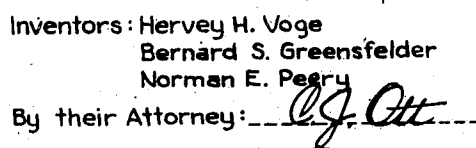


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PRODUCTION OF GASOLINE

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PRODUCTION OF GASOLINE

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This invention relates to the production of gasoline from hydrocarbon oils boiling above the gasoline boiling range through catalytic cracking.

In the production of gasoline from heavier hydrocarbon oils through catalytic cracking, the hydrocarbon oil to be cracked is contacted with the solid cracking catalyst under suitable cracking conditions. The percentage of hydrocarbon oil converted into products boiling outside of the range of the hydrocarbon oil feed is usually designated "depth of cracking" and this quantity is often used as a characterization factor of the operation. The depth of cracking depends upon the activity of the catalyst, the character of the oil being cracked, and the reaction conditions, particularly the temperature. With a given catalyst and oil, the depth of cracking is increased with increasing temperature. However, as the temperature is increased to increase the depth of cracking, the quality of the gasoline changes.

In order to obtain a large production capacity and at the same time produce a gasoline of superior quality, two-step processes have been resorted to in some cases. In such processes the oil is cracked under relatively severe conditions, the gasoline is separated from the product, and the gasoline is passed over the same catalyst or a similar catalyst under lower temperature and space velocity conditions. This latter step, since it gives no appreciable cracking, is sometimes referred to as "repassing." Such combination processes give gasoline of excellent quality even when the depth of cracking in the first cracking step is quite high. However, there is a large loss of gasoline in the repassing treatment, and such processes have also the inherent disadvantage of not utilizing the plant capacity to fullest advantage since only half of the plant is utilized in cracking to produce gasoline.

In the cracking process the more easily crackable constituents of the oil naturally tend to crack in preference to more difficultly crackable or refractory constituents. The unconverted oil is therefore more refractory than the original feed. This oil, referred to as catalytic gas oil, is sometimes recycled in part. However, it is quite refractory and consequently it contributes little towards the gasoline yield upon being recycled. Recycle of this oil is therefore rarely profitable except when there is insufficient virgin feed to fully utilize the plant capacity.

Gasoline of excellent quality may be produced in better yields and with better utilization of plant capacity according to the process of the

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present invention which in general outline is carried out as follows:

The hydrocarbon oil feed, for example, virgin gas oil, is subjected to catalytic cracking in admixture with a hydrogenated oil fraction produced as hereinafter specified. The product is separated into a normally gaseous fraction, an olefinic gasoline fraction, and a refractory gas oil fraction containing unconverted oil (catalytic gas oil). The catalytic gas oil fraction is subjected to a catalytic hydrogenation treatment. The hydrogenated product is separated into a hydrogenated gas oil fraction boiling up to about 470° F. and a hydrogenated gas oil fraction boiling above about 470° F. The hydrogenated gas oil fraction boiling above 470° F. is mixed with the virgin oil feed as specified above. The hydrogenated fraction boiling below about 470° F. is commingled with the olefinic gasoline fraction specified above and the mixture is subjected to a second catalytic cracking treatment at a temperature and at a space velocity somewhat lower than those prevailing in the first mentioned catalytic cracking step. Cracked gasoline is recovered from the product of the second catalytic cracking step.

In the process of the present invention the catalytic gas oil is hydrogenated and the hydrogenated gas oil is then separated into two fractions; only the higher boiling fraction is recycled. This fraction may be advantageously cracked to give large yields of gasoline under the relatively severe conditions pertaining in the cracking zone. The remainder of the hydrogenated catalytic gas oil is mixed with the catalytic gasoline produced in the first step and subjected to a second catalytic cracking operation carried out under milder conditions than those pertaining in the first catalytic cracking step. This operation serves a manifold purpose. Firstly, the catalytic gasoline produced in the first catalytic cracking step may be produced in excellent yields under conditions affording a higher depth of cracking. The gasoline is then materially improved in quality through contact with the catalyst at the somewhat lower temperatures and space velocity conditions prevailing in the second catalytic cracking step. Secondly, loss of gasoline in the second step is decreased due to the presence of the hydrogenated catalytic gas oil fraction. (While it is not desired to be bound by any theory, it is believed that the decreased loss may be explained as follows: In the ordinary repassing operation an appreciable saturation of the gasoline takes place, the neces-

sary hydrogen coming from degradation of part of the gasoline. In the catalytic cracking of the lower boiling fraction of the hydrogenated catalytic gas oil, the larger part of the necessary hydrogen comes from the hydrogenated gas oil fraction rather than from the catalytic gasoline.) Thirdly, in this operation the second step is not a simple repassing treatment; the reactor capacity is utilized for the production of gasoline. The fraction of hydrogenated gas oil boiling below about 470° F. is cracked in part and produces gasoline of excellent quality when cracked under the relatively low temperature conditions. Fourthly, in the catalytic hydrogenation of the catalytic gas oil small but appreciable amounts (for example, 5%–10%) of material boiling in the gasoline boiling range is produced. This gasoline is of relatively poor quality. In the present process this small amount of gasoline is improved in quality by its inclusion in the fraction of the hydrogenated gas oil subjected to the second cracking step.

The process of the invention is described in further detail in connection with the attached drawing, wherein there is shown by means of conventional figures not drawn to scale a plant adapted for operation in accordance with the principles of the invention.

Referring to the drawing, the feed, for example, a reduced crude, flashed distillate or gas oil, introduced by line 1 and feed pump 2, is commingled with a heavy hydrogenated gas oil fraction in line 3. Cracking catalyst in the form of a powder is stored in catalyst hopper 4. Any of the known solid cracking catalysts may be used. One suitable catalyst is, for example, the treated clay cracking catalyst presently sold under the name "Filtrol." The catalyst is made up into a slurry with a suitable oil, for example, part of the feed oil, in mixer 5. A portion of the catalyst slurry is continuously fed into the feed stream in line 3. The amount of catalyst added by the slurry may vary, but is generally between about ¾ pound and 10 pounds per barrel of feed. The mixture then passes via line 6 to furnace 7. The feed, prior to entering the furnace, may also be commingled with a quantity of refractory oil entering via line 8. The order of combining the components of the mixture may be changed from that just described. The mixture containing virgin oil feed, hydrogenated heavy oil, refractory oil, fresh catalyst and partially spent catalyst, is passed through the coils 9 of furnace heater 7 under conditions to produce substantial cracking. The temperature at the exit of coil 9 is suitably between about 950° F. to 1260° F. The pressure is preferably at least 100 p. s. i. for example, between 150 and 900 p. s. i. Immediately upon issuing from the cracking coil, the mixture is quenched by the injection of a suitable quench oil. Thus, in the operation illustrated in the drawing, reflux condensate from fractionator 10 is withdrawn via line 11 and used for this purpose. The product is then passed through pressure reducing valve 12 into fractionator 10. In the fractionator the lighter products are separated from unconverted and partially converted oil and catalyst. The lighter products are withdrawn overhead via line 13. The gasoline produced in this step is quite olefinic and is not of the best quality. The end point of the fraction removed overhead may vary, but is preferably in the order of 400° F. Reflux condensate substantially free of catalyst is withdrawn via line 14. The heavy oil containing spent catalyst in sus-

pension is withdrawn from the bottom and passed to a thickener 15. Clarified oil issuing via line 16 is preferably combined with the heavy refractory condensate in line 14. A part of it may also be recycled to the cracking coil via lines 17 and 8 and/or a portion of it may be withdrawn via line 18. This material is a refractory high boiling material of high aromatic content. It is of little value as a cracking feed, but is useful for some special purposes such as a source of an insecticidal material. The bottom product from the thickener is a heavy slurry of spent catalyst. This product may be withdrawn via line 19. However, it may be advantageously passed by line 20 to the feed to the catalytic cracking step to be described. The reflux condensate, containing if desired some clarified oil from the thickener, is preheated in heat exchanger 21 and charged to reactor 22 wherein it is hydrogenated with hydrogen introduced via line 23. Reactor 22 is charged with any one of the many hydrogenation catalysts available for similar purposes. One excellent catalyst by way of example is a pelleted mixture of sulfides of tungsten and nickel. The conditions in reactor 22 are adjusted according to the catalyst used to effect substantial hydrogenation. Typical conditions are as follows:

Temperature	-----°F.	500–820
Pressure	-----p. s. i.	100–1,000
LHSV	-----	0.2–5

(LHSV, i. e. liquid hourly space velocity, is defined as the volumes of reactant, measured as a liquid, passed in contact with a unit volume of catalyst bed per hour.) The product is passed to a separator 24. Unused hydrogen is removed via line 25 and the hydrogenated product is recovered by line 26. The hydrogenated product is fractionated in fractionator 27 to separate a lighter hydrogenated gas oil fraction and a heavier hydrogenated gas oil fraction. The final boiling point of the lighter hydrogenated gas oil fraction withdrawn overhead via line 28 may vary from about 430° F. up to about 610° F. but is preferably about 470° F.±30° F. The heavy fraction withdrawn from the bottom is passed via line 29 to scrubber 30 wherein it is utilized to remove traces of catalyst fines from the spent regenerator gas. In view of its high boiling point, this material is particularly suited for this purpose. The heavy fraction of the hydrogenated oil now containing a small amount of catalyst passes via line 3 to be commingled with the virgin feed as hereinbefore described.

The gasoline fraction from fractionator 10 and the light gas oil fraction from fractionator 27 are withdrawn from surge tanks 31 and 32, respectively, commingled in line 33 and passed to reactor 34. The heavy slurry of spent catalyst from line 20 is also commingled to produce a three-component mixture. This mixture picks up hot freshly regenerated catalyst from standpipe 35 of regenerator 36 and carries it to the reactor. The amount of catalyst introduced is usually in the order of from about 5 to about 20 parts by weight with respect to the oil. Reactor 34 is partially filled with a bed of powdered cracking catalyst in a fluidized or pseudo liquid condition. Partially spent catalyst is continuously removed from the reactor by line 37 and is picked up by a stream of air entering via line 38 and carried to the regenerator via line 39. The spent regeneration gas containing a small amount of suspended catalyst "fines" is passed to the scrub-

ber via line 40 and the scrubbed gas escapes via line 41. Reactor 34 and regenerator 36 are seen to constitute a conventional fluidized catalyst catalytic cracking system. The temperature in the reactor is usually between about 750° F. and 990° F., and the pressure is usually between 1 atmosphere and about 10 atmospheres. The vaporous product from the reactor is passed via line 42 to a fractionator 43 wherein it is separated into a lighter fraction consisting of gasoline and lighter products and a heavier fraction consisting of unconverted and partially converted products. The lighter fraction is removed overhead via line 44, condenser 45 and surge tank 46. The heavier fraction which also contains some suspended catalyst "fines" is removed from the bottom via line 47. This fraction is advantageously recycled via line 8 as described. All or a portion of this material may, however, be removed from the system via line 48.

In typical example of the process, the oil feed is a flashed distillate having a molecular weight of about 300 produced by the vacuum flashing of California petroleum. The catalyst is the synthetic silica-alumina composite cracking catalyst sold under the trade name "Aerocat." The catalyst, in the form of a powder passing a 100-mesh sieve, is introduced as a slurry in the described fraction of hydrogenated catalytic gas oil to give about 2.5 lbs. of catalyst per barrel of feed. The mixture of feed and catalyst is subjected to cracking conditions to give a depth of cracking of about 45%, the pressure being about 250 p. s. i. and the temperature about 990° F. The gas oil from the catalytic cracking step is hydrogenated with a cobalt molybdate-alumina catalyst (11% Co+Mo in mol ratio of 1:5) under the following conditions:

Temperature	° F.	890
Pressure	p. s. i.	900
Liquid hourly space velocity		1.0
Recycle gas (60%–80% H ₂)	cu. ft./bbl.	500

In this operation about 15% of low octane number gasoline is produced. The hydrogenated gas oil is fractionated into two fractions, the cut point being about 470° F. The higher boiling fraction is cracked in the liquid phase with the virgin feed. The lower boiling fraction is blended with the catalytic gasoline from the liquid phase cracking step and the mixture is subjected to catalytic cracking with the same catalyst in a conventional fluidized catalyst catalytic cracking plant. The conditions are as follows:

Temperature	° F.	810
Pressure	p. s. i.	12
Liquid hourly space velocity		0.5
Catalyst/oil, weight ratio		9:1

In this particular example, the described scrubbing of the regenerator flue gas is not employed.

A characteristic feature of the process is that the catalytic gas oil is hydrogenated and then separated into two fractions which are utilized in different manners in accordance with their different composition. Thus, each fraction is treated in such a manner as to obtain full benefit from the oil as well as to enhance the operations with respect to other materials treated. The lighter portion of the hydrogenated catalytic gas oil is particularly suited for cracking under mild conditions while at the same time affording a substantial improvement in the second treatment of the cracked gasoline. The higher boiling portion of the hydrogenated catalytic gas oil is less

suited for this purpose, but is advantageously cracked under the higher temperature conditions of the first catalytic cracking step.

Features of the preferred embodiment of the invention are noted. Fresh catalyst is continuously charged to the system in small amounts through the slurry. This allows continuous replacement of the catalyst in the fluidized catalyst system to maintain the catalyst activity. Only one catalyst regenerator is required for the two catalytic cracking steps. The operation is capable of producing large yields of superior gasoline with little production of tar, coke and similar undesired products. The operation allows application of existing thermal cracking equipment. (In this connection it should be pointed out that while the first catalytic cracking step is illustrated as carried out in coil 9, the soaking tank used in some existing thermal cracking units may also be included.) The feature of charging the partially spent catalyst from the first catalytic cracking step to the second catalytic cracking step provides a simple and efficient means for separating the spent catalyst from occluded oil and bringing it to regeneration. While this advantage is mechanical, it is nevertheless of importance from a practical point of view. Other features of secondary importance will be apparent to those skilled in the art.

While the invention has been described in some detail, in its preferred embodiment it is to be understood that the process is not limited to the use of the particular catalysts disclosed. In general, any of the numerous known solid catalytic cracking catalysts and hydrogenation catalysts may be used. Those mentioned are commercially available and are given only by way of example. Also, although the cut point of the hydrogenated catalytic gas oil fraction and the relative conditions in the two catalytic cracking steps are important, the absolute conditions with respect to any variable of condition may be varied widely as will be apparent to those skilled in the art. It is therefore desired that the invention not be limited to any of the reaction conditions except as specified in the following claims.

The invention claimed is:

1. Process for the production of gasoline from hydrocarbon oils boiling above the gasoline boiling range which comprises subjecting the hydrocarbon oil feed in admixture with a hydrogenated gas oil fraction produced as hereinafter specified to catalytic cracking, separating the product into a normally gaseous fraction, an olefinic gasoline fraction and a refractory gas oil fraction containing unconverted oil, hydrogenating said refractory gas oil fraction, separating the hydrogenated product by distillation into a hydrogenated fraction boiling below about 470° F. and a hydrogenated gas oil fraction boiling above about 470° F., commingling the higher boiling hydrogenated gas oil fraction with the oil feed as specified above, commingling the said hydrogenated gas oil fraction boiling below about 470° F. with said olefinic gasoline fraction and subjecting the mixture to a second catalytic cracking treatment at a temperature somewhat lower than that prevailing in the first mentioned catalytic cracking step, and recovering cracked gasoline from the product of said second catalytic cracking step.

2. In a process for the production of gasoline from higher boiling hydrocarbon oils through catalytic cracking, the steps of subjecting the oil to be cracked to catalytic cracking at a relatively

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high temperature in the presence of a hydrogenated catalytic gas oil fraction boiling above about 470° F., separating the product into a normally gaseous fraction, an olefinic gasoline fraction and a refractory catalytic gas oil, hydrogenating said catalytic gas oil, separating the hydrogenated product into fractions boiling above and below about 470° F., catalytically cracking the higher boiling hydrogenated fraction in the above mentioned catalytic cracking step, commingling the lower boiling hydrogenated gas oil fraction with the said olefinic gasoline fraction and subjecting the mixture to catalytic cracking at a relatively low temperature, separating gasoline and gas oil from the product, and subjecting the gas oil to catalytic cracking in said first mentioned catalytic cracking step at a relatively high temperature.

3. Process for the production of gasoline from higher boiling hydrocarbon oils through catalytic cracking which comprises subjecting the oil to be cracked to catalytic cracking at a relatively high temperature in the range of 950° to 1260° F. in the presence of heavy hydrogenated catalytic gas oil, separating the product into a normally gaseous fraction, an olefinic gasoline fraction and a refractory gas oil fraction, hydrogenating said gas oil fraction, separating the hydrogenated gas oil by distillation into light and heavy hydrogenated gas oil fractions, catalytically cracking the higher boiling hydrogenated gas oil fraction in the above mentioned catalytic cracking step, commingling

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the lighter hydrogenated gas oil fraction with the olefinic gasoline fraction and subjecting the mixture to catalytic cracking at a relatively low temperature in the range of 750° F. to about 990° F., and separating gasoline from the product.

4. Process according to claim 3 in which the concentration of catalyst in the first catalytic cracking step is between $\frac{3}{4}$ and 10 pounds of catalyst per barrel of feed to the cracking zone.

5. Process according to claim 3 in which the partially spent catalyst from the first catalytic cracking step is charged to the vapor phase second catalytic cracking step.

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