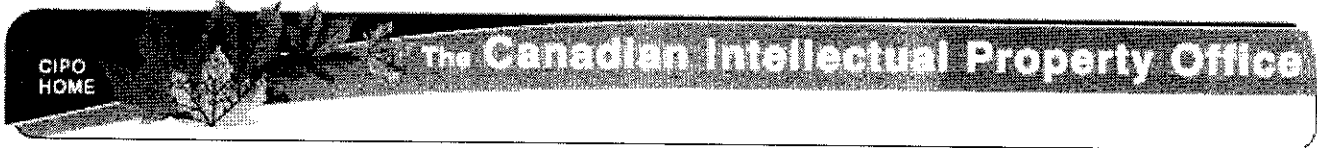


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(12) Patent:

(54) HYDROCARBON PRODUCTION FROM CARBON MONOXIDE AND HYDROGEN PLUS ADDED OLEFINS

(54) PRODUCTION D'HYDROCARBURE D'OXYDE DE CARBONE ET D'HYDROGENE AVEC OLEFINES AJOUTEES

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This invention relates to a process for the conversion of mixtures of hydrogen and carbon monoxide into hydrocarbons containing more than one carbon atom in the molecule. More particularly, the present invention relates to such a process wherein the anti-knock properties of the gasoline boiling range product obtained in such a conversion are materially improved.

When hydrogen and carbon monoxide are caused to react in the presence of a catalyst to form hydrocarbons synthetically in the manner now practiced in the art, the reaction products consist essentially of straight-chain hydrocarbons ranging from normally gaseous to normally liquid to normally solid compounds. The octane number of the refined fraction boiling in the gasoline range is roughly 40 - 50, which is obviously too low for use as motor fuel without further treatment.

It is an object of the present invention to provide a process for the synthesis of hydrocarbons from carbon monoxide and hydrogen wherein a gasoline boiling range fraction having substantially increased octane number is obtained as a product of the reaction.

It is a further object of the present invention to provide a process for the hydrogenation of carbon monoxide in the presence of particular hydrocarbon components which will simultaneously interact during the synthesis reaction.

In accordance with the present invention I have found that in the synthesis of hydrocarbons containing components boiling in the gasoline range, an improvement in the anti-knock properties may be effected or the octane number of the gasoline boiling range fraction may be materially increased

by introducing into the usual CO + H₂ feed branched chain olefin hydrocarbons having 4-6 carbon atoms per molecule. Such olefins include: isobutylene, 2-methylbutene-1, 2-methylbutene-2, 3-methylbutene-1, 2,3-dimethylbutene-2, and 3-methylpentene-2, or mixtures thereof.

In carrying out the present process a volume of the desired branched chain olefins equal to or less than that of the synthesis gas entering the reaction zone is admixed with the feed. Preferably less than 20 per cent of the added olefin based on volume of feed is used.

In addition to the increase in octane number achieved, I have found that a partial control of heat of reaction may be effected by introducing the olefin in liquid phase at one or a plurality of points along the path of flow of reactants. Thus, heat of reaction will be removed as heat of vaporization and sensible heat.

The hydrocarbon synthesis reaction for the production of gasoline range and higher boiling hydrocarbons may be carried out in the manner known to the art. In general, using cobalt catalysts or those containing substantial portions thereof, reaction temperatures in the range of 175-225 C. may be used with the optimum temperature being in the neighborhood of 185-190 C. Ordinary iron catalysts operate best in a narrow range close to 240 C. while sintered iron catalysts require temperatures in the neighborhood of 320 C.

The synthesis reaction is usually carried out at atmospheric or medium pressures, depending on the composition of product desired and the catalyst used. A preferred range of pressures suitable for general use is from 5 to 15 atmospheres, but solid and liquid hydrocarbons may be produced in good yields

at pressures of atmospheric to 150 atmospheres or higher.

Flow rates are variable, depending also on catalyst, cooling means used and products desired. Increasing contact time results in a lower catalyst operating temperature and higher yields per pass with less formation of methane. In order to obtain a satisfactory rate of production suitably rapid flow rates must be provided. With cobalt catalysts, for example, space velocities of about 95-115 cubic feet of synthesis gas per hour per cubic foot of catalyst are usually preferred. A space velocity of 113 cubic feet gives a conversion of about 70 per cent per pass at 185 C. With sintered iron catalysts, much higher space velocities may be used, and velocities of 10,000-30,000 cubic feet of synthesis gas per hour per cubic foot of catalyst have given satisfactory results.

Since the reaction is highly exothermic, cooling means must ordinarily be provided. Such means include cooling tubes through which water or other cooling fluid is circulated such tubes being positioned in or surrounding the catalyst zone. The use of direct heat exchange with non-reactive liquids directly introduced into the reaction zone has also been suggested.

The synthesis gas is usually composed of 2 parts of hydrogen to 1 of carbon monoxide. For iron catalysts which produce large amounts of CO_2 , however, the optimum ratio is 3 parts of hydrogen to 2 parts of carbon monoxide. However, the composition of the synthesis gas may vary from 1 to 3 parts of hydrogen for each part of CO.

In addition to the iron and cobalt catalysts referred to herein, other desirable catalysts include nickel-

manganese-alumina on kieselguhr, nickel-thoria on kieselguhr, and cobalt-thoria-copper on kieselguhr.

The practice of the invention may be illustrated by reference to the accompanying drawing, which represents a flow sheet describing one form of the invention. In the drawing, a synthesis gas mixture comprising CO and H₂ in the proportion of 1/4-2 parts of CO for each part of hydrogen, is introduced via line 1 into reactor 2 containing a hydrocarbon synthesis catalyst 3. The reactor may, if desired, be surrounded by a heat exchange jacket (not shown) through which a cooling fluid is circulated. Other heat exchange means may also be provided, such as cooling tubes inserted through the catalyst mass. The reactor is operated at the desired reaction temperature and an iso-olefin fraction containing C₄-C₆ iso-olefins is introduced into the reaction zone through line 4, and one or more of the branch lines 5, 6, 7, 8. The amount of iso-olefin so introduced may correspond to an equal gaseous volume or less of the synthesis gas, but a minor proportion and preferably less than 20 per cent by volume of the iso-olefin based on the synthesis gas is ordinarily utilized. During the reaction, hydrocarbons are synthesized from CO and H₂ while the iso-olefins introduced participate in the reaction by simultaneously forming a high proportion of isoparaffins boiling in the gasoline range. The synthesis effluent is passed through line 9 into fractionator 10 from which a C₄-C₆ fraction is removed via line 13. The C₄-C₆ olefins are separated from the paraffins in contactor 15 where the olefins may be selectively dissolved in sulfuric acid or in a selective solvent, such as furfural, acetone, methyl-ethylketone, or any other solvent having high selectivity for olefins over paraffins. In certain types of operation,

such as by using sintered iron catalysts, substantial proportions of isoparaffins and iso-olefins are produced and it is in such operations that it is particularly desirable to recycle the entire C_4-C_6 olefin fraction since the fraction contains a substantial proportion of iso-olefins. Where it is desired to separate the iso-olefin in the C_4-C_6 fraction from the normal olefins, selective absorption in dilute sulfuric acid, for example, 65-70 per cent acid, may be carried out in the absorber. The iso-olefins are selectively dissolved therein and recovered for use in the process by stripping. The olefin solution is removed via line 17 and stripped from the solvent in stripper 18. A solvent boiling above the iso-olefin-containing mixture is removed overhead via line 19 and is introduced into the reactor through lines 19, 20 and 4. The C_4-C_6 paraffins are removed from the absorber via line 16. Unreacted synthesis gas and C_1-C_3 hydrocarbons are removed from the fractionator through line 14. A gasoline fraction of improved octane number is removed via line 12, while oils and heavier material are moved from the bottom of the fractionator through line 11. All or any portion of the desired iso-olefin may be obtained from any desired source, as by separation from a cracked hydrocarbon by conventional methods, and separately introduced via line 21, instead of, or in addition to the fraction obtained from the synthesis. Where the C_4-C_6 fraction is low in iso-olefins, it is particularly desirable to introduce iso-olefin from another source and dispense with recycle of the C_4-C_6 fraction.

EXAMPLE

A synthesis gas containing 32.5 per cent of CO and 65.5 per cent of H_2 , together with about 2 per cent of

inert material, is contacted with a mass of catalyst consisting of 100 parts cobalt, 18 parts thorium oxide, and 100 parts kieselguhr at a temperature of 223 C. The temperature is maintained by circulating cooling water in a spaced zone surrounding the catalyst chamber. A pressure of 100 psi gauge was utilized. The space velocity was 120. The reaction products are fractionated and a gasoline fraction is obtained which has an unleaded octane number of about 50.

The same procedure is carried out except that 10% of a C₄ material containing about 65% isobutylene is introduced along with the feed. The gasoline fraction obtained has an unleaded octane number of about 62 indicating substantial reaction of iso-olefin and resulting formation of isoparaffins.

I CLAIM:

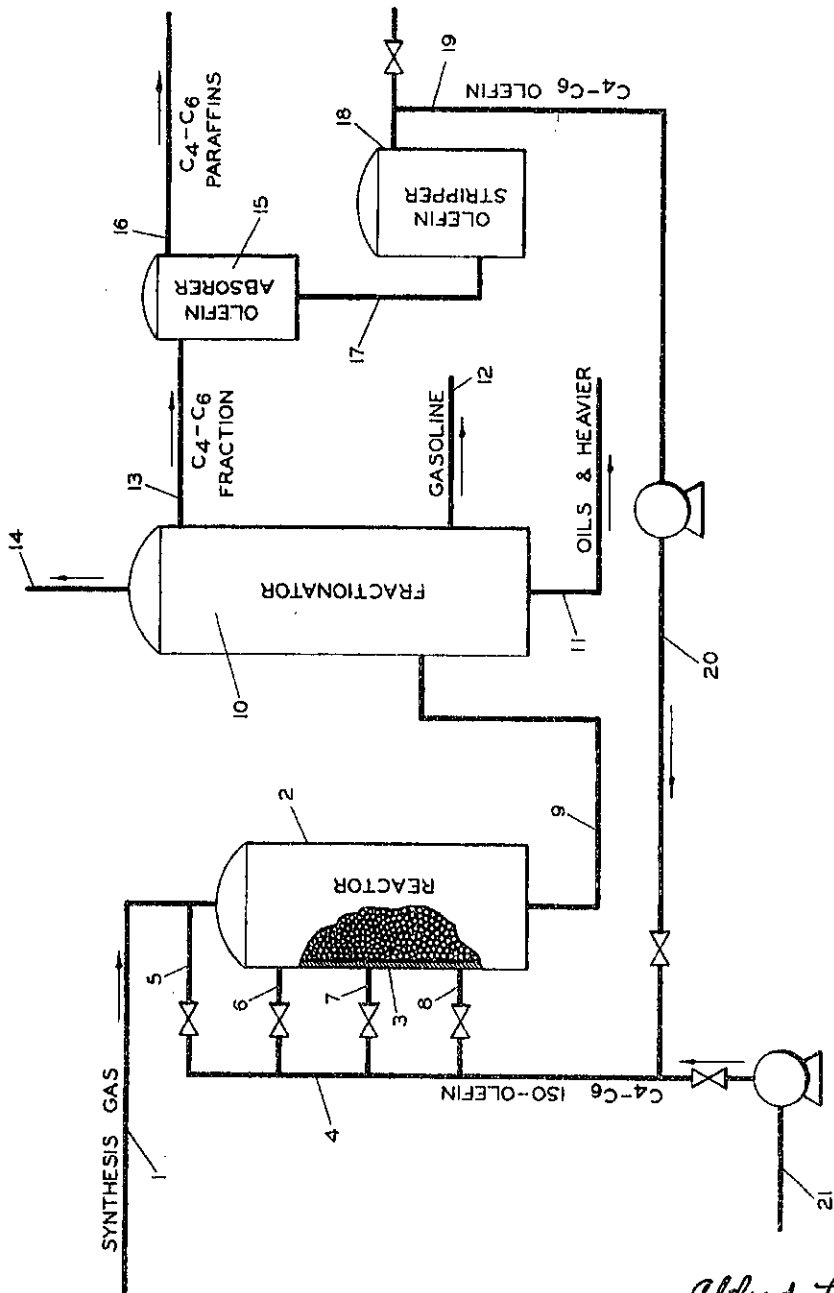
1. In the synthesis of hydrocarbons boiling in the motor fuel range by flowing a synthesis gas mixture containing hydrogen and carbon monoxide through a reaction zone containing a catalyst for said synthesis under conditions of pressure and temperature suitable therefor, the method of increasing the octane number of said motor fuel range hydrocarbons which comprises introducing into said reaction zone along with said synthesis gas a branched chain olefin having 4-6 carbon atoms.

2. A process according to claim 1 wherein C_4 to C_6 olefins comprising iso-olefins are formed as a product of synthesis reaction and wherein the C_4 to C_6 olefin fraction containing said iso-olefins is separated from products of the reaction and reintroduced into the reaction zone.

3. A process according to claim 1 wherein the catalyst comprises sintered iron and wherein the products of the synthesis reaction comprise substantial proportions of C_4 - C_6 iso-olefins which are re-introduced into said reaction zone.

4. A process according to claim 1 wherein the catalyst is one comprising cobalt and thoria.

5. A process according to claim 1 wherein the iso-olefin is introduced in minor proportion by volume with respect to the volume of synthesis gas.



Certified to be the drawing referred
to in the specification hereunto annexed.
Ottawa, Canada, Dec 7, 1946.

Alfred Clark
INVENTOR

By

Smart & Biggar
ATTORNEY