June 20, 1944. V. VOORHEES 2,351,793

CONVERSION OF HYDROCARBON OILS WITH CATALYSTS

Filed July 31, 1940 2 Sheets-Sheet 1

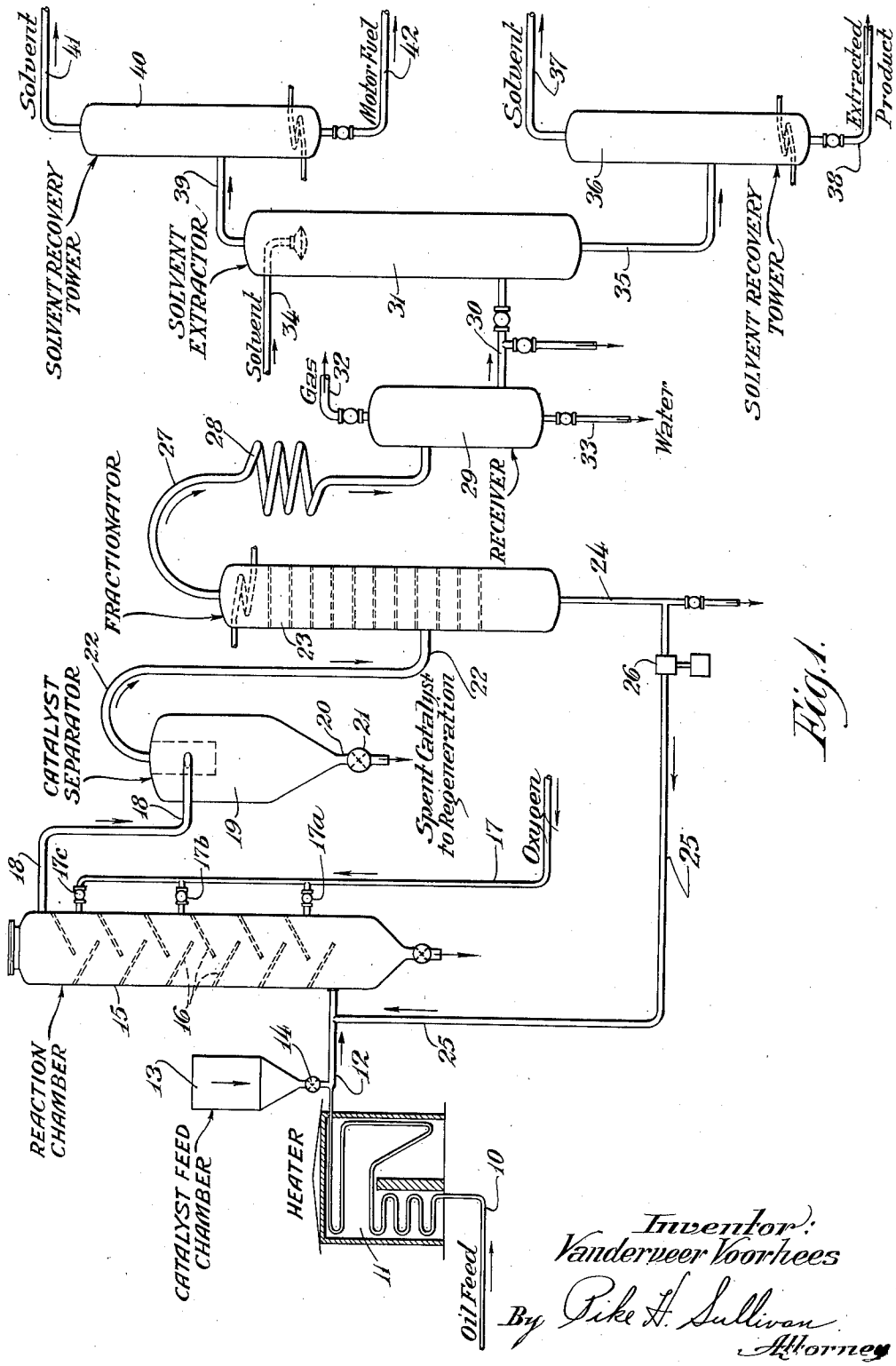


Fig. 1.

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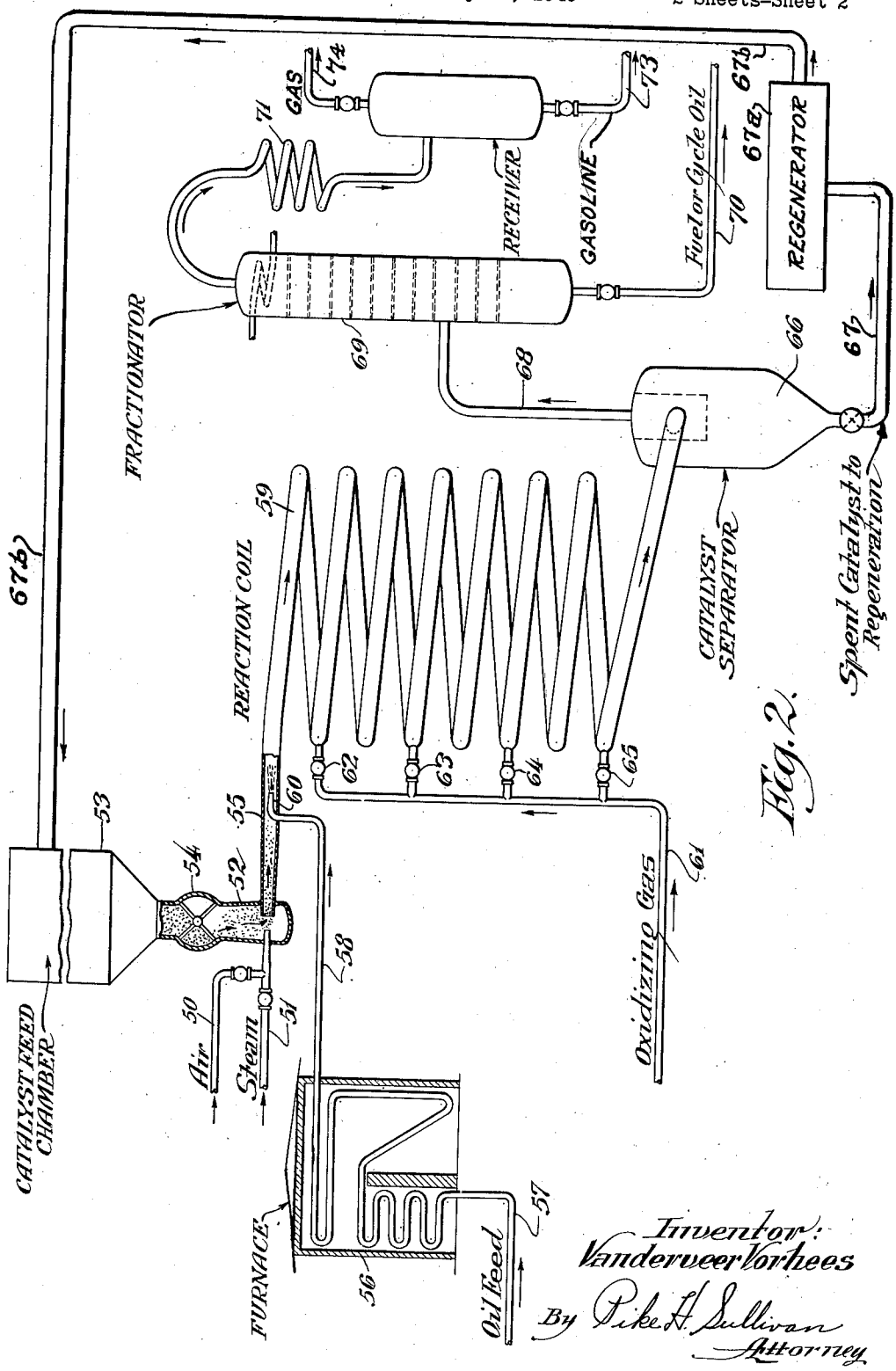


FIG. 2.

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CONVERSION OF HYDROCARBON OILS WITH CATALYSTS

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Application July 31, 1940, Serial No. 348,710

13 Claims. (Cl. 196—52)

This invention relates to a process of converting hydrocarbon oils into motor fuels and other useful products and it relates particularly to the treatment of petroleum hydrocarbons, naphthas, kerosene, gas oil and heavier vaporizable hydrocarbons with suspended catalysts and oxygen in the vapor phase.

One object of the invention is to provide a method and apparatus for converting petroleum hydrocarbons into high knock rating gasoline in a more efficient manner than has heretofore been effected. Another object of the invention is to recover useful by-products from conversion of petroleum hydrocarbons into gasoline in the presence of oxidizing gases. A more specific object of the invention is to provide a method of cracking gas oil and similar petroleum hydrocarbon stocks in the vapor phase with suspended cracking catalysts in a continuous manner to obtain a high degree of conversion of the stock without the necessity of applying external heat during the reaction, thereby avoiding thermal cracking which has heretofore resulted from the indirect application of heat to catalytic cracking reactions. Other objects of the invention will become apparent from the description which follows:

Apparatus for carrying out the process is illustrated in the accompanying drawings which are a part of this specification, wherein Figure 1 shows a schematic layout of a plant for conducting the process using a baffled reaction chamber and Figure 2 shows a modification in which the reaction is conducted in a flowing stream in an elongated passage or coil.

Referring to the drawings—Figure 1—vaporizable petroleum oil feed stock such as gas oil or straight run heavy naphtha is introduced by line 10 into heater 11 where it is vaporized and heated to a temperature in the low cracking range, for example, 850° F. On account of the short time involved, substantially no cracking will occur thermally at this temperature in the transfer line 12 before the introduction of catalyst from catalyst feed chamber 13. However, lower temperatures, as low as 750 to 800° F., may be employed in the transfer line 12. Also, under some conditions and with certain stocks, such as the straight run naphthas, and refractory fractions from thermal cracking operations such as cracked heavy naphtha and middle oils, I may use higher temperatures, for example, 900 to 950° F.

Catalyst in the form of a fine powder is introduced into the stream of vaporized hydrocarbons by a suitable feeding arrangement such as rotating star valve 14, the rate of introducing the catalyst being regulated as desired. The amount of catalyst required can be ordinarily from 1 to 6 times the weight of the hydrocarbon treated or even more, depending on the character of the catalyst and the stock treated as well as other conditions of the operation. In a typical operation, using an argillaceous catalyst, I use from 2 to 4 parts of catalyst by weight to each part of oil treated. In the case of certain types of catalyst, the amount can be reduced to less than equal weight, for example, about ¼ to ½ of the weight of the oil treated can be employed.

The catalysts which I may employ are generally of the argillaceous or alumino-siliceous type and they usually contain a high percentage of active silica in combination with basic oxides of the second or third group metals, such as magnesium and aluminum. They may be prepared synthetically or from natural products such as the argillaceous earths, more particularly the colloidal clays, fuller's earth, bentonite, etc., generally by acid treatment to render them active for the conversion of hydrocarbons. Infusorial earth may also be used as a base for these catalysts. Synthetic catalysts of high activity may be prepared from silica gel activated with other oxides, particularly aluminum and magnesium oxides, either by intimate mixing or chemical combination. In general, silica will compose more than 50% of the weight of the catalyst and commonly 80 to 95%, whereas, alumina, magnesia, etc. will usually compose, together or separately, about 5 to 35% of the catalyst. Other metal oxides may be present as promoters, particularly the oxides of metals of the fifth and sixth groups of the periodic system. Thus, a small amount of vanadium, chromium or molybdenum oxides, generally less than 10% and commonly about 0.2 to 5%, may be used under some conditions. Manganese and copper oxides may also be used as promoters.

The catalyst in the form of a fine powder, usually finer than 100 mesh, and frequently sufficiently fine for most of it to pass 200 to 300 mesh, is dispersed in the oil vapor stream in transfer line 12 and is carried thereby to reaction chamber 15 which is suitably equipped with baffles 16 to insure uniform contacting of the oil vapors with the catalyst suspended therein. The baffles are preferably inclined at the angle of slip for the catalyst. The rate of flow of vapors through chamber 15 is generally sufficiently low to per-

mit partial sedimentation of catalyst to occur therein, thereby increasing the time of contact between the catalyst and the oil vapors. Times of contact of ½ second to 10 seconds or longer are thereby attained. The conversion of the oil vapors into lower molecular weight hydrocarbons within the gasoline boiling range is ordinarily accompanied by a drop in temperature resulting from the endothermic heat of the conversion reaction. For reasons which will hereinafter become apparent, it is generally desirable to convert a large percentage of the oil into gasoline in a single pass through the system. For example, it is frequently desirable to convert 40 to 50% of the oil with the result that a very considerable fall in temperature occurs. The reaction rate is, therefore, ordinarily very greatly reduced making it difficult to maintain the desired rate of conversion. Numerous attempts have heretofore been made to supply heat to the reaction but serious difficulties stand in the way. Specially designed apparatus with heating coils of various types have been proposed and tested. One of the difficulties is the coating of the heating surfaces with powdered catalyst, thus seriously reducing the heat transfer rate and increasing local overheating at the surfaces. Another difficulty is the effect of locally overheating areas which result in no-uniform conversion conditions. Catalyst in the overheated areas becomes foul with carbonaceous matter as a result of the excessive heating, and the amount of undesirable fixed gases, carbon, etc. in the conversion products is thereby increased.

In order to avoid these disadvantages and yet obtain high conversion rates, I employ an internal oxidation reaction to maintain the desired conversion temperature, and also to prevent the deposition of carbonaceous matter on the surface of the catalyst. This internal reaction is accomplished by the introduction to the catalyst-hydrocarbon vapor mixture of oxygen or oxygen-containing gases by line 17 with branches 17*a*, 17*b* and/or 17*c* by which the oxygen is distributed throughout the reaction chamber as desired. Air may be employed as a convenient oxygen-containing gas and I may also use oxygen mixed with other inert gases, steam, CO_2, etc. It is desirable to introduce the oxygen at high velocities to obtain rapid distribution in the reaction chamber, thereby avoiding any sort of local combustion. Sufficient dilution with inert gas and sufficient turbulence is employed at the point of mixing to obtain a uniform oxidizing reaction in the hydrocarbon vapor and on the surface of the catalyst suspended therein. By this means I am enabled to obtain perfectly uniform temperatures in the reaction chamber insuring maximum conversion of hydrocarbons to desirable products and increasing the effectiveness of the catalyst employed. The pressure used in the reaction chamber 15 is generally low, of the order of 5 to 50 pounds per square inch. Atmospheric pressure may be used if desired. The temperature may be maintained uniform throughout the reaction chamber or it may be somewhat increased toward the end of the reaction chamber to increase the conversion of the more refractory hydrocarbons.

The vapors from 15 and spent catalyst are conducted by line 18 to catalyst separator 19 which may be of the centrifugal or cyclone type. The catalyst separated in 19 flows by gravity through outlet 20 controlled by outlet valve 21. The catalyst removed at this point is spent to a considerable degree and is preferably regenerated by heating in air under carefully controlled temperature conditions. A part of the catalyst, however, may be recycled directly to the catalyst feeder 13 where it is mixed with other fresh catalyst and introduced continually into the system. Vapors from 19 pass by line 22 to fractionating tower 23. Any catalyst remaining suspended in the vapors will usually be collected in the reflux liquid in 23 and withdrawn as a liquid suspension by line 24 leading away from the unit or recycled by line 25 and pump 26 back to the reaction chamber 15. If desired, a portion of the reflux may be recycled and a portion withdrawn and processed elsewhere. Likewise, a lighter fraction may be withdrawn from an intermediate point of fractionator 23.

The hydrocarbon vapors leaving the top of fractionator 23 pass by line 27 to condenser 28 and receiver 29 where the liquid products are collected and conducted by line 30 to solvent extractor 31. Uncondensed gases are largely withdrawn from the system by line 32. Any water which is produced in the process may be collected in the bottom of receiver 29 and withdrawn by line 33. In extractor 31 the products may be treated with a suitable solvent for separating oxidation products of the reaction from hydrocarbon products. For this purpose liquid sulfur dioxide may be used as well as various other solvents such as the alcohols, methyl and ethyl alcohol, acetone and other polar liquids incompletely miscible with gasoline. The solvent is introduced by line 34 and the solvent extract withdrawn by line 35 leading to solvent recovery tower 36 wherein the solvent may be distilled from the extract and withdrawn as a vapor by line 37, the extracted products being removed by line 38. The hydrocarbon fraction is withdrawn from extractor 31 by line 39 leading to solvent recovery tower 40 from which the solvent is withdrawn by line 41 and the motor fuel products by line 42. The oxygenated products obtained from line 38 will usually consist of mixtures of aldehydes, ketones, alcohols and organic acids. They may be processed to produce valuable solvents for paints, varnishes, and for other purposes. However, the major product of the reaction is a hydrocarbon separated by line 42. Because of the combined action of the catalyst and the oxygen, the hydrocarbon product contains a high percentage of aromatic and cycloparaffinic hydrocarbons which give to it a high knock rating when used in motor fuel.

Referring now to Figure 2, showing a modification of the foregoing process, air and steam or other inert gas are introduced by lines 50 and 51 respectively into catalyst dispersing chamber 52 into which powdered catalyst is introduced from chamber 53 and regulating feeder valve 54. The Venturi pump principle may be employed in disperser 52 for the purpose of maintaining a low pressure, e. g., atmospheric pressure in 52 and building up a pressure in the catalyst discharge line 55. To this end, air, steam or other inert gas is forced through 52 at high velocity in an unconfined stream. The pressure in line 55 may be from 5 to 50 pounds per square inch, if desired. Hydrocarbon oil vapors are generated in furnace 56, for example, from gas oil feed stock, by line 57. The hot vapors, for example, at a temperature of 900° F. are conducted by transfer line 58 to the entrance of reaction coil 59. The oil vapors and catalyst suspension are brought together at contact point 60 where the oil vapors

are preferably introduced by a nozzle at high velocity. If desired, however, part or all of the oil vapors may be conducted directly from furnace 56 to dispersing chamber 52.

Reaction coil 59 may be an elongated pipe coil into which there is introduced at intervals an oxidizing gas, for example, air or air diluted with inert gas, from line 61, with branches 62, 63, 64 and 65. The oil vapors and suspended catalyst are conducted from reaction chamber 59 to catalyst separator 66. The admission of oxidizing gas in coil 59 may be regulated to provide a uniform temperature throughout the coil or a progressively rising temperature may be employed in the coil to compensate for the decrease in activity of the catalyst while passing therethrough. Thus, the temperature at the beginning of the coil may be 850° F. and at the end of the coil it may be 950° F., a uniform rise in temperature being effected by the exothermic oxidation reaction.

The catalyst separated in cyclone separator 66 and withdrawn at outlet 67 may be regenerated at 67a, then recycled to the system by 67b and catalyst feeding chamber 53. The vapors of the product withdrawn from separator 66 are conducted by line 68 to fractionator 69 wherefrom the heavy fraction is withdrawn by line 70. The heavy fraction may be recycled to the converter 59 or discharged from the system for use as a fuel oil, a solvent, drying oil or for other special purposes. The lighter products are removed as a distillate from fractionator 69, condensed in condenser 71 and collected in receiver 72 from which the gasoline fraction is removed by line 73 and gases by line 74. The gasoline fraction may be further refined as previously indicated to remove oxygen-containing products.

The presence of oxygen in the catalytic conversion reaction not only effects a desirable temperature regulation but increases the catalytic activity, by adsorption of oxygen on the surface of the catalyst. As a result of this combined effect, it is possible to obtain conversions of 50 to 60% or more in a single passage through the apparatus. Heretofore where attempts have been made to introduce oxygen into a hydrocarbon conversion process, either no catalyst was employed or the catalyst was employed in the form of a fixed bed where local oxygen concentrations were necessarily high resulting in the destruction of the hydrocarbon stock. Where no catalyst was present in the reaction zone, it was impossible to direct the reaction in the manner desired. The result was that excessive amounts of oxidation products were produced in the reaction. The present process avoids these difficulties by obtaining rapid dispersion of the oxygen in the hydrocarbon vapors in the presence of a large amount of catalyst to direct the course of reaction. Dehydrogenation catalysts when employed in the reaction may direct the oxidation to hydrogen with the production of water as a by-product rather than organic oxygen-containing compounds sometimes not desired. Chromium, vanadium, molybdenum, manganese, nickel, cobalt or copper oxides in amounts of 0.1 to 5% of the alumino-silicate catalyst may be employed for this purpose.

Having thus described my invention, what I claim is:

1. The process of converting hydrocarbon oils which comprises vaporizing the oil and dispersing in the vapors thereof at elevated temperature a finely divided solid hydrocarbon conversion catalyst, maintaining the suspension of catalyst and hydrocarbon vapors at a conversion temperature, introducing oxygen into the hot suspension to assist in maintaining said conversion temperature by the exothermic heat of oxidation, separating the finely divided catalyst from the hydrocarbon conversion products and fractionating the products.

2. The process of claim 1 wherein the suspension of catalyst in hydrocarbon vapors is conducted through an elongated reaction zone and regulated amounts of oxygen-containing gas are introduced into the suspension at intervals to control the said conversion temperature.

3. The process of claim 1 wherein the suspension of catalyst in hydrocarbon vapors is conducted through an elongated reaction zone and regulated amounts of oxygen-containing gas are introduced into the suspension at intervals to maintain the reaction temperature substantially constant therein.

4. The process of claim 1 wherein the hydrocarbon conversion catalyst is an argillaceous earth.

5. The process of claim 1 wherein the hydrocarbon conversion catalyst is comprised of active silica and alumina.

6. The process of claim 1 wherein the hydrocarbon conversion catalyst consists essentially of silica activated with magnesia.

7. In the process of converting hydrocarbon oils into high knock rating motor fuels wherein said oils are vaporized and heated to conversion temperature and the resulting vapors are subjected to the action of an oxygen-containing gas, the improvement comprising directing the oxidizing action toward the formation of high knock rating hydrocarbon motor fuels by dispersing in said hot hydrocarbon vapors a finely divided siliceous hydrocarbon conversion catalyst before introducing said oxygen-containing gas, separating the catalyst from the reaction products and recovering the desired hydrocarbon motor fuels from the remaining vapors.

8. The process of claim 7 wherein the weight of catalyst employed is about 1 to 6 times the weight of hydrocarbon treated.

9. The process of claim 7 wherein the siliceous catalyst employed is activated by the oxide of a metal selected from the class consisting of the metals of the second and third groups of the periodic system.

10. The process of claim 7 wherein the siliceous catalyst employed is activated by the oxide of a metal selected from the class consisting of the metals of the second and third groups of the periodic system and promoted by a small amount of the oxide of a metal selected from the class consisting of the metals of the fifth and sixth groups of the periodic system.

11. The process of controlling the oxidation of petroleum hydrocarbons in the vapor phase at conversion temperatures above about 750° F. which comprises conducting the oxidation by adding oxygen to said vapors at conversion temperature in the presence of finely divided, highly dispersed siliceous catalysts present to the extent of about ¼ to 6 times the weight of the hydrocarbon oil treated.

12. The process of converting petroleum hydrocarbon oils into motor fuels of high knock rating which comprises continuously vaporizing a stream of said oil and heating the vapors to a cracking temperature, introducing a finely divided solid catalyst into said vapor stream and dispersing it

therein, introducing regulated amounts of oxygen into the resulting hot dispersion of catalyst and hydrocarbon vapors in a reaction zone, separating the finely divided solid catalyst from the reaction products, fractionating the reaction products, recovering therefrom a motor fuel distillate fraction boiling substantially in the range of gasoline and a heavier recycle oil fraction, conducting said recycle oil fraction to said reaction zone and subjecting it therein to further oxidizing action, thereby producing additional high knock rating motor fuels.

13. The process of producing from petroleum hydrocarbons, oxidation products having valuable properties which comprises oxidizing said petroleum hydrocarbons in the vapor phase with atmospheric oxygen at elevated temperatures, above 750° F., and controlling the character of the oxidation by conducting the reaction in the presence of a large proportion of finely divided, highly dispersed solid siliceous hydrocarbon conversion catalyst, supplying oxygen to the reaction by introducing oxygen-containing gas into the dispersion of conversion catalyst and hydrocarbon while at said elevated temperature, separating the catalyst from the reaction products, regenerating said catalyst by burning with air and recycling said catalyst to said oxidation reaction.

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