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PROCESS FOR UPGRADING HYDROCARBON SYNTHESIS OIL

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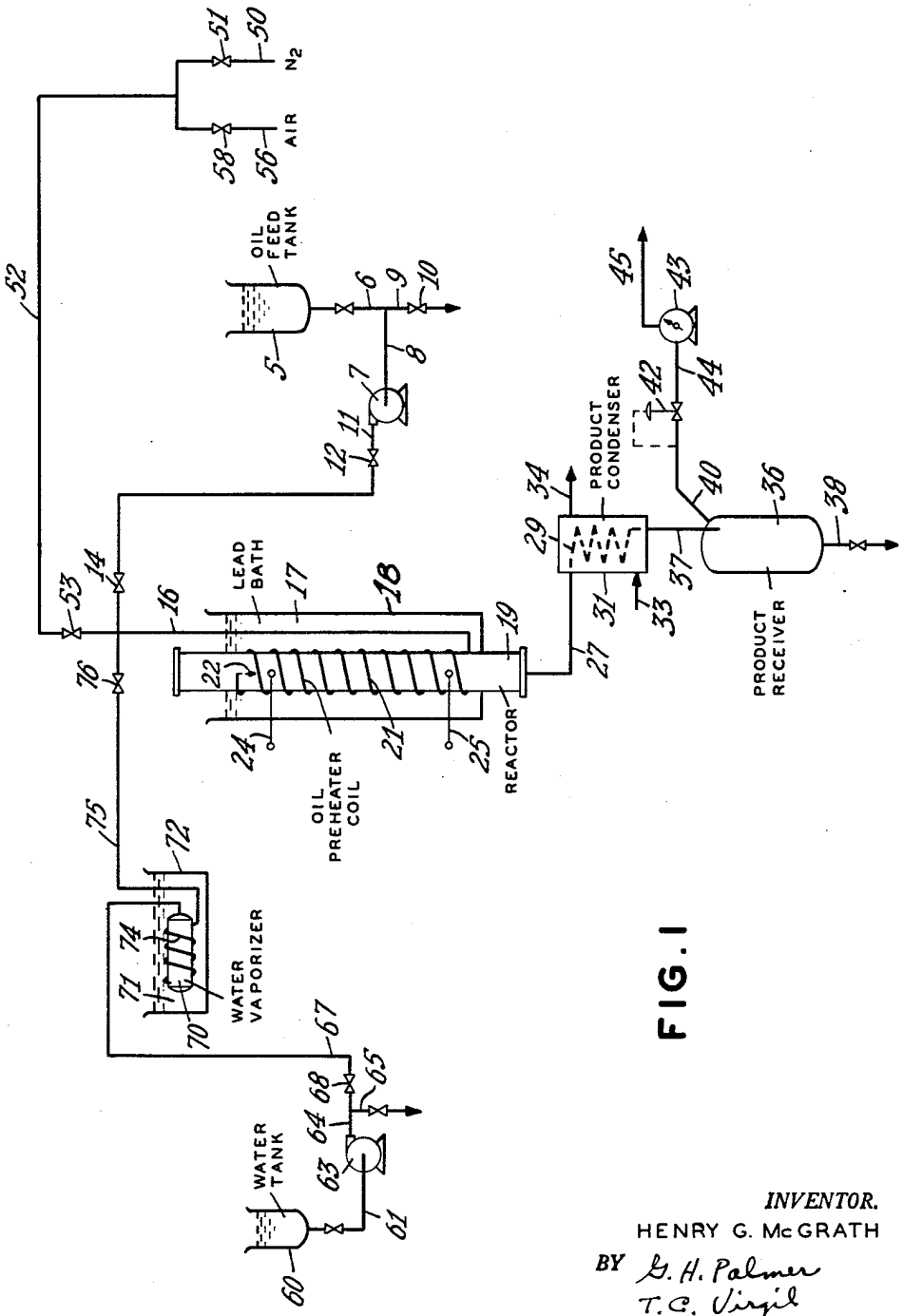

FIG. 1

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PROCESS FOR UPGRADING HYDROCARBON SYNTHESIS OIL

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5 Claims. (Cl. 260—450)

This is a continuation-in-part of application Serial No. 725,835, filed February 1, 1947, now Patent No. 2,598,647, application Serial No. 89,107, filed April 22, 1949, now Patent No. 2,700,676, and application Serial No. 282,150, filed April 14, 1952.

This invention relates to an improved process for upgrading or treating a hydrocarbon oil containing oxygenated organic compounds to yield a product of higher octane quality and stability, and more particularly pertains to an improved process for treating an oil product derived by the synthesis of carbon monoxide and hydrogen to improve the anti-knock quality and stability of the gasoline product and the stability of the diesel fraction.

The presence of oxygenated organic compounds in hydrocarbon oils is disadvantageous from the standpoint of stability when such materials are present in gasoline and diesel oil fractions. The presence of the oxygenated organic compounds renders the diesel oil and gasoline products unstable by reason of the corrosive action and/or further oxidation or decomposition of the oxygen-containing compounds. This problem is particularly acute in the case of diesel oils and gasoline products which are produced by the synthesis of carbon monoxide and hydrogen. Normally, in a hydrocarbon synthesis operation, a substantial part of the product is constituted of oxygenated organic compounds, both the water soluble and water insoluble types. The oil product is usually subjected to a separation treatment in order that the various compounds of the product can be utilized in the best manner known. It is difficult to completely separate all of the oxygenated organic compounds from the normally liquid hydrocarbon materials, and even if such an operation is possible, it is not economical for use on a commercial scale. As a result, it is usually found that a small amount of the oil product which has undergone a separation treatment consists of oxygenated organic compounds. Therefore, it has been the practice to subject the entire hydrocarbon material or the gasoline fraction thereof containing small amounts of oxygenated organic compounds to a treating step whereby the hydrocarbon fractions are upgraded for specific uses, e. g., the anti-knock quality of the gasoline product, as well as for deoxygenation of the hydrocarbon fractions.

It was found that the treatment of the entire oil product leads to serious operating difficulties, because of the presence of metal contaminants in the oil product, as well as the high boiling components, comprising the wax fractions, which are present in the oil. The metal contaminants cause plugging of the heating means wherein the oil product is preheated to a desired temperature. Furthermore, these metals contaminate the catalytic material which is employed for the upgrading treatment, and cause serious adverse effects upon product distribution. The high boiling components in the wax fraction have a higher coke producing tendency than the lower boiling materials and as a result they are readily converted to coke and normally gaseous products which possess little or no economic value. Therefore, any

upgrading operation in which the oil feed contains the wax fraction results in an undesired conversion of the oil feed material to such products as coke and normally gaseous materials. This phenomenon is to be avoided because of the economic loss incurred.

In order to avoid the production of coke and normally gaseous materials in the upgrading treatment, it was suggested heretofore that the oil feed be diluted with an inert gas, such as for example, steam, nitrogen, etc., to reduce the oil partial pressure and obtain a less severe upgrading treatment. The presence of an inert diluent during the upgrading treatment does result in lower yields of coke and normally gaseous materials, but it was also found that such a practice may adversely effect the deoxygenation of the oil product. This indicates that the reactions involving the removal of oxygen from the oxygenated organic compounds takes place at a slower rate than those reactions involving the upgrading treatment of the hydrocarbon materials. Normally, in the upgrading treatment, the gasoline production is improved by isomerization reactions involving the shift of the double bond from the terminal position in the olefins to a position farther from the terminal carbon atoms in the molecule. To a lesser extent, the molecule undergoes branching. In the case of the oxygenated organic compounds, the removal of oxygen is effected mainly by decarboxylation and dehydration reactions. As a result, there is produced water, CO and CO_2 in the deoxygenation and upgrading treatment. It can be seen therefore, that while the use of an inert diluent has reduced the loss of oil product through the formation of coke and normally gaseous materials, the upgrading treatment is deficient insofar as oxygen removal is concerned.

The processing of the gasoline fraction alone results in a decreased quantity of upgraded product by reason that a portion thereof is converted to coke and normally gaseous product materials. Heretofore, it was attempted to overcome the disadvantage of lower yields of upgraded gasoline product by processing the entire oil product including gasoline, diesel oil and wax fraction, and as previously indicated, this technique resulted in an undesirable loss of feed material to coke and gas by reason of the coke forming tendencies of the high boiling components in the wax fraction and/or the presence of metal contaminants. When an upgrading operation is conducted for maximum production of high quality gasoline, the aforementioned procedures are not as efficient as is desired, consequently, it is proposed to overcome this problem by means of the present invention.

It is an object of this invention to provide an improved upgrading treatment for a hydrocarbon material containing oxygenated organic compounds.

Another object of this invention is to provide an improved process for the upgrading of an oil product derived by the synthesis of carbon monoxide and hydrogen.

Still another object of this invention is to provide an improved method for deoxygenation of gasoline fractions containing oxygenated organic compounds whereby the yields are substantially improved.

A further object of this invention is to provide a method for deoxygenating a diesel fraction containing oxygenated organic compounds.

A still further object of this invention is to provide an improved method for the cetane improvement of diesel fractions which are derived by the synthesis of carbon monoxide and hydrogen.

Other objects and advantages of this invention will become apparent from the following description and explanation thereof.

By means of the present invention, it is contemplated improving the quality of hydrocarbon materials having

included therein oxygenated organic compounds by the method which comprises contacting the said hydrocarbon material having an end point of between about 650° and 750° F. with an alumina-containing upgrading catalyst at an elevated temperature sufficient to deoxygenate a substantial amount of the oxygenated organic compounds and improve the quality of the hydrocarbon material.

More particularly, the present invention is concerned with an upgrading treatment for an oil fraction which is derived by the synthesis of carbon monoxide and hydrogen and which contains oxygenated organic compounds by the method which comprises separating that portion of the oil product which boils above about 650° or above about 750° F. from the remainder of the oil product, contacting the separated oil fraction boiling below about 650° or below about 750° F. with an alumina-containing upgrading catalyst at a temperature sufficient to deoxygenate a substantial part of the oxygenated organic compounds contained therein and to improve the quality of the hydrocarbon material which is present in the fraction.

The present invention is applicable for improving the hydrocarbon material having present therein oxygenated organic compounds regardless of the source from which this material is derived. The hydrocarbon material can comprise a diesel oil alone or a mixture of diesel oil and gasoline fractions. The hydrocarbon oil to be processed has an end point between about 650° and 750° F. When this oil constitutes diesel oil alone, it can have an initial boiling point of about 400° to about 500° F.; whereas the gasoline fraction when processed with the diesel oil can have an initial boiling point of about 85° to 325° F. and an end point of about 350° to about 450° F. The present invention is particularly applicable for upgrading a hydrocarbon synthesis product, e. g., a fraction boiling from about 100° to 650° F. and about 400° to 650° F. The product derived by the reaction of carbon monoxide and hydrogen contains a variety of compounds boiling in the gasoline and diesel oil and heavy oil or wax fractions. In addition, the oil product from hydrocarbon synthesis contains a variety of oxygenated organic compounds, both of the water soluble and water insoluble types. Normally, a substantial part of the oxygenated organic compounds are removed by a simple water washing operation. It is to be expected that a small amount of the water soluble oxygenated organic compounds remain in the oil product, however, for the most part the oxygenated organic compounds which remain are water insoluble. Such organic compounds are of high molecular weight and thus readily solubilize with the hydrocarbon materials. Another technique for the removal of at least part of the oxygenated organic compounds, as well as those materials which are normally gaseous under atmospheric conditions involves partial condensation of the reactor effluent from the synthesis operation in one or more steps. The oil product is normally condensed and further processed to improve the quality of the desired products. An unusually effective method of separation which is adapted especially for use with the present invention involves a two-stage condensation of the reactor effluent from the hydrocarbon synthesis operation. In the first condensation step, the temperature is controlled in order to condense substantially all of the heavy oil or wax fraction with or without all or a part of the diesel oil fraction. This partial condensation is effected at a temperature of about 150° to 450° F. and a pressure of about 150 to 650 p. s. i. g. Preferably the partial condensation is effected at a temperature of 300° F. and a pressure of 250 p. s. i. g. In the second step, the gasoline fraction is condensed with or without all or a part of the diesel oil fraction. By this technique, the volume or quantity of the oil product which must be subjected to a preliminary separation treatment for the separation of the heavy oil having an initial boiling point of about 650° to about 750° F. is kept to a minimum. This results in reduced operating costs for the preliminary separation as well as a decrease in the equipment investment which is required for the preliminary separation. As previously indicated, it is desirable to separate the wax or heavy oil fraction having an intial boiling point of about 650° to about 750° F., because of the loss of material which results in the upgrading treatment through coke and normally gaseous materials, as well as the decline in catalyst activity in the upgrading treatment resulting from contamination of the catalyst with the metal normally used in the synthesis operation as catalyst, as well as the metal which is picked up by having the oil product in contact with steel equipment.

The synthesis of hydrocarbons is conducted by contacting hydrogen and carbon monoxide in suitable relative quantities over a catalyst comprising a group VIII metal or a carbide of the group VIII metal. Generally, on a volumetric basis, about 0.5–10:1 of hydrogen to CO are employed in the reaction. In the case of the iron type of catalyst, it is preferred to use about 2–5:1 of hydrogen to CO on a volumetric basis. In this respect, cobalt and nickel types of catalyst yield better results by using the preferred volumetric ratio of hydrogen to carbon monoxide in the order of about 2–5:1. The hydrogen and carbon monoxide are in contact with the synthesis catalyst as a vapor or liquid phase reaction. The iron catalyst is employed as, for example, a precipitated iron type derived by reacting an iron salt with a suitable reagent to form iron oxide. Another iron type of catalyst is prepared by fusing iron oxide with an alumina and with or without a suitable metal compound, such as for example, the carbonate, hydroxide and oxide of sodium, potassium, etc. Ordinarily, the cobalt and nickel catalysts contain the catalytic agent supported on a carbon material, such as, for example, kieselguhr, alumina, fuller's earth, pumice, silica-alumina, activated carbon, etc. Oftentimes, cobalt and nickel in the suitable form are precipitated as a basic carbonate on the carrier material in the preparation thereof. An alkali metal oxide is a suitable promotor which is preferably used with the iron type of catalyst. This promoter serves to promote the reaction between hydrogen and carbon monoxide and results in higher yields for a given reaction than is ordinarily obtained without the use thereof. Generally, the group VIII metal types of catalyst are either partially or completely reduced before use in the synthesis operation.

Other types of catalyst which have been used for synthesis reactions involving carbon monoxide and hydrogen are, for example, cobalt-magnesia-thoria-kieselguhr, nickel-manganese-alumina-kieselguhr, zinc oxide-alumina-thoria, molybdena-alkali metal oxide, chromia-alkali metal oxide, etc. Another group VIII metal which has been used successfully for the synthesis of high boiling hydrocarbons from hydrogen and carbon monoxide is ruthenium and its related compounds.

Usually, when a group VIII metal or its related compound is supported on a carrier material for use as a catalyst in a synthesis operation, about 15 to about 50% by weight of the total catalyst constitutes the group VIII metal, etc. In the case of using a promoter for the synthesis catalyst, generally, about 0.1 to about 2% by weight of alkali metal oxide is employed based on the weight of iron calculated as metallic iron.

The synthesis reaction is usually conducted at a temperature of about 300° to about 675° F. In the case of an iron type of catalyst, it is preferred to employ a temperature of about 450° to about 650° F. With a cobalt or nickel type of catalyst, it is preferred to employ a temperature of about 350° to about 475° F. At these temperatures, the reaction pressure may vary from about 1 atmosphere to about 650 p. s. i. g. Synthesizing hydrocarbons with an iron type of catalyst is preferably

conducted at a pressure in the order of about 80 to about 600 p. s. i. g. The cobalt type of catalyst gives better results at a preferred pressure of about 1 atmosphere to about 250 p. s. i. g. The nickel type of catalyst is preferably used at a reaction pressure in the order of about 1 atmosphere to about 75 p. s. i. g. The relationship between the quantity of synthesis gas and the catalyst which is present during the reaction period is conveniently expressed as the volumetric space velocity, namely, the volume of synthesis gas (CO + hydrogen) measured at 60° F. and 760 mm., which is supplied to the reaction zone on an hourly basis per volume of catalyst which is present in the reaction zone. Usually, for the synthesis operation, the volumetric space velocity may vary in the range of about 100 to about 5000 $V_o/hr./V_c$. In the case of an iron catalyst it is preferred to use about 100 to about 500 $V_o/hr./V_c$; whereas the space velocity for a nickel or cobalt type of catalyst is about 100 to about 1000 $V_o/hr./V_c$. Although not necessary, the synthesis operation is conducted for recycling of the normally gaseous material to the reaction zone. This recycle gas is customarily referred to as a tail gas and it is recycled usually at a rate of about 0.5–3.5:1 on a volumetric basis, based on the fresh feed throughput. In the case of an iron type of catalyst, it is preferred to control operating conditions in order to maintain less than about 16% by volume of carbon monoxide in the cooled gas and also preferably less than about 25% carbon dioxide in the inlet feed gas.

The synthesis of hydrocarbons can be conducted as either a fixed or moving bed system involving a fluid or non-fluid technique. In the non-fluid operation, the catalyst is employed as a pelleted or granular material; whereas for fluid operation the catalyst is in a finely divided form having a particle size in the range of about 5 to about 250 microns, preferably about 10 to about 100 microns. In the fluid system, the catalyst is fluidized by the upward passage by gaseous materials through a mass of finely divided catalyst material at a superficial linear gas velocity in the order of about 0.5 to about 25 feet per second, more usually, about 1 to about 7 feet per second. In a high velocity reaction system, the superficial linear gas velocity of the reactants is in the order of about 4.5 to about 7 feet per second.

The oil product from the synthesis operation having included therein water insoluble oxygenated organic compounds and water soluble oxygenated organic compounds is treated in accordance with the present invention in order to upgrade the quality and stability of the diesel oil, with or without doing the same to the gasoline product. This upgrading involves deoxygenating the oxygenated organic compounds and isomerizing the olefins which are present in the product materials. The present invention is effective for the deoxygenation of oxygenated organic compounds whether they are water soluble or water insoluble. As a practical matter, it is desirable to separate as much of the oxygenated organic compounds as is possible from the oil product in order to decrease the cost of operating the upgrading treatment. In this manner, a substantial part of the oxygenated organic compounds can be advantageously utilized for specific purposes. Generally, the hydrocarbon oil to be treated contains about 0.02 to about 0.5 m.e./gm. acidity. If diesel oil alone is processed about 0.004 to about 0.25 m.e./gm. acidity is usually encountered; whereas with the gasoline fraction about 0.03 to about 0.7 m.e./gm. acidity is usually found. Generally, the upgrading treatment is conducted at a temperature in the order of about 700° to about 950° F., preferably about 750° to about 850° F. The operation can be accomplished by employing atmospheric pressure, however, higher pressures can be used in order to facilitate material handling problems, etc. For this purpose, a reaction pressure in the order of about 0 to about 100 p. s. i. g. can be used advantageously, preferably about 0 to about 20 p. s. i. g.

The material to be upgraded is contacted with the catalytic material containing alumina. The catalyst can be solely alumina or alumina in combination with silica or another suitable catalytic material. For the purpose of this specification and the appended claims, "an alumina containing catalyst" is intended to generically include alumina alone as well as catalysts comprising alumina and some other active component, e. g., silica. Better results are obtained in the use of silica and alumina containing catalyst over a catalyst comprised of alumina alone, although an alumina catalyst is useful for the purposes of this invention. Specific examples of catalysts which are used for the purpose of upgrading oil products containing oxygenated organic compounds are bauxite, "Porocel," activated alumina, alumina gel, silica-stabilized alumina, Montmorillonite clays, such as for example, "Superfiltrol," synthetic alumina cracking catalysts, etc. In the case of a silica-alumina containing catalyst generally about 70 to about 99% of the catalyst contains silica and the remainder about 1 to about 30% by weight is alumina, based on the total weight of the catalyst. It is preferred, however, to have about 75 to about 95% of silica and about 25 to about 5% of alumina in the catalyst for this invention.

The oil product to be upgraded is brought into contact with a catalytic material in the vapor phase for a period of about 1 to about 50, preferably about 2 to about 12 hours. It is convenient to express the relative quantities of feed and catalytic material employed in the reaction in terms of the volumetric space velocity which is defined as the volume of liquid feed charged to the reaction zone on an hourly basis per volume of catalyst which is present in the reaction zone. Generally, the space velocity is about 0.2 to about 20 $V_o/hr./V_c$, preferably in the range of about 2 to about 5. As a result of treating the liquid product with the catalytic material under reaction conditions, a carbonaceous material is deposited on the catalyst which causes a decline in catalytic activity. The drop in catalyst activity is temporary, because a catalyst can be regenerated by burning the carbonaceous material with an oxygen-containing gas. Ordinarily, air or oxygen can be used for this purpose, however, in view that small quantities of carbonaceous material are formed in the process, it is desirable for the sake of temperature control to employ diluted air for the regeneration of the catalyst. If a highly concentrated form of an oxygen containing stream were employed for the regeneration of the catalyst, there is a tendency for excessive temperatures to occur by reason of the difficulty to control the regeneration temperature. The regeneration gas stream generally contains about 1 to about 10% by volume of oxygen, preferably about 2 to about 5% by volume of oxygen. The regeneration is usually conducted at a temperature of about 700° to about 1200° F., preferably about 900° to about 1050° F. At the temperature specified the regeneration can be effected at atmospheric pressure or it can be effected at the same pressure employed for the reaction phase of the process. Accordingly, the pressures specified above for the upgrading treatment can also be employed for the regeneration step.

The upgrading operation can be accomplished as a fixed or moving bed system involving the fluid or non-fluid technique. By reason that the quantity of coke formed in the upgrading treatment is relatively small compared to other operations, the reaction phase or period of operation may run for about 1 to about 40 hours in the case of a fixed bed non-fluid system. In the preferred instance, the reaction period is conducted for about 2 to about 8 hours. The regeneration cycle or period may be operated for the same length of time as the reaction period however, generally, it can be run for about 3 to about 50 hours, preferably about 6 to about 24 hours. In a fixed bed system, it is desirable to employ two vessels for the upgrading treatment. In this manner, it is possible to maintain a continuous flow of processing materials. While

one vessel is processing or upgrading the liquid product, the other vessel is being regenerated. The fixed bed system may involve either fluid or non-fluid techniques depending upon the size of the catalytic material. For a fluid system, the catalyst is used as particles having a size in the order of about 2 to about 250 microns, or more usually, about 10 to about 100 microns. The finely divided catalyst material is capable of being fluidized by the upward passage therethrough of the gaseous reactant at a superficial linear gas velocity of about 0.1 to about 50 feet per second, more usually, about 1 to about 6 feet per second. In the conventional dense phase operation, it is preferred to use a superficial linear gas velocity in the order of about 1–2.5 feet per second. On the other hand, it is also contemplated using the high velocity catalyst circulation system in which the superficial linear gas velocity is in the order of about 4.5 to about 7 feet per second. For a moving bed system, a separate vessel is employed as the regenerator and another vessel as the reactor. After the fluid catalyst has been in the reaction zone for a given period of time, it is contaminated with carbonaceous materials which lowers its activity, thus it is continuously withdrawn from the reaction zone and circulated to the regeneration zone wherein the contaminating deposits are removed by combustion. A continuous stream of regenerated catalysts is recirculated to the reaction zone. There is greater flexibility of operation in a fluid system and in some cases, it is a highly desirable method of operation.

In the upgrading treatment, it is also contemplated employing an inert diluent for the purpose of reducing the oil partial pressure and thus the severity of the treating step. While this is not necessary for the purposes of this invention, it may under certain conditions where the oil feed contains an unusual amount of diesel oil be especially effective. Accordingly, inert diluent can be used in the amount of about 10 to about 5000 standard cubic feet per barrel of oil feed (measured at 60° F. and 760 mm.) preferably about 500 to about 200 s. c. f per barrel of oil feed. The inert diluent includes any material which is gaseous under reaction conditions and which will not react or decompose. Specific examples of the inert diluent are steam, nitrogen, normally gaseous hydrocarbons, such as for example, methane, ethane, etc.

The oil feed to the upgrading operation comprises a hydrocarbon material having an end point of about 650° to about 750 F. Ordinarily, the end point specified is sufficient to eliminate in the heavier boiling fractions any of the metal contaminants, as well as those components which have a high tendency to produce carbon and/or normally gaseous materials under treating conditions. In the case of upgrading, the oil product from a hydrocarbon synthesis operation, the selection of an end point for the feed material is dependent upon the type of catalyst employed in the synthesis operation in order to obtain optimum results. For example, the use of an iron type of catalyst in the synthesis operation produces a product containing relatively less wax or heavy oil material than a synthesis operation in which cobalt is employed as the catalyst. Since less wax or heavy boiling material is produced in the synthesis operation using the iron type of catalyst, it is preferred to use as a feed material in the treating operation one which has an end point of not more than about 650° F. Similarly, in the case of upgrading or treating a liquid product which was produced in a synthesis operation employing a cobalt type of catalyst, it is preferred to employ as a feed material to the treating operation one which has an end point of not greater than 750° F. Various gradations of end points of feed materials to the treating operation can be used depending upon the quantity of wax material and the boiling characteristics thereof which are present in the synthesis liquid product. The quality of the disel oil fraction in the liquid product derived from the synthesis operation using the cobalt type of catalyst warrants raising the end point of the diesel fraction in order to obtain the utmost benefits therefrom. On the other hand, a diesel cut having an end point not greater than 650° F. in the case of synthesis by means of an iron type catalyst is preferred because the quality of the material boiling above about 650° F. does not warrant inclusion with the diesel oil fraction.

Various experiments were conducted on a laboratory scale in order to evaluate various conditions for upgrading treatment of hydrocarbon materials containing oxygenated organic compounds. Figure 1 contains a schematic illustration of a laboratory test unit which was used for the purpose of evaluating the upgrading treatment of various hydrocarbon materials.

In Figure 1, the hydrocarbon material was supplied from an oil feed tank **5** and passed from the bottom thereof by means of a valved line **6** which is connected to the suction side of a pump **7** by means of line **8**. The oil can be discharged from tank **5** by means of a vent line **9** containing a valve **10** which is connected to the tank bottom by line **6**. The oil feed was pumped through the discarge line **11** of the pump containing a valve **12**. When the oil feed was discontinued valve **12** was maintained in a closed position in order to avoid any backflow of processing materials which may have leaked through valve **14** which is located at the other end of line **11**. The oil feed was passed through a line **16**, part of which is submerged in a molten lead bath **17** contained in an open ended vessel **18**.

Line **16** extends approximately the entire length of the open ended vessel **18** which contains the molten lead bath, and then it is wound as a coil **21** around the reactor **19**, which is submerged in the molten lead bath for about 2 feet of its length. Coil **21** serves to preheat the oil feed to the desired temperature, and it covers a substantial part of the length of the reactor before entering through the wall thereof at a point about 4 inches from the top end. Coil **21** terminates as oil inlet **22** within the reactor vessel **19**. The reactor is a vessel 30 inches in length and has an internal diameter of 1 inch. The catalytic material in the granular or pelleted form occupied 21 inches of its length for a total volume of 230–250 cc. The reaction temperatures were indicated by two thermocouples, thermocouple **24** is located about 4 inches from the top and thermocouple **25** is located about 3 inches from the bottom of catalyst bed. The reaction product was discharged from the bottom of the reactor through a line **27** and this line is joined with a coil **29** contained within a closed vessel **31**. The coil **29** was surrounded by cooling water which was introduced into vessel **31** by means of an inlet **34** located at the bottom thereof, and it was discharged from the top of vessel **31** by means of a line **34**. The reaction product was cooled at substantially the same pressure as existed within the reactor. The total product passed through coil **29** and then entered a product receiver **36** by means of line **37** therebetween. The product receiver is equipped with a valved line **38** at the bottom thereof for discharging the condensed liquid, and also, with an overhead vapor or gas line **40** at the top thereof. The pressure within receiver was maintained at a desired level by means of a control valve **42**, and thence, the gaseous material passed to the suction side of a wet test gas meter **43** by means of a line **44**. After the gaseous material was measured, it was vented from the system by a line **45**.

When nitrogen was employed as a diluent for the upgrading treatment, it was supplied from a source **50** which contains a valve **51**. The nitrogen then passed from line **50** into a header **52** which contained a valve **53** at the other end to prevent leakage from line **16** into header **52**. Header **52** is directly connected to line **16** thereby permitting nitrogen to flow into the reactor via coil **21**. Similarly, air is supplied from a source **56** which contains a valve **58**. The air line **56** is in turn connected to header **52**. In some experiments, steam was employed as a diluent and in order to avoid introducing

foreign materials, it was generated from vaporizing water. For this purpose, a water tank **60** served as the supply for water which was discharged from the bottom thereof through a valved line **61** to the suction side of a pump **63**. The water was discharged from the pumps through a line **64** which contains a valved bleed line **65** for the purpose of emptying the discharge line of the pump whenever desired. Line **64** is also connected to a line **67** in which is installed a valve **68**, and line **67** is connected to a water vaporizer drum **70**. The vaporizer drum is submerged in a molten bath of lead **71** contained within an open ended vessel **72**. The water is introduced into one end of the vaporizer drum by means of line **67** and steam emerges from the other end thereof by means of line **74** which is coiled around the outer surface of drum **70**. The coiled line **74** terminates outside of the molten bath as line **75**, and in turn it is connected to line **16**. Line **16** also contains a valve **76**, which serves to prevent back-flow of materials from line **16** into the vaporizer drum **70**, when steam is not flowing through line **75**.

In operation the steam produced in the water vaporizer had a temperature of about 750° to about 850° F. The conditions which existed in the product condenser reduced the temperature of the reactor effluent from about 750° F.–850° F. to about 50° F.–90° F. The other conditions existing in the experiments performed are described in the results reported hereinbelow.

Utilizing the equipment which is illustrated in Figure 1, various types of hydrocarbon materials were evaluated by contacting the same with a material containing 77% silica and 23% alumina, based on the total weight of the catalyst, and this catalyst is designated as "A" in the tables below.

The various hydrocarbon materials employed in the laboratory experiments are given in Table I below.

Table I

Feed Designation	I	II	III	IV	V	VI
°API Gravity	42.2	55.1	53.3	53.0	48.5	48.4
ASTM Distillation, °F.:						
IBP	180	101	174	182	218	204
5	240	130	240	250	271	256
10	260	150	254	259	281	270
20	291	180	266	272	302	291
30	314	212	274	279	324	312
40	356	246	288	292	343	337
50	384	280	300	312	373	366
60	423	320	314	328	407	400
70	471	374	330	346	452	444
80	536	444	350	364	507	505
90	(1)	(2)	368	392	576	580
95	88%	-------	388	413	617	632
E. P.	-------	-------	416	434	644	650
Acidity, me./gm.	0.25	0.147	0.15	0.12	0.04	0.078
Water Washed Oil:						
Acidity, me./gm.	0.21	0.072	-------	-------	-------	-------
Iron Content, Wt. Percent (As Fe_2O_3)	0.13	0.008	-------	-------	-------	-------
Distribution of Oil, Vol. Percent:						
Gasoline 430° E. P.	57.7	[3]74.6	-------	-------	-------	-------
Diesel Oil 650° E. P.	21.8	17.0	-------	-------	-------	-------
Wax (650° F.+)	20.5	8.4	-------	-------	-------	-------
430° F., E. P. Gasoline:						
Acidity, me./gm.	0.165	0.05	-------	-------	-------	-------
RVP, p. s. i.	0.8	5.8	-------	-------	-------	-------
CFRM, clear	37.6	54.8	-------	-------	-------	-------
Feed Source for IBP-650° F. or IBP-430° F. Fraction	-------	-------	I	I	I	I
Wt. Percent Fraction, based on feed source	-------	-------	-------	-------	82.4	83.1

[1] Cracked at 580° F.
[2] Cracked at 460° F.
[3] 400° E. P.

The total liquid product which was derived from a synthesis operation was treated in the laboratory equipment shown in Figure 1. The results of these experiments are reported in Table II below.

Table II

Run No.	1	2	3			4
Feed	I	I	II	II	II	II
Catalyst	(1)	(2)	(1)	(1)	(1)	(1)
No. of Regenerations	0	0	0	0	0	0
Length of Run, Hrs.	1.27	1.62	3(0-3)	2(3-5)	1(5-6)	1.12
Operating Conditions:						
Temperature, °F	795	800	800	800	800	800
Outlet pressure, p. s. i.	15	15	15	15	15	10
Vol. of Catalyst, cc.	236	250	230	230	230	230
Vol. of feed (cc.) per Vol of Cat. (cc.)	4.9	8.9	23.5	23.5	23.5	4.7
Feed rate, cc./hr.	910	1,370	890	890	890	960
H_2O rate, cc./hr.	0	0	0	0	0	150
N_2 rate, S. C. F. H.	0	11	9	9	9	5
Yields (Output Basis):						
100% C_4 Gasoline (430 E. P.), Vol. percent	79.8	71.7	84.0	84.7	80.3	89.0
C_4 Gasoline (430 E. P.), Vol. percent	73.4	69.5	74.6	78.0	78.6	83.2
Diesel Cut (650 E. P.), Vol. percent	12.7	20.5	7.5	10.3	13.5	9.7
Polymer (650+), Vol. percent	6.1	8.7	1.8	2.9	3.2	2.2
H_2O produced, Wt. percent	-------	-------	0.6	1.9	1.3	-------
Product Gas, Wt. percent	3.0	2.6	9.2	2.3	2.1	2.2
Carbon, Wt. percent	4.1	0.5	0.4	0.4	0.3	1.3
Inspections:						
C_5–430° E. P. Gasoline—						
Gravity, °API	56.4	54.8	60.2	60.6	60.6	66.7
CFRM, clear	74.4	67.0	75.0	72.9	71.4	75.0
Acidity, me./gm.	0.0002	0.008	0.001	0.003	0.011	0.025
Stability, Hrs. to 2# drop:						
Clear	14+	1.5	8.1	7.1	3.2	1.7
Inhibited	-------	-------	18.2+	12	7.8	2.3
RVP, p. s. i.	3.3	1.8	3.4	3.4	3.3	4.7
Diesel Cut, 650° E. P.—						
Gravity, °API	34.7	38.3	36.5	36.5	36.5	35.4
Octane No.	-------	-------	45.0	45.0	45.0	-------
Acidity, me./gm.	0.001	0.001	-------	-------	-------	0.003
Aniline Point, °F	119	137	137	137	137	133
Wax—650°.+—						
Gravity, °API	23.2	28.1	22.7	26.8	27.9	24.6

[1] A (granules).
[2] A (pellets).
Me./gm. is milli-equivalent of acid per gram of sample tested.

From Table II, it is to be noted that processing the total liquid containing the wax fraction without the use of a diluent gave unusual results with respect to deoxygenation, however, it is to be noted that the carbon yield is undesirably high. Furthermore, this experiment was conducted for a short period of time, in order to avoid the preheater coil, shown as coil **21** in Figure 1, from plugging as a result of coke production and from the deposition of metal contaminants in the oil feed. From other experiments, it was found that in runs of longer operating periods, the quality of the product would suffer appreciably and the preheater coil would become fouled with iron and coke containing deposits. Run No. 2 illustrates the effect of nitrogen dilution in the upgrading of the total oil. It is to be noted that there has been a significant decrease in the amount of deoxygenation, although the carbon yield has been decreased. The decrease in deoxygenation is best illustrated by reference to the 430° end point gasoline. However, the use of a diluent did not prevent the deposition of metal contaminants on the catalyst. Run No. 3 involves an operation of 6 hours during which three samples were taken at the times designated within the table. It is to be noted in the case of the gasoline product, the oxygen content, measured as acidity increased from 0.001 to 0.011 over a three hour period. In these runs, nitrogen was used as the inert diluent, similarly as in the case of Run No. 2. Furthermore, it is to be noted that the octance quality of the gasoline product became poorer as the run proceeded. This is shown by a drop in octane number from 79.0 to 75.4 in a matter of several hours. These data serve to indicate that the catalyst was becoming gradually contaminated with iron, which caused a reduction in the activity thereof. The other possible explanation which will be discussed hereinafter is that the catalyst became contaminated with carbon thus causing catalyst activity to decrease significantly. Run No. 4 in Table II is illustrative of a run in which both nitrogen and water were employed as the inert diluent. It should be particularly noted that while the carbon decreased significantly, the oxygen content of the gasoline product was undesirably high, thus demonstrating that the oil partial pressure was reduced to a greater extent than is desired to effect good oxygen removal.

A series of runs were made in order to determine what effect, if any, the regeneration of the catalyst would have upon the deoxygenation efficiency and octane improvement of the gasoline product when processing the total oil product including the wax fraction from a synthesis operation. These results are reported in Table III below.

Table III

Run No.	1	2	3	4	5
Feed	I	I	I	I	I
Catalyst	(1)	(1)	(1)	(1)	(1)
No. of Regenerations	1	2	3	0	1
Length of Run, Hrs.	2.0	2.88	4.23	4.0	4.0
Operating Conditions:					
Temperature, ° F.	850	750	800	800	800
Outlet Pressure, p. s. i.	15	15	10	10	10
Vol. of catalyst, cc	230	230	230	230	230
Vol. of Feed/Vol. of Cat. (cc.)	10.4	5.5	19.0	14.9	16.3
Feed rate, cc./hr.	1,200	440	1,030	850	940
H_2O rate, cc./hr.	0	0	150	150	150
N_2 rate, SCFH.	11	11	0	0	0
Yields (Output Basis):					
100% C_4 Gasoline (430 E. P.), Vol. Percent	80.3	65.8	67.8	71.0	64.6
C_4 free Gasoline (430 E. P.), Vol. Percent	76.6	63.9	66.6	67.9	64.2
Diesel Cut (650 E. P.), Vol. Percent	16.7	24.1	23.6	24.6	21.4
Polymer, (650+), Vol. Percent	4.1	5.7	10.2	6.1	15.6
H_2O produced, Wt. Percent	3.0	4.2	-------	1.1	-------
Product Gas, Wt. Percent	3.7	2.4	1.2	1.8	0.4
Carbon, Wt. Percent	-------	0.7	0.2	-------	-------
Inspections:					
C_5–430 E. P. Gasoline—					
Gravity, ° API	56.1	54.6	54.3	56.2	53.0
CFRM, clear	73.0	65.8	62.5	71.4	49.8
Acidity, me./gm.	0.005	0.083	0.185	0.129	0.200
Stability, Hrs. to 2# drop:					
Clear	5.4	1.0	0.6	0.6	2.0
Inhibited	8+	0.9	0.7	0.9	4.8
RVP, p. s. i.	2.4	1.2	1.9	2.2	1.0
Diesel Cut, (650 E. P.)—					
Gravity, ° API	34.9	39.2	39.2	38.2	40.8
Cetane No.	-------	-------	-------	-------	-------
Acidity, me./gm.	0.002	0.007	0.026	0.020	-------
Aniline Point, ° F.	127	137	128	123	-------
Wax—(650° F.+)—					
Gravity, ° API	22.1	26.1	26.9	25.6	26.5

[1] A (granules).

Runs 1, 2 and 3 in Tables III above involve regeneration of catalyst after each of the runs shown in the table. It should be noted that the oxygen content of the gasoline product, measured as acidity, became progressively worse despite the regeneration of the catalyst after each run. For example, in run 1, the acidity for the gasoline produce wat 0.005; whereas the acidity of the same product in run No. 3 was 0.185. This clearly establishes that carbon deposition on the catalyst is not the prime factor for the poor deoxygenation which is obtained when processing the total liquid product from a synthesis operation. Furthermore, it should be noted that the octane improvement of the gasoline product became progressively worse after continued use of the catalyst even with intermittent regeneration as indicated in runs 1–3, inclusive. Runs 4 and 5 involved a 4 hour reaction period with the use of steam as an inert diluent. After each run a sample of material which was plugging the preheater coil, shown as **21** in Figure 1, was analyzed for iron content. The sample showed 88.71% by weight of iron determined as Fe_2O_3. Hence, it is to be noted that the presence of steam was not effective in overcoming the tendency for the preheater coil to plug. Furthermore, in another experiment a sample of the catalyst was analyzed for iron content and the analysis showed that 5.58% by weight of iron determined as Fe_2O_3 was present. These series of runs illustrate that metal contamination of catalyst and plugging of the preheater coil due to the presence of metal contaminants in the oil feed are serious operating difficulties, notwithstanding the use of inert diluents, such as nitrogen and steam, in order to reduce the oil partial pressure under reaction conditions.

A series of runs were also made on the gasoline product obtained from the synthol operation. These data serve to give an indication of the oxygen removal and octane quality improvement which can be effected, with-

out the adverse effect caused by the presence of the wax fraction in the feed material.

Table IV

Run No.	1	2	3	4	5
Feed	III	IV	IV	IV	IV
Catalyst	(1)	(1)	(1)	(1)	(1)
No. of Regenerations	0	1	2	3	4
Length of run, Hrs.	2	2	2	2	2
Operating Conditions:					
Temperature, ° F.	800	800	800	800	800
Outlet Pressure, p. s. i.	10	10	10	10	10
Vol. of Catalyst, cc.	230	230	230	230	230
Vol. of Feed/Vol. of Cat.	9.4	8.4	8.4	8.6	8.4
Feed Rate, cc./hr.	1,075	970	970	1,000	970
H_2O rate, cc./hr.	0	0	0	0	0
N_2 rate, S. C. F. H.	0	0	0	0	0
Yields (Output Basis):					
100% C_4 Gasoline (430 E. P.) Vol. Percent	95.3	94.7	95.2	93.2	95.7
C_4 free Gasoline (430 E. P.), Vol. Percent	87.1	88.2	88.4	87.4	89.8
Polymer (430+), Vol. Percent	3.5	4.3	3.8	3.7	2.5
H_2O produced, Wt. Percent	3.0	1.6	1.7	2.2	2.5
Product Gas, Wt. Percent	2.2	2.7	2.6	2.0	2.4
Inspections:					
C_5-430° F. Gasoline—					
Gravity, ° API	60.7	56.7	58.6	58.3	57.8
CFRM, clear	75.5	74.4	74.5	74.2	74.0
Acidity, me./gm.	0.001	0.002	0.003	0.002	0.003
Stability, Hrs. 2# drop:					
Clear	3.5			6.3	5.5
Inhibited					8+
RVP, p. s. i.		2.9	3.1	2.6	2.8

[1] A (granules).

From Table IV above, it should be noted that the extent of deoxygenation and the octane quality of the product remains substantially the same over a 10 hour period, with intermittent regeneration after each 2 hour reaction period. As would be expected the gasoline feed material did not contain any metal contaminants and consequently, there was absent any evidence of catalyst deactivation and preheater coil plugging.

Another series of runs were made involving the evaluation of a liquid product from a synthol operation including only the gasoline and diesel oil products. The results of these runs are reported in Table V.

notwithstanding the long period of treatment. During these series of runs, it was noted that the preheater coil did not plug nor was there evidence of plugging at the end of run No. 5 in the above table. In the first five runs, steam was employed as the inert diluent and the results obtained therefrom show good octane improvement of the gasoline product as well as effective deoxygenation. Run No. 6 in Table V involves an operation in which an inert diluent was not employed. This run was made over a 4 hour period following which there was no evidence of preheater coil plugging and as is noted from the table above, still better deoxygenation and gasoline product upgrading was achieved than the previous runs.

The important feature of processing the gasoline and

Table V

Run No.	1	2	3	4	5	6
Feed	V	V	V	V	V	VII
Catalyst	(a)	(a)	(a)	(a)	(a)	(a)
No. of Regenerations	0	1	2	3	4	0
Length of Run, Hrs.	4	4	4	4	4	4
Operating Conditions:						
Temperature, ° F.	802	800	800	801	806	807
Outlet pressure, p. s. i.	10	10	10	10	10	10
Space Vel., V_o/hr./V_c	4.3	4.2	4.3	4.1	4.1	4.1
Feed Rate, cc./hr.	998	958	994	950	956	954
H_2O rate, cc./Hr.	166	190	158	160	152	
Yields (Output Basis):						
100% C_4 Gasoline (430° E. P.), Vol. Percent	86.9	83.9	82.7	82.4	84.1	87.1
430 E. P. Gasoline (C_4 free), Vol. Percent	80.8	79.5	79.4	79.7	81.1	79.6
Diesel Cut (650 E. P.), Vol. Percent	[b] 11.7	[c] 8.6	[c] 11.2	[d] 4.4	[d] 4.1	11.5
Polymer (650+), Vol. Percent	0.6	1.5	1.3	1.5	0.9	1.1
H_2O produced, Wt. Percent	3.0	3.2	1.4	2.3	1.3	2.4
Product gas, Wt. Percent	2.1	1.7	1.4	1.2	1.3	2.8
Inspections:						
C_4 free—430 E. P. Gasoline—						
Gravity, ° API	57.8	57.1	56.1	56.1	56.1	58.6
Octane No. CFRM, clear	74.9	73.2	72.0	71.3	71.5	74.9
Acidity, me./gm.	0.04	0.05	0.07	0.07	0.07	0.001
RVP, p. s. i.	2.9	2.5	2.0	1.9	1.7	3.3
Stability, Hrs. to 2# drop:						
Clear	4.0		5.5	3.4	3.9	6.1
Inhibited	4.5	5.0	6.0	5.6		15.0
Diesel Cut—						
Gravity, ° API	34.9	35.7	37.5	35.0	35.4	32.3
Cetane No.	45	47	47			45
Aniline Pt., ° F.				152	152	
Maximum Pour Pt., ° F.				+25	+25	+10

[a] A (granules).
[b] 470–650° F.
[c] 500–650° F.
[d] 550–650° F.

In Table V above, it is demonstrated that the deoxygenation remains fairly constant over an extended period of time, namely, 20 hours, with intermittent regeneration of catalyst after each 4 hour period of reaction. Furthermore, the quality of the gasoline is substantially the same diesel fractions together is that effective deoxygenation and octane improvement of gasoline are obtained at substantially higher yields than is obtained by processing the gasoline fraction alone. When processing gasoline alone, the yield of treated gasoline is less than 100% because part

of the gasoline is converted to material boiling higher than gasoline, dry or product gas and carbon. On the other hand, processing the mixture of gasoline and diesel oil results in yields of gasoline which are higher than what is originally present in the feed. In the case of feed No. V, there is present about 76.6 volume per cent of 430° F. end point gasoline. In every run involving the treatment of feed No. V, significantly more than 76.6% by volume of 430° F. end point gasoline is produced. Therefore, from the standpoint of gasoline production, it is advantageous to treat the gasoline and diesel fractions together, rather than treat the gasoline fraction alone, or the entire oil including gasoline, diesel oil and wax fraction. By comparison of run No. 1 in Table IV with run No. 6 in Table V, it is seen that it is easier to remove oxygenated compounds from the gasoline fraction alone to a figure of 0.001 acidity than when processing diesel oil plus gasoline to obtain a gasoline of the same acidity. The greater severity required for the gasoline plus diesel oil feed results in higher yields of gasoline product because of decomposition of diesel oil. Further, it is not desirable to include the wax fraction with the diesel fraction for the upgrading operation, because the wax fraction contains compounds of high coke forming tendencies and/or it may contain metal contaminants.

The treatment of diesel oil alone in accordance with this invention is illustrated in Table VI below. In this operation activated alumina was employed as catalyst, and the treatment was effected at 850° F., one atmosphere pressure, a space velocity of 1.8 $V_o/hr./C_c$, and for a period of 8 hours.

Table VI

	Raw	Treated
Gravity, °API	44.9	44.8
ASTM Distillation, °F.:		
IBP	369	430
10	451	460
50	496	500
90	589	596
E. P.	640	650
Mol Percent Olefins	62.3	65.8
Aniline Pt., °F	153	161
Diesel Index	69	72
Max. Pour, °F	+5	+10
Flash, PMCC, °F	160	185
SSU @ 100° F.	34.9	35.0
Cetane No.	59	61

From Table VI above, it is to be noted that the treated diesel oil had improved in performance quality, and the amount of water, CO and CO_2 produced indicated that deoxygenation was also attained.

Having thus described my invention by reference to specific examples, it should be understood that no undue limitations or restrictions are to be imposed by reason thereof, but that the scope of the present invention is defined by the appended claims.

I claim:

1. A method of upgrading the quality of a synthetic normally liquid hydrocarbon product derived from the reaction of carbon monoxide and hydrogen in the presence of a synthesis catalyst, the product characterized by having an end point of about 650° to about 750° F. and containing oxygenated compounds, which method comprises contacting said product with an alumina containing catalyst at an elevated temperature and such other conditions that substantial deoxygenation occurs and the quality of the hydrocarbon material is improved.

2. A method of upgrading the quality of a synthetic normally liquid hydrocarbon product derived from the reaction of carbon monoxide and hydrogen in the presence of a synthesis catalyst, the product consisting essentially of diesel oil and gasoline is characterized by having an end point of about 650° to about 750° F. and contains oxygenated compounds, which method comprises contacting said product with an alumina containing catalyst at an elevated temperature and such other conditions that substantial deoxygenation occurs and the octane quality of the gasoline fraction is improved.

3. A method of upgrading the quality of a synthetic normally liquid hydrocarbon product derived from the reaction of carbon monoxide and hydrogen in the presence of a synthesis catalyst, the product consisting essentially of gasoline and diesel oil is characterized by having an end point of about 650° to about 750° F. and contains oxygenated compounds, which method comprises contacting said product with an alumina containing catalyst at a temperature of about 700° to about 950° F., a total pressure of 1 atmosphere to about 100 p. s. i. g., and a volumetric space velocity of about 0.2 to about 20 such that substantial deoxygenation occurs and the octane quality of the gasoline fraction is improved.

4. A method of upgrading the quality of a synthetic normally liquid hydrocarbon product derived from the reaction of carbon monoxide and hydrogen in the presence of a synthesis catalyst, the product consisting essentially of gasoline and diesel oil is characterized by having an end point of about 650° to about 750° F. and contains oxygenated compounds, which method comprises contacting said product with an alumina containing catalyst at a temperature of about 750° to about 850° F., a total pressure of about 1 atmosphere to about 20 p. s. i. g. and a volumetric space velocity of about 2 to about 5 such that substantial deoxygenation occurs and the octane quality of the gasoline fraction is improved.

5. A method for upgrading the quality of a synthetic normally liquid hydrocarbon product derived from the reaction of carbon monoxide and hydrogen in the presence of a synthesis catalyst which comprises removing from said liquid hydrocarbon product of said synthesis reaction a high boiling wax fraction having an initial boiling point between about 650 and about 750° F. and recovering a lower boiling liquid fraction containing oxygenated organic compounds, contacting said lower boiling fraction containing oxygenated organic compounds with an alumina containing catalyst at an elevated temperature and such other conditions that substantial deoxygenation occurs and the quality of the hydrocarbon material is improved.

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