PREPARATION OF SOLID HYDROCARBONS

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3 Claims. (Cl. 260—449.6)

1 The present invention relates to the synthesis of hydrocarbons by the catalytic conversion of gaseous mixtures comprising carbon monoxide and hydrogen. In a more particular aspect it relates to an improved method for obtaining an increased yield of solid hydrocarbons in such a conversion.

When carbon monoxide is reacted with hydro-
gen in the presence of cobalt, nickel, iron and other catalysts, as in a Fischer-Tropsch type process, at somewhat elevated pressures and temperatures of the order of about 100 pounds per square inch and 200° C., the reaction effluent comprises a complex mixture of solid, liquid and gaseous hydrocarbons. The normally gaseous fraction of the product contains hydrocarbons such as methane and ethane and the C3 and C4 hydrocarbons. The normally liquid fraction contains hydrocarbons that boil in the gasoline boiling range and higher. The normally solid fraction is a hydro-
carbon wax. When partial condensation of the reaction effluent is practiced, the liquid conden-
sate obtained usually contains solid components in solution.

The hydrocarbon waxes obtained by these methods have been found to possess considerable value in a number of applications such as for use in dielectric, impregnating, and coating compositions, and as intermediates in the preparation of various useful materials such as those obtained by oxidation, cracking or dehydrogenation. It is, therefore, frequently desirable to obtain increased yields of wax in a process of the type described. Fischer and Pickler in U.S. Patent 2,206,500 have disclosed increasing the yield of wax from a Fischer-Tropsch process by using a vertical cata-
litic reactor from which normally solid hydrocar-
bons which are liquid under the reaction condi-
tions continuously drain. However, this process does not describe any means for regulating the reaction conditions so as to produce a greater proportion of wax within the reaction itself.

It is therefore, an object of the present invention to obtain an increased yield of normally solid hydrocarbons by the synthetic conversion of carbon monoxide-hydrogen mixtures. It is a fur-
ther object of the present invention to effect the preparation of hydrocarbon waxes by the syn-
thetical conversion of carbon monoxide and hydro-
gen in the presence of a Fischer-Tropsch type catalyst. Other objects of the invention will be apparent from a consideration of the following disclosure.

In accordance with the present invention, I have discovered that contrary to what might be expected from a knowledge of the prior art, when the carbon monoxide-hydrogen feed to a Fischer-
Tropsch conversion contains more than 40% of an inert diluent, unusually high yields of normally solid hydrocarbons are obtained. In addition the yield of gasoline is as high as that obtained from feeds which contain little or no diluent, and fur-
thermore, the resultant gasoline contains a higher proportion of olefinic material than gasoline which is obtained by the conversion of diluent free feeds.

According to the prior art the incorporation of up to 40% of nitrogen in the feed will increase the proportion of relatively low-boiling com-
pounds. (Ellis, Chemistry of Petroleum Deriva-
tives, vol. 2, page 1236.) This effect is predict-
able from the teachings of Crawford (Trans. Far-
aday Soc., vol. 35, pages 946-958 and pages 966-
967, (1939)), Storch (Industrial Engineering
Chemistry, June 37, page 340, (1945)), and Tsune-
oaka et al. (Journal of Society of Chemical Indus-
y, vol. 37, Supplemental Binding, pages 704-
711 (1934)).

In accordance with the present invention, the feed gas to the Fischer-Tropsch conversion unit and which contains carbon monoxide and hydro-
gen in a mol ratio of about 1:2, is diluted with a sufficient amount of an inert diluent such as nitrogen, methane or CO2, to provide a com-
position containing more than 40% of the diluent and preferably from about 42 to 70% of such diluent. A suitable composition of feed gas is approximately as follows: 50 volume per cent nitrogen, 16 volume per cent carbon monoxide, and 34 volume per cent hydrogen. Such a feed gas may be prepared by adding the desired pro-
portion of nitrogen to a carbon monoxide-hydro-
gen mixture prepared by any of the methods known to the art. One especially convenient method for preparing feed gas for use in the process of this invention is by partial combus-
tion of methane with air in the presence of a nickel cata-
yst. The effluent gas from such a combus-
tion step contains approximately 40 volume per cent nitrogen as well as carbon monoxide and hydrogen in a mol ratio of about 1:2. This effluent gas may be converted to hydrocarbons with-
out further adjustment of composition, but, prefer-
ably, sufficient nitrogen is added to give a nitrogen content of approximately 42-70 per cent by volume.

The feed is then passed to a reactor, or series of reactors, in the presence of a catalyst suitable for conversion of carbon monoxide and hydrogen to hydrocarbons. In practicing this invention,
prefer to use a cobalt-containing catalyst such as one consisting of metallic cobalt, thorium, and kieselguhr in the ratio of 100:18:100 parts by weight, respectively. When this catalyst is used, suitable reaction conditions are: pressure, about 100 p.s.i.; temperature, about 200° C.; space velocity, 100 to 200 volumes per volume of catalyst per hour.

Other cobalt-containing catalysts may be used such as cobalt alone or cobalt-nickel-alumina and the like on various supports. In general with cobalt catalysts reaction temperatures in the range of about 175 to 225° C. may be used at pressures of atmospheric to 150 atmospheres or higher and preferably 5 to 15 atmospheres. Other metallic Fischer-Tropsch type catalysts may be used, but cobalt has been found to give preferred results.

The reactor may be one of any of the types known to the Fischer-Tropsch art, but is preferably of the vertical type, since, from this type of reactor, the wax formed may be continuously drained. The reactor is preferably provided with suitable cooling means for temperature control.

The effluent from the conversion step is treated by customary methods, such as fractional distillation, to separate the various components as desired.

**Example**

Four carbon monoxide-hydrogen feeds containing different proportions of nitrogen were passed through a reactor containing a catalyst consisting of metallic cobalt, thorium, and kieselguhr in the weight ratio 100:18:100. In each feed, the mol ratio of carbon monoxide to hydrogen was 1:2. The reaction temperature was 200° C., and the pressure was 100 p.s.i. Other operating data were as follows:

<table>
<thead>
<tr>
<th>Run</th>
<th>Duration, hr.</th>
<th>N₂ in Feed, vol. percent</th>
<th>Space Velocity, vol./vol./hr.</th>
<th>Volume Percent Wax in Gaseoline-Free Residue</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>42</td>
<td>0</td>
<td>100</td>
<td>16</td>
</tr>
<tr>
<td>2</td>
<td>26.5</td>
<td>10</td>
<td>100</td>
<td>20</td>
</tr>
<tr>
<td>3</td>
<td>45.5</td>
<td>30</td>
<td>100</td>
<td>25</td>
</tr>
<tr>
<td>4</td>
<td>63</td>
<td>60</td>
<td>100</td>
<td>28</td>
</tr>
<tr>
<td>5</td>
<td>28</td>
<td>0</td>
<td>100</td>
<td>20</td>
</tr>
</tbody>
</table>

The effluents from the five consecutive runs were separately distilled to an end point of 400° F. and the distillation residues were cooled to room temperature and compared. The residue from run 1 was mostly liquid and contained some undissolved wax. The residue from run 2 contained somewhat more undissolved wax, and the residue from run 3 contained still more. The residue from run 4 was solid at room temperature. The residue from run 5 was similar to that from run 1. Substantially equal yields of material boiling above 400° F. were obtained in all five runs. Substantially the same volume of gasoline boiling material was obtained in run 4 as in runs 1 and 5 but this gasoline on analysis was found to be much higher in olefinic content than in runs 1 to 3 and 5. With a diluent concentration below about 42%, the yield of wax is substantially smaller than that which is obtained within the range of about 42% to 70% of diluent in the feed. For example, a 20% increase in N₂ concentration of from 10% to 30% in the feed caused only a 25% increase in wax concentration (from 20% to 25% in the gasoline-free residue). On the other hand when the N₂ concentration was increased from 30% to 50%, a 100% increase in wax concentration resulted (from 25% to 50% in the gasoline-free residue). 70% N₂ is selected as an upper limit, since this represents an economic limit beyond which the total yield based on CO consumed begins to decrease, while the quantity of N₂ required to be compressed and recycled becomes excessive for practical operation. With a decrease in yield, the wax production based on CO reacted also decreases beyond this point.

I claim:

1. A process for the production of wax in high yields which comprises reacting a gaseous mixture containing carbon monoxide and hydrogen in a mol ratio of 1:2 and containing about 50 per cent nitrogen by volume in the presence of a cobalt synthesis catalyst at a temperature within the range of 175 to 225° C. and a pressure of from 5 to 15 atmospheres, at a space velocity of from 100 to 200 volumes gas per volume catalyst per hour, and treating the effluents of the reaction to recover therefrom a high yield of wax as a product of the process.

2. A process according to claim 1 wherein the temperature is 200° C.

3. A process according to claim 1 wherein the temperature is 200° C. and the pressure is 100 pounds per square inch.

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**REFERENCES CITED**

The following references are of record in the file of this patent:

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