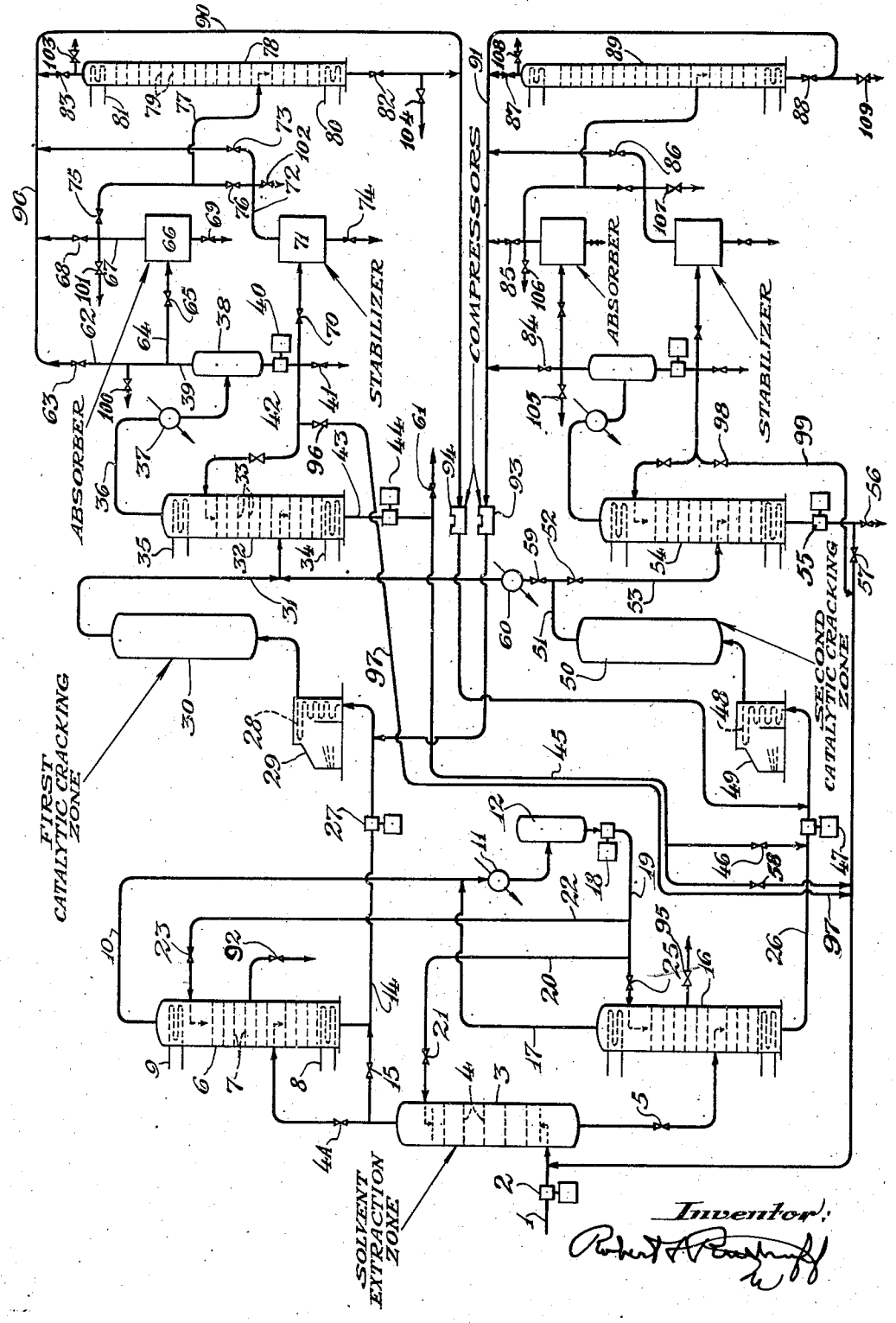
March 26, 1946. R. F. RUTHRUFF 2,397,329

SELECTIVE CATALYTIC CRACKING

Filed Dec. 1, 1941



Patented Mar. 26, 1946

2,397,329

UNITED STATES PATENT OFFICE

2,397,329

SELECTIVE CATALYTIC CRACKING

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Application December 1, 1941, Serial No. 421,143

6 Claims. (Cl. 196—52)

This invention relates to the selective catalytic cracking of hydrocabon oils. More particularly, this invention relates to the separation of hydrocarbon oils into a relatively refractory component and a relatively non-refractory component and separately subjecting the two components to catalytic cracking under conditions selected primarily on the basis of the refractoriness of said components.

A primary object of my invention is to provide an improved selective catalytic cracking process for treating hydrocarbon oils whereby a maximum yield of motor fuel of superior antiknock quality is obtained.

Another object of my invention is to provide an improved selective catalytic cracking process for treating hydrocarbon oils wherein said hydrocarbon oils are separated into a plurality of components of differing refractoriness which are subjected to separate catalytic conversion processes whereby a maximum yield of motor fuel of superior antiknock quality is obtained.

A further object of my invention is to provide an improved selective catalytic cracking process for treating hydrocarbon oils wherein said hydrocarbon oils are subjected to solvent extraction to form a plurality of components of differing refractoriness which are subjected to separate catalytic conversion processes whereby a maximum yield of motor fuel of superior antiknock quality is obtained.

An additional object of my invention is to provide an improved selective catalytic cracking process for treating hydrocarbon oils wherein said hydrocarbon oils are separated into a plurality of components of differing refractoriness which are subjected to separate catalytic conversion processes wherein byproducts from certain of said separate catalytic conversion processes are introduced into other of said separate catalytic conversion processes whereby a maximum yield of motor fuel of superior antiknock quality is obtained.

Another object of my invention is to provide an improved selective catalytic cracking process for treating hydrocarbon oils wherein said hydrocarbon oils are subjected to solvent extraction to form a plurality of components of differing refractoriness which are subjected to separate catalytic conversion processes wherein byproducts from certain of said separate catalytic conversion processes are introduced into other of said separate catalytic conversion processes whereby a maximum yield of motor fuel of superior antiknock quality is obtained.

Further objects and advantages of my invention will become evident as the description thereof proceeds.

Various selective thermal conversion processes for separately transforming a plurality of hydrocarbon fractions into motor fuel are well known in the art. For example, it is known to fractionate crude oil into light naphtha, heavy naphtha, gas oil and reduced crude following which the heavy naphtha is thermally reformed, the gas oil is thermally cracked while the reduced crude is thermally viscosity broken. Reaction products from the thermal cracking zone and the thermal viscosity breaking zone are combined and fractionated to give gasoline plus gas, light cycle gas oil, heavy cycle gas oil and tar. The light cycle gas oil is recycled to the thermal cracking zone while the heavy cycle gas oil is recycled to the thermal viscosity breaking zone. Reaction products from the thermal reforming zone are fractionated to give reformed gasoline. The virgin light naphtha, reformed gasoline and cracked gasoline from the thermal cracking and thermal viscosity breaking zones are blended to give the desired ultimate product of the process. In this, and similar schemes, a plurality of components produced by fractionation are subjected to separate thermal conversion processes wherein byproducts from certain of said separate thermal conversion processes are introduced into other of said separate thermal conversion processes whereby a high yield of motor fuel is obtained.

Also, in my copending application, Serial No. 334,741, filed May 13, 1940, now U. S. Patent 2,312,445, issued March 2, 1943, a selective catalytic conversion process is described for separately transforming a plurality of hydrocarbon fractions, wherein byproducts from certain of the separate catalytic conversion processes are introduced into other of said separate catalytic conversion processes whereby a high yield of motor fuel of high antiknock value is obtained.

The selective conversion processes of the prior art are primarily concerned with the efficient treatment of charging stocks of wide boiling range. To accomplish this, the charging stock selected is fractionated into a plurality of cuts of narrower boiling range which are each separately processed under conditions best suited for each particular fraction. Obviously, the operating conditions are selected for each individual conversion zone primarily on the basis of the boiling range of the particular fraction charged to said zone. In contradistinction to this, in the instant invention, the charging stock, which is

preferably of comparatively narrow boiling range, for example, one of the fractions employed in prior art selective conversion processes, is separated into a plurality of components of the same or approximately the same boiling range as that of the original charge but of differing refractoriness and these are separately processed under catalytic conversion conditions best suited for each particular component. Here the operating conditions are selected for each individual catalytic conversion zone primarily on the basis of the chemical characteristics of the particular fraction charged to said zone. The boiling range of the several components being identical or approximately so, this factor need not be considered in fixing operating conditions.

Many variations are possible in the practice of my invention and accordingly it is impractical to encompass all of them in a brief or even a detailed exposition thereof. However, to indicate the spirit, but not the scope, of my invention, the following brief description of a single illustrative and non-limiting embodiment thereof is included:

A suitable hydrocarbon oil is separated into a relatively refractory portion and a relatively non-refractory portion, for example, by solvent extraction. The relatively non-refractory portion is subjected to catalytic cracking under relatively mild conditions in the presence of an active catalyst, the products being separated into gas, gasoline and cycle stock. The cycle stock is added to the relatively refractory portion of the charge and the resulting mixture is subjected to catalytic cracking under relatively severe conditions in the presence of an active catalyst, the reaction products being again separated into gas, gasoline and cycle stock. This second cycle stock may be discarded while the two gasoline streams are blended to form the desired ultimate product of the combination.

For the better understanding of this invention, reference may be had to the accompanying figure, forming a part of this specification and wherein said figure is a diagrammatic representation in elevational view of one form of apparatus suitable for accomplishing the objects of this invention.

Turning now to a more detailed consideration of the figure, a suitable hydrocarbon charge, for example, straight run gasoline, heavy naphtha, light gas oil, heavy gas oil, reduced crude or the like enters the system through line 1 and is moved by pump 2 to the solvent extraction tower 3. It is well known in the art to treat petroleum fractions with various solvents in order to separate said fractions, at least partially, into their respective components. For example, it is well known to treat petroleum fractions with solvents, solvent mixtures or modified solvents selected from the class of solvents having a preferential selectivity for the relatively hydrogen poor components (aromatics, naphthenes, olefines) as compared with the relatively hydrogen rich components (paraffins) of the petroleum fractions. Solvents of this class include, for example, phenol, phenol plus water, benzene plus acetone, furfural, sulfur dioxide, aniline, dichloro diethyl ether and the like. The petroleum fraction and the selected solvent may be contacted in any suitable manner, as for example in a single or multi-stage batch operation. The petroleum fraction and the selected solvent however, are usually contacted in a countercurrent treating tower such as is indicated by the reference numeral 3. Here the lighter phase, usually the oil, is introduced near the bottom of tower 3 and the heavier phase, usually the solvent, is introduced near the top of tower 3. Tower 3 is preferably provided with means to facilitate liquid-liquid contact, for example, perforated plates 4, but other suitable means, such as bubble trays, Raschig rings, Berl saddles or the like may be employed. The respective liquids flow countercurrently, contacting each other under conditions to form a raffinate or solvent poor phase which is discharged through valved line 4A and an extract or solvent rich phase which is discharged through valved line 5.

The exact nature of the selective solvent employed is determined largely by the boiling range and the chemical nature of the particular hydrocarbon oil being extracted. Generally, a selective solvent is used having a boiling point or boiling range below, preferably appreciably below, the initial boiling point of the particular hydrocarbon charge being extracted although it is obvious that this is largely a matter of convenience rather than an absolute requirement, especially in the case of lower boiling hydrocarbon oils, but it might be a matter of some difficulty to find a satisfactory selective solvent boiling above the range of heavy gas oil or reduced crude. Liquid sulfur dioxide is frequently employed in the solvent extraction of gasoline, heavy naphtha, kerosene and similar fractions of relatively low boiling range while one of the higher boiling solvents previously mentioned or other suitable materials of similar nature may be employed while extracting light gas oil, heavy gas oil, reduced crude and similar fractions of relatively elevated boiling range.

The operating conditions to be employed in solvent extraction tower 3, for example, temperature and solvent to oil ratio and the like, are largely conditioned by the nature of the solvent selected and the hydrocarbon oil being treated. Sulfur dioxide is usually employed at rather low temperatures for obvious reasons, for example, in the temperature range 0° F. to —110° F. or even lower. However higher temperatures may be employed if the extraction zone is operated under pressure. The other solvents mentioned as well as other selective solvents also have preferred operating temperatures. Furfural, for example, is generally what may be considered a high temperature solvent, being used frequently in the neighborhood of 200° F., more or less.

The solvent extraction step per se forms no part of the instant invention except in the combination shown and since such processes are familiar to those skilled in the art, further discussion is unnecessary.

The raffinate phase, which is poor in solvent and rich in hydrocarbon components of high hydrogen content, is sent to fractionating tower 6. This tower is provided with means to facilitate liquid-vapor contact, for example, bubble trays 7, bottom heating means, for example, coil 8 and top cooling means, for example, coil 9. Vaporized solvent passes overhead through line 10, is condensed in cooler 11 and passes to reservoir 12. Raffinate oil is removed through line 14 to be processed as described subsequently. This description, and that to follow, is obviously based on the supposition that the solvent is lower boiling than the oil. If the opposite obtains the required changes will be obvious to those skilled in the art.

In some cases it is possible to remove solvent from the raffinate phase by water washing or by a similar extraction process with a suitable

second solvent. Fractionation of the raffinate phase can then be dispensed with. Obviously in such cases, the extract phase may be worked up similarly if desired and also it is not necessary to select a primary solvent that boils either above or below the boiling range of the hydrocarbon oil being processed. Also, with a very few solvents, the raffinate phase is solvent free or practically so. Under such circumstances tower 6 may be dispensed with and raffinate sent directly from valved line 4A to line 14 via valved line 15.

The extract phase, which is rich in solvent and in hydrogen-poor hydrocarbon components, is sent to fractionating tower 16 which is similar to tower 6. Solvent vapors pass overhead through line 17, are condensed in cooler 11 and sent to reservoir 12. Solvent in reservoir 12 is moved by pump 18 to manifold 19, line 20 and valve 21 to extraction tower 3. A part of the solvent may be sent through line 22 and valve 23 to the top of tower 6 to provide open reflux therein while part may be sent through valve 25 to tower 16 for the same purpose. Extract oil is removed from tower 16 by line 26 to be processed as subsequently described.

Raffinate oil in line 14 is moved by pump 27 through coil 28 in furnace setting 29 wherein the charge is brought to the desired catalytic cracking temperature. Since the charge is of a relatively non-refractory nature, the desired catalytic cracking temperature is relatively low, being generally in the range 500° F. to 900° F., more or less, the exact temperature depending upon the boiling range of the stock and other operating conditions as will be more specifically set forth hereinunder. The thus heated charge, preferably in the vaporized state, is sent to reactor 30 which contains a suitable cracking catalyst of high activity. Among suitable contact agents for the purpose may be mentioned certain natural clays, especially activated clays of the bentonite, montmorillonite or sepiolite types; synthetic silica-alumina complexes or synthetic silica-magnesia complexes. The clay type catalysts are preferably activated by being treated for several hours with acid or with aqueous solutions of salts of magnesium, aluminum, manganese or the like, then washed and finally converted to any desired physical form. The synthetic silica-alumina complexes are preferably made by first precipitating silica gel from water glass solution with acid. The gel is washed and, if desired, dried or partially dried and then activated by hydrolytic adsorption of alumina thereon. Or the gel is washed and, if desired, partially or completely dried and then impregnated with an aluminum nitrate solution, then dried and heated to 850°–1050° F. to decompose the aluminum salt. Alternatively, the washed and, if desired, dried or partially dried silica gel may be mechanically homogenized with aluminum hydroxide. Or, the silica gel may be simultaneously precipitated with aluminum hydroxide by mixing a water glass solution with a solution of an aluminum salt. Numerous other methods of catalyst preparations may be employed but they will not be described in further detail since the particular catalyst used forms no feature per se of the instant invention. Synthetic silica-magnesia catalysts may be made as described above, substituting magnesium compounds for aluminum compounds. Silica gel may be activated by other materials in addition to or in place of magnesia or alumina, for example, zirconia or boron oxide. Also, various activated carbons and carbon blacks may be used as catalysts. Carbons that have been activated by heating to above 400° C., for example, 950° C., or even higher in an inert or oxidizing atmosphere may be used.

Reaction products from reactor 30 pass by line 31 to fractionating tower 32 which is provided with means to facilitate liquid-vapor contact, for example, bubble trays 33, lower disposed heating means, for example, coil 34 and upper disposed cooling means, for example, coil 35. Overhead from tower 32, consisting of gasoline and gas, passes through line 36, is condensed in 37 and separated in 38. Gas passes overhead from the separator through line 39 while gasoline may be moved by pump 40 to storage through valved line 41. Part of the gasoline may be recycled through the valved line 42 to tower 32 to provide open reflux therein.

Cycle stock is removed from tower 32 by line 43. This material is considerably more refractory than the raffinate oil from which it was obtained and accordingly it is moved by pump 44 through line 45 and valve 46 to line 26 where it is admixed with relatively refractory extract oil. The blend is moved by pump 47 through heating coil 48 in furnace setting 49. During passage through coil 48 the charge is brought to a relatively high catalytic cracking temperature, for example, a temperature in the approximate range 850° F. to 1050° F., more or less. The thus heated charge passes to reactor 50 which contains a suitable cracking catalyst of a nature previously described. Reaction products from reactor 50 pass by line 51, valve 52 and line 53 to tower 54 which is similar to tower 32. Cycle stock from tower 54 is moved by pump 55 and since it is usually very refractory it may be discharged through valve 56 for disposal. If desired however, part or all of this cycle stock may be sent through valved line 57 to solvent extraction tower 3.

Many variations of the above described single embodiment are possible. Among these may be mentioned the following:

(1) Cycle stock from tower 32, instead of being combined with the extract oil, is instead sent through valved line 58 to extraction tower 3, valve 46 being closed. In this way, only the relatively refractory portions of this stock are processed in reactor 50, the relatively non-refractory portions being recycled, after extraction, to reactor 30. Cycle stock from tower 54 is then either discharged through valved line 56 or is sent in part or entirely to the solvent extractor 3.

(2) If desired, reaction products from reactor 50 may be sent to fractionating tower 32 by closing valve 52 and opening valve 59. In this scheme of operation, tower 54 may be dispensed with, including its auxiliary equipment. If desired, material from reactor 50 may be slightly cooled in 60 prior to entering tower 32. When operating in accordance with this scheme, cycle stock from tower 32 is preferably eliminated from the system through valved line 61 but part or all of it may be sent to the solvent extraction zone and/or to the second catalytic cracking zone by paths previously outlined.

(3) If desired, the liquid hydrocarbons of lower boiling point than that of the charge which are produced in reactor 30 and/or reactor 50 may also be extracted in extractor 3. For example, liquid

reaction products of lower boiling range than that of the charge which are products of reactor 30 may be passed through valve 96 and line 97 to the lower part of the extraction tower 3. In such a case, fractionating tower 6 is provided with means for removing a side stream, e. g., valved line 92. Tower 6 then produces (*a*) solvent as overhead through line 10, (*b*) the raffinate portion of liquid hydrocarbons of lower boiling point than that of the charge produced in reactor 30 as an intermediate cut through valved line 92 and (*c*) the raffinate oil portions of the hydrocarbon charge as bottoms through line 14. When operating in this way it is obvious that a selective solvent of low boiling point, e. g., sulfur dioxide is used but if a high boiling solvent is employed it may be eliminated as bottoms by obvious modifications as has already been mentioned. Similarly, when operating in the manner described, tower 16 produces (*a*) solvent as overhead through line 17, (*b*) the extract portions of liquid hydrocarbons of lower boiling point than that of the charge which are produced in reactor 30 as an intermediate cut through valved line 95 and (*c*) the extract oil portions of the hydrocarbon charge as bottoms through line 26.

It will be noted that when operating as described immediately above, if the bottoms from tower 32 are to be recycled to the solvent extraction tower 3 by pump 44, line 45 and valve 58, there is no need for tower 32 and its auxiliary equipment. Reaction products from reactor 30 are cooled and separated, the liquid portions then being sent to the solvent extraction tower 3. Fractionation of the reaction products is then accomplished, after solvent extraction, in fractionating towers 6 and 16.

By operating as described under (3), liquid reaction products of low olefine content and high octane number are obtained via valved line 92. These are eminently suitable for aviation use. On the other hand, less suitable products for aviation use but which are eminently suited for automotive use are obtained as an intermediate fraction from tower 16 via valved line 95.

Liquid hydrocarbon conversion products of lower boiling range than the charge and produced in reactor 50 may similarly be solvent extracted in part or entirely. This is accomplished by sending the liquid conversion products obtained as an overhead from tower 54 to extractor 3 through valve 98 and line 99. Again, if all the cycle stock eliminated as bottoms from tower 54 is to be sent to solvent extraction tower 3 along with the liquid conversion products made in reactor 50, then tower 54 may be dispensed with, the reaction products from reactor 50 being cooled and separated, the liquid portions thereof being sent to extraction tower 3, the reaction products made in reactor 50 being fractionated in towers 6 and 16.

The above described variation is useful when it is desired to produce a high octane number light naphtha of low olefine content from a heavy naphtha charge or a high octane number gasoline of low olefine content from a gas oil charge. For reasons to be given subsequently, this scheme of operation is not necessary to accomplish this result when the conversion zones are maintained at high superatmospheric pressure.

Returning now to the flow shown in the figure, light products may be worked up as desired. Considering in detail the overhead system following the first catalytic cracking zone (which is identical with the overhead system following the second catalytic cracking zone), most simply, gas may be taken overhead from separator 38 through lines 39, 62 and valve 63 and disposed of as desired. The net gasoline, as mentioned before, may be sent to storage through valve 41. As is well known to those skilled in the art, when operating in this simple manner, the gas invariably contains more or less normally liquid components which may be separated therefrom by absorption while the liquid contains more or less undesired gaseous components which may be separated therefrom by stabilization, both conventional and well known processes. For example, valve 63 may be closed and the gas sent from separator 38 through lines 39, 64 and valve 65 to a conventional absorber represented by reference numeral 66. Dry gas may be removed via line 67 and valve 68 for disposal as desired while absorption gasoline is discharged through valved line 69. Also, liquid from separator 38 may be sent through valved line 70 to a conventional stabilizer represented by reference numeral 71, valve 41 being closed. Dry gas may be removed via line 72 and valve 73 for disposal as desired while stabilized gasoline may be discharged through valved line 74.

If desired, valves 68 and/or 73 may be closed and the gas from absorber 66 and/or stabilizer 71 may be passed through valved lines 75 and/or 76 to manifold 77 and thence to fractionator 78. Fractionator 78 is conventional, being provided with means to facilitate liquid-vapor contact, for example, bubble trays 79, lower disposed heating means, for example, coil 80 and upper disposed cooling means, for example, coil 81. Relatively light gaseous components may be eliminated through valved line 83 for disposal as desired, while relatively heavy gaseous components may be eliminated through valved line 82 for disposal as desired. As has been mentioned previously, the overhead system following the second catalytic reactor 50 may be operated similarly.

It will be noted that at the choice of the operator one or more gas streams of practically any desired characteristics become available. In general, the characteristics of the several gas streams are approximately as follows:

From lines containing valves 63 and 84: Approximately total gas somewhat deficient however in heavier gaseous components and containing some normally liquid hydrocarbons.

From lines containing valves 68 and 85: Similar to above but lacking normally liquid components.

From lines containing valves 73 and 86: Gas rich in heavier gaseous components.

From lines containing valves 83 and 87; Gas rich in lighter gaseous components.

From lines containing valves 82 and 88: Gas rich in heavier gaseous components.

Obviously, the nature of the gas eliminated from the top and bottom of fractionators 78 and 89 depends upon the nature of the gas charged thereto and the exact manner in which these fractionators are operated on this charge. The charge may be relatively heavy gas, relatively light gas or total gas. The fractionators separate their respective charges into a relatively heavy and a relatively light fraction.

If desired, the various gas streams, or portions thereof, may be vented from the system; gas from separator 38 through valve 100, gas from absorber 66 through valve 101, gas from stabilizer 71 through valve 102, overhead gas from fractionator 78 through valve 103 and bottoms gas

from fractionator 78 through valve 104. In the overhead system following reactor 50 the corresponding valves are designated 105, 106, 107, 108 and 109.

It should be emphasized that the gas produced in reactor 30 is relatively poor in olefines while that produced in reactor 50 is relatively rich in olefines.

It is possible to send, if desired, a portion or all of a selected gas stream or streams from the overhead system following reactor 30 to the second catalytic cracking zone by manifold 90 and compressor 94 and likewise it is possible to send, if desired, a portion or all of a selected stream or streams from the overhead system following reactor 50 to the first catalytic cracking zone by manifold 91 and compressor 93.

An especially valuable embodiment may be employed when the liquid conversion products have been solvent extracted as previously described. When operating in this manner part or all of the liquid hydrocarbon conversion products boiling lower than the original charge are separated into a raffinate portion of low olefine content and high octane number and an extract portion of high olefine content and high octane number. Highly olefinic gas from the second catalytic cracking zone, 50, may be used to alkylate by known methods the raffinate portion of the conversion products to produce a high yield of saturated alkylate of high octane number and/or gas of low olefine content from the first catalytic cracking zone, 30, may be alkylated by known methods by the extract portion of the conversion products to produce a high yield of saturated alkylate of high octane number.

For simplicity, in the figure, the catalytic reactors 30 and 50 are each represented by single vessels. As is well known to those skilled in the art, cracking catalysts decline in activity more or less rapidly while on stream due to the deposition of carbon or carbonaceous residues thereon. To restore catalytic activity, it is necessary to remove said carbon or carbonaceous residues periodically at rather frequent intervals. This is usually accomplished by burning said materials from the catalytic surfaces with air or dilute air. For continuous operation, it is obvious that provision must be made for catalytic material of adequate activity to be available at all times. Many methods are known for accomplishing this, several being described in some detail in my copending applications, Serial Number 313,898, filed January 15, 1940, now U. S. Patent 2,323,728, issued July 6, 1943, and Serial Number 334,741, filed May 13, 1940, now U. S. Patent 2,312,445, issued March 2, 1943, viz:

1. Plural reactors containing a stationary bed of catalyst.

2. Reactors designed for use with moving catalysts.

3. Reactors designed for use with suspended catalysts.

For reasons of simplicity none of the above schemes are shown in the figure but it is to be understood that for continuous operation one such method or its equivalent is employed.

Having now described in general terms one form of apparatus suitable for accomplishing the objects of my invention, more specific illustrative but non-limiting details with respect to the treatment of certain selected charging stocks in accordance thereto will now be given. The process of this invention is particularly adapted to the treatment of hydrocarbon oils of relatively narrow boiling range as exemplified by gasoline, heavy naphtha, light gas oil, heavy gas oil, reduced crude and the like but is not necessarily limited thereto.

Any gasoline (which term includes hydrocarbon oils boiling within the approximate range 60° F. to 500° F.) may be employed as charge in the process but virgin gasolines from mixed base crudes, for example, gasolines from Midcontinent and East Texas crudes are especially suitable. Such gasolines, by solvent extraction, give appreciable amounts of both a relatively refractory extract oil and a relatively non-refractory raffinate oil. The relatively non-refractory raffinate oil may be vaporized at a comparatively low temperature, for example, 500° F. to 900° F., more or less and passed over a catalyst of a nature previously described at a rate of from 0.2 to 15 volumes, more or less, of liquid charge per hour per volume of catalyst (hereinafter designated by v./hr./v.). In general, a moderate to low operating pressure is employed, sufficient to overcome pressure drop, for example, 50 pounds per square inch or less, for example, 25 pounds per square inch. Under certain conditions however, to be outlined in detail subsequently, high superatmospheric pressures are employed. Obviously, such operating variables as temperature, contact time, pressure and catalyst activity are more or less interchangeable. For example, a high operating temperature may be compensated for to a greater or lesser extent by increasing flow rate (reducing contact time), decreasing the activity of the catalyst employed or by operating at a lower pressure or by any combination of these changes. The corresponding relatively refractory extract oil is processed under more severe conditions than outlined above for the raffinate oil. For example, the extract oil may be vaporized at a relatively high catalytic cracking temperature in the neighborhood of 850° F. to 1050° F. more or less, and passed at the flow rates and in the pressure ranges previously described over the catalyst selected. More specific and obviously non-limiting examples of the treatment of gasolines will be found below.

Example 1

East Texas gasoline (110° F. to 415° F. A. S. T. M. boiling range) was solvent extracted using sulfur dioxide. The raffinate oil was vaporized at 850° F. and passed at 50 pounds per square inch pressure and the temperature mentioned over Super Filtrol (a trade name for an acid activated bentonite), the charge rate being 3 v./hr./v. The liquid recovery was 95% and the knock rating of the total liquid product was 10 units above that of the charge. This liquid was fractionated and material of 260° F. endpoint and 74 octane number (A. S. T. M. designation D357–39) was reserved. The resulting bottoms were mixed with the extract oil and the blend was passed over Super Filtrol at 50 pounds per square inch pressure, 900° F. and a flow rate of 2 v./hr./v. The product was fractionated, giving 83% gasoline of slightly higher octane number than the above mentioned light naphtha from the catalytic cracking of raffinate oil. The two overhead fractions were blended to give a high yield of gasoline of just under 76 octane number. Cycle stock from the extract oil conversion step may be sent in part or entirely to the solvent extraction zone or, if desired, may be thermally reformed.

Example 2

Similar to Example 1, except that the heavy naphtha obtained from the reaction mixture from

processing raffinate oil, instead of being admixed with the extract oil, was sent to the solvent extraction zone.

Example 3

The East Texas virgin gasoline was solvent extracted as previously described and tower **6** was so operated that solvent was taken overhead through line **10**, a light naphtha (260° F. endpoint) was eliminated from the system as a side stream through valved line **92** while the heavy naphtha was removed from tower **6** through line **14** and was processed as described in Example 1. On distilling the catalytically cracked heavy naphtha raffinate oil, a 260° F. endpoint light naphtha of 80 octane number was obtained. The remaining cycle stock was admixed with extract oil and processed as described in Example 1. The gasoline obtained was above 76 octane number. The virgin light naphtha, light naphtha from processing heavy naphtha raffinate oil and gasoline from processing the extract oil-cycle blend were mixed. The cycle stock from the extract oil conversion zone may be sent in part or entirely to the solvent extraction zone or it may be thermally reformed.

Example 4

Similar to Example 3 except that the cycle stock from the processing of heavy naphtha raffinate oil was sent to the solvent extraction zone.

Example 5

An East Texas heavy naphtha (250° F. to 400° F. boiling range) was solvent extracted with sulfur dioxide. The raffinate oil was catalytically cracked in the presence of Super Filtrol at 50 pounds per square inch pressure, 850° F. and a charge rate of 2.5 v./hr./v. A 35% yield of 78 octane number light naphtha was obtained. The cycle stock was blended with the extract oil and was passed at 900° F., 50 pounds per square inch pressure and a flow rate of 2 v./hr./v. over Super Filtrol, in a second catalytic cracking zone. The total liquid obtained was of 76 octane number, the light naphtha was 80 octane number. The cycle stock from the extract oil conversion zone may be sent in part or entirely to the solvent extraction zone or it may be thermally reformed.

Example 6

Similar to Example 5 except that the cycle stock from raffinate oil conversion was returned to the solvent extraction zone.

Gasolines prepared in accordance with Examples 1–6 above have an appreciable olefine content and hence a high acid heat. Such characteristics make these materials unsuitable for use in aviation gasolines. By operating at low temperatures, for example, 500° F. to 800° F., preferably at 600° F. to 700° F., and at high pressures, for example, above 300 pounds per square inch, preferably above 750 pounds per square inch, for example, in the pressure range 1500 to 6000 pounds per square inch, gasolines of low acid heat are obtained.

Example 7

An East Texas heavy naphtha was solvent extracted with sulfur dioxide and the raffinate oil was brought to a pressure of 6000 pounds per square inch and heated to 625° F. Under these conditions it was contacted with Super Filtrol at a charge rate of 0.5 v./hr./v. The product formed boiling up to 250° F. had an acid heat of only 1° F. (A. S. T. M. designation D481–39), was of 79 octane number and the yield was 22% based on the raffinate oil charge. The cycle stock from this operation was blended with the extract oil and the mixture was catalytically cracked in a second zone at 675° F., 6000 pounds per square inch pressure and a flow rate of 0.5 v./hr./v., using Super Filtrol. The 250° F. endpoint material from the reaction products had an octane number of 80, an acid heat of 3° F. and the yield was 26%. Cycle stock from the extract oil conversion zone may be sent in part or entirely to the solvent extraction zone or it may be thermally reformed.

Example 8

Similar to Example 7 above except that the cycle stock from raffinate oil processing was sent to the solvent extraction zone.

It is highly desirable to conduct catalytic cracking operations in the vapor phase. When operating at low pressures this occurs automatically with light to moderately heavy stocks but at the high superatmospheric pressures previously mentioned a vaporization aid may be required, especially when the charging stock is moderately high or high boiling, for example, of the nature of light gas oil, heavy gas oil, reduced crude or the like. With gasolines or heavy naphthas such vaporization aids are usually not essential even at high pressures but may be used if desired. One of the most convenient vaporization aids is the gas produced by the unit. In Examples 7 and 8, above, for example, 5% by weight, more or less, of gas (based on liquid charge) may be compressed and added to the raffinate oil charge and/or the extract oil charge prior to passage to the proper conversion zones. As mentioned, when operating at high pressures and employing stocks boiling above the usual gasoline boiling range a vaporization aid is almost essential. For example, when charging materials of the boiling range of light gas oil, about 13 cubic feet of total butane free gas per gallon of liquid charge may be used. When extremely heavy stocks are employed even at moderate to low pressures a vaporization aid is highly desirable. For example, a vaporization aid is almost essential when charging materials of the nature of reduced crude and highly desirable when charging materials of the nature of heavy gas oil.

In addition to aiding in vaporizing the charge, components of the added gas react to a greater or lesser extent under the conversion conditions with the liquids present thereby increasing the yield of desired products. This effect is not very pronounced under the operating conditions outlined in Examples 7 and 8. There are two reasons for this. In the first place, the gas produced under such conditions is practically olefine free and hence comparatively unreactive and in the second place the operating temperature is low. However, when the raffinate and extract oils are processed under more normal conditions as regards to temperature, the gases produced contain appreciable olefines and the reaction temperatures are sufficiently high to bring about alkylation and/or gas reversion if the gas is recycled. Since the operating conditions in the raffinate oil conversion step are less severe than in the extract oil conversion step, the relatively low olefine gas from the raffinate oil conversion is less reactive than that from the extract oil conversion. Accordingly, when it is desired to take advantage of this alkylation and/or gas reversion effect it is preferable to send relatively non-reactive gas from raffinate oil conversion to the relatively severe conditions of the extract

oil conversion zone and to send relatively reactive gas from extract oil conversion to the relatively mild conditions of the raffinate oil conversion zone. This is clearly shown in the figure. When gas is recycled to secure the gas reversion and/or alkylation effect it is preferable to remove therefrom and discard at least hydrogen and methane before recycling the remainder. Preferably, C_2 hydrocarbons are also removed and discarded. The best gas to recycle consists of C_3 and/or C_4 hydrocarbons.

Example 9

A light Midcontinent gas oil of 36° A. P. I. gravity and 430° F. to 730° F. boiling range was solvent extracted, using furfural. The raffinate oil was passed at a flow rate of 1.5 v./hr./v. and a temperature of 850 F. over Super Filtrol, the inlet pressure to the heating coil being 50 pounds per square inch. Exactly 50% by volume of 81 octane number gasoline formed. The cycle stock (40% by volume) was added to the extract oil and the mixture was brought up to 50 pounds per square inch pressure, heated to 900° F. and passed over Super Filtrol at a rate of 1 v./hr./v. A 55% by volume yield of 81 octane number gasoline was obtained. The cycle stock from this second catalytic cracking operation may be sent in part or entirely to the solvent extraction zone or, if desired, it may be thermally cracked to completion.

Example 10

Similar to Example 9 above except that the cycle stock from raffinate oil cracking is sent to the solvent extraction zone instead of being mixed with the extract oil.

When a heavy stock, especially a heavy stock of a residual nature is to be processed, for example, reduced crude, it is desirable to deasphalt the stock prior to charging to the solvent extraction zone. In this way, components having little potential gasoline value are removed and by so doing deterioration of catalytic activity is retarded since the asphalt and resin-like components, if retained in the charge, deposit on the catalytically active surfaces and bring about an extremely rapid decline in activity. The deasphalting may be accomplished, for example, by dissolving the charge in a liquefied normally gaseous hydrocarbon such as propane or the butanes. On increasing the temperature to about the critical temperature of the normally gaseous hydrocarbons, asphalts and resins are precipitated and may easily be removed. By methods well known to those skilled in the art, deasphalting and solvent extraction may be accomplished in one step.

Example 11

An East Texas reduced crude was dissolved in 8 volumes of liquid propane and the solution was heated under pressure to 200° F. Precipitated material was separated and the solvent removed. The deasphalted charge was solvent extracted using furfural. The raffinate oil was mixed with gas from the extract oil conversion zone at a rate of 25 cubic feet of gas per gallon of oil and the whole was brought to a pressure of 50 pounds per square inch, heated to 900° F. and passed over Super Filtrol at a rate of 1 v./hr./v. Gasoline (40% by volume, 78 octane number) was separated together with the gas and the cycle oil was admixed with the extract oil. To this blend, gas from the raffinate oil catalytic cracking zone was added at a rate of 25 cubic feet per gallon of oil, the mix was brought to 50 pounds per square inch pressure, heated to 975° F. and passed over Super Filtrol at a rate of 1 v./hr./v. A little over 40% of 79 octane number gasoline was obtained. Cycle stock from the extract oil catalytic cracking zone may be sent in whole or in part to the solvent extraction zone or may be thermally viscosity broken.

Example 12

Like Example 11 above except that cycle from the raffinate oil catalytic cracking zone is sent to the solvent extraction zone instead of being mixed with the extract oil.

In all of the above examples, to facilitate comparisons, Super Filtrol was used as catalyst in both conversion zones. It is to be understood however that other suitable contact agents may be employed in either or both zones, for example, alumina hydrolytically adsorbed on silica gel, synthetic silica-alumina mixtures or complexes, synthetic magnesium silicates and the like. As the activities of the several catalysts vary, obviously operating conditions should be adjusted when changing from one contact agent to another.

While virgin charging stocks are employed in all of the above examples, the invention is not limited thereto. For example, such stocks as coker gas oils and viscosity breaker gas oils may be used if desired. Also, cracked gasolines or cracked heavy naphthas may be processed. When this is done, the extract oil catalytic cracking zone produces a large amount of valuable gas rich in C_4 hydrocarbons, especially isobutane and isobutene. Such gas is very suitable as a charge to catalytic polymerization or catalytic alkylation units. When available, cracked gasolines of low quality, for example, coker gasolines and viscosity breaker gasolines may be processed in this way to great profit.

While solvent extraction has been exclusively described as the process suitable for separating the selected hydrocarbon charge into a relatively refractory component and a relatively non-refractory component, other procedures may be employed for accomplishing the same ends, for example, fractionation. By accurate fractionation the hydrocarbon oil charge may be separated into a plurality of narrow fractions of differing refractoriness. These cuts may be treated separately in accordance with the teachings of this invention or, fractions of like or similar refractoriness may be combined and the resulting blends treated as described. In most cases, separation by fractionation is of limited applicability, being best suited for use in connection with hydrocarbon oils of comparatively low boiling range, for example, gasoline, heavy naphtha, kerosene and the like. With oils of higher boiling range, the mixture of hydrocarbons is usually so complex that separation by fractionation is practically impossible.

Separation of hydrocarbon oils into relatively refractory and relatively non-refractory components may also be accomplished by fractional crystallization. This method is generally of wider applicability than fractionation, in fact it is particularly suited for removal of relatively non-refractory waxes from oils of comparatively high boiling range.

It is obvious that, if desired, cycle stock from the first catalytic cracking zone obtained through line 43 may be recycled in part or entirely to the

first catalytic cracking zone through heating coil 23 in furnace setting 29 and/or cycle stock from the second catalytic cracking zone obtained as bottoms from tower 54 may be recycled in part or entirely to the second catalytic cracking zone through heating coil 48 in furnace setting 49. Means for accomplishing this recycling are so obvious that the necessary lines are not indicated in the figure.

Be it remembered that while the instant invention has been described by means of several specific examples thereof, it is to be understood that these examples are illustrative only and the invention is not limited to the specific disclosures therein. Also, it will be obvious that certain features and subcombinations are of utility and may be employed without reference to other features and subcombinations. This is contemplated by and within the scope of the appended claims. It is further to be understood that various changes may be made in details within the scope of the appended claims without departing from the spirit of my invention. It is accordingly to be understood that my invention is not to be limited to the specific details shown and described.

I claim:

1. In the catalytic conversion of a hydrocarbon oil, the steps including heating the raffinate oil obtained from said hydrocarbon oil by solvent extraction as hereinafter described to a relatively low catalytic cracking temperature, contacting said heated raffinate oil with a cracking catalyst for a time sufficient to effect substantial conversion of said raffinate oil to hydrocarbon conversion products of lower boiling point than said raffinate oil, fractionating the resulting reaction products in a first fractionating zone into gas, the aforementioned liquid hydrocarbon conversion products and cycle stock, admixing said liquid hydrocarbon conversion products with the aforementioned hydrocarbon oil, solvent extracting the mixture and fractionating the raffinate phase in a second fractionating zone into substantially saturated hydrocarbon conversion products and the previously mentioned raffinate oil.

2. In the catalytic conversion of a hydrocarbon oil, the steps including heating the raffinate oil obtained from said hydrocarbon oil by solvent extraction as hereinafter described to a relatively low catalytic cracking temperature, contacting said heated raffinate oil in a first catalytic cracking zone with a cracking catalyst for a time sufficient to effect substantial conversion of said raffinate oil to liquid hydrocarbon conversion products of lower boiling point than said raffinate oil, heating the extract oil obtained from said hydrocarbon oil by solvent extraction as hereinafter described to a relatively high catalytic cracking temperature, contacting said heated extract oil in a second catalytic cracking zone with a cracking catalyst for a time sufficient to effect substantial conversion of said extract oil to liquid hydrocarbon conversion products of lower boiling point than said extract oil, fractionating the resulting reaction products from both catalytic cracking zones in a first fractionating zone into gas, the aforementioned liquid hydrocarbon conversion products and cycle stock, admixing said liquid hydrocarbon conversion products with the aforementioned hydrocarbon oil, solvent extracting the mixture, fractionating the raffinate phase in a second fractionating zone into substantially saturated hydrocarbon conversion products and the previously mentioned raffinate oil and fractionating the extract phase in a third fractionating zone into highly unsaturated hydrocarbon conversion products and the previously mentioned extract oil.

3. In the catalytic conversion of a hydrocarbon oil, the steps including heating the raffinate oil obtained from said hydrocarbon oil by solvent extraction as hereinafter described to a relatively low catalytic cracking temperature, contacting said heated raffinate oil in a first catalytic cracking zone with a cracking catalyst for a time sufficient to effect substantial conversion of said raffinate oil to liquid hydrocarbon conversion products of lower boiling point than said raffinate oil, fractionating the resulting reaction products in a first fractionating zone into gas, the aforementioned liquid hydrocarbon conversion products and cycle stock, admixing said liquid hydrocarbon conversion products with the aforementioned hydrocarbon oil, solvent extracting the mixture, fractionating the raffinate phase in a second fractionating zone into substantially saturated hydrocarbon conversion products and the previously mentioned raffinate oil, fractionating the extract phase in a third fractionating zone into highly unsaturated hydrocarbon conversion products and extract oil, admixing extract oil with the aforementioned cycle stock, heating the mixture of extract oil and cycle stock to a high catalytic cracking temperature and contacting said heated mixture of extract oil and cycle stock in a second catalytic cracking zone with a cracking catalyst for a time sufficient to effect substantial conversion of said last-named mixture to liquid hydrocarbon conversion products of lower boiling point than said last-named mixture.

4. The process of claim 3 further characterized by the fact that the reaction products from the conversion of said mixture of extract oil and cycle stock in said second catalytic cracking zone are fractionated in a fourth fractionating zone into gas, the last-named liquid hydrocarbon conversion products and cycle stock and the last-named liquid hydrocarbon conversion products are admixed with the aforementioned hydrocarbon oil.

5. In the catalytic conversion of a hydrocarbon oil, the steps including heating the raffinate oil obtained from said hydrocarbon oil by solvent extraction as hereinafter described to a low catalytic cracking temperature, contacting said heated raffinate oil in a catalytic cracking zone with a cracking catalyst for a time sufficient to effect substantial conversion of said raffinate oil to liquid hydrocarbon conversion products of lower boiling point than said raffinate oil, cooling the reaction products, separating the reaction products into gas and liquid, admixing said liquid with the aforementioned hydrocarbon oil, solvent extracting the mixture and fractionating the raffinate phase into substantially saturated hydrocarbon conversion products and the previously mentioned raffinate oil.

6. In the catalytic conversion of a hydrocarbon oil, the steps including heating the raffinate oil obtained from said hydrocarbon oil by solvent extraction as hereinafter described to a low catalytic cracking temperature, contacting said heated raffinate oil in a first catalytic cracking zone with a cracking catalyst for a time sufficient to effect substantial conversion of said raffinate oil to liquid hydrocarbon conversion products of lower boiling point than said raffinate oil, cooling the reaction products, separating the reaction products into gas and liquid, admixing said liquid

with the aforementioned hydrocarbon oil, solvent extracting the mixture, fractionating the raffinate phase in a first fractionating zone into substantially saturated hydrocarbon conversion products and the aforementioned raffinate oil, fractionating the extract phase in a second fractionating zone into highly unsaturated hydrocarbon conversion products and extract oil, heating said extract oil to a high catalytic cracking temperature, contacting said heated extract oil in a second catalytic cracking zone with a cracking catalyst for a time sufficient to effect substantial conversion of said extract oil to liquid hydrocarbon conversion products of lower boiling point than said extract oil, fractionating the resulting reaction products from said second catalytic cracking zone in a third fractionating zone into gas, said liquid last mentioned hydrocarbon conversion products and cycle stock and admixing said last mentioned liquid hydrocarbon conversion products with the aforementioned hydrocarbon oil.

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