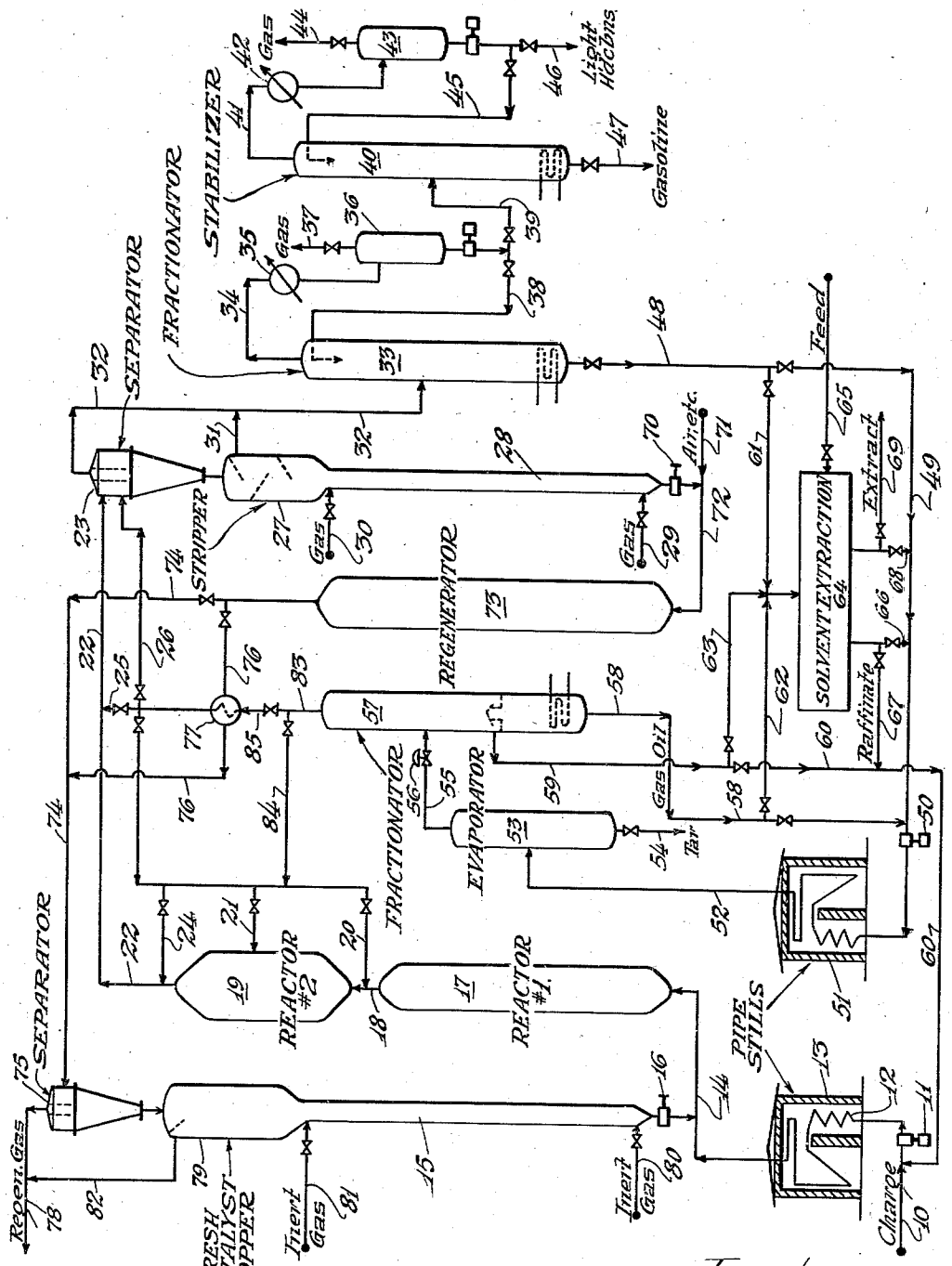
July 10, 1945. E. A. JOHNSON 2,379,966

HYDROCARBON CONVERSION SYSTEM

Filed Dec. 31, 1940



Inventor:
Everett A. Johnson

By Donald E. Payne
Attorney.

Patented July 10, 1945

2,379,966

UNITED STATES PATENT OFFICE

2,379,966

HYDROCARBON CONVERSION SYSTEM

Everett A. Johnson, Park Ridge, Ill., assignor to Standard Oil Company, Chicago, Ill., a corporation of Indiana

Application December 31, 1940, Serial No. 372,509

10 Claims. (Cl. 196—52)

This invention relates to a hydrocarbon conversion system and it pertains more particularly to a system for converting gas oils or heavier hydrocarbons into high quality motor fuels.

Catalytic cracking processes produce high octane number gasoline and low gravity gas oils. The heavier components of such gas oils may be cracked more satisfactorily by thermal processes than by catalytic processes. The gasoline produced by the thermal conversion of these heavier hydrocarbons is characterized by a lower octane number than the catalytically cracked product. Heretofore it has been necessary to subject the thermally cracked naphtha to a separate conversion step such as reforming or isoforming in order to increase its clear octane number. An object of my invention is to obtain this clear octane number increase in the thermally cracked naphtha without the necessity of employing a separate conversion system.

A further object of the invention is to provide an improved method and means for utilizing a cracking catalyst more fully and to greater advantage than it has been utilized in any previous conversion system. A further object is to provide a new and improved integration of thermal and catalytic processes which will greatly reduce capital investments and operating costs and, at the same time, increase the quality and yields of gasoline obtainable from a given charging stock.

A further object is to provide a method and means for simultaneously treating thermally cracked naphtha with catalytic conversion products in a moving catalyst system so that the catalyst which has already produced some catalytic conversion of the gas oil will in a later stage simultaneously effect cracking of gas oil and octane improvement of the thermally cracked naphtha. A further object is to provide an improved means for controlling the final stage of catalytic gas oil cracking operation and for preventing undesirable reactions therein.

A further object is to provide an improved system for correlating solvent extraction with thermal and catalytic cracking systems whereby deleterious materials may be removed both from the charging and recycle stocks to the thermal and to the catalytic conversion steps. Other objects will become apparent as the detailed description of the invention proceeds.

In practicing my invention I prefer to employ the so-called fluid catalyst system wherein a solid catalyst is suspended in reaction vapors during the conversion step, is then separated from conversion products, is next regenerated while suspended in a regeneration gas and is finally returned for effecting further reaction. The reaction products are fractionated to separate a cycle gas oil from the gasoline and lighter hydrocarbons. This cycle gas oil may be solvent extracted to remove polycyclic aromatics or other components which may be undesirable in subsequent conversion steps.

The gas oil or gas oil raffinate is then passed through a thermal conversion system and the thermal conversion products are roughly fractionated to remove tar and to separate a naphtha from one or more gas oil fractions, the latter being charged to either the thermal or catalytic conversion steps either before or after solvent extraction. The hot thermally cracked naphtha either with or without the addition of further heat is then introduced into the catalytic conversion stream at such a point that it will not interfere with the desired catalytic cracking of the gas oil and will not itself be over-treated by the catalyst but will undergo a reforming change which markedly improves its octane number.

In many cases the hot thermally cracked naphtha may be introduced into the catalytic cracking reaction stream at the point wherein the stream is introduced into the separation stage since the contact of the thermally cracked vapors in the separator may be sufficient to markedly improve its octane number. In other cases the thermally cracked naphtha may be introduced in the final stage or one of the latter stages of the catalytic cracking or in the transfer line leading to such stage or stages or in the transfer line leading from the last stage to the separation stage. In any event, the thermally cracked vapors will contact catalyst which has already performed its function in the catalytic conversion of gas oil and which has become coated with a carbonaceous deposit and has thus become partially spent. I have found that this spent catalyst is still effective to effect an increase in the octane number of the thermally cracked naphtha and that this increase can be effected directly in the latter part of the catalytic conversion system. The use of a separate reforming system is thus eliminated and the reformed thermal naphtha is separated from the catalyst and fractionated in the same system with the cracked gas oil products.

My invention not only provides a means for more complete utilization of catalyst and for increasing the clear octane number of thermally cracked naphtha without appreciable additional expense but it provides a means whereby unde-

sirable reactions may be inhibited in the latter stages of the catalytic conversion of gas oil. The invention is applicable to moving bed catalyst systems as well as to the powdered or "fluid type" systems.

The invention will be more fully understood from the following detailed description and from the accompanying drawing which forms a part of the specification and which is a flow diagram schematically illustrating a preferred embodiment of my invention.

The charging stock to my system may be a gas oil or heavier hydrocarbon produced from petroleum or from any other source. Synthetic hydrocarbons resulting from the Fischer process of carbon monoxide-hydrogen synthesis or hydrocarbons from the ordinary hydrogenation of carbonaceous material provide excellent sources for such charging stock. I will describe the invention, however, as applied to the conversion of a 35° A. P. I. gravity Mid-Continent gas oil.

The catalyst employed in this system may be an activated clay such as the acid treated bentonite commercially marketed as Super Filtrol. Alternatively, it may be a synthetic catalyst of the silica-alumina or silica-magnesia type. Such a catalyst may be prepared by depositing alumina or alumina and zirconia on silica gel or by incorporating these or other catalytic metal oxides in silica gel, for instance, by forming the silica gel itself in a solution of aluminum and zirconium salts, washing, drying and heating. An excellent catalyst may be prepared by ball milling calcined magnesia and silica gel with sufficient water to form a paste or doughy mass which is then dried and heated to about 1000° F. No invention is claimed in any particular catalyst and since cracking catalysts are well known in the art a further description of them is unnecessary. The best catalysts are of the metal oxide type, particularly of the silica-metal oxide type.

In the fluid type system I prefer to employ the catalysts in the form of a powder ranging in particle size from about 200 to 400 mesh. Such a powder in compacted form has a density of about .7, i. e., it weighs about 40 to 45 pounds per cubic foot. When aerated at a gas velocity of about .05 to .2 feet per second, the catalyst becomes fluent and may have a density of about 20 to 40 pounds per cubic foot. At gas or vapor velocities of about .3 to 3 feet per second, preferably about 1 to 2 feet per second, the catalyst density may be about 10 to 20 pounds per cubic foot and I prefer to employ such catalyst density in my reaction and regeneration zones.

Referring to the drawing, the gas oil charge is introduced through line 10 by pump 11 to coils 12 of pipe still 13 wherein the oil is vaporized and heated to give a transfer line temperature of about 800 to 1100° F., for example, 900° F. and a transfer line pressure of about atmospheric to about 50 pounds per square inch, preferably about 10 to 15 pounds per square inch.

As the heated vapor passes through transfer line 14, it picks up hot powdered catalyst from standpipe or catastat 15. The catalyst is introduced into the transfer line in amounts regulated by slide valve or star feeder 16. It should be understood, of course, that steam or a mechanical screw or any other suitable means may be used for introducing the catalyst into transfer line 14 and that the catalyst is carried by the vapors in said line to up-flow reactor 17. If desired, the catalyst may be injected directly into the reactor instead of being introduced into the transfer line. I prefer to employ catalyst-to-oil weight ratios of about 1:1 to 5:1, for example about 3:1. The temperature in the reactor may be 800 to 1000° F., for example 925° F.

Reactor 17 may be a cylindrical vessel with a conical inlet and outlet respectively and of such size and cross-sectional area as to retain the necessary amount of catalyst for effecting the desired amount of conversion. The cross-sectional area should be such as to insure a vertical vapor velocity of about .3 to 3 feet per second if the reaction is to be effected under the desired dense phase conditions. It should be understood, however, that my invention is not limited to any particular reactor size and shape and that it is only necessary to provide a contact of the vapors with a sufficient amount of catalyst to effect the desired conversion. For a catalyst holding time in the reactor of about 3 minutes the oil contact time may be about 10 seconds in order to obtain about 40% conversion. My invention is not limited to the particular conditions above recited; generally speaking the vapor velocities in the reactor should be sufficient to maintain a catalyst density therein of about 1 to 35 pounds per cubic foot, preferably about 10 to 20 pounds per cubic foot. The amount of catalyst in the reactor for a given amount of conversion is dependent on the activity of the catalyst which is dependent in turn on its residence time in the reactor. I prefer to use a residence time and amount of catalyst as defined by the following equation:

$$T = at^{.534}$$

where "T" is tons of catalyst in the reactor per 100 barrels of stock charged thereto, "a" is a constant ranging from .3 to 3.0, preferably about 1.2, and "t" is catalyst residence time in minutes in the total reactor space.

Vapors carry catalyst from the top reactor 17 through line 18 to reactor 19 at the same rate as catalyst is introduced into reactor 17. Reactor 19 is preferably of larger cross-sectional area so that about the same vapor velocities may be obtained therein as were obtained in reactor 17 in spite of the addition of a large amount of hot thermally cracked naphtha vapors introduced through line 20. These thermally cracked naphtha vapors may be characterized by octane number of about 65 to 70 while the octane number of catalytically cracked naphtha may be about 80. The catalyst which has already effected the catalytic cracking of gas oil vapors is in accordance with my invention utilized for obtaining an octane number increase on the thermally cracked naphtha of as much as 5 to 15 units and this increase in octane number is obtained without any appreciable loss in thermally cracked naphtha yield.

The time of vapor contact in reactor 19 may be only about ½ to 1/50 of that required for the catalytic cracking of gas oil although it should be understood that gas oil cracking takes place in reactor 19 simultaneously with the reforming of the thermally cracked naphtha. I prefer to introduce the thermally cracked naphtha through line 20 at a temperature of about 900° F. In reactions wherein quenching is desired the temperatures of this introduced stream may be as low as 800 or 875° F. Usually, however, I prefer to add heat at this point in order to effect a further catalytic cracking of the gas oil in reactor 19 along with the reforming of the thermally cracked naphtha. For this purpose the tempera-

ture of the added stream may be about 950 to 1050 or 1100° F.

Instead of introducing the hot thermally cracked naphtha through line 20 I may introduce it through line 21 at an intermediate point of the reactor. In fact, I may use a single reactor in place of reactors 17 and 19 and merely introduce the hot thermally cracked naphtha near the top of said single reactor. This latter expedient is less desirable in dense phase operations than in operations wherein there is uniform movement of the catalyst through the reactor.

The reaction vapor stream together with suspended catalyst leaves the top of reactor 19 through line 22 and is conveyed therein to cyclone separator 23. The thermally cracked naphtha may be introduced into this line 22 through line 24 or line 25 or it may be introduced directly to the separator through line 26. The exact point or points of introduction will depend partly upon the amount of thermally cracked naphtha vapors to undergo reforming or isoforming, partly upon the nature of the catalyst and the extent to which it has previously been coated with carbonaceous deposit and partly upon reaction conditions. As hereinabove stated, the treatment is only ½ to 1/50 of that required for the catalytic conversion itself.

The catalyst separated from vapors in separator 23 falls into hopper or stripper 27 which in turn discharges the catalyst into standpipe or catastat 28. This standpipe is aerated by means of an inert gas such as steam introduced through line 29 and additional gas may be introduced through line 30 for maintaining desired aeration or stripping in hopper 27. Gases from hopper 27 are vented through line 31 to line 32 which is the line conveying reaction vapors from separator 23 to further catalyst separators (not shown) if required and thence to fractionating tower 33.

Gasoline and gases are taken overhead from tower 33 through line 34 and cooler 35 to receiver 36. Gas may be vented from this receiver through line 37. A portion of the liquids may be recycled through line 38 as reflux for tower 33. The rest of the liquid is introduced through line 39 to stabilizer 40.

Propane and lighter gases are taken overhead from the stabilizer through line 41 and cooler 42 to receiver 43 from which gases may be vented through line 44. A portion of the liquefied light hydrocarbons may be recycled as reflux through line 45 and the remainder withdrawn from the system through line 46. Stabilized gasoline is withdrawn from the system through line 47.

Gas oil from fractionator 33 is withdrawn through line 48 and may be introduced directly through line 49 by means of pump 50 to coils 51 of furnace 52 wherein the gas oil is subjected to temperatures and pressures required for thermal conversion. I prefer to use relatively high temperatures and low pressures in this conversion step although the pressure and soaking factors should be sufficient to obtain the desired crack per pass, usually about 15 to 45%, preferably about 25 or 30%. In a preferred example, a transfer line temperature of about 975° F. and pressure of about 200 to 300 pounds per square inch may be employed. Thermal cracking temperature may range from about 850 to 1100° F. and pressures may range from about atmospheric to 1000 pounds per square inch.

The thermal cracking may be effected in the coils themselves or in a separate soaking drum (not shown) and then introduced by line 52 to evaporator tower 53 from which tar is drawn off through line 54. Overhead from the evaporator is discharged through line 55 and reducing valve 56 into fractionator 57 from which heavy gas oil is withdrawn through line 58, and, if desired, a lighter gas oil through line 59. In a preferred method of operation the heavy gas oil is recycled to line 49 for further conversion and the lighter gas oil of about 600 to 700 end point is returned through line 60 to line 10.

Gas oil fractions from any or all of lines 48, 58 and 59 may be introduced through lines 61, 62 and 63 respectively to solvent extraction system 64. Similarly, the original feed stock to the system may be charged to this extraction system through line 65. In the extraction system the gas oil may be countercurrently or in any other conventional manner extracted with a selective solvent such as sulfur dioxide, nitroparaffins such as nitro methane and nitroethane, nitroparaffin-SO_2, benzol-acetone, furfural, SO_2-benzol or any other solvent known to the art for the removal of polycyclic aromatic hydrocarbons or any other components which may be detrimental in either the thermal or catalytic conversion systems Likewise the solvent extractions can be used to select the cracking stock most suitable for thermal and catalytic cracking respectively. While a single solvent extraction system is represented in the drawing it should be understood that separate extraction systems may be used for separate stocks or the separate stocks may be separately or simultaneously extracted in a single system. The raffinate or raffinates from such system or systems may be introduced through line 66 to the thermal conversion system or through line 67 to the catalytic conversion system. Heavy polynuclear extracts are undesirable in the catalytic conversion system but may be introduced into the thermal cracking system through line 68 or withdrawn through line 69 to storage.

Spent catalyst from catastat 28 is introduced through valve or star feeder 70 by means of an oxygen containing gas such as air from line 71 into line 72 and conveyed therein to up-flow regenerator 73. Here again it should be understood that the catalyst may be introduced directly into the regenerator. The regenerator may be a cylindrical vessel similar in size and shape to reactor 17 since I prefer to burn the carbonaceous deposit from the catalyst while the catalyst is in the suspended dense phase condition that is obtainable with the use of vertical vapor velocities of about 1 or 2 feet per second.

Regeneration temperatures may be held within close limits, preferably below 1050° F. by recycling cool regenerated catalyst, by introducing steam or cooling gases (provided that this can be done without exceeding desired vapor velocities) or by the use of heat exchange coils in the regenerator. Regenerated catalyst is carried out of the top of the regenerator either through line 74 directly to cyclone separator 75 or through line 76 and heat exchanger 77. The regeneration gases separated from the catalyst in separator 75 are withdrawn through line 78 and both heat and catalyst may be recovered therefrom in any conventional manner.

Catalyst from separator 75 falls to hopper 79 and thence to standpipe or catastat 15. Aerating gas is introduced through lines 80 and 81

and such gas is preferably withdrawn from the top of hopper 79 through line 82.

The hot thermally cracked naphtha vapors from the top of fractionator 57 may be passed directly through lines 83 and 84 for introduction into the last portion of the catalytic reaction system through lines 20, 21, 24, 25 or 26. Alternatively, these hot thermally cracked naphtha vapors may be passed through line 85 and heat exchanger 77 before being introduced into the catalytic system through any of the aforesaid lines. It should be understood that while heat exchange has been illustrated between the hot naphtha vapors and the hot regeneration gases, heat exchange may be effected by passing the hot naphtha vapors through coils in regenerator 73 or through coils in either furnace 52 or furnace 13. In fact, a single furnace may be used for heating coils 12 and 51 respectively and the last increment of heat may be added to the hot cracked naphtha vapors by passing said vapors through another coil in this same furnace.

Various other modifications of the invention will be apparent to those skilled in the art from the above description and I do not limit myself to any of the details hereinabove set forth except as defined by the following claims.

I claim:

1. In a hydrocarbon conversion system wherein gas oil is cracked by a catalyst suspended in gas oil vapors and is subsequently separated from said vapors and wherein a thermally cracked naphtha is produced by thermal cracking of heavier-than-gasoline hydrocarbons separated from catalytically cracked gasoline, the method of increasing the octane number of said thermally cracked naphtha which comprises contacting said thermally cracked naphtha vapors at a temperature of about 800 to 1100° F. with a catalyst that has previously become coated with a carbonaceous deposit in said gas oil cracking step.

2. The method of converting a heavier-than-gasoline hydrocarbon charging stock into large yields of high quality motor fuel which comprises vaporizing and heating said stock to a temperature of about 800 to 1100° F., suspending a solid catalyst in said heated vapors and contacting said vapors with said catalyst in an elongated reaction zone, introducing hot thermally cracked naphtha vapors into said reaction zone at a point in said zone wherein substantial conversion of the charging stock has already been effected whereby catalyst which has already effected catalytic conversion of charging stock effects reforming of said thermally cracked naphtha vapors, separating the products of cracking and reforming from said catalyst and separating gasoline from said products.

3. The method of claim 2 wherein the thermally cracked naphtha vapors are produced by thermally cracking a gas oil charging stock which contains the heavier-than-gasoline components of products resulting from the catalytic cracking.

4. The method of converting a hydrocarbon fresh feed heavier-than-gasoline into large yields of high octane number motor fuel comprising the steps of catalytically cracking at least a fraction of said fresh feed to produce hydrocarbons in the gasoline boiling range and a catalytically cracked gas oil, thermally cracking at least a part of said fresh feed to produce a thermally cracked naphtha and a thermally cracked gas oil, recycling at least a part of said thermally cracked gas oil to one of said cracking steps, and commingling thermally cracked naphtha vapors and partially spent cracking catalyst in a later stage of the catalytic cracking operation, thereby increasing the octane number of said thermally cracked naphtha.

5. The method of converting a hydrocarbon charging stock heavier than gasoline into large yields of high octane number motor fuel, the steps comprising solvent-extracting the said charging stock, recovering a raffinate and an extract therefrom, catalytically cracking said raffinate to produce gasoline and a catalytically cracked gas oil, thermally cracking said extract to produce a thermally cracked naphtha and a thermally cracked gas oil, recycling at least a portion of one of said gas oils to one of said cracking steps, and contacting said thermally cracked naphtha vapors with the partially spent catalyst in a later stage of said catalytic cracking operation whereby the octane number of said thermally cracked naphtha is increased.

6. In a combination thermal and catalytic cracking system the method of increasing the octane number of thermally cracked naphtha produced by thermal cracking of heavier-than-gasoline hydrocarbons, which method comprises catalytically cracking a charging stock in first and second zones and introducing hot thermally cracked naphtha vapors at a temperature of about 800 to 1100° F. into said second catalytic cracking zone along with partially cracked gas oil vapors from the first catalytic cracking zone.

7. The method of claim 6 which includes the steps of effecting the catalytic cracking with powdered catalyst at a temperature within the approximate range of 800 to 1000° F., and maintaining a catalyst density in at least the first catalytic cracking zone within the approximate range of 1 to 35 pounds per cubic foot.

8. The method of claim 6 wherein the time of contact of the thermally cracked naphtha with the cracking catalyst is within the approximate range of ½ to 1/50 of the time of contact of said charging stock with said catalyst.

9. The method of claim 6 wherein the thermally cracked naphtha vapors are introduced into said second zone at a temperature which is higher than the temperature of cracked gas oil vapors from the first zone.

10. The method of claim 6 which includes the steps of effecting catalytic cracking by means of a continuously moving catalyst stream, contacting gas oil vapors with said stream in both of said first and second zones and contacting said thermally cracked naphtha with said moving stream in only the second of said zones.

EVERETT A. JOHNSON.