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UTILIZATION OF NORMALLY GASEOUS HYDROCARBONS

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8 Claims. (Cl. 196—9)

Procedure for utilizing gaseous hydrocarbons such as propane and butanes, for obtaining higher boiling hydrocarbons has heretofore been awkward. Paraffin gases have been dehydrogenated as a first operation; but the equilibrium for this is in general unfavorable. In accordance with the present invention, gaseous hydrocarbons may however be utilized in conversion to higher boiling products in conjunction with aromatization in a manner particularly effective and convenient, this being an object of the invention. Other objects and advantages will appear as the description proceeds.

To the accomplishment of the foregoing and related ends, the invention, then, comprises the features hereinafter fully described, and particularly pointed out in the claims, the following description setting forth in detail certain illustrative embodiments of the invention, these being indicative however, of but a few of the various ways in which the principle of the invention may be employed.

The gas may conveniently be for instance relatively pure butanes, or mixtures of butanes with butenes and/or with lower hydrocarbons, or in general those below a five carbon atom structure (the latter being commonly accounted as starting the liquid or gasoline range). The gas is, in accordance with the invention, subjected along with a vaporized higher boiling nonbenzenoid hydrocarbon, to the action of a particular catalyst, at high temperature, and relatively low pressure, the catalyst having the characteristics of being a gel type contact catalyst containing 18–30 mol per cent of chromic oxide and 82–70 mol per cent of aluminum oxide, or at least 70 mol per cent of aluminum oxide, and there can be present correspondingly minor amounts of oxides of such elements as copper, antimony, tin, etc. The proportions in this catalyst as affecting the present process are critical, and there is a peculiar peak of activity with the chromic oxide and aluminum oxide at 20:80 mol per cent. The higher boiling non-benzenoid hydrocarbon may be aliphatic or paraffinic and olefinic in character, or naphthenic, or mixtures, naphthas, distillates, etc. And, the gases, as indicated may be paraffinic or olefinic, or mixtures of both. They may be gases formed in aromatization or any other convenient source. The process operates equally well with paraffins, which thus distinguishes it from the known catalytic reversion processes. Also, reversion i. e. alkylation with aromatics can be carried out more favorably than with ordinary gasoline as heretofore practiced.

The temperature in the catalyst zone may be 750–1200° F. Pressure should in general be relatively low, pressures above 200 pounds per square inch being peculiarly unfavorable. Desirably, the pressure should be atmospheric to 180 pounds per square inch, and preferably around 100 pounds. The rate of feed may involve ratios of gas to liquid hydrocarbon, for example naphtha, of 0.1–5 mols of gas to 1 of naphtha. The now rates of naphtha may be 0.1–10 liquid volumes per volume of catalyst per hour. At the higher temperatures the shorter contact times may be used. Hydrogen or hydrogen-containing gas may or may not be added, but preferably is, as it helps to lessen coke formation.

Where desired, the primary product of the treatment may be extracted by an extracting agent, as for example liquid sulphur dioxide or a high boiling amine or phenol, or combinations of such or other solvents, and the undissolved or non-benzenoid portion, can be returned to contact with the catalyst. The gases formed may be recycled in part as desired. When the catalyst activity declines to a predetermined level, it may be regenerated in situ by applying, the temperature being 750–1200° F., an oxygen-containing gas, as air or oxygen diluted for example with nitrogen. Preferably, the regenerating gas is dried. At intervals of 1–3 weeks, the catalyst may be regenerated at a higher temperature, as 1200–1300° F.

As an example: Butane-butene mixed gas in mol ratio of 0.87 to 1 of a vaporized naphtha from Illinois petroleum is subjected to the action of a 20:80 chromium and aluminum oxide catalyst, at a temperature of 1025° F. and pressure of 100 pounds per square inch. With a naphtha flow rate of 0.585 volume per hour per volume of the catalyst, and hydrogen in mol ratio 3 to 1 of naphtha, the yield based on naphtha feed is 86 weight per cent of gasoline having an A. S. T. M. knock rating of 80.5 and Kattwinkel test 54. If the naphtha stock be supplied to the catalyst under similar conditions without the supply of butane, the yield for the same knock rating product is more than 20 per cent lower.

As another example: With butane at a mol ratio of 1.8 to 1 of a similar Illinois naphtha, hydrogen not being supplied, and with operating temperature 970° F. and 100 pounds pressure, the product yield is 83.8 weight per cent of gasoline of A. S. T. M. knock rating 81 and Kattwinkel test 53. This is over 20 per cent more gasoline yield than when the butane is absent. If the naphtha feed be shut off, the

gaseous hydrocarbon alone gives no appreciable yield of liquid products.

As seen, the ability of this process to operate with paraffins distinguishes it from catalytic reversion processes heretofore known; and the high yields of the gasoline product are notable. The gasoline produced moreover, has an especially good blending octane number, and lead susceptibility is better than when butane is not added.

Other modes of applying the principle of the invention may be employed, change being made as regards the details described, provided the features stated in any of the following claims, or the equivalent of such, be employed.

I therefore particularly point out and distinctly claim as my invention:

1. A process of aromatizing and reacting forming-aromatics and gaseous hydrocarbons of four carbon atoms and less, which comprises subjecting butane and vaporized naphtha to the action of a gel type contact mass consisting of 18–30 mol per cent of chromic oxide and not less than 70 mol per cent of alumina, at high temperature and about 100 pounds pressure per square inch.

2. A process of aromatizing and reacting forming-aromatics and gaseous hydrocarbons of four carbon atoms and less, which comprises subjecting butane and vaporized normally liquid non-benzenoid hydrocarbon to the action of a gel type contact mass consisting of 18–30 mol per cent of chromic oxide and not less than 70 mol per cent of alumina, at high temperature and about 100 pounds pressure per square inch.

3. A process of aromatizing and reacting forming-aromatics and normally gaseous hydrocarbons, which comprises subjecting such gaseous hydrocarbon together with a vaporized naphtha to the action of a gel type contact mass consisting of 18–30 mol per cent of chromic oxide and not less than 70 mol per cent of alumina, at high temperature and about 100 pounds pressure per square inch.

4. A process of aromatizing and reacting forming-aromatics and normally gaseous hydrocarbons, which comprises subjecting such gaseous hydrocarbon together with a vaporized normally liquid non-benzenoid hydrocarbon to the action of a gel type contact mass consisting of 18–30 mol per cent of chromic oxide and not less than 70 mol per cent of alumina, at high temperature and about 100 pounds pressure per square inch.

5. A process of aromatizing and reacting forming-aromatics and normally gaseous hydrocarbons, which comprises subjecting butane and vaporized naphtha to the action of a gel type contact mass consisting of 18–30 mol per cent of chromic oxide and not less than 70 mol per cent of alumina, at high temperature and pressure of atmospheric to 180 pounds per square inch.

6. A process of aromatizing and reacting forming-aromatics and normally gaseous hydrocarbons, which comprises subjecting butane and vaporized normally liquid non-benzenoid hydrocarbon to the action of a gel type contact mass consisting of 18–30 mol per cent of chromic oxide and not less than 70 mol per cent of alumina, at high temperature and pressure of atmospheric to 180 pounds per square inch.

7. A process of aromatizing and reacting forming-aromatics and normally gaseous hydrocarbons, which comprises subjecting such gaseous hydrocarbon together with a vaporized naphtha to the action of a gel type contact mass consisting of 18–30 mol per cent of chromic oxide and not less than 70 mol per cent of alumina, at high temperature and pressure of atmospheric to 180 pounds per square inch.

8. A process of aromatizing and reacting forming-aromatics and normally gaseous hydrocarbons, which comprises subjecting such gaseous hydrocarbon together with a vaporized normally liquid non-benzenoid hydrocarbon to the action of a gel type contact mass consisting of 18–30 mol per cent of chromic oxide and not less than 70 mol per cent of alumina, at high temperature and pressure of atmospheric to 180 pounds per square inch.

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