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2,816,906

**CATALYTIC TREATMENT OF HYDROCARBONS
CONTAINING OXYGENATED COMPOUNDS****William I. Gilbert and William A. Horne, Oakmont, Pa.,
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This invention relates to the catalytic treatment of the total liquid hydrocarbon product obtained by the reaction of carbon monoxide and a hydrogen-containing gas in the presence of a Fischer-Tropsch catalyst.

The catalytic hydrogenation of carbon monoxide in the presence of a Fischer-Tropsch catalyst at temperatures up to about 750° F. under superatmospheric pressures produces a variety of substances, the predominance of a particular substance depending upon the particular operating conditions employed in carrying out the synthesis. In general, the materials which are produced by the synthesis reaction comprise organic oxygenated compounds and hydrocarbons. The hydrocarbons thus produced comprise essentially straight chain olefins and paraffins. The present invention is concerned with the conversion of oxygenated compounds to hydrocarbons and the improvement of olefins through isomerization.

The hydrocarbons which are separated from the reaction products obtained in the synthesis process invariably contain a small amount of organic oxygenated compounds. The organic oxygenated compounds which may comprise alcohols, aldehydes, ketones and acids are undesirable in hydrocarbons boiling in the motor fuel boiling range in that they greatly decrease the octane number of the motor fuel. Likewise, the oxygenated compounds have a deleterious effect on the cetane number of hydrocarbons boiling in the diesel fuel boiling range.

Attempts have been made to hydrogenate carbon monoxide to produce hydrocarbons devoid of oxygenated compounds but invariably small amounts of the latter are formed. Methods have been devised for separating the oxygenated compounds from the hydrocarbons but these methods for one or more reasons have not been entirely satisfactory.

The present invention is directed to a process which not only converts to more desirable compounds the objectionable oxygenated compounds which are associated with the hydrocarbons produced by the reaction of carbon monoxide and hydrogen in the presence of a Fischer-Tropsch catalyst but also improves the octane rating and the cetane rating of the hydrocarbons boiling in the motor fuel and diesel fuel boiling ranges, respectively. The process of the invention has the further advantage in that it makes more economic use of the catalyst.

The process of the present invention comprises separating the total liquid hydrocarbon product containing olefins and oxygenated compounds obtained by the reaction of carbon monoxide and a hydrogen-containing gas into a fraction boiling in the motor fuel boiling range, a fraction boiling in the diesel fuel boiling range, and a residual fraction comprising a waxy residue boiling above the diesel fuel fraction. The motor fuel fraction is contacted under deoxygenation conditions comprising a temperature of about 500° to about 1100° F. in the presence of a catalyst comprising alumina impregnated with anhydrous hydrogen chloride. The diesel fuel fraction is contacted at a temperature between about 500° and 1100° F. under substantially non-isomerizing conditions in the

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presence of catalyst withdrawn from the deoxygenation reaction zone.

By the term "deoxygenation" as used herein and in the appended claims we are referring to the simultaneous deoxygenation of oxygenated compounds to olefins and isomerization of straight chain olefins to branched chain olefins. The process of deoxygenation while simultaneously isomerizing a synthetic motor fuel is defined in U. S. Patent No. 2,589,273 to Charles W. Montgomery and William I. Gilbert.

The process of the invention comprises a cyclic catalytic process wherein a synthetic diesel fuel fraction is deoxygenated in the presence of catalyst withdrawn from the deoxygenation of a synthetic motor fuel fraction and the synthetic motor fuel fraction is deoxygenated in the presence of regenerated catalyst from said deoxygenation reaction.

The catalyst which is withdrawn from the deoxygenation zone is partially spent insofar as its promoting to any great degree further isomerization. We have found, however, that this catalyst is an effective catalyst for promoting deoxygenation reactions. In order that the hydrocarbons boiling in the diesel fuel range will not be isomerized, we have found it advantageous to employ a small amount of ammonia in combination with the diesel fuel fraction. While the ammonia is advantageously passed in combination with the diesel fuel fraction over the spent deoxygenation catalyst, good results can be obtained by treating this catalyst with ammonia prior to contacting the hydrocarbons boiling in the diesel fuel range with the catalyst.

Deoxygenation in the presence of ammonia can be carried out either at atmospheric or superatmospheric pressure, i. e. pressures from 0 to 200 pounds per square inch gauge. Good results are obtained at a temperature of about 550° to 750° F. and atmospheric pressure. The amount of ammonia added to the charge is relatively small in comparison with the hydrocarbon charge. The amount of ammonia added is at least sufficient to maintain the pH of the aqueous product released by the deoxygenation reaction above about 6.5. The exact amount of ammonia will vary depending upon the acidity of the charge and also upon the extent to which the deoxygenation catalyst has been spent. In general, however, the ratio of ammonia to liquid hydrocarbons comprises about 0.0005 to 0.0025 volume of liquid ammonia per volume of liquid hydrocarbon charge. When the catalyst is intermittently treated with ammonia, the amount of ammonia so employed is approximately equal to that which would be employed if the ammonia were added continuously. Treating of the catalyst with ammonia is continued until the olefin isomerizing activity of the catalyst is substantially destroyed.

The catalyst which we employ for deoxygenation of the motor fuel fraction comprises alumina impregnated with anhydrous hydrogen chloride. As the catalyst is used, it gradually loses some of its hydrogen chloride content with the result that its isomerizing activity is decreased. This catalyst, however, is satisfactory for deoxygenation so that prior to its being burned-off and reactivated with anhydrous hydrogen chloride, the spent catalyst is used for deoxygenation of the Diesel fuel fraction. After the catalyst has been used for deoxygenation, it is then burned-off and reactivated for further deoxygenation. The catalyst is preferably in powdered or finely divided form with about 95 to 100 percent passing through a 100 mesh screen. The amount of make-up catalyst is relatively small. However, when necessary, make-up catalyst is advantageously added in the form of powdered alumina to the deoxygenation reaction zone. Instead of alumina, we may use bauxite, fuller's earth, or the like.

The present invention will be described more fully hereinbelow in conjunction with the accompanying flow diagram which illustrates diagrammatically a preferred embodiment of the invention.

Now referring to the drawing, hydrocarbon charge containing olefins and oxygenated compounds obtained, for example, from the reaction of carbon monoxide and hydrogen in a Fischer-Tropsch process (not shown) is introduced by pump 10 through conduit 11 to heater 12. The hydrocarbon charge may comprise up to 5 weight percent butanes and lighter, 50 to 80 weight percent boiling within the range, from room temperature to 400° F. comprising hydrocarbons boiling in the motor fuel boiling range, 10 to 20 weight percent boiling within the range 400° to 650° F. comprising hydrocarbons boiling in the diesel fuel boiling range, and 10 to 25 weight percent waxy residue boiling above about 650° F.

Heated hydrocarbon charge is then passed through conduit 13 to fractionator 14. In fractionator 14, the charge is separated into three fractions. A fraction comprising hydrocarbons and oxygenated compounds boiling in the motor fuel boiling range is removed overhead from fractionator 14 by conduit 16 through condenser 17 and conduit 18 to receiving vessel 19. Any light gases present are removed from vessel 19 by conduit 21. A fraction comprising hydrocarbons and oxygenated compounds boiling in the diesel fuel boiling range is removed from fractionator 14 by conduit 22 and collected in a receiving vessel 23. A waxy residual fraction comprising hydrocarbons and oxygenated compounds boiling above about 650° F. is removed from the bottom of fractionator 14 through conduit 24.

The motor fuel fraction collected in vessel 19 is recycled in part as reflux to fractionator 14 by conduits 26 and 27 and pump 28. The remainder of the motor fuel fraction is passed through conduits 26 and 29 by pump 31 to heater 32. The motor fuel fraction is heated in heater 32 to a temperature of about 500° to about 1100° F. and then passed through conduit 33 to catalyst transfer conduit 34. The catalyst in transfer conduit 34 comprises regenerated catalyst which is removed from regenerator 48 by catalyst leg 35. Anhydrous hydrogen chloride is introduced into the motor fuel fraction by conduit 36. Instead of introducing the anhydrous hydrogen chloride with the motor fuel fraction, the anhydrous hydrogen chloride can, if desired, be passed by valved-conduit 30 into catalyst transfer conduit 34 prior to contacting the catalyst with the motor fuel fraction. The amount of anhydrous hydrogen chloride is sufficient to improve the isomerizing activity of the alumina and ordinarily comprises about 1 to 20 volumes of anhydrous hydrogen chloride per volume of catalyst. The motor fuel fraction and catalyst passes from conduit 34 into deoxygenizer 37. Deoxygenizer 37 is advantageously provided with a perforated plate 40 designed to retard the downward flow of catalyst. In deoxygenizer 37 the fraction boiling in the motor fuel boiling range is simultaneously deoxygenated and isomerized. Simultaneous deoxygenation and isomerization is advantageously carried out at about 500° to about 1100° F. in the presence of a finely divided catalyst comprising alumina impregnated with anhydrous hydrogen chloride.

The anhydrous hydrogen chloride which is introduced with the motor fuel fraction maintains the isomerizing activity of the catalyst over a prolonged period of time. Chlorine, however, has a detrimental effect upon the lead susceptibility of the product. Therefore, the product should be treated to insure that no chlorine is present. Accordingly, the hydrocarbon product which is removed from the top of the deoxygenizer 37 through cyclone separator 38 is passed by conduit 39 to bauxite treater 41. The treating is advantageously carried out at about 400° to about 950° F. and space velocity of 0.1 to 30 volumes of gasoline per volume of bauxite per hour. The de-

chlorinated product is removed from bauxite treater 41 by conduit 42.

Catalyst which has lost a substantial part of its isomerizing activity is withdrawn from the bottom of deoxygenizer 37 by spent catalyst leg 46, advantageously of sufficient length that the dense body of catalyst therein forms an effective seal against the upward passage of gases from deoxygenator 49. A flow valve 44, advantageously of the slide valve type, controls the downward flow of catalyst. A portion of the catalyst withdrawn by catalyst leg 46 is passed by transfer conduit 47 to regenerator 48. The amount of catalyst sent to regenerator 48 through transfer conduit 47 is controlled by valve 45. The spent catalyst in transfer conduit 47 is picked up by a current of hot air and/or flue gas introduced by conduit 71. The remainder of the catalyst withdrawn by catalyst leg 46 is passed to deoxygenator 49. Any make-up catalyst which is required is introduced into catalyst leg 46 by conduit 51.

The fraction comprising diesel fuel containing olefins and oxygenated compounds collected in receiving vessel 23 is passed by pump 52 through conduit 53 to heater 54. The diesel fuel fraction is heated to a temperature of about 500° to about 1100° F. in heater 54. The heated diesel fuel fraction is then passed through conduit 56 to conduit 57 wherein it is admixed with a small amount of ammonia which is introduced into conduit 57 by flow control valve 58. The amount of ammonia introduced is controlled by pH meter 59. When the pH of the aqueous product separated from the diesel fuel product falls below about 6.5, flow valve 58 opens to allow more ammonia to be introduced with the diesel fuel fraction.

The combined diesel fuel and ammonia stream is introduced into deoxygenator 49 which is maintained at about 500° to about 1100° F. The ammonia need not be introduced with the diesel fuel fraction. If desired, the catalyst can be contacted with ammonia prior to introducing the diesel fuel fraction. In such case, the ammonia can be introduced into catalyst leg 46 by valved-conduit 60. Deoxygenator 49 is advantageously provided with a perforated plate 50 designed to retard the downward flow of catalyst and to promote uniform contact of the diesel fuel fraction and ammonia with the catalyst. Deoxygenated diesel fuel product and water are removed from the top of deoxygenator 49 through cyclone separator 61 and conduit 62. The product then is passed through condenser 63 and conduit 64 to diesel fuel receiving vessel 66. Any excess ammonia present or light gases formed during deoxygenation are vented from the top of vessel 66 through conduit 67. Water which is formed during deoxygenation is removed from vessel 66 by conduit 68 containing pH meter 59. Diesel fuel is removed from vessel 66 by conduit 69.

Spent catalyst from deoxygenator 49 is withdrawn through spent catalyst leg 72 which is advantageously of sufficient length that the dense body of catalyst therein forms an effective seal against the upward passage of conveying medium introduced by conduit 74. A conventional valve 73 suitably of the slide valve type for controlling the downward flow of catalyst is interposed in catalyst leg 72. From catalyst leg 72, the spent catalyst is picked up by a current of hot air and/or flue gas from heater 75 and carried upwardly through riser pipe 76 to regenerator 48. Since the amount of diesel fuel hydrocarbons produced in a Fischer-Tropsch process may be about one-fifth the amount of gasoline boiling range hydrocarbons, the amount of catalyst passing to regenerator 48 in riser pipe 76 may be about one-fifth the amount of catalyst in transfer conduit 47. It will be understood, however, that this is not a set proportion and that the proportionate amount of catalyst in the various units will vary depending upon the make-up of the total hydrocarbon charge.

Regenerator 48 is advantageously provided with a perforated plate 81 designed to retard the downward flow

of catalyst. Burning carbonaceous deposits from the catalyst is accomplished with air and flue gas which is used to introduce the spent catalyst into the regenerator. In some instances it is desirable to purge the catalyst first with flue gas and then regenerate with air and flue gas or steam if necessary. Burning-off is carried out at a temperature below the sintering temperature of the catalyst, i. e., below about 1200° F. After the catalyst has been burned off, it gravitates through the perforations in plate 81 and forms a dense phase in catalyst leg 35. Catalyst leg 35 has a flow valve 82 interposed in the lower extremity thereof to control the amount of catalyst which is put back into the system. The regenerated catalyst is then picked up by the stream of vaporized or partially vaporized motor fuel fraction and anhydrous hydrogen chloride and returned to the deoxygenizer 37. From the upper section of regenerator 48, the hot products of combustion pass through cyclone separator 83 and out through conduit 84.

Obviously, many modifications and variations of the invention as hereinbefore set forth may be made without departing from the spirit and scope thereof and, therefore, only such limitations should be imposed as are indicated in the appended claims.

We claim:

1. In a process for simultaneously deoxygenating and isomerizing a motor fuel fraction comprising hydrocarbons boiling within the range of from room temperature to 400° F. and deoxygenating a diesel fuel fraction comprising hydrocarbons boiling within the range 400° F. to 650° F., each fraction having been obtained by the reaction of carbon monoxide and a hydrogen-containing gas, the improvement which comprises (1) deoxygenating the diesel fuel fraction in the presence of ammonia in an amount sufficient to substantially inhibit hydrocarbon isomerization with unregenerated catalyst selected from the group consisting of alumina, bauxite and fuller's earth which has been directly withdrawn from simultaneously deoxygenating and isomerizing the motor fuel fraction and (2) simultaneously deoxygenating and isomerizing the motor fuel fraction with regenerated catalyst from the diesel fuel deoxygenating reaction.

2. In a process for simultaneously deoxygenating and isomerizing a motor fuel fraction comprising hydrocarbons boiling within the range of from room temperature to 400° F. and deoxygenating a diesel fuel fraction comprising hydrocarbons boiling within the range of 400° to 650° F., each fraction having been obtained by the reaction of carbon monoxide and a hydrogen-containing gas, the improvement which comprises (1) contacting the diesel fuel fraction together with ammonia with unregenerated catalyst selected from the group consisting of alumina, bauxite and fuller's earth which has been directly withdrawn from simultaneously deoxygenating and isomerizing the motor fuel fraction and (2) contacting the motor fuel fraction together with anhydrous hydrogen chloride with regenerated catalyst from the diesel fuel deoxygenating reaction.

3. In a process for simultaneously deoxygenating and isomerizing a motor fuel fraction comprising hydrocarbons boiling within the range of from room temperature to 400° F. in the presence of alumina impregnated with anhydrous hydrogen chloride and deoxygenating a diesel fuel fraction comprising hydrocarbons boiling within the range 400° to 650° F., each fraction having been obtained by the reaction of carbon monoxide and a hydrogen-containing gas, the improvement which comprises withdrawing catalyst consisting of finely divided alumina impregnated with anhydrous hydrogen chloride from the zone wherein the motor fuel fraction is simultaneously deoxygenated and isomerized, said catalyst being partially spent insofar as its promoting further isomerization; dividing said withdrawn catalyst into two portions; passing one of said portions into a regeneration zone and passing the remaining portion together with ammonia

into the diesel fuel deoxygenating zone; withdrawing spent catalyst from the diesel fuel deoxygenating zone; passing said spent deoxygenating catalyst to the regeneration zone; regenerating the catalyst in the regeneration zone; and passing the regenerated catalyst to the zone wherein the motor fuel fraction is simultaneously deoxygenated and isomerized.

4. A process for the catalytic treatment of the total liquid hydrocarbon product containing olefins and oxygenated compounds obtained by the reaction of carbon monoxide and a hydrogen-containing gas which comprises separating said liquid hydrocarbon product into a fraction boiling within the range of from room temperature to 400° F. comprising hydrocarbons boiling in the motor fuel boiling range, a fraction boiling within the range 400° to 650° F. comprising hydrocarbons boiling in the diesel fuel boiling range, and a residual fraction comprising a waxy residue boiling above the diesel fuel fraction; simultaneously deoxygenating and isomerizing the motor fuel fraction at a temperature of about 500° to 1100° F. in the presence of finely divided alumina impregnated with anhydrous hydrogen chloride; and deoxygenating the diesel fuel fraction in the presence of ammonia in an amount sufficient to substantially inhibit hydrocarbon isomerization and to maintain the pH of the aqueous product released in the diesel fuel deoxygenation reaction above about 6.5 at a temperature of about 500° to about 1100° F. with unregenerated catalyst comprising catalyst which has been directly withdrawn from simultaneously deoxygenating and isomerizing the motor fuel fraction.

5. A process for the catalytic treatment of the total liquid hydrocarbon product containing olefins and oxygenated compounds obtained by the reaction of carbon monoxide and a hydrogen-containing gas which comprises separating said liquid hydrocarbon product into a fraction boiling within the range of from room temperature to 400° F. comprising hydrocarbons boiling in the motor fuel boiling range, a fraction boiling within the range 400° to 650° F. comprising hydrocarbons boiling in the diesel fuel boiling range, and a residual fraction comprising a waxy residue boiling above the diesel fuel fraction; contacting the motor fuel fraction together with anhydrous hydrogen chloride at a temperature of about 500° to about 1100° F. in a zone containing finely divided alumina; passing motor fuel thus obtained over bauxite at about 400° to about 950° F. and a space velocity of 0.1 to 30 volumes of motor fuel per volume of bauxite per hour; and contacting the diesel fuel fraction together with ammonia in an amount sufficient to substantially inhibit hydrocarbon isomerization and to maintain the pH of the aqueous product released in the diesel fuel deoxygenation reaction above about 6.5 at a temperature of about 500° to about 1100° F. with unregenerated catalyst which has been directly withdrawn from the zone wherein the motor fuel fraction has been treated, said withdrawn catalyst being partially spent insofar as its promoting further isomerization.

6. A process for the catalytic treatment of the total liquid hydrocarbon product containing olefins and oxygenated compounds obtained by the reaction of carbon monoxide and a hydrogen-containing gas which comprises separating said liquid hydrocarbon product into a fraction boiling within the range of from room temperature to 400° F. comprising hydrocarbons boiling in the motor fuel boiling range, a fraction boiling within the range 400° to 650° F. comprising hydrocarbons boiling in the diesel fuel boiling range, and a residual fraction comprising a waxy residue boiling above the diesel fuel fraction; contacting the motor fuel fraction together with anhydrous hydrogen chloride at a temperature of about 500° to about 1100° F. in a zone containing finely divided alumina, the ratio of anhydrous hydrogen chloride to alumina comprising about 1 to 20 volumes of anhydrous hydrogen chloride per volume of alumina; passing

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the motor fuel thus obtained over bauxite at about 400° to about 950° F. and a space velocity of about 0.1 to 30 volumes of motor fuel per volume of bauxite per hour; and contacting the diesel fuel fraction together with ammonia in an amount sufficient to substantially inhibit hydrocarbon isomerization and to maintain the pH of the aqueous product released in the diesel fuel deoxygenation reaction above about 6.5 at a temperature of about 550° to about 750° F. with unregenerated catalyst which has been directly withdrawn from the zone wherein the motor fuel fraction has been treated, said withdrawn catalyst being partially spent insofar as its promoting further isomerization.

7. The process of claim 6 wherein the alumina comprises a mixture of regenerated spent catalyst from the zone wherein the motor fuel fraction has been treated and regenerated spent diesel fuel deoxygenating catalyst.

8. The process of claim 6 wherein the alumina comprises a mixture of spent catalyst from the zone wherein

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the motor fuel fraction has been treated and spent diesel fuel deoxygenating catalyst which has been regenerated by burning off carbonaceous deposits at a temperature below about 1200° F.

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