The Texas Company

T O M REEL 55

Item 95

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Problem: 628

Hydrocarbon synthesis from CO and H_2

Research workers: Breywisch, Geiseler

Status as of August 1, 1943

1) Synthesis reactors (Dr. Breywisch)

The three 700 l. pipe reactors (458/1, 2 and 4) were operated in 3 steps without removing the carbonic acid. The conversion was 1:100. The alcohol and olefin content in the products of the 3 reactors was normal and corresponded with the results which were obtained with the three 1. reactors in Me 776.

2) Catalyst reduction

For a 2½ m^3 plate reactor which will be constructed for the recycle method (see Monthly Report of June 1, 1943) 1, 2 m^3 catalyst was reduced in 3 charges. The hydrogen recycle in the reduction equipment is dried with silica gel. For this purpose 2 towers of 800 liter content each are connected in parallel which alternately are introduced in the cycle and dried. In order to study accurately whether the absorptivity of the silica gel may eventually decrease, one of the two towers was filled with fresh silica gel. The old filling consisted of about equal parts of

silica gel A and B. The silica gel A (finely porous) was almost spent while the B part was still fully active. Exact results can only be furnished when at the time of the next reduction charge both fillings can be compared.

3) A distillation column ($\frac{1}{2}$ m^3 content) which belongs to the alcohol processing equipment was set in operation after enlarging the heating surface.

4) The preparation of alcohols, by esterification with boric acid, was first started after the equipment had been altered. So far three runs have been made. The results corresponded with those obtained with the small apparatus in Me 225. In order to dry the boric acid an apparatus heated with high pressure steam was also installed.

Small technical experiments in Me 776 (Dr. Geiseler)

1) The reactor 21 (gasoline synthesis with recycle gas; see Monthly Report of June 1, 1943) does not show any slackening in activity after having been operated for more than 3 months. Only after some changes (the reactor was cut off for several days from steam and gas and held under H_2) did the boiling range of the resulting product change in favor of the high boiling portion. Methane formation decreased from about 12-13% to about 8-9%. Distillation of the products before and after the changes is shown in Table 1.

TABLE 1

Fraction	Before the change Weight %	After the change Weight %
-200 deg.	57.0	32.5
-230 deg.	0.5	2.5
-350 deg.	18.0	17.8
-400 deg.	4.5	4.2
400 deg.	20.0	43.0

2) After the reactor 20 had been operated for about 50 days (reactor test with 30 cm boiler tubes) it was shut off; in this experimental period the activity of the catalyst remained unchanged. This shows that most likely the elimination of the reaction heat by means of the cycle gas and boiling water under pressure takes place to the extent that the temperature in the catalyst granule does not rise over a certain maximum point, above which the activity decreases rapidly. In order to see how the catalyst acts when the heat decrease is not affected by recycle gas, the reactor was operated under otherwise unchanged conditions, i.e., the same rate without recycling. The catalyst did not get out of control, but its activity decreased very quickly and after a few days it had already dropped to half.

3) The 180 l. reactor equipped with external catalyst tubes (No. 22) which during the past report period had been changed so that it can be operated with recycle gas, was filled with W.K. 17 (grain size 0.3-1.0 mm) and operated under gasoline conditions. At a temperature of 186 deg. and a fresh gas charge of 1:280, a conversion of 1:160 is obtained. 63% of $CO + H_2$ in the synthesis gas are converted. The conversion yield is between 150 and 160

g/m^3. 58% of the oxygen from the CO appears in the reduction water and only about 12% in the CO_2 formed, while the balance appears chiefly in the organic compounds; 5-9% of the synthesis gas is converted to methane.

The recycle tests have shown that the blowers (bearings and gears) are strongly affected by corrosion. In order to protect the blower a caustic scrubber was installed directly behind the cooler. Details are illustrated by diagram 1. K indicates the cooler, LW = caustic scrubber, KW= cold separator, and LV = caustic storage. After an operating period of more than 3 weeks with the built-in scrubber practically no corrosion could be noticed.

Drawing

(Too faint to be reproduced)

This method of neutralizing the acid soon caused difficulties in the operations. Since on account of the relatively high CO_2 content of the recycle gas, considerable caustic is charged (in 4 hours about 3-4 liters 15% NaOH), bicarbonate particles (mist) which were entrained very soon obstruct the preheater (in order to keep the temperature of the preheater constant, the steam pressure must be increased continuously). The analysis of a product taken out of the preheater showed 52% bicarbonate, 5% Fe_2O_3, 4% soot and the rest water and organic products. In order to prevent further entrainment of bicarbonate as mist in the preheater, the experimental arrangement was made in such a way that the recycle gas is washed alone; reaction water and cold separator

product are thus previously drawn off and then the washed recycle gas passes through a centrifugal separator.

Diagram 2 shows the present status of the experimental arrangement of reactor 22. In the drawing are: O = reactor, HA_1 & HA_2 = hot separator, K = cooler, LW = caustic scrubber, ZA = centrifugal separator, KA = cold separator, G = blower, U_1 and U_2 = gasometers, LV = caustic storage , V = preheater, M = orifice meter, and TB = separator vessel.

Drawing

(See following page)

Laboratory Work in Me 245 - Separation of alcohol from mixtures with hydrocarbons by adsorption with silica gel.

1) Time spent in charging the gel

To be able to answer the question, how much time should be spent in order to obtain the best saturation with the least filtering thru of the product, the following experiment was made. Through a column of 1.0 m length and 1½ cm inside width corresponding to an amount of 140 g fresh dried gel, in three experiments 400 cm^3 of a Synol fraction of 168-173 deg. C. with 10% alcohol were filtered thru in three different time periods. The product which drains off or drops off at the lower end of the tube was collected in portions of 50 cm^3 each and tested for its alcohol content. The filtering time in the three experiments amounted to 20, 90 and 360 minutes. The result of the test is shown in Graph 3.

Drawing

(Too faint to be reproduced)

As can be seen from the Graph 3, the characteristics of the three curves are very little different in spite of the extremely different time periods which had been chosen, i.e., the adsorption from the liquid to the gel goes exceedingly fast and complete saturation is obtained within a short period of time. Technically, this fact means that the duration period has to be neglected when considering the other operating periods necessary for washing, removing of gel, and drying.

2) Experiment to remove the adsorbed alcohols from the silica gel by means of water.

a) 214 g freshly dried gel was agitated for 1 hour with 600 g Synol-Cg-alcohol, the supernatant solution poured off and the gel extracted in a Soxhlet for 2 hours with petroleum ether. The gel so treated was now agitated three times with 1 liter of water, the aqueous extracts combined and the upper layer separated. After drying the oil, 26 g alcohol remained, corresponding to a yield of 12.1 g/100 g gel.

b) 200 g freshly dried gel were treated exactly as under (a), i.e., with a Synol product of the fraction of 170-180 deg. with an alcohol content of 45%. By shaking with water, 27 g oil were obtained containing petroleum ether with 85% alcohol, which equals a yield of 11.5 g/100 g gel.

Whether the used gel continuously regenerated can be reused must be determined by series and duration tests. From the

experiments so far made it could be established that when the gel had been regenerated twice or several times, emulsions occurred when treated with water (alcohol - water - petroleum ether). When fresh gel was used no formation of emulsion occurred. However, the formation of the emulsion can easily be prevented by using warm water of about 60-70 deg. C. instead of cold water. The experiments are being continued.

Signed: Dr. Breywisch