

# The Texas Company

T O M REEL 55

Bag 2523

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Item 96

Assignment: 628

Hydrocarbon Synthesis from Carbon Monoxide and Hydrogen

Research Workers: Breywisch, Geiseler

Status as of June 1, 1943

Synthesis reactors: (Dr. Breywisch)

In the time allotted for a report on this work reactor 2 (14 mm tubular reactor with 700 l. catalyst) was started. First, a fine-granular catalyst (0.3-1 mm as compared with 1-2 mm granular size in previous experiments) was used. The depth of the bed was 4 m. Corresponding to the small scale tests in Me 776, an approximately 10 deg. lower operating temperature was required for equal conversion. Then, as the second step, the reactor was connected behind reactor 4 (700 l. capacity of 1-2 mm granular catalyst) with intermediate separation of the products but without extraction of the CO<sub>2</sub>. In agreement with the small scale tests which were carried out with recycle gas, it was shown that the CO<sub>2</sub> acts only as inert gas and in no way causes damage to the catalyst or a noticeable increase in the operating temperature.

The plate reactor, put to use for the first time in the previously reported period (2.5 m<sup>3</sup> capacity, was freed of paraffin by extraction. Work was begun on the removal of the catalyst. According to the results to date, approximately 250 man hours would be necessary. From this point of view, the use of plate

reactors for synthesis with fused catalysts, as is customary in the Fischer plants, is very disadvantageous in contrast to the reactor developed in Leuna during the course of the last year which consists of a system of cooling tubes without the use of plates.

### CORROSION

All reactors, at the point where the mixture of hot gaseous products enters the hot separator, were provided with a gooseneck, which is fed with caustic soda or a soda solution. Since the soda, due to the CO<sub>2</sub> content in the gas (15-25%) is converted to bicarbonate, the acids are not removed quantitatively. In the products of the second cooling stage, an acid number of 0.2-0.8 (in contrast to 10-20 without alkali addition) is always found. However, in no case was corrosion noticed. The washing was carried out at a temperature of 110-130 deg.

#### I. Small Scale Technical Experiments in Me 776: (Dr. Geiseler)

##### 1. Gasoline Synthesis - Recycle Method

Reactor 20 (gas recycle test) operated in the past reported period under Synol conditions, was transferred after a period of about two months to gasoline conditions. Next, under extreme synthesis conditions (extensive conversion of the fresh gas charge with the highest possible yield), the yield was to be evaluated with regard to the liquid and gas portions, the composition of the product and the extent to which the activity of the catalyst alters on use. The catalyst operates at 200 deg. C., with an initial rate of 1:500 and a conversion of 1:350 (69% of the fresh gas with

reference to CO plus hydrogen is converted). The oxygen of the carbon monoxide, not used in forming the reaction product, is converted up to 30% to CO<sub>2</sub> and up to 47% to reaction water. 30% of the converted gas is changed into methane. The liquid yield amounts to about 135 g/m<sup>3</sup> of converted gas. The following Table 1 shows the composition of the product.

Table 1

Fraction	Weight %	Weight % Olefins	Weight % Alcohols
28-200	73.5	44.7	40.7
-230	0.8	22.7	33.2
-350	12.4	32.3	45.5
-400	3.0	27.8	26.0
400	10.3	--	--

2. Gasoline Synthesis with Recycling - One Stage Operation

Reactor 21 was rebuilt as a second unit for the gas recycle operation. The experimental procedure remained essentially the same as described for reactor 20, only there was a centrifugal separator between the blowers and cold separator in order to precipitate the liquid product entrained through mist formation. The hot separator is now heated with high pressure steam; the high boiling portions therein separated have a dropping point of about 114 deg. C. The reactor was operated under gasoline conditions and study should be made as to how the synthesis conditions must be chosen, if the largest portion of the fresh gas (about 85-90% of the CO and hydrogen mixture) is to be converted and the highest possible conversion is to be attained (operation in one stage). The reactor operates at present at a temperature of 196

deg. With an initial rate of 1:200 and a conversion of 1:160, it converts about 85% of the CO and hydrogen mixture. About 35% of the oxygen of the carbon monoxide not going into the organic products reacts to form CO<sub>2</sub> and 50% to form water. The liquid yield amounts to an average of 140 g/m<sup>3</sup> of converted gas, the spent gas contains about 40% carbon dioxide, and 10-12% of the converted gas is changed to methane. As synthesis gas a mixture of O-water gas and methanol-fresh gas is used which is so made up that carbon monoxide and hydrogen under the given conditions are present in the exhaust gas in the ratio of 1:1. The mixture was so chosen in order to prevent concentrating one of the two components and to offer a check to a far-reaching conversion of the gas. The cold separator product has the following composition (Table 2):

Table 2

Fraction	Weight %	Weight % Olefins	Weight % Alcohols
30-200	55.3	31.9	40.3
-230	2.0	40.6	30.8
-350	18.2	33.6	46.8
-400	4.0	31.2	31.0
400	20.5	—	—

### 3. Reactor experiment

To determine whether the condenser tubes in the 12 cm reactor should have a distance of 11 or 15 mm, reactor 20 was fitted with a cooling aggregate of 20/25 mm tubes, which had a distance of 30 mm, was filled with WK 17 of granular size 1-2 mm, carefully started and brought slowly to standard conditions.

At a temperature of 197 deg. and an initial rate of 1:350, the reactor converted about 180 m<sup>3</sup> gas/m<sup>3</sup> catalyst/hr. By this experiment it is shown that with the cooling installation at hand, the heat of reaction is still carried off to the extent that the reactor still remained under control. How far under the given conditions the catalyst is attacked cannot yet be said; this decision must be determined by long-term experiments. In any case the experiment shows that the condenser tubes can have a distance of 15 mm without danger to the synthesis in the recycle method, a distance which at present has advantages in the removal of the catalyst.

#### 4. Synthesis Pressure - Experimental

On the basis of the recycle method and the approximately 10-15 deg. lower synthesis temperature achieved thereby, it seemed of interest to determine whether the optimum synthesis pressure was still at approximately 25 atmospheres or whether under the now chosen operating conditions higher pressure could be used. For this reason experiments were carried out in which the synthesis pressure was increased from 25 atmospheres to 80 atmospheres. The resulting product is essentially darker colored and its odor indicates a definite decomposition. The composition of the product has shifted in favor of the alcohols (since as a result of the pressure increase the synthesis temperature can be kept lower), but on the whole no particular advantages have resulted. (See Table 3.)

Table 3

Reactor	Rate	Synthesis Temp.	Pressure atms.	Weight % alcohol in the fractions				Comments
				-200	-230	-350	-400	
20/4	1:7000	183	24	43.7	47.6	71.8	81.7	Recycle
19/6	1:10,000	165	80	66.5	68.9	79.6	53.4	Fresh gas, one stage

### 5. Preparation of amines

If one mixes ammonia with the synthesis gas (CO plus hydrogen), it is to be expected that the alcohols formed on the catalyst are further converted to amines. In order to establish the influence of ammonia on the synthesis products, an experimental procedure was chosen as is shown in Ill. 1. (This illustration cannot be reproduced. - Translator) In it L signifies a caustic tower through which the synthesis gas bubbles for the purpose of separating the CO<sub>2</sub>; A is a container filled with 10% ammonia water. At a determined velocity, the synthesis gas carries the ammonia into the reactor with a definite partial pressure. The synthesis temperature was 175 deg. and about 50 m<sup>3</sup> gas/m<sup>3</sup> catalyst/hr. were converted at a fresh gas charge of 1:350. The resultant product is distinguished by an intensive amine odor, which, however, soon diminishes after extended standing in the air (low boiling amines). In this experiment, the amine portion of the total liquid product was approximately 10% without considering the amines already lost through evaporation before working up the product. The alcohol and olefin contents are given in Table 4.

Table 4

Fraction	Weight %	Weight % Olefins	Weight % Alcohols
-200	40.4	36.0	31.6
-230	1.0	31.5	31.1
-350	23.1	40.1	33.0
-400	8.4	20.0	42.0
400	27.1	---	---

## II. Laboratory Work in Me 245: (Dr. Geiseler)

### 1. The separation of alcohols from mixtures with hydrocarbons by means of adsorption-distillation

Based on the work of G. Hesse and B. Tschachatin (Naturw., 30, 387 (1942)), experiments have been made since January to separate alcohol-hydrocarbon mixtures through adsorption-distillation. For this purpose an apparatus was constructed as is shown in Ill.

2. (Too faint to be reproduced.) In round-bottom flask R is placed the alcohol-hydrocarbon mixture; in column K (internal diameter 2.5 cm, height of bed 1 m), very porous silica gel B of grain size 1-2 mm, which has been dried with dry hot nitrogen at approximately 180 deg. for more than 6 hours. The column is kept at 100 deg. by means of steam. Through the capillary tubes reaching into the round-bottom flask passes a nitrogen stream of approximately 3-4 lit/hr., this rate being controlled by a flow-meter. Temperature measuring points are in the flask and in the uppermost layer of the gel. At the beginning of the experiment the temperature is always higher than towards the end but nevertheless always a few degrees under 100 deg. The distillate is collected in narrow fractions and examined as to composition.

Experiments were carried out:

1. with mixtures composed of equal boiling fractions of hydrocarbons and alcohols (Ill. 3, Curve I)
2. with mixtures which had been obtained through vacuum distillation of the primary product obtained in the semi-technical unit Me 458 (Curve II); and
3. with mixtures obtained by distillation of the primary product under normal pressure (Curve III).

Experiment: 43/4 (Curve I in Ill. 3) (See following page.)

Charge: 300 cm<sup>3</sup> gel, 75 cm<sup>3</sup> Synol mixture (192-200 deg.), 65% alcohol, 18.5% olefins

Table 5

Frac- tion	Temp. Oil Bath	Temp. Flasks	Temp. Column	Vacuum mm	CO <sub>2</sub> Stream mm	Distil- late cm <sup>3</sup>	% Al- cohol	% Ole- fins
1	102	82	101	5	2	5	1.4	40.8
2	102	87	101.5	5	2	5	1.4	51.4
3	112	93	105	5	2	5	0.8	51.3
4	119	99	107	5	2	5	0.85	54.5
5	123	100.4	103	5	2	5	60.4	22.5
6	133	100.5	100	5	2	5	87.9	8.2
7	140	103.5	99	5	80	5	97.1	5.5
8	144	100.5	99	5	80	4.5	97.1	4.5

Extraction of the gel: 24.5 cm<sup>3</sup>

Ice cooling: 3.5 cm<sup>3</sup>

The fractionating action of this method is based on the facts that:

1. the temperature-vapor pressure curves of the alcohols and hydrocarbons do not run parallel but rather diverge strongly with decreasing vapor pressures so that, therefore, the difference in the distillation points increases (details on this are given in the work of Dr. Reisinger);



2. the carrier (nitrogen, carbon dioxide, water, etc.) forces the molecules to be separated through the column and reduces the partial pressures;

3. the adsorbability of the components varies.

In the hydrocarbon-alcohol mixtures here being considered the difference in adsorption of both components is so great that at the end of the experiment it is not possible to carry off with the carrier gas the alcohol adhering to the gel, not even with the use of a many times increased gas charge. The experiments showed that the mixtures mentioned under (1) could be most easily separated and those noted under (2) the least easily. The separation effect of the latter is based solely on the difference in adsorption between alcohol and hydrocarbon, since separating action, as a result of distillation under decreased pressure, can no longer occur because the product introduced was fractionated under corresponding conditions (vacuum column in Me 458).

Should the fractions to be separated be selected too broadly, the fractionating action is reduced and one gets flat, distorted curves. The rise of the curve is still<sup>0</sup> dependent on various other factors, for example, on the temperature to which the gel tower is brought - it should lie only slightly over the boiling point of the vaporizing mixture - and on the carrier gas which serves as a means of elution. The perpendiculars Ia, IIa, and IIIa added to the curves in III. 3 would result with an ideal separation.

2. Experiment on the isolation of high molecular alcohols from high boiling primary products through adsorption on silica gel.

For the isolation of alcohols from mixtures of hydrocarbons through adsorption on silica gel the assumption must be made that

the products be as non-viscous as possible and in case of high viscosity still be readily soluble in the solvents particularly suitable for this procedure. Since the high boiling residue is very viscous in the molten state and furthermore is very difficultly soluble in all solvents, the separation was fraught with considerable difficulties. It was therefore thought best to proceed in the following manner: 100 g hot separator product (dropping point: 95 deg., OH-No.: 14.0) were dissolved in 1.5 liters of Xylol under heating; 200 g freshly dried gel added and this mixture kept at approximately 90 deg. for 90 minutes while well stirred; the still warm Xylol solution was decanted and the gel washed for two hours in the Soxhlet with petroleum ether and next extracted for 10 hours with acetone. The experiment yielded the following data:

	<u>g</u>	<u>OH-No.</u>
Xylol extract	33.5	11.0
Petroleum ether extract	4.5	6.9
Acetone extract	4.0	92.0

The acetone extract obtained has a dark brown color and is essentially softer than the initial product. Its dropping point is 72 deg. C.

Translated by E. Spiekerman