------------------------------|
| 160-180 | 10-11 | 26.5% | 35% | 40.5% | } 23% | 11-12 |
| 180-220 | 12-13 | 38% | 23.5% | 39% | | 13-14 |
| 220-260 | 14-15 | 17.5% | 11% | 8.5% | | 15-16 |
| 260-290 | 15-16 | 22% | 10% | 9.6% | | 16-17 |
| 290-310 | 17-18 | 6.0% | 9% | 2.4% | | 18-19 |
| | | 100% | | 100% | | |

Table C.

| Sample Reference | SO ₂ % SO ₂ | SO ₂ Raffinate Temp. | Oxo-Treatments of SO ₂ Raffinates | | | | Crude, Oxo-Treatment, Product | % Oxo-Treated Calculated in terms of Untreated Oil | % Oxo-Treated Calculated in terms of Crude Yield | |
|--------------------------------|-----------------------------------|---------------------------------|--|-------------------|--------|-------------|-------------------------------|--|--|------|
| | | | Characteristic Numbers of the Untreated Oil | D ₂₀ 4 | S.P.L. | I. No. Haus | | | | |
| E.U. I 10 | 50% | -30 | 0.813 | 41 | 53 | 0.830 | 0.0 | 48 | 18.5 | 14.5 |
| E.U. I 60 | 50% | -30 | 0.803 | 33 | 46 | 0.815 | 0.0 | 35 | 14.0 | 11.5 |
| E.U. II 10 | 50% | -50 | 0.820 | 40 | 48 | 0.825 | 0.0 | 46 | 17.5 | 15.5 |
| E.U. II 60 | 500% | -50 | 0.803 | 35 | 48 | 0.813 | 0.0 | 35 | 14 | 11.5 |
| Hungarian Cracked Cassil Crude | - | - | 0.835 | 49.5 | 55 | 0.847 | 0.0 | 50 | 19.2 | 19.2 |

Table D.

| Fraction Deg.C. | Weight % | Characteristic Numbers of the Raw Material | | | | | | | | | | Crude Oxo-Treatment Yield | | | | | |
|------------------------------------|----------|--|--------|----------|-----------|------------|------|-------|--------|--------|----------|---------------------------|------------|--|--|--|--|
| | | OH No. | CO No. | Acid No. | Sapn. No. | Iodine No. | S | d | OH No. | CO No. | Acid No. | Sapn. No. | Iodine No. | | | | |
| below 200 and with intense cooling | 10 | 0.803 | 5 | 0 | 1.2 | 5 | 93.7 | 0.854 | 12.2 | 0.66 | 0.82 | 6 | 68.7 | | | | |
| 200-250 | 10 | 0.85 | 4 | 0 | 0.8 | 3.3 | 61.7 | 0.854 | 12.2 | 0.66 | 0.82 | 6 | 68.7 | | | | |
| 250-300 | 15 | 0.87 | 3 | 0 | 0.8 | 3.8 | 60 | 0.877 | 20 | 1.5 | - | 9.2 | 28.7 | | | | |
| 300-end point residue | 35 | 0.885 | 4 | 0 | 0.8 | 3 | 63.3 | 0.896 | 29 | 0 | - | 8.5 | | | | | |

The Texas Company
Item 8

TECHNICAL OIL MISSION; REEL 55,
BAG 2523, DOCUMENT 70

Project: 813

Problem: Reaction of CO and H₂ on Olefins (Oxo-Reaction).

Investigators: Gemassmer, Berg, Ballaus

Status on October 1, 1943.

I. Product Studies (Gemassmer, Berg)

Oxo-Treatment of Carbonization Gasoline from Brux and Deuben.

Attempts were continued to introduce the Oxo-treatment as a refining process for the manufacture of high grade gasoline from carbonization gasolines. Larger quantities of carbonization gasoline were now available for the experiments. The gasoline was cut in three fractions in order to facilitate the separation of the Oxo-alcohols by distillation. The Oxo-treatment was carried out as a batch process (autoclave) in Me 458a. Even with the Oxo-treatment and the hydrogenation on a large scale it was not possible to hydrogenate completely these sulfur-rich materials.

The gasoline separated by distillation still showed appreciable carbonyl numbers, which can be traced partly to Oxo-aldehydes, which were not hydrogenated, and partly to ketones already present in the raw material. Ketones are more difficultly removed by hydrogenation than aldehydes.

The observation frequently made with sulfur-containing materials was again confirmed that sulfur-containing compounds are not affected by an Oxo-treatment and, thus, sulfur is concentrated in the first fraction primarily.

The gasoline was handed (after elimination of Oxo-alcohols) to Dr. Welz for further treating and testing.

Other Oxo-reaction products from carbonization gasolines were subjected to a secondary hydrogenation over the sulfide contact catalyst 3076 before separating the Oxo-alcohols by distillation. This was done in order to eliminate aldehydes and to separate the Oxo-alcohols from the gasoline by distillation. The gasoline samples obtained by secondary hydrogenation of Oxo-reaction products were also handed to Dr. Welz.

Production of Oxo-Alcohols from Primary Olefins.

The experiments on the formation of Oxo-alcohols from olefins were completed. The separation of these Oxo-alcohols by distillation could be carried out conveniently with the laboratory columns. Only the alcohols with higher molecular weights ($C_{18}-C_{20}$) could not be separated in this way. The alcohols with higher molecular weights could also only be concentrated in the laboratory columns.

Oxo-Treatment of Hungarian Cracked Gas Oils.

Experiments were continued on the Oxo-treatment of narrower cuts of the Hungarian cracked gas oil and on the separation of the components that can be sulfonated with chlorosulfonic acid.

Crude Tar Obtained by Alkylation.

Experiments were started to separate the crude tar, which is obtained by alkylation from acid tar, into acidic and neutral fractions by neutralization with aqueous methanol lye. It is planned to subject the neutral fraction to the Oxo-synthesis after

investigation of its behavior on distillation and of its composition.

Experiments on Secondary Hydrogenation.

In connection with the difficulties encountered with plant olefins (yellow oil) and sulfur-containing materials during the hydrogenation step following the Oxo-treatment, numerous experiments were carried out during the report period in the small size reactor and on a larger scale in the chamber 1a in Me 333a.

a) Experiments with the small size reactor (reactor 43).

The experiments on after-hydrogenation were carried out with a sulfidic catalyst (3076). The contact length was 30 cm. Oxo-reaction products from carbonization gasoline from Brux and Deuben were used for the experiments. These products were led over the catalyst with half space velocity. The purpose of these experiments was to hydrogenate the aldehydes and ketones without hydrogenating the aromatic components. The complete hydrogenation of the more difficultly hydrogenated ketones succeeded with about 10-11 MV. In order to learn about the behavior of aromatics under these conditions, experiments with benzene were carried out and it was found that hydrogenation takes place also with 11 MV. The content of cyclohexane formed was determined with a refractometer. According to the experiments in the small size reactor hydrogenation of aldehydes and ketones does not seem possible without hydrogenation of the aromatics.

b) Experiments in the Chamber 1a in Me 333a.

~~Experiments were done with regard to the construction of~~

an after-hydrogenation stage in Me 458a. The experiments showed that the considerably greater contact length (4.5 meter instead of 30 cm. in the small reactor) makes it possible to accomplish the same degree of hydrogenation at about 3 MV lower temperature. Various materials were led over the catalyst 3076 with a velocity of a single charge per hour.

As a preliminary experiment on the after-hydrogenation of Oxo-treated carbonization gasoline fractions, the behavior of benzene was investigated. The experiments were done at increasing temperatures and 200 atm. hydrogen and with a single charge per hour. With 100% pure benzene, hydrogenation occurred already at 6-7 MV. The same thing was true in case of benzene diluted with Mepasin. With the carrying out of the after-hydrogenation on this scale, the beginning of the hydrogenation was clearly observable by an increase in temperature, caused by the large evolution of heat due to the hydrogenation of aromatics.

The hydrogenation of aldehydes goes to completion already at 6 MV. These runs show also that a complete hydrogenation of aldehydes is hardly possible without hydrogenating part of the aromatics. The conditions are more difficult still when besides aldehydes also ketones are present together with the aromatics. This is the case with cracked gasolines. An Oxo-treated cracked gasoline fraction was after-hydrogenated at 8 and 10 MV. The products which were hydrogenated at 8 MV still showed carbonyl numbers, which probably resulted from ketones only. The products which were hydrogenated at 10 MV showed only slight carbonyl

numbers. Hydrogenation of aromatics, however, occurred at 10 MV. This had to be concluded from the difficulty of keeping the temperature constant and from the lower density of the reaction products. To what extent hydrogenation of aromatics took place with these sulfur-containing materials and whether a partial hydrogenation of aromatics took place also at 8 MV, was not determined. Both products were handed to Dr. Welz after separation of Oxo-products by distillation for further testing.

Hydrogenation of alcohols occurs only above 9 MV. Runs are being carried out about increasing further the charge velocity over the catalyst. This is of particular importance for the after-hydrogenation stage to be constructed in Me 458a. Hydrogenation runs with sulfur-containing materials are also being done, since hydrogenation with a cobalt catalyst is possible only to a limited degree and since the after-hydrogenation chamber is to be used in the first place for the hydrogenation of sulfur-containing materials.

II. Tests Run in Me 458a.

1) Oxo-Treatment of (different) Charge Stocks

Several fractions of carbonization gasolines from Deuben and from Brux were Oxo-treated during the report period. The Oxo-treatment took place with all oils without difficulty and yielded better results than with the autoclave run(s). The hydrogenation did not go to completion in spite of the use of a fresh catalyst, because of the higher sulfur content. A short summary of the most important results is given in the attached table.

The purification of the Oxo-treated fraction was effected by distillation in the laboratory Me 225.

Besides the carbonization gasolines dehydrated neutral extract from the ester oil plant was Oxo-treated. It was a neutral extract obtained from the manufacture of the ester 455, which was manufactured from the isobutyl fraction 140-180°C. It was found that this neutral extract had a very high content of olefins and could be Oxo-treated to form alcohols to about 80-85%. It can be concluded from these observations that fundamentally always more olefins can be produced from the neutral extracts from the ester oil plant than from the neutral extracts from the carboxylic acid plant, since in the manufacture of ester oils always a larger excess of alcohol has to be used, which goes into the neutral extract together with the real neutral components and secondary alcohols.

Samples of the alcohols obtained from the neutral fraction were given to Dr. Kollek, Lu and (Miss) Dr. Rossig (lubricating oil tests Dr. Zorn).

2) Distillations in Me 458a.

During the report period the old dephlegmators of both columns which were too small were modified and replaced by new, larger dephlegmators. The cooling surface was 46 m² instead of 18 m² as before. Distillation of diisobutyl alcohols showed at once that operation was now easier and could be done with smaller losses.

3) Production of Methyl Adipol.

Work on the production of methyl adipol was resumed, but had to be interrupted because of a leak in the high pressure steam heating unit.

4) Status of the Improvement of the Oxo-Plant for Auxiliary Production.

The work did not progress as much in the report period as could have been expected. The high pressure section came quite close to completion and soon the mounting of gauges and control units can be started. The low pressure section was insulated and completed and the production control units were connected. The filters were put in operation in a trial run and it was found that the center of gravity was too far from the center of rotation. This made it impossible to fix the swing filters in the desired positions. The filters were weighed and a 100 kg heavy plate was fastened on the lighter side. Now the filters can be fixed in every desired position without difficulty. The filter candles were all tight and the attained filter times correspond quite well to expectations and, therefore, the filter stage can be considered to be sufficient.

5) Construction of an After-Hydrogenation Stage in Me 458a.

Taking into account the experiences obtained in Me 333a, Ka la, a start was made with planning the construction of an after-hydrogenation stage. In this stage materials which were not completely hydrogenated will be subjected to a secondary hydrogenation by percolating them through the solid catalyst (3076). An outline and details will be communicated in the next work report.

6) Trying out Cobalt Carbonyl.

While modifying a HD-separator, it was found that it contained about 500 g crystallized cobalt carbonyl. This separator was placed behind a gas condenser of an aggregate which was operated

temporarily as an Oxo-reaction furnace. This cobalt carbonyl will be tried out in some special experiments.

III. Investigator Dr. Ballaus.

Experiments to dimerize Oxo-aldehydes while being produced in the autoclave were(words are missing in German original).... after preliminary experiments with isohexyl - and isoheptyl aldehyde had shown (as observed also before by Dr. Zerrweck and Dr. Lowenberg) that the reaction takes place without side reactions only at temperatures around 30°C. But the Cannizarro reaction(words are missing).... to the main reaction was interrupted.

1) Production of Oxo-Aldehydes Free from Carbonyl Compounds.

It was attempted to produce Oxo-aldehydes as free as possible from cobalt compounds and then to condense these Oxo-aldehydes. The elimination of cobalt carbonyl by hydrogenation in the presence of sodium ethylate did not succeed without hydrogenating at the same time a large portion of the aldehydes (autoclave runs 58/26, 58/28, 58/29, 58/30, 62/31). In the same way the use of sodium salts of fatty acids, sodium acetoacetic ester, or sodium malonic ester did not lead to the desired goal. The partial hindering of hydrogenation found by Dr. Meusel is caused, as shown by experiments 59/27, 58/33 and 56/41, by the formation of sodium formate or methyl formate, which compounds (experiment 60/61) also strongly hinder hydrogenation.

A more thorough elimination of cobalt carbonyl and of other cobalt compounds from the Oxo-reaction yield succeeded with

carbon dioxide under increased pressure and at higher temperatures. The determination of cobalt was carried out with standard comparison solutions in the absence of a solvent-resistant colorimeter. The determination gave cobalt contents of 3-10 mg Co per liter with several runs. With the numerous experiments 30-50 atm carbon dioxide from a cylinder was always used and then the materials were heated 1-2 hours at 140-180°C. In a sample of the effluent gas 0.35% carbon monoxide was found. (Runs 58/37, 58/39, 58/49, 44/50, 58/51, 60/52 and other runs).

2) Experiments with Oxidic Cobalt Catalysts.

When decomposing cobalt carbonyl a precipitate with the color of cobalt carbonate was formed and thus was present in addition to the unchanged catalyst. Because of this, it was tried to use also cobalt carbonate, cobalt oxide and used catalyst. After some initial erring it was established that oxidic cobalt compounds cause the Oxo-reaction to take place only in presence of alkalies and reducing substances, as e.g., hydroquinone which is used for stabilizing olefins (0.01% of the olefins) (together with Dr. Hula) (experiment numbers 58/49, 58/51, 60/52, 44/55, 60/56, 44/69, 58/71, 58/74, 44/75 etc.).

OXO-TREATMENT OF CARBONIZATION OILS

| Raw Material | Boiling Range | Density at 20°C. | S ?? | Iodine Number | Crude Oxo-Reaction Product | | % Reacted in Terms of Raw Material | |
|-------------------------------|---------------|------------------|------|---------------|----------------------------|-----------|------------------------------------|----------------------------|
| | | | | | Density | OH Number | CC Number | Calculated from OH Numbers |
| Carbonization Oil from Deuben | 50-135° | 0.820 | 85% | 80 | 0.857 | 92 | 51 | 38% |
| | 135-185° | 0.841 | 81% | 71 | 0.864 | 130 | 28 | 31% |
| Carbonization Oil from Brux | 80-140° | 0.804 | 85% | 88 | 0.846 | 100 | 63 | About 35% |
| | 140-185° | 0.823 | 79% | 90 | 0.850 | 86 | 46 | About 35% |

The Texas Company

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

Project: 813

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

Investigators: Gemassmer, Berg, Ballaus

Status on August 1, 1943.

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

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

Dr. Meusel found with a condensation experiment, tried in the autoclave, that hydrogenation is already hindered appreciably with 0.2% sodium methylate present. Although methylate tends to promote condensation of aldehydes, appreciable quantities of aldehyde could be found in the reaction products. A C_8 -aldehyde, which was obtained in this way, was condensed with solid NaOH at 30-40°C. and gave a 80% yield of the C_{24} -glycol monoester. Before the condensation experiments, however, are continued, it is necessary to accomplish the elimination of the cobalt carbonyls without decomposition of the aldehydes. Experiments about this point are in progress.

signed: Ballaus

Appendix to

Project: 813

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

Investigator: Meusel

Status on August 1, 1943

Ester Hydrogenation

a) BBE-Catalyst

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

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

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

b) Sulfur Resistant Ester Hydrogenation Catalysts.

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

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

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

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

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

signed: Meusel

TOM Reel 55, Document 71 (Continued)

Project: 813

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

Investigators: Gemassmer, Berg

Status on August 1, 1943

1) Product Studies on Laboratory Scale

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

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

Cracked Gas Oil from Hungarian Petroleum

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

About 50% is absorbable in phosphoric-sulfuric acid.

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

Carbonization Gasolines from Brux and Light Oil from Deuben

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

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

Estonian Shale Oil from the Tunnel Furnace

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

Centrifuge Experiments with a Technical Centrifuge

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

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

Runs in Me 458a

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

Fractionations in Me 458a

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

Trials to Improve the Sedimentation Stage

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

Enlarging the Oxo-Plant Me 458a for Auxiliary Production

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

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

Status of the Construction of the Enlarged Oxo-Plant

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

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

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

Methyladipol

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

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

The Texas Company

TECHNICAL OIL MISSION; REEL 55,
BAG 2523, DOCUMENT 72

Project: 813

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

Investigators: Gemassmer, Berg, Meusel

Status on June 1, 1943

1. Investigation of Materials on a Laboratory Scale

Primary Olefin from "Ruhrechemie"

This olefin, which will be the raw material for the large scale industrial Oxo-plant in Holten, was made available to us by the "Ruhrechemie" in larger lots (4.5 m³). This material is produced by the "Ruhrechemie" in an industrial pilot reactor. It is produced with a cobalt catalyst, and by varying the operation technique (recycling of the gases and changing the CO:H₂ ratio to 1:1) the product obtained contains about three times as much olefins as the ordinary Fischer kogasin from the medium pressure process. The product was fractionated into numerous sharp fractions which were Oxo-treated and accurately tested analytically. By determining the various characteristic numbers for all fractions accurate estimates were obtained for the content of olefins, of alcohols, of esters, etc. The olefin content decreases with increasing number of carbon atoms. With the lower boiling fractions it is 40-45% and increases to 12-13% with the highest fractions (C₂₀). The olefin fraction C₁₁-C₁₈ which is solvent extractable, had an average olefin content of 30%. Calculated in terms of the total raw material available to us, the

content of olefins with chain lengths C_{11} - C_{18} is 20%.

The alcohol content decreases from 10-12% for the lower fractions to 5% for the higher boiling fractions. Esters are not present in the lower fractions, while 3-5% esters are present in the highest boiling fractions. Aldehydes cannot be detected and only traces of acids. The accurate analytic investigation led to an exact knowledge of the possibilities of Oxo-treatments. The results, obtained with Oxo-treatments, a description of the alcohols and a study of the alcohol sulfates so obtained will be presented and discussed in a special report.

The Oxo-treatment of the olefins was more than 95-96% effective. After the pure alcohols have been isolated by distillation on a laboratory scale, a start will be made with the purification by fractionation on a (semi) pilot plant scale.

2. Synol Recycle Product (Product Obtained from the Cold Separator)

A larger quantity of the "Synol" product, obtained by the new recycle process, was used in order to investigate possibilities of getting increased yields of alcohols with Oxo-treatments. The material under investigation came from reactor (illegible) 776. The material was fractionated without eliminating the esters and the following sharp cuts were obtained:

1. - 110°
2. 110 - 175°
3. 175 - 218°
4. 218 - 255°
5. 255 - 290°

6. 290 - 320°

7. 320 - 360°

The individual fractions were accurately tested and all characteristic numbers were determined. The alcohol was found to be 55% on the average except for the lowest and highest boiling fractions. The alcohol content decreases to 35% for the highest boiling fractions. The determination of alcohol content was done by means of the OH number and by way of sulfonation with chlorosulfonic acid. Remarkable is the relatively high ester content, which is as high as 20% for the highest boiling fractions. The average content of acids is 0.5%. The aldehyde content varies between 3 and 7%. The olefin content varies between 15 and 20% with all fractions. Remarkable is the high value of the S.P.L. (?) which has an average value of 80% for all fractions. Thus, a total alcohol content of 80% should be obtainable from the crude Synol product by transforming the olefins and aldehydes into alcohols and by hydrogenation of the esters to alcohols.

The Oxo-treatment of the sharp fractions was done in the autoclave. The resulting products were tested also by accurate determination of the characteristic constants. It was found that the Oxo-treatment produced materials which were much more uniform. The aldehydes and the olefins were transformed into alcohols almost completely and the alcohol content after Oxo-treatment and hydrogenation was about 70-75% with almost all fractions. With the highest boiling fractions the alcohol content obtained was almost 60%. One can see from these few figures that the increased production by means of an Oxo-treatment still is appreciable also

with the material obtained with the Synol recycling process.

The detailed results of these investigations will be reported in a special report.

Investigations in the Semi-Commercial Plant Me 458a

1. Continuous Oxo-Treatment of Yellow Oil

The experiments on the continuous Oxo-treatment and hydrogenation of yellow oil were continued. With the hydrogenation certain improvements were obtained. The contact times, when endeavoring to obtain a complete hydrogenation with a used "Ruhrechemie" catalyst, were still unsatisfactory. The aftertreatment in a hydrogenation stage (percolating process) appears to be unavoidable in case it is desired to obtain alcohols completely free from aldehydes.

2. Investigation of the Influence of the Oxo-Treatment Conditions on the Properties of the Resulting Alcohols

In order to learn about the dependence of the properties of the Oxo-alcohols on the treatment conditions, a series of runs with pure "Ruhrechemie" cracked olefins was carried through (Exp. 252-268). The following results were obtained:

In case the Oxo-treatment is started at once at a higher temperature (170-190°), the resulting Oxo-alcohols have a low melting point. In case the treatment is done in this way that one starts at low temperatures (100-130°) and the temperature is increased while the Oxo-treatment is going on toward completion, then one obtains alcohols with appreciably higher melting points. Apparently, the migration of the double bond caused by the cobalt carbonyl catalyst does not occur except at higher temperatures,

while at low temperatures the direct Oxo-treatment without double bond migration is the main reaction.

Since with industrial olefins a rather high temperature is required for complete reaction, it is important, in case primarily straight chain alcohols are desired, to start at lower temperatures and to complete the reaction at higher temperatures. With a continuous Oxo-treatment it is essential to subdivide the Oxo-treatment chamber in zones with different temperatures.

Oxo-Treatment of Primary Olefins from the "Ruhchemie"

The crude primary olefins were fractionated partly in 458a, partly in the pilot plant. The following 8 sharp cut fractions were obtained:

1. 50 - 150° (C₆ - C₉)
2. 150 - 175° (C₁₀)
3. 175 - 217° (C₁₁ - C₁₂)
4. 217 - 256° (C₁₃ - C₁₄)
5. 256 - 292° (C₁₅ - C₁₆)
6. 292 - 310° (C₁₇)
7. 310 - 320° (C₁₈ - C₁₉)
8. 320 - 350° (C₂₀)

The larger parts of the individual fractions were Oxo-treated batchwise in 458a, charges 269-287. The operating conditions were chosen in order to obtain a most favorable Oxo-treatment. The temperature was kept below the lowest temperature at which reaction occurs while admitting the raw material into the furnace. Then, the temperature was increased after the gases had been started re-

oyling. The reaction went to completion to about 95-96% as calculated from the analytic data before and after Oxo-treatment and hydrogenation. The yields will be fractionated in order to obtain the pure alcohols.

Content of Cobalt Carbonyl in the Mash after the Oxo-Stage

In order to determine how the cobalt carbonyl content of the mash after Oxo-treatment varies with varying Oxo-treatment conditions, numerous cobalt determinations were run on oil freed from catalyst after completion of the Oxo-stage. These runs were done with batches 255-268 and with the continuous run 44 for varying Oxo-treatment conditions. This is the picture obtained: With short contact time in the Oxo-furnace (10-15 minutes) the carbonyl content of the Oxo-treated mash always is low and was found to be in the range 170 (?) - 450 mg cobalt per liter oil. These values indicate that 2-5% of the cobalt present in the catalyst went into solution as carbonyl. If the contact time in the Oxo-furnace is increased to one hour or longer, then up to 40% of the cobalt present in the catalyst goes into solution as carbonyl. Under normal conditions one should count on a carbonyl content of about 1 g cobalt per liter oil.

Upon increasing the temperature to 180-190° at the end of an Oxo-treatment, the carbonyl content decreases to about 200 mg cobalt per liter oil. This decrease of carbonyl content must be explained by a decomposition of the carbonyl at the high end temperature.

Carbon Monoxide Corrosion

When extending the piping, the orifices (Linsen) at the

gas exit of the Oxo-reactor showed especially heavy corrosion. Of one connection (orifice?) only a thin ring remained due to frequent tightening. As a trial copper plated and brass plated orifices were mounted.

Clogging of the Product Preheater in the Hydrogenation Stage

The preheater which is placed in the mash injector connection immediately before the hydrogenation furnace became completely clogged up during the report period. The heating tubing was cut open and showed layers of deposit, which layers consisted primarily of metallic cobalt and catalyst material. It has to be assumed that the preheater got clogged by thermal decomposition of the cobalt carbonyl which dissolved in the mash. The preheater before the hydrogenation furnace has to be eliminated and it will be tried to accomplish preheating of the mash in the hydrogenation furnace in such a way that the cobalt carbonyl is not decomposed at the hot walls of the hydrogenation furnace but in the hot mash itself.

Extracting Cobalt Carbonyl from the High Pressure Circulating System

In order to prevent spraying over of the wash oil from the high pressure bubble cap scrubber, a 1/2 meter long piece of high pressure pipe was mounted on the extractor as a settling zone. In this way it was possible to prevent the spraying over of oil and to eliminate the danger of flooding the gas circulating pumps.

Distillations in 458a

During the report period, in addition to reacted yellow

oil and crude primary olefins from "Ruhchemie A. G.", there was distilled by Dr. Jagemann also a larger quantity of methyl adipic dimethyl ester. In the distillation of this last material about 800 liters of the 8300 liters were completely cracked in the kettle. A dark resinous residue resulted which finally had to be removed by hand after several trials to dissolve it with middle oil, methanol and water.

Production of Methyladipol in 458a

The production of methyladipol was carried further during the entire report period, but then had to be interrupted because of other demands for using the filters.

The results with hydrogenation were not so good as were to be expected in view of the results with previous runs in the adipol furnace in Me 225. While an average hydrogenating time of 6-7 hours was counted on, an average hydrogenating time of 19 hours was required even with a fresh catalyst. With further use of the same catalyst, the hydrogenating time had to be increased further. A detailed account of the results will be given in a report together with Dr. Diericks, as soon as the experiments have been completed. It has to be mentioned even now that the production of methyladipol from the esters, then available in the Organic Department, is not a process suitable for regular operation.

Status of the Extension of the Oxo-plant 458a

During the report period the Construction Department has completed the extension and has started mounting the new dumping filters and the necessary measuring devices, etc.

Aldol Formation from Aldehydes During the Oxo-reaction (Dr. Meusel)

It was tried to obtain aldol condensation of oxo-aldehydes at the moment of formation by adding alkaline substances and by varying pressure and temperature. With subsequent hydrogenation, diols should be obtainable or otherwise unsaturated or saturated primary alcohols with the double number of C atoms in case the secondary OH groups are easily split off as water and the double bond so formed is then hydrogenated. The following materials were tried: Aqueous sodium hydroxide, methyl alcoholic sodium hydroxide, sodium methylate, solid sodium hydroxide, calcium oxide, sodium carbonate and aqueous ammonia, but no major effect in the desired direction could be established. Variation of pressure and temperature had a much greater effect on the quantity of higher boiling material. Increasing both variables appreciably more higher boiling material is obtained. The high boiling residue so obtained, however, contains extremely few OH groups, and thus it is suspected that the actual reaction did not take place at all via aldol.

Two quite interesting observations resulted from these experiments:

1) The Oxo-reaction is almost completely inhibited in the presence of aqueous ammonia.

~~85% of the original olefins were recovered completely~~
unchanged, probably because the cobalt-ammin complex thus formed is more stable than the cobalt carbonyl complex and thus the content of cobalt carbonyl in the catalyst required for the Oxo-

reaction decreased. This might well be a proof thus far lacking that cobalt carbonyl is required and essential for the Oxo-reaction.

2) In the presence of sodium methylate, the hydrogenation is completely inhibited while the Oxo-reaction occurs uninhibited. It might well be possible this way to produce aldehydes free from cobalt carbonyl in case the carbonyls are destroyed during a hydrogenation following the Oxo-stage while the aldehydes are not affected.

At this stage the investigations were left to Dr. Ballaus for further work.

signed: Gemassmer, Berg, Meusel

The Texas Company

TOM REEL 55, BAG 2523, DOCUMENT 73

Problem: 813

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

Investigators: Gemassmer, Berg

Status on April 1, 1943

Investigation of Materials on a Laboratory Scale.

In the report period the various investigations and reaction studies of lignite carbonization products were finished. Light oil from the Lurgi-gas circulation (spulgas) process from Deuben. The light oil had a density of 0.932 and a boiling point range between 150-360°C. The light oil was fractionated. The cuts were freed from acidic materials and phenols by thorough extraction with caustic, then were washed with dilute sulphuric acid and then were distilled again. This purification was necessary with all these materials in order to obtain color stable alcohols after Oxo-treatment and hydrogenation. The purification on a laboratory scale is rather tedious and time consuming and larger losses of materials are hardly avoidable.

The Oxo-treatment takes place without difficulties. The Oxo-treatment temperature should be kept at about 190° in order to secure complete transformation. Further increase of the temperature does not give additional conversion. The hydrogenation takes place to an insufficient degree with a cobalt catalyst because of the high sulfur content of the material (about 2%). One always had to reckon with the treatment of lignite carbonization oils by an after hydrogenation with a sulfidic catalyst. After-hydrogena-

tion experiments with a sulfidic catalyst were not carried out, but no major difficulties should be expected in view of the experiences with other materials. In addition to the light oil from the Lurgi gas circulation process, also fractions from the Rolle reactor (carbonization tar) were investigated. With this material the same preliminary purification as with the Lurgi light oil was required and also otherwise the treatment and precautions were the same.

From part of the crude reaction products pure alcohols were prepared by means of the boric esters. These were tested by determining the physical constants. The alcohols have a high density, low melting point and a peculiar odor.

All experiments were done in an autoclave on a laboratory scale and gave only an approximate picture. For an accurate confirmation of the results and for obtaining the required operating conditions for the process, further experiments on a (semi)pilot plant scale had to be performed.

II. Repetition of the Oxo-treatment Procedure of Ludwigshafen (With Dissolved Catalyst).

In order to obtain a more accurate picture of the Oxo-treatment, using a dissolved catalyst, as worked out by the main laboratory in Ludwigshafen (Dr. Reppe), a few experiments were done in a small reactor. As a basis for these experiments the orally communicated experiences of Ludwigshafen were used. These were recorded in the minute notes 116/42 and 12/43.

Preparation of the Catalysts

The procedure of Ludwigshafen uses a dilute solution of cobalt salt in olefin, which percolates over pumice stone charged

Table I
Investigation and Oxo-treatment of Lurgi Light Oil

| Boiling Range of Cut | % by Wt. in Terms of Total Sample Light Oil | Density 20° | Sulfuric-Phosphoric Acid Soluble | Iodine Number According to Hanus | Crude Oxo-Product | | | % Convertible as Calculated from OH and CO Numbers |
|----------------------|---|-------------|----------------------------------|----------------------------------|-------------------|----------------------|----------------------|--|
| | | | | | Density | OH (Hydroxyl) Number | CO (Carbonyl) Number | |
| 150-200° | 8% | 0.860 | 77% | 61 | 0.852 | 45 | 36 | 30% |
| 200-300° | 63% | 0.923 | 83% | 50 | 0.907 | 50 | 30 | 35% |
| 300-350° | 18% | 0.950 | 82% | 70 | 0.930 | 45 | 10 | 27% |
| Over 350° | 11% | -- | -- | -- | -- | -- | -- | -- |

Table II
Investigation and Oxo-treatment of Rolle Carbonization Tar

| Boiling Range of Cut | % by Wt. in Terms of Total Sample Light Oil | Density 20° | Sulfuric-Phosphoric Acid Soluble | Iodine Number According to Hanus | Crude Oxo-Product | | | % Convertible as Calculated from OH and CO Numbers |
|----------------------------|---|-------------|----------------------------------|----------------------------------|-------------------|----------------------|----------------------|--|
| | | | | | Density | OH (Hydroxyl) Number | CO (Carbonyl) Number | |
| 150-200° | 5% | 0.837 | 84% | 123 | 0.865 | 84 | 0.0 | 26% |
| 200-250° | 18% | 0.833 | 84% | 102 | 0.897 | 56 | 7 | 22% |
| 250-300° | 21% | 0.913 | 83% | 90 | 0.918 | 40 | 0.0 | 18% |
| 300-350° | 14% | -- | -- | -- | -- | -- | -- | -- |
| Residue Boiling Above 350° | 42% | -- | -- | -- | -- | -- | -- | -- |

with cobalt, under oxo reaction conditions. We used as solid catalyst a pumice stone with 5% cobalt (catalyst No. 4491), which catalyst after being placed in the reactor was reduced at 400° with hydrogen. As cobalt salt we used the cobalt salts of light (Vorlauf) fatty acids, which were prepared by heating cobalt acetate with light fatty acids. The cobalt salts dissolve in olefins only after adding at least as much higher alcohols as the weight of the cobalt salts. By adding the double weight of alcohols to the cobalt salts one obtains a viscous concentrated cobalt solution, which dissolves in olefins without forming a precipitate or turbidity.

For the conversion a small reactor with copper lining (reactor 42 in Me 225) with 50 cc. catalyst volume and 350 mm. length of the catalyst layer was used. Although the conditions were varied, the temperature between 5 and 10 mV, the amount of dissolved cobalt between 0.001-0.1%, injection rate between 10 and 50 cc. per hour, it was impossible to increase the conversion to above 80%. It seems possible that the yield would improve by increasing the percolation length. It was found that, when starting up, the conversion is low initially and the yield reaches the maximum value only after two days. This result is also obtained if the reactor is again switched to the Oxo reaction before cobalt elimination.

The same reactor served for the elimination of cobalt. For this temperature was kept at 3 mV. The elimination of cobalt showed a similar trend as the Oxo-treatment. At first the elimination of cobalt was very inefficient but improved after a few

days of operation. But even after 14 days cobalt could still be detected in the filtrate. It is possible that the cobalt salt is harder to destroy than the cobalt carbonyl and that because of this traces of cobalt always escape elimination. Increasing of the percolation length might yield more complete transformation. During the elimination of cobalt the product is hydrogenated to about 90%.

Summarizing one may say that the Ludwigshafen developed procedure for Oxo-treatments with dissolved catalyst is quite satisfactory. Further experiments in more adequate apparatus must show, whether the obtainable transformation will approach that of the mash (suspension) process.

III. Determination of the Catalyst Grain Size.

Of the different methods for determining grain size the one chosen was the sedimentation method which was applied by Krczil (Kolloidzeitschrift 55 (1931) p.25) to ceramic raw materials. Instead of aqueous suspensions, as used by Krczil, suspensions in benzol were used, since the catalyst did not tend to agglomerate in benzol. With a used catalyst it is not possible to obtain the proper wetting in water because of traces of oil adhering to the surface. The procedure was briefly as follows:

The catalyst is freed from oil by extraction with pentane and after drying 10 g. is suspended in 1 liter benzol. The suspension was placed in a measuring cylinder and after different times 10 ccm of the suspension were removed with a pipet from 10 ccm depth of submersion and the catalyst still remaining in the samples was weighed after evaporation of the benzol. From these data and the density of the catalyst the grain size can be calculated

with the formula of Stokes.

$$v = \frac{2}{9} \cdot \frac{v^2}{n} \cdot (D - d) \cdot g$$

v = sedimentation velocity cm/sec.

d = particle diameter

D = catalyst density = 2.8

d = density of benzol = 0.87865/20°C.

n = viscosity of benzene 0.00642 centipoises/20°C.

g = gravitation constant

With a fresh catalyst 97% is larger than 0.02 cm, 1.5% is between 0.01 and 0.02 and traces are between 0.005 and 0.01, particles smaller than 0.005 are not present with fresh catalyst.

In contrast the following data were obtained with a catalyst which had been used during several months and which had been reactivated by adding regularly fresh catalyst.

5.5% larger than 0.02; 6% between 0.01 and 0.02; 84% between 0.01 and 0.005; 2% between 0.002 and 0.005; traces under 0.002. It was tried to follow the decrease in particle size with time during a longer continuous run in Me 458a. No appreciable decrease in particle size of the catalyst was found, but no clear picture was obtained. These investigations will be repeated as soon as a larger amount of olefin will be available for an extended continuous run.

Determination of the Viscosity of Oxo-alcohol and Oxo-alcohol-Hydrocarbon Mixtures

Since the oil viscosity is of great importance for the sedimentation velocity and thus also for the centrifugal separation

of the catalyst, the viscosities were determined with a Ubbelohde viscosimeter in order to determine the dependence on the temperature.

It was found that with higher Oxo-alcohols at 100° a viscosity is reached which is five times the viscosity of benzol at 20°. Thus, the times required for sedimentation and also for centrifuging may have to be increased five times.

Centrifuge Experiments with Cobalt Catalyst-Suspensions

With an exact knowledge of the grain size of the catalyst and of the viscosity of the oil, it is possible to estimate the efficiency of a centrifuge of known speed and dimensions without performing further experiments. As a matter of fact, experiments with different centrifuges gave a quite satisfactory agreement with the calculated values. Further details of the calculations, measurements and basic figures will be communicated in a special report, since these calculations and results are of great importance for the operation of suspension processes.

Determination of the Degree of Reduction of the Catalyst

It appeared of interest to know whether the degree of reduction of the cobalt catalyst in the Oxo-synthesis has a similar effect on the activity as is the case with the Fischer-synthesis. Several catalysts were investigated in this respect. Furthermore, it was tried to establish whether the decrease of activity while the process is operating has to do with a degree of oxidation of the catalyst. This was determined by measuring the volume of hydrogen evolved when a weighed quantity of the catalyst is decomposed with hydrochloric acid. The impression obtained at present is as

follows:

1) Catalysts, reduced in Me 458a and containing more than 90% of the cobalt in the reduced form, show no noticeable difference during operation from the Fischer synthesis catalysts, containing only up to 40% metallic cobalt. The variation of the degree of reduction with length of operation could not be determined very well as the values found did not give a clear picture. The experiments will be repeated with the next long and continuous experiment in Me 458a.

Progress Made in the Semi Pilot Oxo-plant Me 458a.

Fractionations

During a fractionation it was suddenly no more possible to get the reflux back in the column. It was found that the reflux tubing, which runs inside the vapor tubing, was torn apparently by heat tensions. Further investigation showed that the reflux tubing of column I was torn also. Because of these failures, which may have been for some time, only part of the predetermined reflux went back into the column. In this way the sharpness of the fractionations may have suffered. A few coils of tubing were placed in the reflux conduit as compensating lengths in order that such failures could not happen again.

Interferences Caused by Cobalt Carbonyl

With the continuous Oxo-treatments the cooler of the reaction product suspension coming from the Oxo-furnace was placed after the Widia sludge discharge valve. Clogging occurred in the discharge tubing. This was subjected to a closer investigation. The high pressure part of the tubing was completely free up to the

Widia valve and showed no trace of deposits. Immediately behind the valve and down to the cooler, the tubing was lined with a heavy layer of cobalt and iron. This showed that, on releasing the pressure on the hot cobalt carbonyl containing suspension, that the cobalt carbonyl is decomposed immediately beyond the point of pressure release and that the connections become clogged in spite of the high flow velocity. In order to avoid clogging in this way, the suspension cooler was placed in the high pressure section, and thus the pressure on the cobalt carbonyl containing suspension was released only after cooling.

During the report period two tank cars of yellow oil from the i-butyl oil synthesis were received in Me 458a for a further study of the Oxo-treatment of this material. It was found with all these experiments that hydrogenation is not easily carried through to completion. Since these hydrogenation difficulties occur primarily when yellow oil is treated, it is possible that this material contains components which easily form resins interfering with the hydrogenation. It appears imperative to provide for an after-hydrogenation stage when treating yellow oil.

Production of Methyladipol in Me 458a

The production of methyladipol was continued during the whole report period and will still take several months, as the obtained yields fell much short of the scheduled production. This work and the results will be discussed in a special report.

Extension of the Oxo-pilot Plant Me 458a for the Auxiliary Production of 100 Tons of Alcohol Per Month

During the report period the planning of the necessary

extension was pushed along so far that all necessary apparatus could be ordered. The construction department started the construction of the building annex for the plant extension. The planned operation of the process will be discussed in the next report.

TOM REEL 55, BAG 2523, DOCUMENT 73 (Continued)

Problem: 813

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

Investigators: Gemassmer, (Berg, Meusel, Ballaus)

Status on February 1, 1943

Process Development: Gemassmer

I. Investigation of Materials on a Laboratory Scale

a) Rumanian cracked benzine of the company Astra Romana was cut into two fractions 80-155° and 155-200° and was oxo-treated. With the fraction 80-155° (C₇-C₉; SPL = 50%; olefin content = 47%) 32% of the total raw material could be transformed into alcohols in the autoclave at 8.5 mV (193°). This corresponds to a conversion of ?? % of the olefin content as estimated by means of the analytic iodine number.

With the fraction 155-200° (C₉-C₁₂; SPL = 50%; olefin content 45%) only 21% of the raw material could be converted under the above conditions in the autoclave, corresponding to 47% of the analytically determined olefin content.

b) Carbonization products, obtained from lignite according to different procedures, were subjected to a preliminary refinement, were distilled, and oxo-treated. These runs are not completed as yet and will be discussed at length in the (next?) report.

c) Triisobutylene, which on order by Dr. Fischer was prepared from isobutanol, was oxo-treated in a number of autoclave experiments. 50% of the raw material, corresponding to about 65% of the olefins as estimated analytically, could be converted into

alcohols. The fraction convertible by Oxo-treatment was 20% larger as compared with the large scale material, of which only 40% could be converted.

??? oil derived from a Hungarian crude oil from the company Apollo in Pressburg was investigated on a laboratory scale. The iodine number according to Hanus showed an olefin content of about 30%, while 47% was absorbable in sulfuric-phosphoric acid. It was possible to convert only 12-15% of the oil by Oxo-treatment, which amounts to about 50% of the olefin content as determined by the iodine number.

Work in Progress in the Pilot Oxo-plant Me 458a

During the report period several series of runs with cracked olefins from Ruhrchemie were done in 458a, in order to clarify some fundamental questions.

1) Dependence of the Constitution of Oxo-alcohols on the Reaction Conditions

Investigating a C_{16} -olefin fraction it was found that the melting points of the purified alcohols depend markedly on the temperature of the Oxo-treatment. The melting point decreases with increasing temperature. It appears that the displacement of the double bond induced by the cobalt carbonyl is much more temperature dependent than the Oxo-conversion and happens much faster at higher temperatures. These experiments could not be carried further as no suitable raw material was further available.

2) Pressure Dependence of the Oxo-conversion

As part of the general investigation of the Oxo-conversion, the experiments for determining the influence of the pressure

on the Oxo-conversion were carried further. The continuous runs in the pilot plant gave the following picture.

The Oxo-reaction is markedly pressure dependent contrary to the experiences with the runs with fresh catalyst in autoclaves. Pressure dependence is not very marked when putting in a new fresh catalyst, while a once used catalyst shows following behavior.

(32nd continuous run in 458a):

conversion up to about 10% at 50 atm.
conversion up to about 50 at 100 atm.
conversion up to about 70-80 at 150 atm.
conversion up to about 95% at full supply line
pressure of 225 atm.

These values hold for a residence time of one hour in the Oxo-reactor. Quite interesting seems the fact that the Oxo-reaction is rather temperature independent when the pressure is too low. Also no improvement of conversion can be obtained by a 20° increase in temperature.

The results of these runs can be considered as rather well established, but must be extended by further investigations which have been planned. Summarizing it can already be said that the Oxo-conversion is strongly dependent on the pressure and that plant operation at pressures under 150 atm. is out of the question.

Investigation of Materials in 458a

Rumanian cracked gasoline, fraction 80-155. At first a few batches were converted, and then the major quantity (7.6 m³) was Oxo-treated in a continuous run. A conversion of 32-35% was obtained, calculated in terms of the raw material. Hydrogenation went without a hitch.

Rumanian cracked gasoline, fraction 155-200°C. Again,

several batches of this fraction were converted, and then the major quantity (4 m³) were subjected to a continuous Oxo-treatment and a hydrogenation. 22-24% of the raw material were converted. Difficulties were encountered with the hydrogenation of this material. About 25% of the converted material still were composed of unchanged aldehydes after passing through the hydrogenation stage. The sulfur content of the raw material was 0.12%. By re-hydrogenation over a sulfidic catalyst (118) Dr. Meusel succeeded immediately in hydrogenating all aldehydes and to obtain a further increase in yield by splitting part of the esters.

Synol material, fraction 109-320°. 3.4 m³ synol product from Me 458, boiling range 109-320°, were Oxo-treated and hydrogenated. The olefin content of the Synol material was converted almost completely into alcohols. The converted material was fractionated and the solvent extractable alcohols (C₁₂-C₁₈, Synol- and Oxo-alcohols together) will be tried out as detergent raw materials.

Technical Improvements in Me 458a

In order to use the reactors efficiently, when operating continuously with high efficiencies, tubular preheaters were mounted for the liquid injection materials.

It proved necessary, to free the recycle water gas of the Oxo-stage from cobalt carbonyl in order to prevent clogging of the gas preheaters. In a high pressure duct of 90 mm. diameter and 1 m. length, a bubble plate column was mounted for washing the material coming from the reactor. Each bell had 12 slits with a total slit area of 1.8 cm². Five partitions are built in the column. Extraction experiments were done for different gas and liquid velocities

with these results:

| Liquid velocity liters oil per hour | Gas velocity Nm ³ CO/H ₂ /h | Degree of extraction % total cobalt |
|--|--|--|
| 2 | 20 | 95 |
| 2 | 30 | 90 |
| 2 | 60 | 75 |
| 5 | 20 | 96 |
| 5 | 30 | 93 |
| 5 | 60 | 90 |
| 10 | 20 | 97 |

Only untreated olefin was used as extraction liquid with these experiments. Runs to do the extractions with crude alcohol are in progress. It is seen that the washing effect of the column is very good but that too few plates are provided to accomplish complete removal of CO.

Plans for the Extension of the Experimental Plant Me 458a

The experimental Oxo-plant Me 458a will be extended for regular production according to the fundamental plans detailed in the notes of the minutes A.N. 94/1942. It is tentatively planned to reserve two reactors for experimental purposes while four reactors will be used for production. A start is made with working out details for the project. The present schedule calls for August 1943 as the deadline for starting production.

Production of Methyladipol in Me 458a

In view of the experiences of Dr. Dierichs, sections of the plant in Me 458a were changed over for the production of Methyladipol according to the fundamental plans recorded in the minutes 92/42 of 8 October 1942. For the production of methyladipol the following units were segregated from the other units of the plant,

2 high pressure reactors, 1 filter, 1 suspension container, 1 pressure release unit and a gas circulating pump. This was done in order to prevent mixing of gas and liquid.

Several tons of methyladipic dimethyl ester were fractionated in 458a. The first batches were hydrogenated during the present report period. Nothing very definite can be said as yet about efficiency etc.

Catalyst Studies

In view of difficulties encountered with the filtration of the suspension in Me 458a, which difficulties occurred with a longer use of the Fischer-synthesis catalyst, experiments were started to determine the grain size of the catalyst. The determination is done by means of a sedimentation method. The purpose of the experiments is to establish the decrease of grain size with length of use in operation, and to investigate how well the catalyst might be separated by centrifuging.

The Texas Company

TOM REEL 55, BAG 2523, DOCUMENT 74

Problem: 813

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

Investigators: Gemassmer, Berg, Meusel, Ballaus

Status on December 1, 1942

I. Process Development: Gemassmer

1. Investigation of Materials on a Laboratory Scale

a) Estonian shale oil, boiling range 200-300°, was treated with lye and dilute sulfuric acid and was then Oxo-treated (20% conversion). The product was distilled and the alcohols were purified via the boric acid esters and then sulphonated. The sulphonation product was light yellow and was found on testing by Dr. Richter equivalent in quality to Mesapon.

b) Gasoline from the "Sump" Phase of the Leuna Hydrogenation Process

The gasoline under investigation had the following properties:

d = 0.729; boiling range 60-110°; C-number = (?)⁵ (possibly 6.5 or 8.5 because illegible. Trans.) and was well freed by Dr.

Kolb from ketones by extraction. According to the iodine number

(Hanus = 55; Kaufmann = 54; Klein = 52) the content of olefins is about 20%, while 31% are absorbed by phosphoric sulfuric acid.

With the Oxo-treatment it was found necessary to keep the tem-

perature at 190°. Hardly 20% of the raw material was convertible

into products containing oxygen. No further experiments were done with this product and with the alcohols.

c) Propylene Polymerization Products

Dr. Fischer forwarded three samples of 10 liters each of propylene

polymerization products.

1) Raw Polymer

Boiling range 126-260°, C₈(?)-C₁₅. In spite of the iodine number, which indicates an olefin content of 80-90%, only 52% were convertible by Oxo-treatment.

2) Distillate I

Boiling range 77-150°C.; C₇-C₉. According to the iodine number 75-80% is olefinic, but only 50% is Oxo-convertible.

3) Distillate II

Boiling range 150-200°C.; C₉-C₁₂. The iodine numbers indicate 90% olefins, but it was possible to convert only 54% into oxygen containing compounds.

Several batches of each of the different propylene polymerization samples were treated in autoclave experiments. The purification of the alcohols by fractionation and the testing as plasticizer and ester oil component are still in progress.

d) German Shale Oil (Botternhausen) and Carbonization Products

Samples of German shale oil and different lignite carbonization products from Riebeck were distilled, refined and tested analytically. They will be Oxo-treated shortly.

Continuous Runs in Me 458a

Roumanian Cracked Oil

Fourteen tons Roumanian cracked oil from the firm "Astra Romana" were first distilled (in order to clear the material) and then Oxo-treated in a continuous run. The sulfur content of the oil was 0.24%. In spite of the sulfur content, it was possible to hydrogenate completely the aldehydes obtained

after Oxo-treatment. This went without difficulties. The sulfur content of the material did not interfere with the hydrogenation as wrongly expected. By following the sulfur content of the circulating gas and the reaction product, it was established that the sulfur of this material is bound so strongly, that under the conditions of the Oxo-synthesis and the hydrogenation no hydrogen sulfide nor other volatile organic sulfur compounds are developed and thus the hydrogenation is not interfered with.

Fifteen per cent of the oil could be converted into alcohols. Since all the oil of the boiling range 235-320°C. was used, the subsequent distillation of the alcoholic reaction products achieved merely an increase of concentration to 40% alcohol content. Part of the alcohols which were concentrated by distillation were purified by Dr. Berg by way of the boric acid esters and then sulfonated. Another part was sulfonated directly. The testing of extraction qualities is still to be done. A major part (3.2 m³) of the yield concentrated by distillation was condensed (fused?) in the carboxyl acid plant Me 494 by Dr. Gericke and then was fractionated. Both the alcohols and the carboxylic acids have a peculiar odor.

The alcohols have a definitely higher density. 0.860-0.880 as compared to 0.832-0.835 for the products obtained from cracked olefins. The melting point is more than 10° lower.

From the high density it may be concluded that rings are present as structural components of the alcohols. As to the sulfur content of the material, it was found that the alcohols obtained by Oxo-conversion were almost free from sulfur; the non-converted

neutral oils showed a definite increase of sulfur content.

Roumanian Cracked Oil from the Company Romana Americana

13 m³ of this cracked oil were Oxo-treated in a continuous run in Me 458a. In spite of repeated variations of operation conditions no more than about 12% could be converted into alcohols. The same can be said generally for this material as has been said about the cracked oil from the Astra Romana. The sulfur content was 0.17% and did not show up during conversion.

Neutral Part from the Esteroil Plant 160-200°C.

About 37 m³ of a dehydrated neutral part from the ester-oil plant was Oxo-treated in the 31st continuous run. About 50% of this material can be converted into alcohols by an Oxo-treatment. At the same time the temperature dependence of the reaction was studied. It was found that at 100 and 150 atm. CO/H₂ pressure the conversion is unsatisfactory and does not proceed further than 10%. At 175 atm., however, a 70-75% conversion was attained. Thus, it seems as if the Oxo-conversion possesses a certain threshold pressure. These results were obtained with a catalyst which had been used in operation during a considerable time. Experiments with a fresh catalyst show that Oxo-conversion is possible also at lower pressures, or in other words that the threshold pressure depends on the activity of the catalyst. Experiments for a more detailed study of these questions are now in progress.

Plant Experiences in Me 458a

Cobalt carbonyl, which is available in the Oxo-gas

cycle, caused gradual clogging of the preheaters, which are kept at 200°. For that reason, a small bubble plate column was ordered, for scrubbing the gas in a high pressure separator at the furnace exit.

The wear and tear of "Widia" valves was considerably reduced by inserting a seat, and no valve had to be replaced after keeping them in operation for more than two months.

Further Treating and Testing of Oxo Yields: Berg

A) Sulfonation of Oxo-alcohols

a) Runs in Me 244

1) Procedure

The sulfonation and neutralization was performed as described in the last progress report (10-1-42). To speed up the separation of the neutral oil, the alcohol sulfate solution was warmed to 40-50° after neutralization. It will be tried also to do the extraction at higher temperatures. In this way it should be possible to obtain a little more concentrated solutions of alcohol sulfates.

Concentrating the alcohol sulfate solution in the coil (Dr. Elbel) did not succeed very well even after mounting a valve for regulating the vapor pressure. The same difficulties occurred as those described in the progress report 10-1-42. The ~~ease of concentrating in the coil~~ appears to depend on the concentration of the alcohol sulfate solution fed in. More concentrated solutions can be better concentrated further than more diluted solutions. A further study of this aspect will be undertaken.

The concentrating was tried also in this way that a further length of tubing (70 mm. diameter) is inserted and mounted on a slant. This length of tubing is heated, the solution is admitted at the top, the further concentrated solution is drained at the bottom end, while the formed vapors are sucked away. By varying the angle of inclination of the tube, it was possible to accomplish that a 10% was concentrated to 30%. In this way, it was possible for us to achieve concentration in Me 244 in a satisfactory way. An advantage of the continuous evaporation in the slanting tube was this, that the alcohol sulfates were not exposed to higher temperatures for such a long time as is the case when concentrating in a kettle. Difficulties were encountered in so far that crusts were formed in the tube from time to time. This can be ascribed probably to non-uniform flow, and will be studied further.

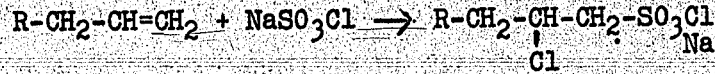
2) Sulfonation of Oxo-alcohols from Roumanian Cracked Middle Oil

Experiments were started to sulfonate Oxo-alcohols, which were obtained from cracked Roumanian petroleum in Me 458a. Both crude alcohol as obtained by Oxo-conversion and hydrogenation (containing high boiling material) and also alcohols freed from high boiling materials by distillation were sulfonated. The preparation of dry alcohol sulfates freed from salts on the drum was not possible because of the stickiness at the higher temperatures. The products easily decomposed on the drum. Drying of alcohol sulfates mixed with sodium sulfates, however, is possible. The experiments are carried further.

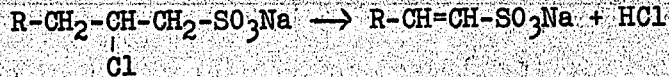
b) Laboratory Runs

1) Sulfonation with NaSO₃Cl

As indicated in the American patent 2,240,920, it was tried to sulfonate olefins with NaSO₃Cl. The sodium salt of chlorosulfonic acid was prepared with sodium chloride and sulfur trioxide. The sulfonation is supposed to go according to the following equation:



Since the sulfonation is done according to the patent at higher temperature (150°), the intermediate product splits off hydrogen chloride



In view of the experiments carried out thus far, the sulfonation of cracked olefins according to the patent occurs only slightly. A great disadvantage is that the sulfonation agent is a solid. The sulfonation of alcohols could not be accomplished under similar conditions. The initially formed alcohol sulfates decomposed at these temperatures in accordance with previous experiences. A simultaneous sulfonation of a mixture of olefins and alcohols, as e.g. Synol-material, is not possible by this method.

2) Another difficulty was encountered after the sulfonation of alcohol hydrocarbon mixtures. The separation of the acid ester from the mixture with hydrocarbons does not succeed by means of resins which can combine with acids. The resin combines primarily