TOM Reel 101 – Doc. PG-21579 – NID>

"INVESTIGATION OF THE REACTION WATER OBTAINED FROM MIDDLE-PRESSURE SYNTHESIS EXPERIMENTS WITH IRON CATALYSTS AND HYDROGEN-RICH STARTING GAS, F. Weinrotter, April 30, 1941"

PRELIMINARY OBSERVATIONS

The first step in the investigation was to separate the water obtained during the synthesis from the liquid and solid hydrocarbon reaction products. The water was colorless at first, but after a few days, it acquired a light brownish hue. The reaction water was acid towards litmus. Certain quantities of iron salts were shown to be present.

QUANTITATIVE DETERMINATION OF THE ALCOHOLS AND FATTY ACIDS IN THE REACTION WATER

Saponification

735 cc. of the reaction water were refluxed for several hours with an excess of sodium hydroxide.

Analysis of Saponification Fraction Boiling Below 100°C

At this point, a 73.2 cc. fraction boiling up to 100°C and containing the alcohols could be separated. Qualitative tests on this fraction revealed the presence of ketones (acetone, methyl ethyl ketone) and the absence of aldehydes.

The boiling point curve obtained by distillation of this alcohol fraction in a well-designed micro column (15 theoretical plates) is shown in Figure 5.

From the boiling point curves, and the constant boiling azeotropic mixture of ehtyl and propyl alcohol with water, the percent of pure alcohol in the reaction water could be calculated. The figures are given in Table 3.

Table 3.- Content of Pure Alcohols in the Reaction Water Expressed in Weight Percents

Methyl alcohol	0.6
Ethyl alcohol	3.2
N-propyl alcohol	1.3
N-butyl alcohol	0.5 (to 0.6)*
Total	5.6

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*The fraction boiling at 92°C. (indicated in Figure 5) was assumed to be the azeotropic mixture of butyl alcohol and water. Owing to lack of information in the literature, this cannot be considered conclusive.

Analysis of Saponification Fraction Boiling Above 100°C.

The fraction boiling above 100°C. was evaporated on the water bath, and the sodium salts thus obtained were decomposed with dilute sulfuric acid.

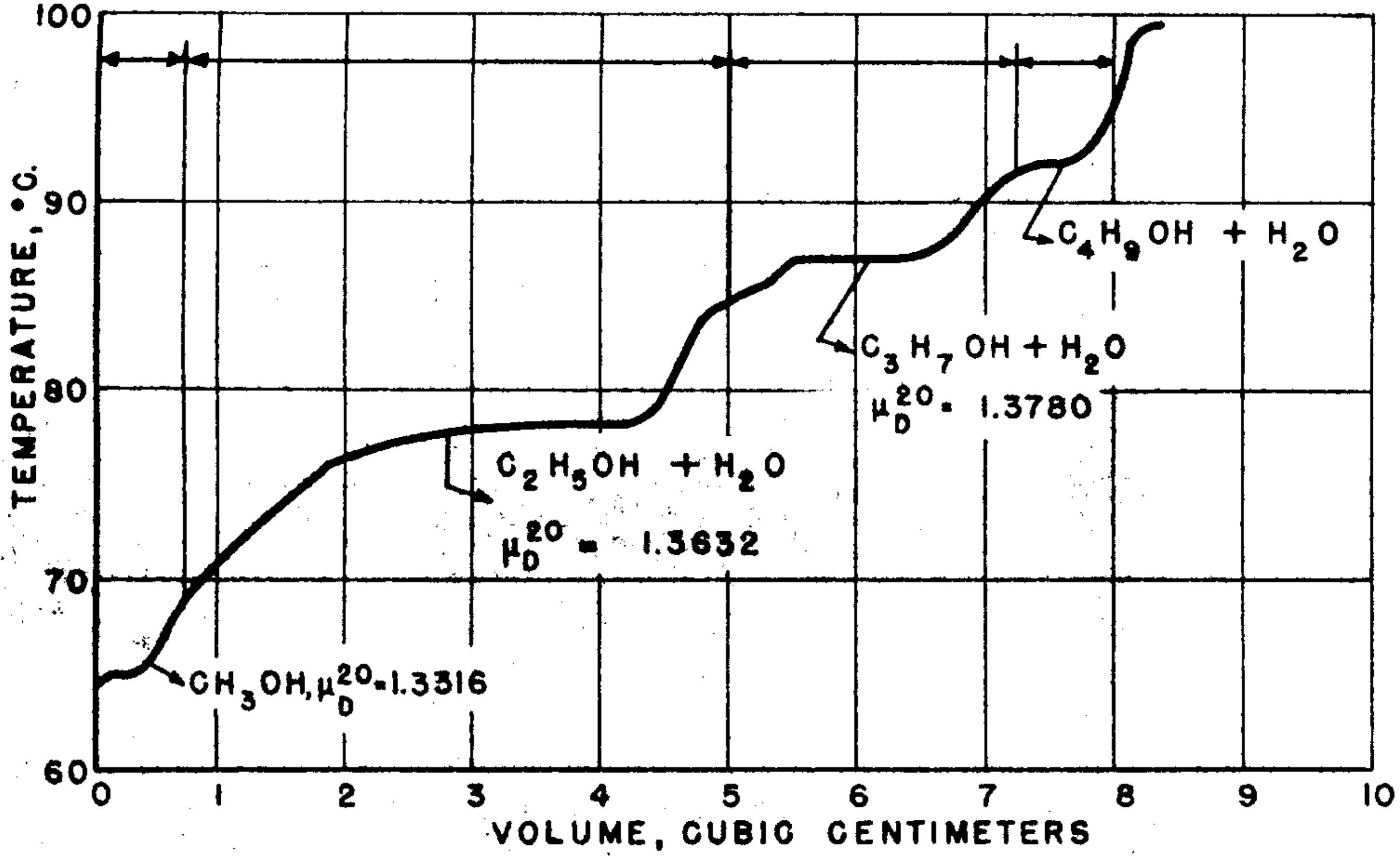

Figure 5.– Analysis of reaction water after saponification; micro distillation of 10 cc. of the fraction boiling below 100 °C.

The solution was then saturated with sodium chloride, and extracted for 150 hours with ether in a Kutscher-Steudel apparatus. Removal of the ether by distillation produced a 1.7-gram residue of pure fatty acid which, referred to the total quantity of reaction water analyzed, amounted to 0.23 weight percent.

FURTHER TESTS

For further identification, the fatty acids were esterified with methanol in the presence of sulfuric acid and the mixture of esters distilled in a micro column.

The only fraction which was obtained was 1.8 cc. of methyl acetate, since at high temperatures, the mixture of the esters of the higher fatty acids decomposes in presence of sulfuric acid. Methyl formate was not present.

The quantity of acetic acid calculated from the methyl acetate fraction was 1.36 grams so that the fatty acid mixture contained approximately 80 percent by weight acetic acid. The remainder was composed of the higher homologs of the fatty acid series, and could be recognized by their characteristic odors. Formic acid was not present or if present, only in very small traces. In the original reaction water, fatty acids were present in free form up to approximately 80 percent. This was evident from the acid- and esterification-values and from the distillation curve of the fraction of the original reaction water which boiled below 100°C. (Figure 6). This fraction closely resembles the corresponding fraction obtained by saponification of the reaction water.

Figure 7 shows the variation in reaction temperature with synthesis gas composition, and Figure 8 summarizes graphically hydrocarbon and water yields versus synthesis gas composition, after four weeks of operation. (This refers to a one-stage operation.)

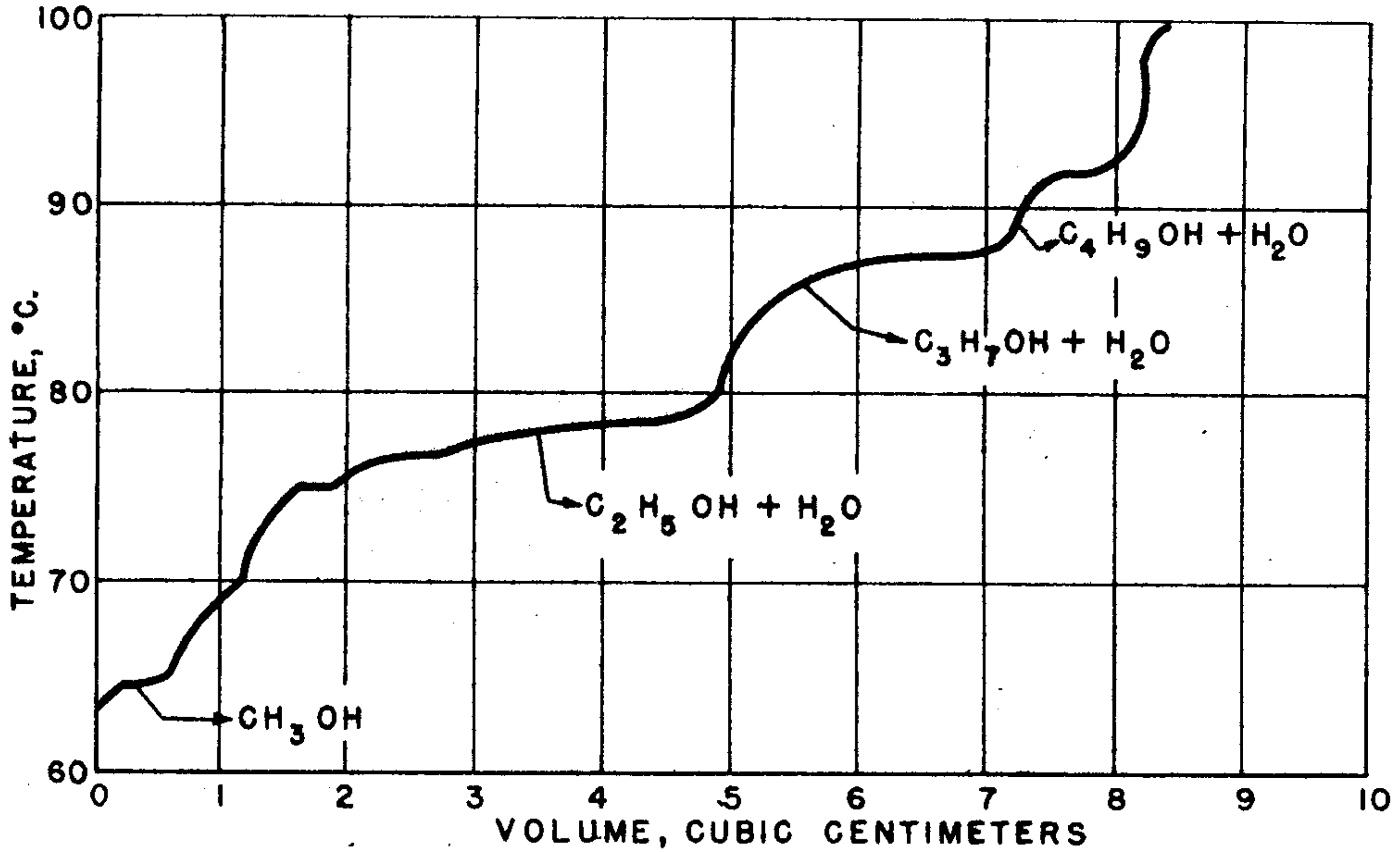

Figure 6.— Analysis of reaction water; distillation of fraction boiling below 100 °C.

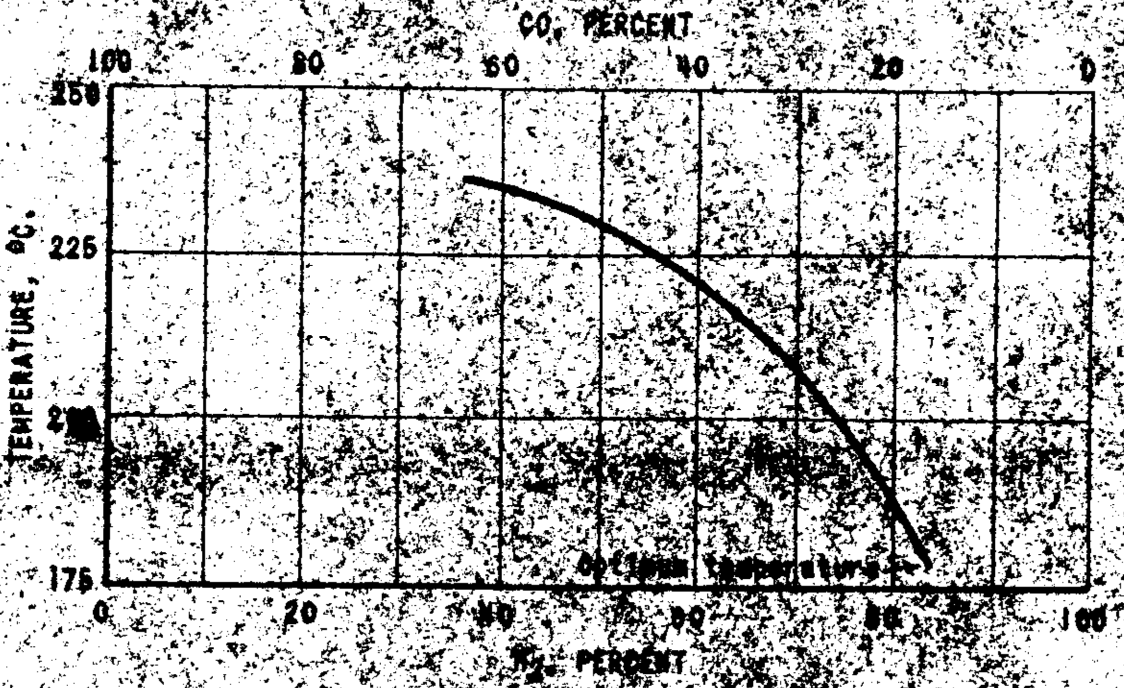

Figure 7. - Variation in temperature with synthesis gas composition.

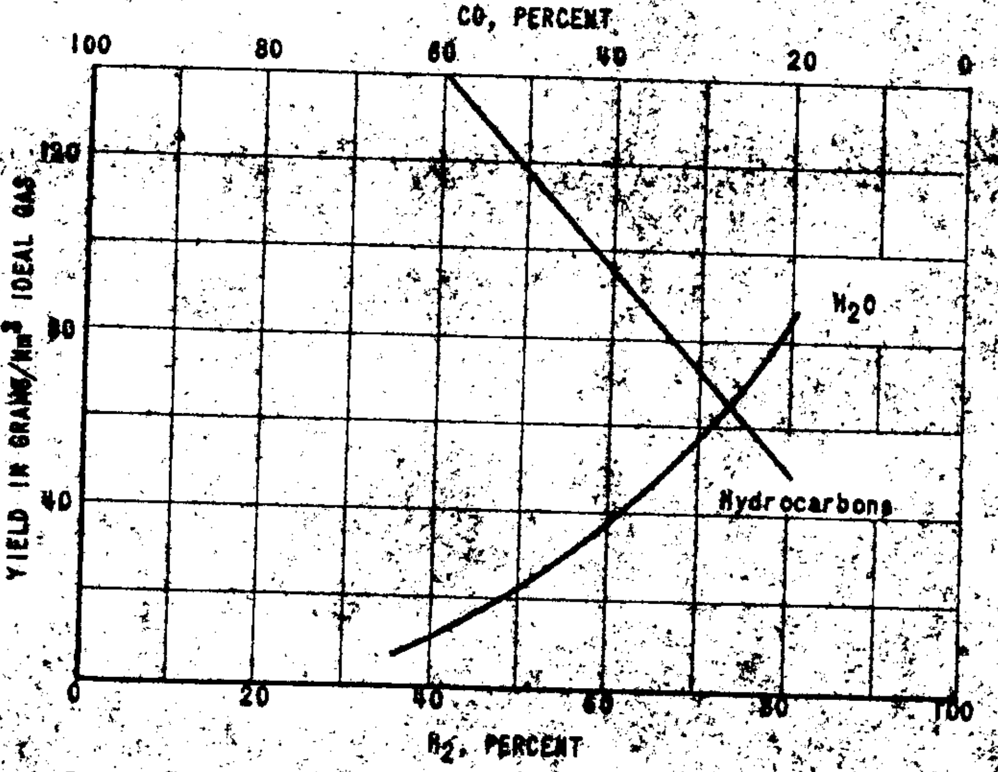

Figure 8. -- Variation in yield with synthesis gas composition.