

Niley

UNITED STATES
DEPARTMENT OF THE INTERIOR
BUREAU OF MINES
OFFICE OF SYNTHETIC LIQUID FUEL
LOUISIANA, MISSOURI

1474

From Dr. M. Pier's file

F-437

W. M. Sternberg
January 14, 1948

I. G. Ludwigshafen
Ammonia Laboratory Oppau

July 28, 1941

HYDROCARBON SYNTHESIS WITH IRON CATALYSTS

We have operated with activated iron catalysts of the most diversified composition. Our principal aim was the production of straight chain paraffins as a starting material for the oxidation of paraffins.

At present, using a synthesis gas $\text{CO} : \text{H}_2 = 1 : 2$, a product can be obtained at $215 - 225^\circ\text{C}$, 70 percent of which boils above 320°C , while the balance is distributed about equally among the fractions boiling below 200° and $200 - 320^\circ\text{C}$. The fraction of the primary product boiling above 320°C consists of about 90 percent straight chain paraffins. $1/3$ of these 70 percent have a boiling point range between 320 and 450°C , the balance boils at higher temperatures. This high boiling fraction can, however, be cracked to paraffins with a boiling point range of $320 - 450^\circ\text{C}$ with a 70 percent yield, so that 50 percent of the total primary product is available for oxidation. Operations

on the large scale must be done with a circulation of the products or in several stages, with washing out the carbon dioxide and deposition of the products.

The calculated yield amounts to 180 g/nbcm of converted gas, and were we to consider 80 percent of this amount as being actually realizable, we will obtain 145 g/nbcm.

A preferential formation of olefins can be obtained with the synthesis gas mixture $\text{CO} : \text{H}_2 = 1 : 1$. With a CO consumption of about 30 percent with a single pass and temperatures of 210 - 250°C, a product could be obtained which consists of about 50 percent olefins in the higher fractions (above 200°C) without any important changes in the distribution of the product among the different boiling point ranges. About 80 percent of the product is composed of straight chain hydrocarbons (the conversion of $\text{CO} : \text{H}_2$ takes place in a proportion of 1 : 1, or in the same proportion as they are present in the starting gas).

This method of operation furnishes the possibility of using the middle fractions for the oxo reactions, while the higher boiling fractions can be hydrogenated and used for paraffin oxidation.

When fused iron catalysts are used for the manufacture of olefins, higher operating temperatures are required, with a simultaneous higher (double)

load per li catalysts per hour. The proportion of olefins in the middle and higher boiling fractions amounts to about 70 and 60 percent. The catalyst has the disadvantage that, when changing the synthesis gas composition from 1 : 2 to 1 : 1, and such a gas is led over the catalyst from the start ($\text{CO} : \text{H}_2 = 1 : 1$) it is consumed in the proportion of $\text{CO} : \text{H}_2 = 1.6$, as has been frequently observed with precipitated catalyst of other compositions. The olefins in the boiling range of $200 - 320^\circ\text{C}$ are about 65 percent straight chain, and about 75 percent in the higher fractions.

The required higher synthesis temperature, as well as the consumption of a synthesis gas in a different proportion than supplied permits to consider the greater use of precipitated catalyst in the olefin synthesis in the future.

Alcohols

Attempts have been made to produce alcohols from CO and H_2 at middle and higher pressures, using fused iron-catalysts, calcined iron and precipitated iron catalysts, without as yet being able to give any conclusive results.

Only a qualitative difference in results was clearly recognizable when the different above named

catalysts were used. There are, however, well grounded opinions that at higher pressures (in excess of 50 atm) very good yields of higher alcohols can be obtained with the precipitated catalysts and without any noticeable carbonyl formation; these alcohols were suitable for conversion to the fatty acids. We have thus e.g. obtained:

<u>Boiling Point</u>	<u>Percent</u>	<u>Percent Alcohol</u>
-200°C	60	35
200-320°C	20	40
320-450°C	13	43
over 450°C	7	55

The total yield: 70 g with a single pass or 160 g/nbcm of the converted gas: operating conditions 200 atm, catalyst load 500 : 1 using calcined catalysts under similar operating conditions lower alcohols are obtained preferentially e.g. alcohols C₁-C₅ in about equal proportions.

The corresponding work with fused iron catalysts has been discontinued for the time being because of the poor yields obtained with these catalysts under our operating conditions.

underwriters

/s/ Nietzel