TOM REEL 101 - Doc. PG-21576-NID,

"PROCESS FOR THE PRODUCTION OF HYDROCARBON (Patent Application)"*

INTRODUCTION

Iron catalysts have frequently been proposed for the synthesis of hydrocarbons from CO and H_2. It has been demonstrated that the use of high pressures under certain conditions is essential for good conversion. Iron has a great advantage over cobalt and nickel in being less expensive. However, this advantage has hitherto been counter-balanced by the lower activity of the iron catalysts. Iron catalysts yielded essentially smaller yields of hydrocarbons, possessed a shorter lifetime, and had to be operated at higher temperatures.

This third factor becomes important if the cooling medium is water. When the cooling water temperature is 200°C., the corresponding steam pressure is only 15 atmospheres. At 225°C., however, the steam pressure is 25 atmospheres; at 250°C., it is 40 atmospheres; and at 290°C., a steam pressure of 80 atmospheres is required. Obviously, if it should be necessary to operate the reaction at 300°C., the use of water as the heat transfer liquid would be inadvisable.

Experiments have frequently been carried out to improve the activity of the iron catalysts either by the addition of promoters, such as copper, or by preliminary reduction with hydrogen or carbon monoxide-hydrogen mixtures. The results, however, were so unsatisfactory that the use of cobalt for the synthesis was continued.

SCOPE OF PRESENT INVENTION

The present invention describes a procedure which, if followed precisely, overcomes the difficulties heretofore connected with the use of iron catalysts. In the future, therefore, cobalt may be replaced by iron without

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*Apparently this is German Patent No. 736,091 (1943). Ref. TOM Reel 100, Item 20578. (Ed. note).

diminishing the hydrocarbon yields or shortening the lifetime of the catalyst. Moreover, the temperature at which the reaction is carried out is not excessively high.

This surprising and technically important development was the pretreatment of the iron catalysts with CO-rich gases at pressures well below one atmosphere. In order to get very good results, the pressure should be only a fraction of an atmosphere. After the pretreatment of the catalyst, the conversion of CO-H_2 mixtures takes place at elevated pressures of 10 to 30 atmospheres.

It is assumed that by pretreating the iron catalyst in the manner outlined a definite internal change occurs. We are of the opinion that iron carbides are formed, and a well-defined pattern of carbon is dispersed throughout the crystal lattice. This dispersion of carbon and of iron carbides improves the catalytic properties of the iron permanently. Hydrogen should not be used for this induction as only reduction can be effected. Although the presence of CO_2 is known to hinder induction, the carbon dioxide which is formed during pretreatment by the interaction of iron oxide with carbon monoxide is removed from the surface of the catalyst by fresh CO-rich gases so rapidly that it has little opportunity to impede the induction. The CO_2 is removed more quickly at lower pressures. After induction, obviously the presence of CO_2 is no longer detrimental to the catalyst. It has been observed that the activity of the iron catalyst remains unchanged in the presence of a completely converted synthesis gas (that is, the carbon monoxide has been completely used up) containing approximately 60 percent CO_2, and operating under optimum conditions.

We have also found that the optimum induction temperature is higher than the optimum initial temperature of the synthesis. Thus, for an experiment in which the iron catalyst was inducted with pure CO at 1/10 atmosphere, the optimum temperature was 320-340°C., whereas optimum starting temperature of the synthesis was between 220-230°C. For this reason, it is recommended that induction and synthesis be carried out in separate reactors.

OPERATING CONDITIONS

The induction of the catalyst and the synthesis of the hydrocarbons proceed under entirely different conditions. The optimum conditions are discussed below.

Induction

Carbon monoxide-rich gases or better still, pure carbon monoxide should be used. It is also permissible to use CO which has been diluted by an inert gas. If CO and H_2 mixtures are employed, the greater the H_2 concentration the poorer the results.

Pressures should preferably be below one atmosphere and the CO partial pressure should be a fraction of one atmosphere.

The temperature should be above 230°C., preferably between 300° and 350°C.

The contact time should be short in order to keep the partial pressure of the CO_2 as low as possible.

Synthesis.

In order to insure the best results, it is preferable to use a synthesis gas mixture of composition $(1.5 \text{ to } 2)CO + 1H_2$.

The synthesis pressure should be between 10 and 30 atmospheres.

The temperature should be between 200-320°C. at a point at which a satisfactory conversion of CO is maintained. As the catalyst activity decreases, it is necessary to increase the temperature in order to keep the yield constant. The more active the catalyst, the lower the initial synthesis temperature. However, it was found that the increase in temperature occurred more slowly for a properly inducted catalyst. A catalyst which was pretreated at 15 atmospheres pressure with 4 liters per hour of a 1.8:1 mixture of CO and H_2 at 255°C. for 24 hours did not give any conversion when operated with synthesis gas at 230°C. It was necessary to raise the initial temperature directly to 260°-280°C., and the yields were unsatisfactory. However, the same catalyst inducted under similar conditions, but at one atmosphere pressure, produced a satisfactory yield when operated at 15 atmospheres and 250°C. The reaction temperature was increased approximately 2 to 3 degrees for each additional week of operation in order to maintain high conversion. If, however, the same catalyst was inducted at 1/10 atmosphere and otherwise similar conditions, the synthesis could be started at 230°-235°C., and practically complete conversion obtained from the very start. To maintain good conversion, it was necessary to raise the temperature by only 28°C. for the first three months of operation, and 7°C. for an additional three months. Thus, a catalyst was obtained which required a reaction temperature increase of only 35°C. over 1/2 year of operation. If the catalyst was pretreated under the best induction conditions, that is, with 4 liters per hour of carbon monoxide at 1/10 atmosphere and 325°C., it was possible to start the synthesis at 235°C. with compl te conversion of the CO. No increase in reaction temperature was necessary for more than three months.

The contact time should be longer for the synthesis than for the induction. It has been found advantageous to pace the increase in contact time in proportion to the increase in pressure.

EXAMPLE

An iron catalyst precipitated from the nitrates and containing 1/10 percent of alkali was inducted at 1/10 atmosphere for 24 hours at 325°C. with

4 liters of CO per 10 grams of Fe. Then the catalyst was operated with a gas consisting of CO and H_2 in the ratio of 1.8:1 at a pressure of 15 atmospheres and temperature of 235°C. The contraction was 55 percent, corresponding to complete conversion of the CO. The yields of solid, liquid, and gasol hydrocarbons were approximately 150 g./Nm^3 of the CO-H_2 mixture. After three months of operation, the activity of the catalyst was still constant at the same operating temperature.

The liquid hydrocarbons consisted chiefly of relatively anti-knock-proof benzine, boiling up to 180°C. Twenty to thirty grams of the yield were C_3 and C_4 hydrocarbons; the unsaturated portion of this fraction is extremely important for the production of high octane benzine (polymer benzine).

CLAIMS

We claim the following:

A process for the production of higher hydrocarbons from CO and H_2 over iron catalysts pretreated with CO or CO-rich gases at pressures below one atmosphere. Thereafter, the synthesis proper is carried out with CO and H_2 mixtures at elevated pressures, preferably between 2 and 100 atmospheres.

A process according to the above claim in which the synthesis pressures range between 10 and 30 atmospheres.

A procedure according to both of the above claims modified so that induction is carried out at about 300°C. and the synthesis between 200° and 300°C.