

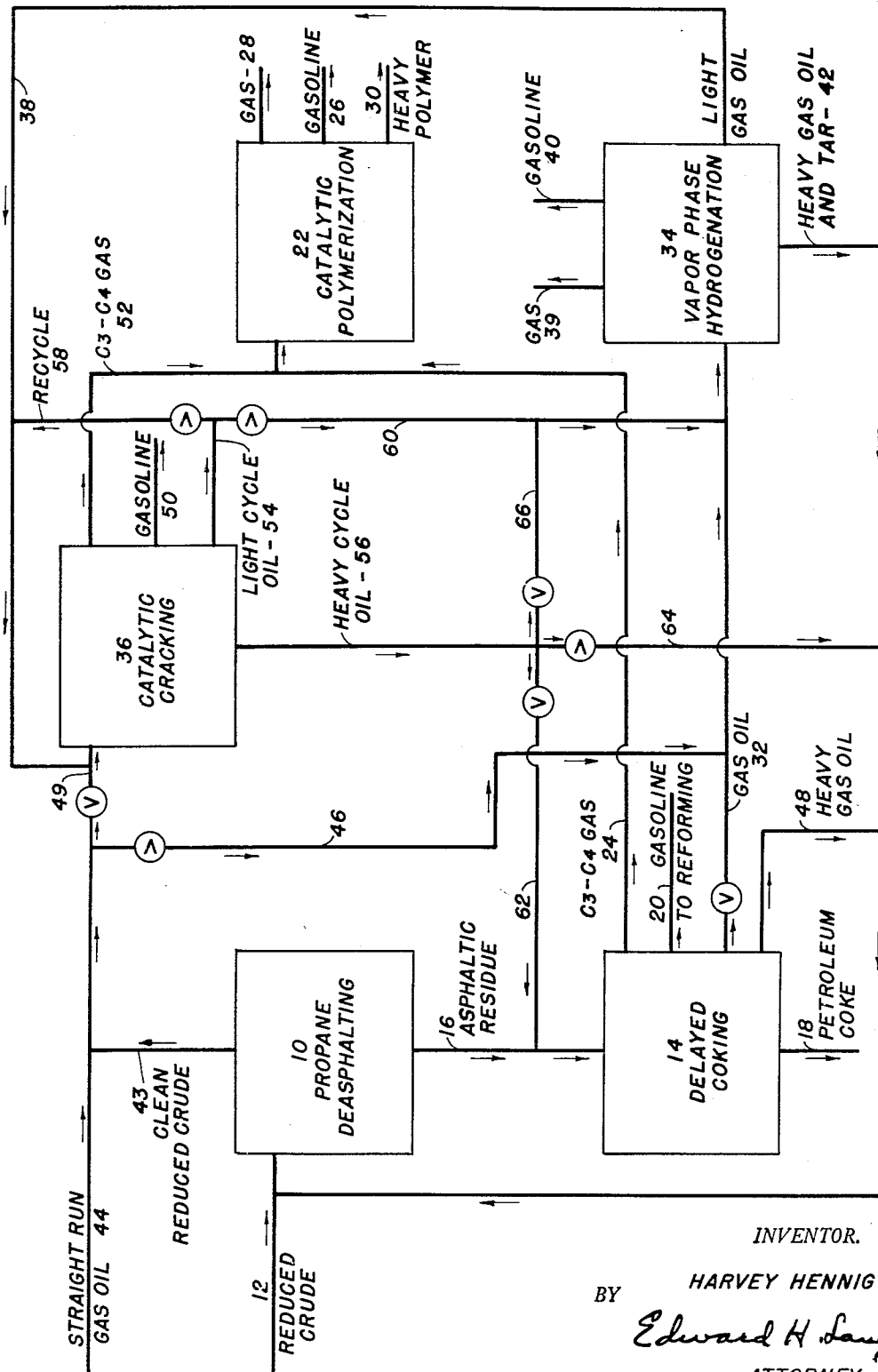
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PROCESS FOR REFINING OF PETROLEUM, SHALE OIL, AND THE LIKE

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**PROCESS FOR REFINING OF PETROLEUM,  
SHALE OIL, AND THE LIKE****Harvey Hennig, Cary, Ill., assignor to The Pure Oil Com-  
pany, Chicago, Ill., a corporation of Ohio****Application December 27, 1951, Serial No. 264,372****7 Claims. (Cl. 196—49)**

This invention relates to a process for treating crude petroleum, shale oils, and the like. More particularly, the invention relates to a process for upgrading crude petroleum, shale oils, and the like to produce high-quality gasoline. In a still more specific aspect, the invention relates to a combination process for producing high-quality gasoline from heavy crude oil fractions, obtained from crude petroleum, shale oil, and the like, by deasphalting, coking, cracking, hydrogenation, and polymerization.

In order to obtain valuable products from crude oils, such as crude petroleum as it comes from the well and shale oil as it comes from the retort, these oils are subjected to a suitable separation process to divide the crude into a gaseous fraction, a fraction boiling in the gasoline range, a gas oil fraction boiling between approximately 550° and 800° F., and a heavy residue boiling above about 800° F. One method of effecting this separation is to pass the crude oils to a preheater, heat the crude to a temperature below the temperature at which cracking will occur, and then fractionate the heated crude to separate gases, gasoline, gas oils and a heavy residue.

The gas oils boiling between about 550° and 800° F., obtained by the above fractionation, are referred to herein as straight run gas oil, and the heavy residue boiling above approximately 800° F. is referred to as reduced crude in this specification and the appended claims.

Due to the increased demands for gasoline and light distillates and the possibility of depleted crude oil supplies, it has now become necessary to utilize reduced crudes to obtain maximum yields of gasoline and light distillates. The upgrading of reduced crude and other high boiling fractions to obtain fractions of relatively lower boiling points may be effected by catalytically cracking the high boiling fractions. However, reduced crudes cannot be economically cracked without some form of intermediate preparation because of the varying amounts of dirt, asphalts and tars, and other contaminants present in the reduced crudes. These contaminants result in premature deactivation of the cracking catalyst due to excessive carbon deposition if they are not removed from the reduced crude prior to catalytic cracking. One method being used to clean up reduced crudes, preparatory to cracking, is propane treating. The heavy residue of dirt, asphalt and the like, referred to herein as asphaltic residue, separated from the reduced crude by propane treating is normally of little value and is suitable for use only as a low grade fuel oil or a road building material.

Efforts have been made to further process this asphaltic residue to obtain products of greater value such as gasoline and gas oils. One method of treating this asphaltic residue is high pressure hydrogenolysis or destructive hydrogenation. However, this method of hydrogenation is carried out under high pressure and is therefore costly and technically difficult to operate. It would therefore be desirable to be able to utilize a less complicated method of accomplishing this hydrogenation operation.

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In addition to dirt and asphaltic contaminants, crude oils, particularly shale oils and high sulfur crudes which are being produced in increasing quantities, often contain comparatively large quantities of sulfur, basic nitrogen, phenolic oxygen and unsaturated hydrocarbons. If straight run gas oils and deasphalted reduced crudes, referred to herein as clean reduced crudes, obtained from these types of crude oils are to be catalytically cracked, it is also highly desirable to remove as much of these contaminants as possible and to saturate the unsaturated hydrocarbons prior to cracking. Hydrogenation under proper conditions is also an effective means for removing contaminating sulfur, nitrogen, and oxygen and for saturating unsaturated components.

In processes wherein heavy oils, such as straight run gas oils and clean reduced crudes, are catalytically cracked, a heavy oil residue is obtained which is more difficult to crack than the original charge oil. This heavy oil residue is referred to as heavy cycle oil in this specification and the appended claims. These heavy cycle oils usually contain large quantities of tar-forming materials. If heavy cycle oil is recycled to the cracking unit excessive formation of coke and carbonaceous deposits will occur and the cracking catalyst will be prematurely deactivated. In addition to carbon-forming constituents, heavy cycle oil from a catalytic cracking unit also contains varying amounts of refractory, condensed-ring aromatics which are difficult to convert by cracking unless they are saturated. Therefore, these heavy cycle oils must be further processed before they are returned to the cracking unit in order to remove carbon-forming materials and to produce a charge stock more amenable to conversion to high yields of gasoline and light distillates.

Catalytically cracking heavy oils, such as straight run gas oils and clean reduced crude, also results in the production of varying amounts of normally gaseous hydrocarbons. In order to obtain maximum yields of gasoline from a crude hydrocarbon material, it is also desirable to convert a portion of these gases to gasoline. One method of obtaining added gasoline products from catalytic cracking effluent gases is to separate C<sub>3</sub> and C<sub>4</sub> hydrocarbons from the effluent gases and then subject this fraction to catalytic polymerization.

It is therefore an object of this invention to provide a method for upgrading hydrocarbon materials. A further object of this invention is to provide a method for upgrading straight run gas oils and reduced crudes to produce maximum yields of high-quality gasoline. Another object of this invention is to provide a combination process for manufacturing high-quality gasoline from straight run gas oils and deasphalted reduced crudes. Another and further object of this invention is to provide a combination process for preparing cracking stock from straight run gas oils and deasphalted reduced crudes. A still further object of this invention is to provide a method of preparing cracking stock from asphaltic residue, obtained by propane deasphalting of reduced crudes, and from heavy cycle oil, obtained by catalytically cracking straight run gas oils and deasphalted reduced crudes. Other and further objects and advantages of my invention will be apparent to those skilled in the art from the following description of my invention.

I have discovered a combination process whereby straight run gas oils and reduced crudes may be treated to prepare catalytic cracking stock and to ultimately obtain high yields of high-quality gasoline.

In a preferred embodiment of my invention reduced crude from petroleum or shale oil is fed to a propane deasphalting unit. The overhead product, after removal of propane, is fed to a vapor phase hydrogenation unit along with straight run gas oil where the gas oils and reduced crude are treated with hydrogen to saturate unsat-

urated components and to remove contaminating sulfur compounds, basic nitrogen and phenolic oxygen. The products of the hydrogenation step include small amounts of gas and gasoline and a light cycle or gas oil as the main product, the last being passed to a catalytic cracking unit where it is upgraded to produce high yields of gasoline. In a situation in which the clean reduced crude and straight run gas oil exhibits a high aniline point and contains little nitrogen, oxygen or sulfur the straight run gas oil and clean reduced crude may be charged directly to the catalytic cracking unit. Light cycle oil from the catalytic cracking unit is recycled to the catalytic cracker or preferably also fed to the vapor phase hydrogenation unit to be saturated into a feed more amenable to catalytic cracking. Heavy cycle oil from the catalytic cracker is charged to a delayed coking unit along with the asphaltic residue of the propane deasphalting unit. Alternately, if conditions are such that the overhead stream from the propane unit is fed to the hydrogenation unit, the catalytic cracker heavy cycle oil can be fed to the propane unit for further separation. Operating conditions in the hydrogenation unit may at times be of sufficient severity that some extra heavy gas oil and tar or asphalt is produced. If such is the case, these heavy fractions can also be sent to the propane unit. The gas oil produced as one of the products of the delayed coker is charged to the hydrogenation unit to be upgraded into a high-quality catalytic cracking stock. If an extra heavy gas oil is produced by delayed coking this material can be sent to the propane unit when the overhead stream from that unit is fed to the hydrogenation unit. C<sub>3</sub> and C<sub>4</sub> gases from the catalytic cracking unit and, if preferred, from the delayed coking unit are charged to a catalytic polymerization unit where they are treated to produce additional quantities of gasoline.

Under certain circumstances it may be desirable to reform straight run and coker gasoline to obtain a gasoline product having an improved octane rating, although slight losses in total gasoline product usually result. This catalytic reforming of a highly naphthenic straight run gasoline may also provide at least a part of the hydrogen required for hydrogenation.

A further understanding of some of the specific aspects of my invention may be had by referring to the accompanying drawing which is a schematic flow diagram showing one arrangement of apparatus elements and flow of materials therethrough suitable for the practice of my invention. Various other valves, pumps and other conventional equipment necessary for the practice of my invention will be familiar to one skilled in the art and have been omitted from this drawing for the sake of clarity.

In accordance with the drawing, a reduced crude obtained by the fractionation of crude petroleum or shale oil and boiling above approximately 800° F. is charged to propane deasphalting unit 10 through line 12. In deasphalting unit 10, the reduced crude is countercurrently contacted with liquefied propane at a temperature of about 130° to 190° F. Asphaltic residue obtained as a bottoms product in deasphalting unit 10 is charged to delayed coking unit 14 through line 16. A coking coil which forms a part of delayed coking unit 14 heats the asphaltic residue to a temperature sufficient to vaporize approximately 30 to 70% of the charge under conditions such that the accumulation of carbon in the coking coil is avoided. The charge passes from the coking coil at a temperature of about 915° F. and a pressure of about 30 pounds per square inch gauge to coking drums, usually operated in pairs, where asphaltic hydrocarbons gradually coke and light products vaporize off. Gas, gasoline, petroleum coke, and gas oil are produced as products of coking unit 14. Petroleum coke is removed by suitable means indicated as line 18. Gasoline discharging through line 20 can be utilized in its present condition or, if preferred, it may be charged to a catalytic reforming unit, not shown,

to increase its octane rating. The catalytic reforming unit could be operated at a temperature of approximately 900° to 1100° F. and a pressure of about atmospheric to 50 pounds per square inch gauge utilizing a catalyst of alumina or magnesia with oxides of metals of the left hand columns of groups IV, V and VI of the periodic table. Although this reforming operation results in reduced gasoline yields, market conditions might dictate the use of reforming to obtain gasolines of higher octane ratings. The C<sub>3</sub> and C<sub>4</sub> constituents of the gases produced by coking unit 14 are charged to a non-selective catalytic polymerization unit 22 through line 24 where they are treated to produce additional quantities of gasoline. Suitable conditions for the operation of polymerization unit 22 include: a temperature of about 400° to 475° F., a pressure of about 200 to 1000 pounds per square inch gauge, and catalysts such as phosphoric acid-on-kieselguhr, copper pyrophosphate-on-charcoal, etc. The products of polymerization unit 22 include a high octane gasoline, gas, and heavy polymers which are discharged through lines 26, 28, and 30, respectively. The gas oil product of coking unit 14 is passed through line 32 to vapor phase hydrogenation unit 34 where it is upgraded to prepare a high-quality catalytic cracking stock. In hydrogenation unit 34 the delayed coker gas oil, in its vapor phase, is contacted with hydrogen and a saturation catalyst such as pure tungsten sulfide at a temperature of about 700° to 900° F. and a pressure of approximately 1000 to 3000 pounds per square inch gauge. In addition to hydrogenating the coker gas oil, hydrogenation unit 34 also removes a majority of the sulfur present in the gas oil thus producing a clean, high grade catalytic cracking stock. Since hydrogenation unit 34 is operated under conditions suitable for the preparation of catalytic cracking stock, a light gas oil, which is charged to catalytic cracking unit 36 through line 38 is the main product. Small amounts of gas and gasoline are also formed in hydrogenation unit 34 and are discharged through lines 39 and 40, respectively. In situations in which hydrogenation unit 34 is operated under more severe conditions a heavy gas oil and tar fraction may also be produced. This heavy gas oil and tar fraction is passed through line 42 to propane deasphalting unit 10 where it is further processed to remove asphaltic materials and is subsequently converted to catalytic cracking stock. The overhead product of deasphalting unit 10 is stripped of propane to produce a clean reduced crude which is discharged from deasphalting unit 10 through line 43. This clean reduced crude is then preferably mixed with straight run gas oils, obtained by the fractionation of crude oils and introduced to the system through line 44. The mixture of clean reduced crude and straight run gas oil may contain large amounts of sulfur compounds, phenolic oxygen, basic nitrogen and unsaturated hydrocarbons. If such is the case, the mixture is passed through line 46 to vapor phase hydrogenation unit 34 where it is treated with hydrogen to saturate unsaturated components, to convert basic nitrogen to ammonia, to convert sulfur and sulfur compounds to hydrogen sulfide, and to convert phenolic oxygen to water. This saturation and purification treatment serves to produce a high grade catalytic cracking stock from the mixture of clean reduced crude and straight run gas oil. When the clean reduced crude is charged to hydrogenation unit 34, any extra heavy gas oils produced in coking unit 14 may be returned to deasphalting unit 10 through line 48 for further treatment. As an alternative, mixtures of clean reduced crude and straight run gas oils which are low in unsaturates and which are substantially free of phenolic oxygen, sulfur and sulfur compounds, and basic nitrogen may be charged directly to catalytic cracking unit 36 through line 49 together with light gas oil from hydrogenation unit 34. When operating with mixtures of clean reduced crude and straight run gas oils of this nature presaturation hydrogenation is unnecessary. Catalytic cracking unit 36 is preferably operated at temperatures of about 850° to

1000° F. and pressures of approximately 0 to 100 pounds per square inch gauge utilizing a moving bed catalyst such as bauxite, montmorillonite, a bentonitic clay or synthetic silica-alumina. However, a fixed bed or fluid type catalyst process may also be advantageously employed. In catalytic cracking unit 36 the heavy charge stocks are converted to hydrocarbons of lower boiling points, the main product being gasoline which is discharged through line 50. C<sub>3</sub> and C<sub>4</sub> gases, separated from the gaseous product of cracking unit 36, are charged to polymerization unit 22 through line 52 where they are treated to produce additional quantities of gasoline. As pointed out above, C<sub>3</sub> and C<sub>4</sub> gases from coking unit 14 may also be charged to polymerization unit 22 along with C<sub>3</sub> and C<sub>4</sub> gases from cracking unit 36. The other products of cracking unit 36 include a light cycle oil and a heavy cycle oil which are discharged through lines 54 and 56, respectively. The light cycle oil is recycled to catalytic cracking unit 36 through line 58, or it may also be charged to hydrogenation unit 34 through line 60 to saturate it into a feed more amenable to cracking, depending upon the character of the oil. The heavy cycle oil produced in cracking unit 36 and boiling in the range of approximately 600° to 850° F. usually contains large amounts of tars and carbonaceous materials which tend to foul a cracking catalyst and, therefore, is unsuitable for recycling to the cracking unit. In addition, this heavy cycle oil is highly refractory and is more difficult to crack than the original charge to the catalytic cracking unit. In order to upgrade this heavy cycle oil to produce a superior catalytic cracking stock the oil is passed through line 62 to delayed coking unit 14. The heavy cycle oil acts as a diluent for asphaltic residue from propane unit 10 as well as a charge stock for coking unit 14. If conditions are such that clean reduced crude from deasphalting unit 10 is fed to hydrogenation unit 34 the heavy cycle oil is charged to deasphalting unit 10 through line 64 for further separation. Alternatively, a heavy cycle oil containing relatively small amounts of tars and carbonaceous materials and containing relatively large amounts of refractory, condensed-ring aromatics may be charged directly to hydrogenation unit 34 through line 66 for upgrading to a cracking stock more amenable to catalytic cracking.

Further advantages of my invention are illustrated by the following example in which calculations have been made to show product yields and gasoline octane numbers obtained when employing the combination of steps of my invention, including: propane deasphalting, catalytic cracking (once-through), delayed coking, vapor phase hydrogenation, and catalytic polymerization of C<sub>3</sub> and C<sub>4</sub> gases, and when employing a combination of treating steps in which the delayed coking and vapor phase hydrogenation steps of my process have been eliminated. Product yields and gasoline octane ratings are listed in Table I in which the combination process of my invention is designated as process A and the combination of steps omitting delayed coking and vapor phase hydrogenation is designated as process B.

Table I

Process	Gasoline Yield (10# R. V. P.) Vol., Percent	Excess C <sub>2</sub> 's Vol., Percent	Dist. Fuel Oil, Vol., Percent	Residual Fuel Oil, Vol., Percent	Coke, Weight Percent
(A)-----	91.1	2.5	0	0	3.7
(B)-----	72.5	0	2.0	19.7	0

## GASOLINE OCTANE NUMBERS

Process	Motor		Research	
	0	3 cc. TEL	0	3 cc. TEL
(A)-----	75.3	88.5	82.9	94.3
(B)-----	74.0	86.0	81.0	91.6

Among the principal advantages of my invention are the elimination of the necessity of hydrogenating asphaltic residues and heavy cycle oils under high pressure liquid phase conditions, by passing these materials through a delayed coking unit prior to hydrogenation and greater utilization of propane deasphalting by treating materials containing excessive amounts of tars and asphalts in the deasphalting unit prior to cracking or hydrogenating these materials. The use of vapor phase hydrogenation rather than liquid phase hydrogenation is extremely advantageous in that the former type of treating process is comparatively simple to operate and is much less expensive than the ordinary liquid phase hydrogenation unit.

Although my process has been described and exemplified in its preferred modifications, it is understood that various changes may be made without departing from the scope of the disclosure and the claims.

I claim:

1. The method for preparing high quality gasoline comprising propane deasphalting at least one oil selected from the group consisting of a reduced crude mineral oil and shale oil in a propane deasphalting zone to obtain a raffinate and asphaltic residue, coking the asphaltic residue to produce coke and a gas oil fraction, subjecting the gas oil fraction in a zone to vapor phase hydrogenation at temperatures and pressures sufficient to bring about substantial saturation of said fraction in the presence of a saturation catalyst, thereby producing a clean cracking stock, and subjecting said clean cracking stock to cracking in a catalytic cracking zone under conditions to produce a substantial yield of high octane gasoline.

2. Method in accordance with claim 1 in which the raffinate is charged to the catalytic cracking zone with the clean cracking stock.

3. Method in accordance with claim 2 in which straight run gas oil is charged to the catalytic cracking zone.

4. Method in accordance with claim 1 in which the raffinate is charged to the hydrogenation zone.

5. Method in accordance with claim 2 in which straight run gas oil is charged to the hydrogenation zone.

6. Method in accordance with claim 5 in which both heavy and light gas oil fractions are separated from the products of the coking zone and the heavy gas oil fraction is recycled to the propane deasphalting zone.

7. Method in accordance with claim 1 in which a tarry fraction is separated from the products of the hydrogenation zone and recycled to the propane deasphalting zone.

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