

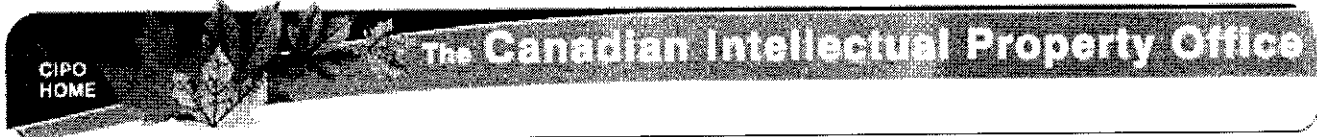


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(12) Patent:

(54) SYNTHESIS OF HYDROCARBON FROM CARBON OXIDES HYDROGEN AND BRANCH CHAINED HYDROCARBONS

(54) SYNTHESE D'HYDROCARBURE D'HYDROGENE D'OXYDES DE CARBONE ET D'HYDROCARBURES A CHAINE BRANCHEE

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Our invention relates to the synthesis of hydrocarbons, and especially to an improved process for synthesizing hydrocarbons of motor fuel range by the hydrogenation of carbon oxides.

The synthesis of hydrocarbons by the hydrogenation of carbon monoxide has been operated on a commercial scale for a number of years, but this process has had certain disadvantages, particularly in the character of the hydrocarbons produced. The motor fuels obtained by this process have not been comparable in anti-knock properties to motor fuels obtainable from petroleum fractions, and have generally had octane numbers considerably below straight run and thermally cracked gasolines.

An object of the present invention is to provide a process for the hydrogenation of carbon oxides to produce motor fuel hydrocarbons of improved anti-knock characteristics.

Another object of our invention is to provide an improved reaction mixture for the vapor phase catalytic hydrogenation of carbon oxides to produce increased yields of hydrocarbons.

A further object of our invention is to provide a suitable continuous cyclic process for effecting our improved hydrogenation reaction.

Other objects and advantages of our invention will be apparent from the following description.

In accordance with the present invention, the reactant mixture for the hydrogenation contains, in addition to hydrogen and a carbon oxide, a substantial proportion of a hydrocarbon component comprising essentially branched chain hydrocarbons. The provision of a branched chain hydrocarbon in

the reaction mixture increases the yield of hydrocarbons of motor fuel range and above, and thus effects a marked improvement in the volumetric efficiency of the catalytic unit. The use of a branched chain hydrocarbon in the reaction mixture also modifies the characteristics of the reaction products, and effects a marked improvement in the anti-knock characteristics of the motor fuel range hydrocarbons. It is believed that the branched chain hydrocarbon reacts with methylene radicals at the catalyst surface to produce branched chain hydrocarbons of higher molecular weight, rather than essentially straight chain hydrocarbons, such as are produced from carbon monoxide and hydrogen alone. However, it is to be understood that our invention is not limited to any particular theory by which it may operate.

Any branched chain hydrocarbon of lower molecular weight than the desired reaction product may be employed in our process, but we prefer to use a branched chain hydrocarbon which is in the vapor state under the hydrogenation conditions employed. Isobutane, isobutylene, isopentane, the methylbutenes and methylpentenes, 2,2-dimethylbutane, and 2,3-dimethylbutane are examples of hydrocarbons of the preferred volatility range. When effecting the reaction with a liquid phase in contact with the catalyst, higher boiling branched chain hydrocarbons such as di-isobutylene, tri-isobutylene, and the corresponding paraffins may be employed. A mixture of such hydrocarbons may be employed if desired, but the recycling of unreacted branched chain hydrocarbon in the substantial absence of straight chain hydrocarbons will be simplified if only a single branched chain

hydrocarbon is used for this purpose. Although any branched chain hydrocarbon will be operative in our process we prefer to use isoparaffins of 4 to 6 carbon atoms, and our invention will be specifically illustrated with respect to the use of isobutane.

The amount of hydrocarbon to be incorporated in the reaction mixture may be varied over relatively wide limits, depending on the particular hydrocarbon employed, and the nature of the synthetic hydrocarbons to be produced. A larger amount of hydrocarbons may be employed when the catalyst and reaction conditions are chosen for the production of a wide range product, including high molecular weight constituents, than is desirable when the synthesis conditions are designed to produce primarily light hydrocarbons of motor fuel range. It is desirable to employ at least 5 mol per cent of isobutane, based on the carbon oxide in the reaction mixture, and corresponding amounts of other branched chain hydrocarbons. Amounts of 5 to 15 mol per cent are suitable for obtaining a substantially modified reaction product. However, a large excess of the branched chain hydrocarbon, e.g., 100 - 1000 mol per cent, may be employed to minimize the formation of the usual carbon oxide hydrogenation products.

Aside from the use of a branched chain hydrocarbon in the reaction mixture, the hydrogenation reaction may be effected in accordance with prior practices in the art. Either carbon monoxide or carbon dioxide may be employed, using the known ratios of hydrogen to carbon oxide in each case. However, carbon monoxide is usually to be preferred, and further discussion herein will refer specifically to carbon monoxide.

The usual catalysts, comprising metals of the eighth group of the periodic system, together with activating constituents, such as aluminum, magnesium, thorium, their oxides, and the like may be employed in our process. Any catalyst which is effective for the reaction of carbon monoxide and hydrogen alone, will be found to be operative with the reaction mixtures of the present invention. Such catalysts may be prepared, reduced, and conditioned in the usual manner, and may be used in the dry state for a fully vapor phase process, or may be used in the form of a slurry in a high boiling hydrocarbon or other liquid carrier.

The temperature and pressure conditions for the reaction may be the same as those employed with the particular catalyst for the reaction of carbon monoxide and hydrogen alone. Temperature of 325 to 550°F., and preferably 390 to 450°F., or in the range about 325 to 700°F., and pressures up to 100 atmospheres but preferably from atmospheric to fifteen atmospheres, constitute suitable conditions with most catalysts.

The contact time need not be modified when incorporating a branched chain hydrocarbon in the reaction mixture, although improved yields of light motor fuel fractions may be obtained in some cases by utilizing a somewhat shorter contact time than would be employed in the absence of a hydrocarbon reactant.

In order to operate the hydrogenation processes economically, it is desirable to recycle the unreacted carbon monoxide and hydrogen, and to utilize the methane and other low molecular weight hydrocarbons which are produced in the process. The fixed gases, including the non-conden-

sable hydrocarbons, may be separated from the reaction product and recycled, but it is usually preferable to oxidize the hydrocarbon component to carbon monoxide prior to recycling. For this purpose, the fixed gases may be mixed with steam or other oxygen-containing gas, and passed over a suitable catalyst, such as nickel, at a temperature of 1200-1500°F. The resulting carbon monoxide-hydrogen mixture, after cooling by suitable heat exchange, may then be recycled to the hydrogenation reaction, preferably being mixed with the fresh make-up reactants prior to entering the reaction vessel. This procedure, and other known expedients for cyclic operation of the hydrogenation process, may be used in conjunction with our present improvements; and our invention is not limited to the use of any particular procedures or reaction conditions for effecting recycle of carbon monoxide and hydrogen.

In order to utilize a branched chain hydrocarbon in the reaction most economically, it is also desirable that the unreacted hydrocarbon be recycled in the process. For this purpose, the particular hydrocarbon employed may be separated from the light liquid hydrocarbon reaction product by conventional methods, such as multiple stage fractionation, azeotropic distillation, and the like.

One advantageous method of separating an unreacted isoparaffin comprises the recovery of a fraction containing only the isoparaffin and the olefins of substantially the same boiling point, reacting the olefin content of this fraction to produce higher boiling hydrocarbons, separating the latter, and recycling the isoparaffin to the hydrogenation reaction. In this type of operation, the olefin content

of the narrow boiling fraction may be subjected to polymerization, alkylation, or other conventional reactions for the production of the higher boiling hydrocarbons. The alkylation reaction is particularly advantageous, however, since the separated narrow boiling fraction contains both the isoparaffin and the olefins required for the alkylation reaction.

The use of isobutane as the branched chain hydrocarbon in the reaction mixture, and the use of alkylation to separate isobutane for recycle, constitutes a preferred procedure for carrying out our invention, and one modification of this process is illustrated in the flow diagram constituting the accompanying drawing. As may be seen from this diagram, the hydrogenation reaction, recovery of reaction products, separation of fixed gases, oxidation of the hydrocarbon content of the fixed gases by catalytic reaction with steam at high temperature, and recycle of the resulting carbon monoxide-hydrogen mixture, are effected in accordance with conventional procedures. This representation, however, is only diagrammatic, and additional expedients which are commonly employed, such as the use of activated charcoal adsorbers to effect complete recovery of products from the gas mixture, may also be used. In this phase of the process, the only distinction of our procedure over prior practices is the incorporation of isobutane in the reaction mixture.

In order to recover isobutane from the reaction product for recycle, the primary fractionator is operated to separate propane and propylene as overhead, and to obtain as a side-cut a light liquid hydrocarbon fraction containing the butanes and butylenes. The latter fraction is then debutan-

ized, and the debutanizer overhead is fractionated to obtain an isobutane-butene distillate, which is employed in the alkylation step of the process.

The alkylation may be effected in accordance with any of the usual methods, utilizing catalysts such as sulfuric acid, hydrofluoric acid, aluminum chloride, and the like. In the modification illustrated, sulfuric acid is used as the catalyst, and the reaction and separation of the reaction product are effected in the conventional manner. The alkylate debutanizer overhead supplies recycle isobutane for either the alkylation reaction, the hydrogenation reaction, or both, as may be desired. The make-up isobutane for the process may likewise be supplied only to the alkylation step, or to the hydrogenation step, or to both, as desired. Generally, we prefer to supply the make-up isobutane to the hydrogenation step and utilize most or all of the recycle isobutane to supply the large excess desired in the alkylation reaction. The particular distribution of the make-up and recycle isobutane, however, will be determined in any case by the relative amounts of reactants employed in the hydrogenation and alkylation reactions.

It may be seen that the procedure described above has the advantage of improving the yield and quality of the motor fuel hydrocarbons produced in the hydrogenation reaction, and also yielding additional motor fuel hydrocarbons of high quality from the gaseous olefins produced in the hydrogenation.

The following specific example illustrates the use of the procedure described above:



EXAMPLE

A hydrogenation catalyst comprising cobaltous oxide with minor amounts of manganese, thorium, and magnesium oxides, supported on kieselguhr, and reduced with hydrogen at an increasing temperature from 650° to 770°F., is employed for the hydrogenation of carbon monoxide, with and without isobutane in the reaction mixture. The charge rates, essential reaction conditions, and the hydrocarbon yields which are obtained under these conditions are shown in the table below:

C H A R G E			TEM- PERA- TURE	PRES- SURE	SPACE VELOCITY cu.ft. of charge/hr. per cu.ft. of cata- lyst	HYDROCARBON YIELD lbs./1000 cu. ft. of charge, recoverable by condensation and adsorption
cu.ft./hr. per cu.ft. of catalyst	Carbon Monoxide	Hydro- gen				
			°F.	atm.		
33.33	66.67	0.00	395	1	100	6.83
31.00	62.00	7.00	395	1	100	11.25

The CFRM octane number of the motor fuel fraction in the first case above is only about 45, whereas the octane number of the motor fuel fraction in the second case may be as high as 65, or even higher. If the sulfuric acid alkylate from the isobutane-butene fraction of the hydrogenation product is blended with the motor fuel fraction, the octane number of the overall motor fuel produced may be increased to 68, or higher.

It is to be understood, of course, that the above example is merely illustrative and does not limit the scope of our invention. Other branched chain hydrocarbons may be

used in the reaction mixture, in place of isobutane, and the reaction conditions may be modified in various respects, as pointed out in the preceding discussion. Similarly, other equivalent procedures may be employed for recovering unreacted branched chain hydrocarbon for recycling to the hydrogenation reaction. In general, it may be said that the use of any equivalents or modifications of procedure which would naturally occur to those skilled in the art, is included in the scope of our invention. Only such limitations should be imposed on the scope of our invention as are indicated in the appended claims.

## WE CLAIM:

1. In a catalytic process for synthesizing hydrocarbons by the hydrogenation of a carbon oxide, the method which comprises continuously passing to a reaction zone a reactant feed comprising carbon monoxide, hydrogen and isoparaffin hydrocarbon having from 4 to 6 carbon atoms per molecule, subjecting the reactant feed in the gas phase to contact with a hydrogenation catalyst comprising a metal of the eighth group of the periodic system, and a minor amount of a metal oxide having the essential promoting action of thorium and magnesium oxides, effecting contact between the reactants and the catalyst at a temperature in the range 325 to 550°F. and under a pressure ranging from atmospheric to about 15 atmospheres, continuously removing from the reaction zone a stream of reaction products comprising unreacted isoparaffin and synthesized hydrocarbons, separating unreacted isoparaffin from the reaction products, and recycling said separated isoparaffin to the reaction zone, the amount of isoparaffin entering the reaction zone being at least 5 mol per cent based on the carbon oxide in the reaction mixture.

2. The method according to Claim 1 in which the isoparaffin is isobutane.

3. The method according to Claim 1 in which the isoparaffin is isopentane.

4. In a catalytic process for synthesizing hydrocarbons by the hydrogenation of a carbon oxide, the method which comprises continuously passing to a reaction zone a

reactant feed comprising carbon monoxide, hydrogen and isoparaffin hydrocarbon having from 4 to 6 carbon atoms per molecule, subjecting the reactant feed in the gas phase to contact with a hydrogenation catalyst comprising a metal of the eighth group of the periodic system and a minor amount of a metal oxide having the essential promoting action of thorium and magnesium oxides, effecting contact between the reactant and the catalyst at a temperature in the range 350 to 450°F. and under substantially atmospheric pressure, continuously removing from the reaction zone a stream of reaction products comprising unreacted isoparaffin and synthesized hydrocarbons, separating unreacted isoparaffin from the reaction products, and recycling said separated isoparaffin to the reaction zone, the amount of isoparaffin entering the reaction zone being about 5 to 15 mol per cent based on the carbon oxide in the reaction mixture.

5. The method according to Claim 4 in which the isoparaffin is isobutane.

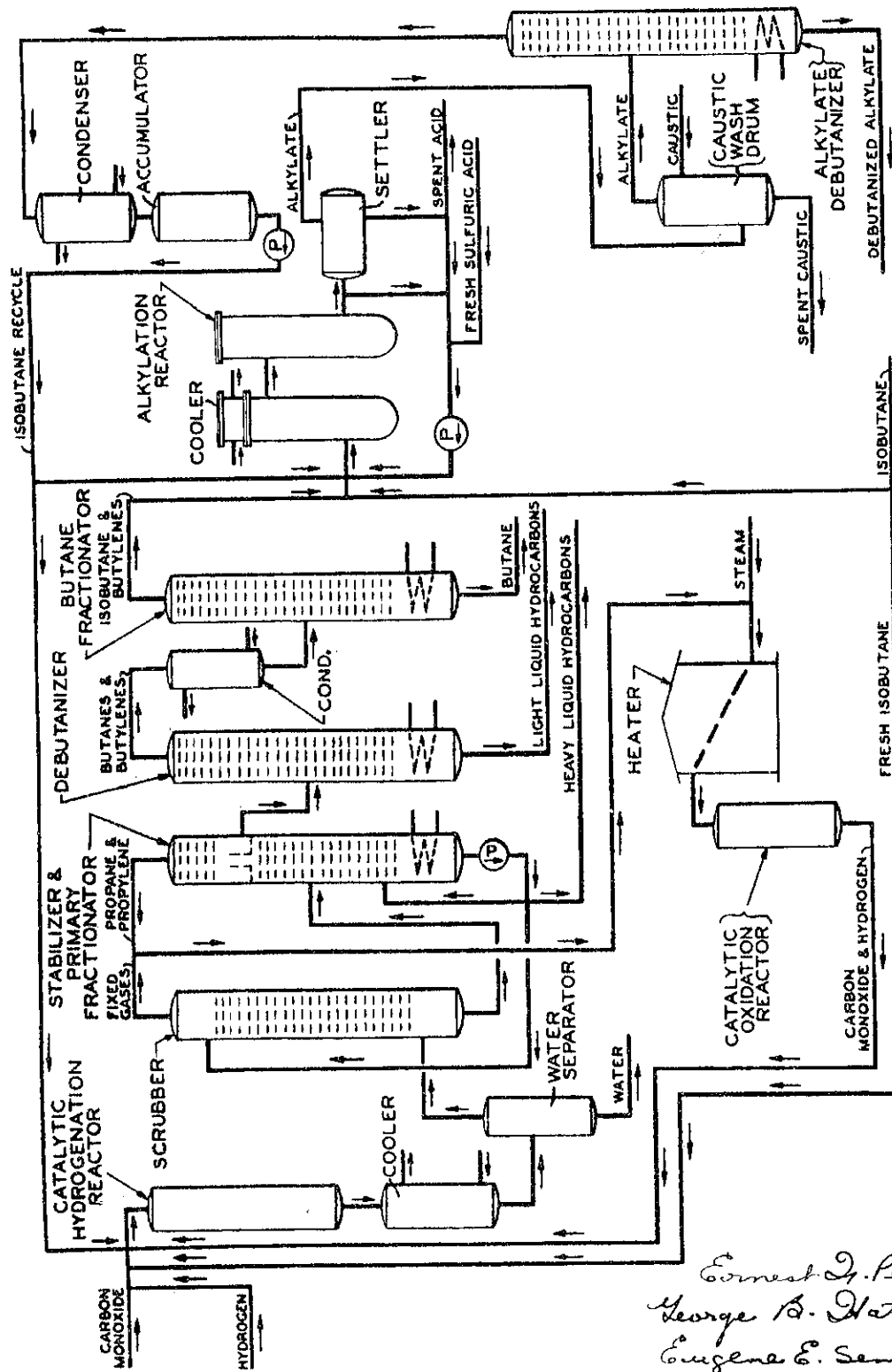
6. The method according to Claim 4 in which the isoparaffin is isopentane.

7. In a catalytic process for synthesizing hydrocarbons by the hydrogenation of a carbon oxide, the method which comprises continuously passing to a reaction zone a reactant feed comprising carbon monoxide, hydrogen and isoparaffin hydrocarbon having from 4 to 6 carbon atoms per molecule, subjecting the reactant feed in the gas phase to contact with an active synthesis catalyst comprising a metal of the eighth group of the periodic system, effecting contact between the reactants and the catalyst at a temperature

in the range about 325 to 700°F. and under a pressure ranging from atmospheric to about 100 atmospheres, continuously removing from the reaction zone a stream of reaction products comprising unreacted isoparaffin and synthesized hydrocarbons, separating unreacted isoparaffin from the reaction products, and recycling said separated isoparaffin to the reaction zone, the amount of isoparaffin entering the reaction zone being at least 5 mol per cent based on the carbon oxide in the reaction mixture.

8. The method according to Claim 7 in which the isoparaffin is isobutane.

9. The method according to Claim 7 in which the isoparaffin is isopentane.



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 INVENTOR

Certified to be the drawings referred to  
 in the specification hereunto annexed.

Ottawa, October 3, 1946

Smart & Beggs  
 ATTORNEY