

The High Pressure Gas Circulation Process for the  
Synthesis of Ethyl Alcohol from CO - H<sub>2</sub> - containing  
Waste Gases

The experiments of Dr. Eduard Linckh in the preparation of hydrocarbons from CO - H<sub>2</sub> under elevated pressure with fused iron catalyst furnish the groundwork for this process. In this connection appreciable quantities of reaction water were formed containing water-soluble alcohols, especially ethyl alcohol. The experiments were continued by Dr. Klenow in order to increase the proportion of alcohols. At the same time Dr. Klenow initiated experiments for the study of fused iron catalysts and to determine new catalyst compositions which would especially favor the formation of water-soluble alcohols.

The Gas Circulation Process

The conversion of carbon monoxide-hydrogen mixtures with fused iron catalysts under pressure necessitates special preparations in order to avoid an excessive reaction in the direction of methane or soot formation. If such measures are not taken, the reaction will be concentrated in the catalyst layer situated near the gas entry to the accompaniment of overheating. As a result of the high reaction heat the reaction continues to proceed rapidly in the narrowest space and spontaneously leads to carbon monoxide decomposition and to loss of control of the reaction temperature.

After several experiments the following measures were taken to control the reaction:

1. The catalyst is arranged annularly in a thin bed inside of a tube. The outside of the tube is jacketed with water under pressure.

in order to surrender a portion of the reaction heat to the water through the tube.

2. The synthesis gas is recirculated so that the carbon monoxide concentration in the circulated gas does not exceed 10 per cent by volume.

3. The catalyst at the gas entry side is copper plated in order to diminish the danger of soot formation.

4. The recirculated synthesis gas is conducted throughout the entire length of the catalyst bed but mainly passes the space free of catalyst in the middle of the tube so that it only sweeps along the annular catalyst, partially penetrating it.

The ration of the quantity of circulating gas to the fresh gas was 3 : 1.

20 - 25 per cent of the fresh gas was constantly released from circulation as final gas.

In general, the circulating depressured gas of the isobutyl alcohol synthesis was used as fresh gas; however, other gas mixtures were experimented with. The experiments were conducted at a pressure of 180 atm. gage and a temperature of 290-320 degrees.

#### Equipment

The reactor consisted of a high pressure tube of 120 mm. internal diameter with a built-in seamless boiling tube of 82 mm. internal diameter. Water, activated by a thermosyphon, was circulated in the outer annular space between both tubes. The inner boiling tube contains a central wire net hose which keeps the middle of the tube free from catalyst for the catalyst is charged into the annular space between the boiling tube and the hose. The diameter of the bed was 10 - 12 mm.

The synthesis gas enters the top of the reactor, passes from top to bottom of the central boiling tube containing the catalyst and is conducted to a hot separator via a small separator, a heat exchanger and a hot cooler. It then passes through a "cold cooler", the cold separator and is washed by oil. The circulating gas is returned to the reactor by means of a gas circulating pump after depressuring a part of the circulating gas and adding make-up gas. Before entry into the reactor the circulating gas passes through a pre-heater and finally the heat exchanger where it is heated to the reactor entry temperature by the hot circulating gas. The depressured gases of the compressed oil wash, as well as the circulating depressured oil, were led through an activated charcoal plant in order to recover highly volatile hydrocarbons.

#### Catalysts

Fused iron catalysts that were obtained by melting the following mixture in a current of oxygen were used in the pilot plant:

- 89.5 % iron powder
- 2.24 % titanium dioxide
- 2.24 % silicon powder
- 2.24 % manganous oxide
- 2.03 % copper powder
- 1.80 % KOH dissolved in some water

If the mixture is carefully added to the melt the copper will burn well and will enter the melt. On the other hand, when copper oxide was employed it was reduced to metal and separated out in the form of molten metallic globules.

### Reduction of the Catalysts

The oxidic fused catalyst cakes were crushed to a particle size of (sic) mm. and then reduced with hydrogen at 650 degrees C. for 3 days. A hydrogen quantity of 500 - 700 liters is used hourly for every liter of catalyst.

The reduction temperature of 650 degrees is the most favorable. Higher temperature markedly impairs catalyst activity. A lower temperature during reduction means greater activity and shows that the synthesis takes place at low temperatures. In this connection, however, the formation of water-soluble alcohols diminishes, and the formation of oil increases.

### Copper Plating of the Catalyst

It was observed over and over again when working in the gas phase that more or less marked formation of soot readily occurred at the side of the catalyst charge turned to the gas entrance. To correct this trouble, which causes catalyst decomposition, copper-plated catalyst was charged into the upper sixth of the reactor. Copper-plating of the catalyst is accomplished by treatment with a weak (5%) nitric acid copper nitrate solution.

In this manner soot deposition was avoided without impairment of activity.

### Synthesis Gas

#### a. Type of Gas

Three different types of fresh gas were used in the various experiments.

1. A mixture of 20 per cent pure CO and 80 per cent zero (Nullgas) gas (2 per cent N<sub>2</sub>).
2. Butyl residue gas enriched to about 45 per cent with pure CO; rediluted to 20 - 22 per cent CO by addition of zero gas (2 per cent N<sub>2</sub>).

3. Pure butyl residue gas (6 - 6.5 per cent  $\text{CO}_2$ , 0.5 - 1 per cent  $\text{C}_n\text{H}_{2n}$ , 20 - 22 per cent CO, 57 - 64 per cent  $\text{H}_2$ , 5 - 6 per cent  $\text{C}_n\text{H}_{2n+2}$ , 5 - 6 per cent  $\text{N}_2$ ).

In these investigations an approximately constant proportion 20 per cent CO was maintained so that differences in result could not be attributed to divergencies in this constituent. The hydrogen proportion showed appreciably greater differences. In the mixture of CO with zero gas it was 80 per cent. In the case of the butyl (Tanol) residue, gas treated according to 2., it was 70 per cent, and in the case of pure butyl (Tanol) residue gas, it was 60 per cent. This gives a ratio of CO : H<sub>2</sub> = 1 : 4, 1 : 3.5, 1 : 3.

The third important difference lies in the "inert gas content particularly with saturated and unsaturated hydrocarbons. In this instance the butyl residue gas clearly has the greatest proportion.

According to the experimental results there is no noticeable difference if the mixed gas consisting of CO - H<sub>2</sub> or the rediluted, or Tanol residue gas is used. However, the use of pure Tanol residue gas immediately resulted in appreciably better yields. This was shown with particular clarity in an experiment in which rediluted gas was used in the first period, iso-gas in the second, and rediluted gas again in the third. The first period yielded 64.35 grams/m<sup>3</sup> fresh gas product, the second 82.1 grams/m<sup>3</sup>, the third 60.75 grams/m<sup>3</sup>. This increase in yield which occurs in several experiments is explained by the proportion of low-molecular carbons and similar compounds which were then synthesized or built up into larger molecules. It is not clear to what extent the CO<sub>2</sub> and methane participate in the conversion. It can be said in general that the use of butyl residue gas is most advantageous. In addition, there is the omission of compression since the gas can be used with the obtained pressure.

b. Space Velocity

The throughput of fresh gas is of further importance in increasing the yield. This is shown by several experiments. Calculations are for a space velocity of  $m^3$  per liter of catalyst per hour. Three experiments were conducted with a special catalyst arrangement ("lower bed installation" with 50 cups") with Tanol flue gas under similar conditions. The use of  $0.65 m^3$ /liter catalyst resulted in  $93.3 \text{ grams}/m^3$  fresh gas;  $0.75 m^3$ /liter gave  $62.28 \text{ grams}$ . Another experiment, conducted with mixed gas consisting of CO-zero gas (Nullgas), resulted in  $58.25 \text{ g}/m^3$ , using  $2.15 m^3$ /liter of catalyst in the first period; a space velocity of  $3.4 m^3$ /liter in the second period gave only  $41.54 \text{ grams}$ . Experimental conditions were almost the same.

c. Pressure

Increase in pressure acts in two directions. Under similar conditions the yield increases with rising pressure and the tendency toward formation of hydrogen-containing products simultaneously increases. An experiment with a bundle of tubes with circulation of water, using a space velocity of  $3.4 m^3$ /hour, gave  $41.94 \text{ grams}/m^3$  at 100 atm. gage, and using a space velocity of  $3.7 m^3$ /hour gave  $44.08 \text{ grams}/m^3$  at 180 atm. gage. In the first case the yield consisted of 30.59 per cent of alcohol; in the second case it consisted of 84.5 per cent of alcohol.

d. Circulating Gas

The quantity of circulating gas is kept as high as necessary, to insure that the entrance gas does not exceed 10 per cent of CO on an average by dilution with fresh gas. Larger quantities of circulating gas are too large to pass through and produce yields that are too little. As a result of increasing enrichment of the CO in the incoming gas the conversion is

altered in favor of the oil content, and finally the reactor tends to get out of control.

In addition to removing a part of the heat of reaction the circulating gas should also act as a safety gas. It is assumed that the first stage of the conversion produces oxygen-containing compounds, in particular alcohols. These compounds, which call for speedy removal, are safeguarded by dilution with non-reactive or slightly reactive compounds. A decrease in the quantity of circulating gas led to an increase in hydrocarbons and similar compounds.

With respect to the formation of alcohols, it was shown to be advantageous to free the circulating gas of volatile compounds by the wash under pressure before returning to the reactor since these compounds again participate in the formation of hydrocarbons and other similar substances during the reaction. The total yield was higher if it was not

e. Final Gas

The final gas carries with itself a greater or lesser amount of highly volatile hydrocarbons, particularly liquefiable hydrocarbons, depending on pre-treatment. It is therefore purified with charcoal, consisting afterwards essentially of hydrogen, methane and nitrogen, along with a percentage of  $\text{CO}_2$  and some non-condensable hydrocarbons. The remainder is the unconverted  $\text{CO}$  is also contained in it. It is available for further working up for fuel purposes. The remainder is about 30 - 40 per cent of the volume of the fresh gas. The quantity of substances which can be removed by active charcoal ranges between rather wide limits, between about 20 grams/ $\text{m}^3$  to about 80 grams/ $\text{m}^3$ , depending on conditions.

### 5. Products

The following products are obtained by the synthesis in the gas phase:

- a. Oils from the cold separator.
- b. Light oils as distillates from the wash oil.
- c. Activated charcoal gasoline.
- d. Liquefiable gas.
- e. Alcohols from the cold and hot separator.

A total yield of 53.31 grams/m<sup>3</sup> of the following composition was found as means value in the 7 large-scale experiments:

|                              |                              |                |
|------------------------------|------------------------------|----------------|
| Oils from the cold separator | - 12.61 g/m <sup>3</sup>     | - 23.28 %      |
| Light oils from the wash oil | - 3.14 "                     | - 5.62 %       |
| Activated charcoal gasolines | - 6.56 "                     | - 12.64 %      |
| Liquefiable gases            | - 4.2 "                      | - 8.49 %       |
| Alcohols                     | - 25.58 "                    | - 49.47 %      |
|                              | <u>58.31 g/m<sup>3</sup></u> | <u>- 100 %</u> |

In this connection fluctuating small quantities of semi-solid, paraffin-containing products, which may contain up to 40 per cent of higher alcohols, are obtained from the hot separator. Because of their small quantity they are calculated as part of the oils from the cold separator.

These fresh, light-colored oils range from colorless to light yellow. They turn brown if kept in the presence of air. They have a pungent odor similar to esters of alcohols. Mean density 0.771. Flakes of small amounts of higher hydrocarbons often float in it. Boiling begins at about 45-50 degrees. 90 - 95 per cent is distilled at 300 degrees, the residue consisting of dark brown, semi-solid paraffinoid masses. The acid number is 10-12; saponification number 30-35; OH number 120-140. The oils still contain appreciable quantities of water-soluble alcohols which can be



scrubbed out in quantities of 18-25 per cent by stirring with water. per cent of the oil is evaporated at 90 degrees during distillation. distillate is divided into two parts. The lower layer (8-10 per cent with a density of 0.896 contains about 75 per cent alcohol in water. upper layer with a density of 0.720 contains about 23-25 per cent of alcohol (water-soluble). The residue of 48-50 per cent of the crude is dark brown and contains about 5-6 per cent water-soluble alcohol. was possible by careful distillation to recover the bulk of the alcohol especially on adding slight quantities of water. The light distillate corresponds substantially to activated charcoal gasoline. The remainder consist principally of fractions corresponding to illuminating oil and oil. The residue consists principally of paraffins with a V.S. of 16. Together with oils of similar origin the oils can be worked up to gas illuminating oils and liquefiable gas.

b. Light Oils from Wash Oil

A light colorless distillate ( $d = 0.680 - 0.702$ ) is obtained from the wash oil of the oil scrubber. The distillate stands between oil from the cold separator and the activated charcoal gasoline, but resembles the latter a great deal. It is therefore mixed into that tar. Boiling starts at 30-35 degrees. This fraction which contains about 10 per cent of the yield can be worked up with activated charcoal gasoline.

c. Activated charcoal gasoline

A condensate with a density of 0.660-0.680 and composed of 85-95 per cent of low-boiling, paraffinic and olefinic hydrocarbons is obtained when the activated charcoal towers are purged with superheat steam. This amounts to 10-15 per cent of the yield. Boiling starts

30-35 degrees and 40 per cent is evaporated at 45 degrees. This distillate forms two layers: the lower layer with a density of 0.962 is composed of 55-60 per cent alcohols and amounts to about 1 per cent of the gasoline; the upper layer (38 per cent) with a density of 0.670 is composed of 16 per cent of alcohols and the distillation residue ( $d = 0.722$ ) another 13-14 per cent of alcohols. The crude gasoline contains roughly 17 per cent alcohol. After preliminary hydrogenation this product can be worked up with other gasolines.

d. Liquefiable Gases

The liquefiable gases, the  $C_3 - C_5$  hydrocarbons, are driven off along with the activated carbon gasoline. They form 8-10 per cent of the yield and, according to current analyses, contain about 90-95 per cent olefinic hydrocarbons. Since no compression is available, they have heretofore not been recovered but their presence merely determined in a part of the residue gases. The bulk of the liquefiable gas (about 90 per cent) is contained in the let down gases of the pressure scrubber along with a large part of the activated charcoal gasoline. In a large plant provision could be made for continuous fractional distillation of the wash oil with fractionated depressuring. The final gasolines and the liquefied gas could be continuously obtained under pressure in a liquified form. It is planned to return the liquefiable gases to the process by injection.

e. Alcohols

The product alcohol is obtained in amounts of 45 - 55 per cent of the yield, in individual cases up to 60 per cent. The bulk is contained in the water from the cold separator which consists of 45-50 per cent alcohol. A solution of 3-10 % alcohol is obtained from the hot separator.

The alcohols are pre-concentrated to a concentrate of 90 per cent  
The crude alcohol contains about 10 per cent water.

|                 |           |
|-----------------|-----------|
| Acetaldehyde    | 2 - 3 %   |
| Acetone         | 3 - 5 %   |
| Methanol        | 10 - 15 % |
| Ethanol         | 60 - 70 % |
| Higher alcohols | 10 - 15 % |

Since the separation of aldehyde and acetone from the al especially ethyl alcohol, by distillation is incomplete, these imp should be converted to the corresponding alcohols by a previous ca hydrogenation. Experiments show that the aldehyde and ketone reac thereby completely disappears.

Literature:

|                 |                           |  |
|-----------------|---------------------------|--|
| French patent   | 833302 )                  | Discovered by Dr. Ed. Lir<br>Dr. Fr. Wir             |
| English patent  | 478318 )                  |  |
| American patent | 2148099 )                 |  |
| German patent.  | 76490, December 23, 1943. | Discove<br>Dr. R. Klen<br>Dr. E. Linc<br>Dr. Fr. Wir |

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Duftschildt