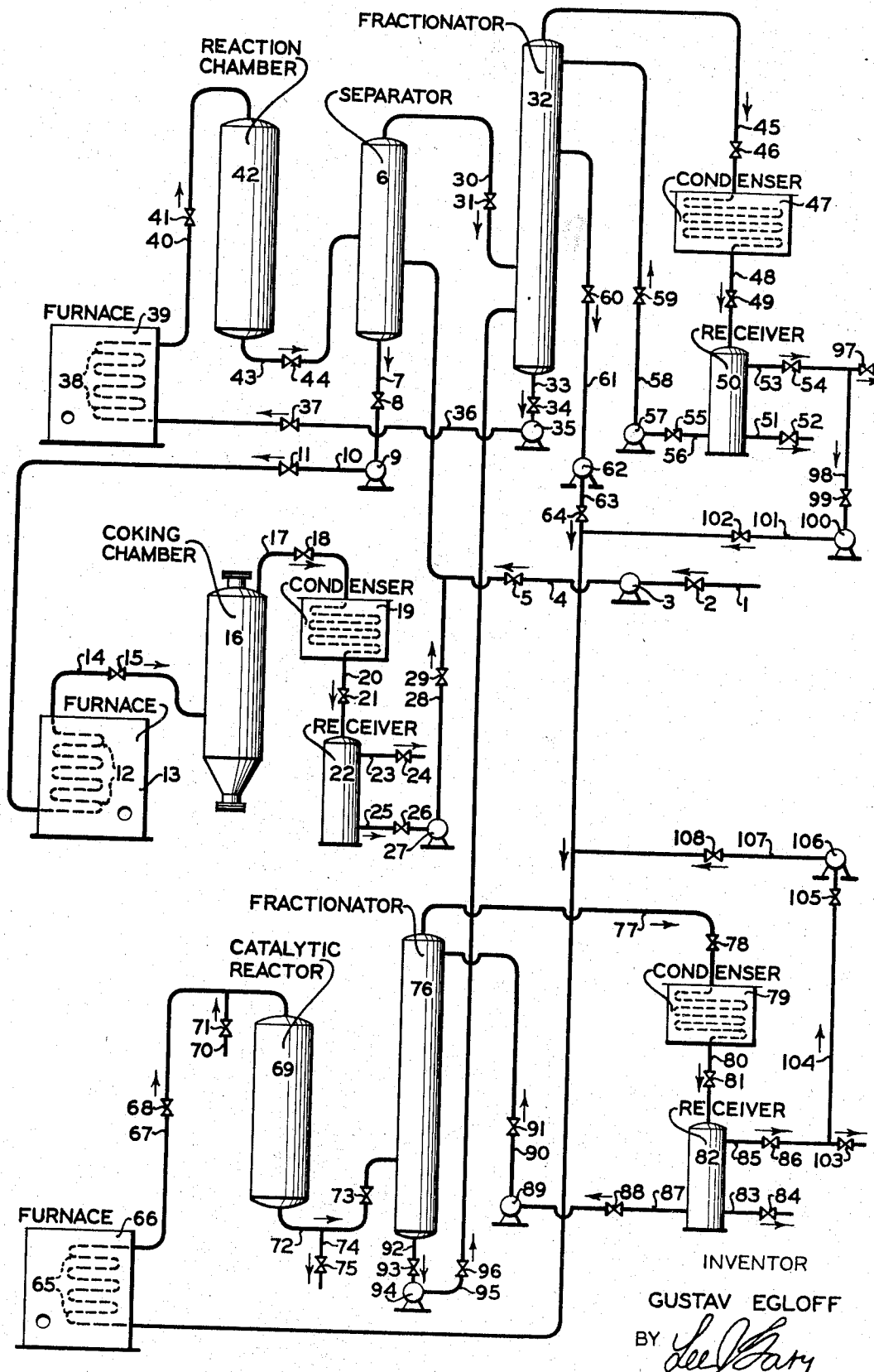
May 9, 1944. G. EGLOFF 2,348,531

TREATMENT OF HYDROCARBONS

Filed Dec. 16, 1940



Patented May 9, 1944 2,348,531

UNITED STATES PATENT OFFICE

2,348,531

TREATMENT OF HYDROCARBONS

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Application December 16, 1940, Serial No. 370,325

4 Claims. (Cl. 196—49)

This invention relates to the treatment of hydrocarbon oils to produce large yields of high antiknock gasoline. More specifically it is directed to the cracking and coking treatment of hydrocarbon oil by catalytic and thermal means so that the oil and conversion products therefrom are effectively utilized in the production of the large yields of high antiknock gasoline.

In the utilization of heavy crude oils, topped and reduced crudes, large yields of gasoline are obtained in the present process by coking the high boiling cracked residues from charging oils of this type to produce gasoline as the preferred liquid product. Hydrocarbons boiling above the gasoline boiling point range and having relatively low coke depositing characteristics are directed to catalytic cracking treatment while substantially higher boiling hydrocarbons of an intermediate, coke depositing nature are subjected to thermal or pyrolytic cracking treatment and the heaviest fractions are directed to said coking treatment.

In one specific embodiment the present invention comprises mixing a hydrocarbon charging oil with non-vaporous, high coke-forming oil and gas produced by thermal cracking as hereinafter described, thermally coking said high coke-forming oil, separating the coke and vaporous products therefrom and condensing said vaporous products, commingling the condensed products with said hydrocarbon charging oil, directing the vaporous oil and gas from said thermal cracking step to fractionating treatment to separate relatively heavy and light reflux condensates from thermally cracked gasoline and gas, subjecting said heavy reflux condensate oil to thermal cracking treatment and separating the conversion products therefrom into non-vaporous and vaporous products for said coking and fractionating treatments, and subjecting said relatively light reflux condensate to contact with a cracking catalyst under cracking conditions to produce reaction products containing a large yield of catalytically cracked gasoline, separating the reaction products into catalytically cracked gasoline and a hydrocarbon fraction boiling above said catalytically cracked gasoline, commingling the said hydrocarbon fraction with the hydrocarbons from thermal cracking and coking undergoing fractionation as above described.

According to the present invention, heavy crude petroleum oils or topped and reduced crude oils are subjected to thermal and catalytic cracking, and coking treatment in such a manner as to effectively utilize the oil charged to the process in producing a large yield of high antiknock gasoline with coke and gas as the main by-products. The heavier constituents of the oil charged to the process which ordinarily yield liquid residues unsuitable for fuel oil purposes when cracking to produce substantial yields of gasoline are thermally coked and the distillate from coking is mixed with the oil admitted to the process. Gasoline vapors are separated from reflux condensate and a heavier reflux condensate fraction is directed to thermal cracking treatment while the lighter reflux condensate fraction is directed to catalytic cracking treatment. As a result of processing in this manner, the major product from the process is a gasoline of higher antiknock value than is ordinarily produced by thermal cracking and coking treatment. In the thermal cracking, temperatures of approximately 850–1050° F. may be employed and pressures of approximately 75 to 600 pounds or more per square inch.

The catalysts utilized in catalytic cracking may be either of natural or synthetic origin. Naturally occurring siliceous and aluminous materials such as many earths, clays, glauconites (greensand), bentonites and montmorillonites which are usually acid-treated, or otherwise modified to give useful catalysts may be employed, or permutites and other active materials including certain phosphates of aluminum, zirconium and titanium. Synthetic catalysts may include various composites of prepared hydrated silica admixed or co-precipitated with hydrous oxides such as those of aluminum, zirconium, magnesium, titanium, vanadium, as well as other hydrous metal oxides. The synthetic cracking catalysts employed may be prepared by numerous methods. The components may be separately, concurrently, or consecutively precipitated. Generally speaking, the primary and major component is a precipitated hydrated silica composited or intimately admixed with a precipitated hydrous metal oxide such as alumina, zirconia or mixtures thereof and present in minor proportions. The composited hydrated oxides may be formed into particles of a size ranging from approximately 2 to 10 mesh by extrusion, pelleting or briquetting, for example, and the preparation is usually washed at some stage of the operation to remove detrimental components such as alkali metal impurities. The drying is at ordinary drying temperatures and the particles are calcined at approximately 1000 to 1600° F.

The temperatures employed in catalytic cracking treatment may vary from approximately 700

to 1100° F. and the pressures employed may vary from substantially atmospheric pressure to pressures of the order of 500 to 1000 pounds per square inch. Space velocities of approximately ½ to 60 may be used, the space velocity being defined as the hourly volume of liquid oil charged to the catalyst per volume of catalyst space in the reactor. Although the catalytic cracking treatment in the presence of these catalysts is described when using the catalyst in a granular condition disposed in a catalytic reactor it is also possible to use essentially the same catalysts in a finely divided condition by mixing the finely divided catalyst with the oil, for example, and subjecting the mixture to cracking conditions of time, temperature and pressure to produce substantial yields of high antiknock catalytically cracked gasoline.

Other features of the invention will become apparent in connection with the description of the flow and operating conditions described in connection with the attached drawing. The drawing illustrates diagrammatically and in conventional side elevation one specific form of apparatus which may be used to accomplish the objects of the invention. It is not drawn to any exact or relative scale and serves only as an illustration of the scope of the process constituting the invention.

Referring to the drawing, charging stock which may be preheated by any suitable means is admitted to the process through line 1 and valve 2 leading to pump 3 which pumps this oil through line 4 containing valve 5 into the separating chamber 6 of the thermal cracking step. The oil is mixed in this separating chamber with conversion products from the thermal cracking step, a portion thereof undergoing vaporization and passing off with vaporous products from thermal cracking while the unvaporized portion is mixed with non-vaporous hydrocarbons from thermal cracking separated in this chamber. The unvaporized and non-vaporous hydrocarbons are removed from separating chamber 6 through line 7 containing valve 8 and leading to pump 9 which pumps this oil through line 10 containing valve 11 and leading to heating element 12 located in furnace 13. The oil is heated to coking conditions of temperature and pressure in heating element 12 and thence directed through line 14 regulated by valve 15 to the coking chamber 16. A plurality of coking chambers may be provided so that one or more coking chambers are in use while one or more coking chambers are in process of cleaning or preparation for use. Vaporous products separated from the coke deposited in chamber 16 is removed from the top of the chamber through line 17 regulated by valve 18 which leads to the condenser 19 and the cooled and condensed products thence flow through line 20 and valve 21 into receiver 22 where gaseous products are separated from the liquid product of the coking step. Gaseous products are removed from receiver 22 through line 23 regulated by valve 24 and the liquid product is removed through line 25 controlled by valve 26. Although this oil may be withdrawn from the system by means not shown it is preferably directed to pump 27 which pumps this oil through line 28 containing valve 29 and thence into line 5 previously described where the oil mixes with the fresh hydrocarbon oil charged to the process and which is being directed to the separating chamber 6. A mixture of vaporized untreated hydrocarbons and thermally cracked hydrocarbons leaves the separating chamber 6 through line 30 controlled by valve 31 and flows into the fractionator 32 from which gasoline vapors and gas are removed overhead and a relatively heavy reflux condensate and a relatively light reflux condensate are separated for thermal and catalytic cracking respectively. Heavy reflux condensate which is not suitable for catalytic cracking and separated in fractionator 32 is removed from the bottom thereof through line 33 regulated by valve 34 leading to pump 35 which pumps this oil through line 36 containing valve 37 and leading to heating element 38 located in furnace 39 where this oil is heated under pressure at thermal cracking conditions. The heated oil then flows through line 40 regulated by valve 41 into the reaction chamber 42 where a reaction period is maintained to favor the production of a large yield of gasoline hydrocarbons. The cracked products are removed from the bottom of reaction chamber 42 through line 43 regulated by valve 44 leading into the said separating chamber 6 where they are mixed with the fresh hydrocarbon oil admitted to the process, and non-vaporous oil is separated from vaporous products and is further processed as has been hereinabove described. Gasoline vapors and hydrocarbon gases produced in the coking and thermal cracking operations and separated in fractionator 32 as has been described are removed through line 45 containing valve 46 leading to the condenser 47 and the cooled and condensed products thence flow through line 48 containing valve 49 into the receiver 50 where the unstabilized gaseous products are separated from the unstabilized gasoline product. The unstabilized gasoline is removed from receiver 50 through line 51 regulated by valve 52 and the unstabilized gases are removed through line 53 regulated by valve 54. A portion of the said gasoline in receiver 50 is directed through line 55 containing valve 56 to pump 57 which pumps this oil through line 58 controlled by valve 59 to the top of the fractionator 32 for the purpose of regulating the end boiling point temperature of the gasoline vapors leaving the top of fractionator 32.

Said relatively light reflux condensate separated in fractionator 32 is removed through line 61 regulated by valve 60 and directed to pump 62 which pumps this oil through line 63 containing valve 64 into the heating element 65 located in the furnace 66 where this oil is heated to catalytic cracking conditions of temperature and pressure. The heated hydrocarbons are then directed through line 67 regulated by valve 68 into the catalytic reactor 69 where granular particles of the above described catalyst are disposed. The catalyst may be arranged in one or more beds in the catalyst reactor and may be provided with means for dissipating or adding heat to the catalyst bed. A plurality of reactors may be provided so that one or more are in use while one or more are in process of being regenerated or prepared for processing. During regeneration an oxygen-containing gas such as flue gas mixed with air may be introduced through line 70 regulated by valve 71 and directed through line 67 while valve 68 is closed into the reactor 69 to oxidize hydrocarbonaceous deposits upon the catalyst. The regeneration gases are removed from the chamber 69 through line 72 containing valve 73, said valve 73 being closed while the regeneration gases are removed through line 74 regulated by valve 75. In the processing period valve 75 in line 74 is closed and the hydrocarbon vapors flow through line 72 and through valve 73 to the fractionator

76 where gasoline boiling hydrocarbons and gases are removed overhead and higher boiling hydrocarbons condensed and separately withdrawn. The gasoline vapors and gases are removed from the fractionator 76 through line 77 containing valve 78 and flow to the condenser 79, the condensed and cooled products thence flowing through line 80 containing valve 81 into the receiver 82 where the unstabilized catalytically cracked gasoline is separated from unstabilized gases. The gasoline is removed from receiver 82 through line 83 regulated by valve 84 and the gases are removed through line 85 regulated by valve 86. A portion of the gasoline hydrocarbons is removed through line 87 containing valve 88 leading to pump 89 which pumps this oil through line 90 regulated by valve 91 into the top of the fractionator 76 in order to control the end boiling point temperature of the gasoline product removed overhead. The hydrocarbons boiling above the gasoline hydrocarbons and condensed in fractionator 76 are removed from the bottom thereof through line 92 containing valve 93 leading to pump 94 which pumps this oil through line 95 containing valve 96 into the fractionator 32 for fractionation in a commingled state with the hydrocarbons from thermal cracking processed therein for the separation of said relatively light and said relatively heavy reflux condensates for catalytic and thermal cracking.

Unstabilized gases from catalytic and thermal cracking removed through lines 85 and 53 respectively may be subsequently stabilized to remove C_5 hydrocarbons present therein and may also be subjected to polymerizing treatment in order to produce additional yields of high octane number gasoline, and a portion of the remaining normally gaseous and essentially saturated hydrocarbons are directed to mixture with the oil processed in the catalytic cracking step. When adding unstabilized gas from receiver 50 removed through line 53 regulated by 54, a portion of this gas may be removed from the process through valve 97, the remainder of said gas being directed through line 98 containing valve 99 to the compressor 100 which compresses this gas and directs the compressed gases through line 101 containing valve 102 into said relatively light reflux condensate flowing through line 63 to catalytic cracking treatment. Similarly when unstabilized gases are further added from receiver 82 through line 85 and valve 86, gases therefrom may be removed in part from the process through valve 103 and the remaining gases directed through line 104 containing valve 105 to the compressor 106 which compresses this gas and directs the compressed gas through line 107 containing valve 108 and into line 63 for admixture with the said relatively light reflux condensate flowing to catalytic cracking treatment.

An example of one specific operation of the process as it may be accomplished in an apparatus such as illustrated and above described is approximately as follows: A 25–26° A. P. I. gravity Mid-Continent topped crude oil is preheated in the process and directed to the separating zone of the thermal cracking section of the process where approximately 30% by volume of the oil charged is withdrawn in an unvaporized condition together with heavy residual oil from thermal cracking and subjected to coking treatment. This oil is heated to approximately 900° F. at a pressure of approximately 50 pounds per square inch after which the oil is directed to the coking chamber and coked. The distillate from coking is directed to said separating zone in admixture with the said oil charged to the process and vaporized charging stock and products from thermal cracking and coking are fractionated to separate the thermally produced gasoline and gas from a relatively light and a relatively heavy reflux condensate fraction. The relatively heavy reflux condensate consisting of a mixture of charging stock hydrocarbons together with partially converted hydrocarbons from the thermal and catalytic treatments are thermally cracked at a temperature of 980° F. and a pressure of approximately 250 pounds per square inch, the average temperature being somewhat lowered in the reaction chamber. The said relatively light reflux condensate consisting of a mixture of hydrocarbons from the charging stock and from thermal and catalytic treatment are vaporized at a temperature of approximately 1000° F. and a pressure of approximately 50 pounds per square inch and directed to the catalyst reaction chamber containing a synthetic cracking catalyst prepared according to the method above described and having the following approximate composition, $100SiO_2:5Al_2O_3$ using a space velocity of 4. When blending the gasoline products from this operation approximately 68% of 400° F. end-point gasoline is produced based on the charging stock having a 73 octane number by the A. S. T. M. motor method.

I claim as my invention:

1. A process for thermally and catalytically cracking, and coking a hydrocarbon oil to produce a substantial yield of high antiknock gasoline which comprises employing as charging oil a hydrocarbon oil having relatively heavy and high coke forming fractions and relatively lighter fractions comprising those within the gasoline boiling range and mixing said charging oil directly with cracked oil and gas obtained from thermal cracking of a relatively heavy reflux condensate fraction, separating therefrom a mixture of non-vaporous cracked and uncracked oil containing said relatively heavy and high coke forming fractions and a vaporous oil and gas, subjecting said mixture of non-vaporous oil to coking treatment to produce coke and a distillate oil, fractionating the said vaporous oil and gas to separate high antiknock gasoline and gas from a relatively light reflux condensate fraction and from the said relatively heavy reflux condensate fraction, condensing, cooling and separating said high antiknock gasoline and gas, directing the said relatively heavy reflux condensate fraction to said thermal cracking treatment and thermally cracking said fraction to produce said cracked oil and gas, directing said relatively light reflux condensate fraction to catalytic cracking treatment to produce cracked products containing substantial yields of high antiknock gasoline, fractionating said cracked products into vaporous high antiknock gasoline and gas, and a higher boiling hydrocarbon oil, condensing, cooling and separating said high antiknock gasoline and gas, and directing said higher boiling hydrocarbon oil directly into said vaporous oil and gas from thermal cracking and undergoing said fractionation.

2. A process for thermally and catalytically cracking, and thermally coking a hydrocarbon oil to produce a substantial yield of high antiknock gasoline which comprises employing as charging oil a hydrocarbon oil having relatively heavy and high coke forming fractions and relatively lighter fractions comprising those within the gasoline boiling range and mixing said charg-

ing oil directly with cracked oil and gas obtained from thermal cracking of a relatively heavy reflux condensate fraction, separating therefrom a mixture of non-vaporous cracked and uncracked oil containing said relatively heavy and high coke forming fractions and a vaporous oil and gas, subjecting said mixture of non-vaporous oil to thermal coking treatment to produce coke and vaporous products, condensing and cooling said vaporous products to separate gas and a distillate oil, adding said distillate oil directly to said charging hydrocarbon oil to be mixed with said cracked oil and gas from said thermal cracking, fractionating the said vaporous oil and gas to separate high antiknock gasoline and gas from a relatively light reflux condensate fraction and from the said relatively heavy reflux condensate fraction, directing the said relatively heavy reflux condensate fraction to said thermal cracking treatment and thermally cracking said fraction to produce said cracked oil and gas, directing said relatively light reflux condensate fraction to catalytic cracking treatment to produce cracked products containing substantial yields of high antiknock gasoline, fractionating said cracked products into vaporous high antiknock gasoline and gas, and a higher boiling hydrocarbon oil, condensing, cooling and separating said high antiknock gasoline and gas, and directing said higher boiling hydrocarbon oil directly into said vaporous oil and gas from thermal cracking and undergoing said fractionation.

3. A process according to claim 1 wherein a portion of said gas separated from said high antiknock gasoline from thermal cracking is mixed directly with said relatively light reflux condensate fraction directed to catalytic cracking treatment.

4. A process according to claim 2 wherein a portion of said gas separated from said high antiknock gasoline from thermal cracking and a portion of said gas separated from said high antiknock gasoline from catalytic cracking are mixed directly with said relatively light reflux condensate fraction directed to catalytic cracking treatment.

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