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OILS INVOLVING HYDROGENATION AND  
CATALYTIC CRACKING

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2 Sheets-Sheet 1

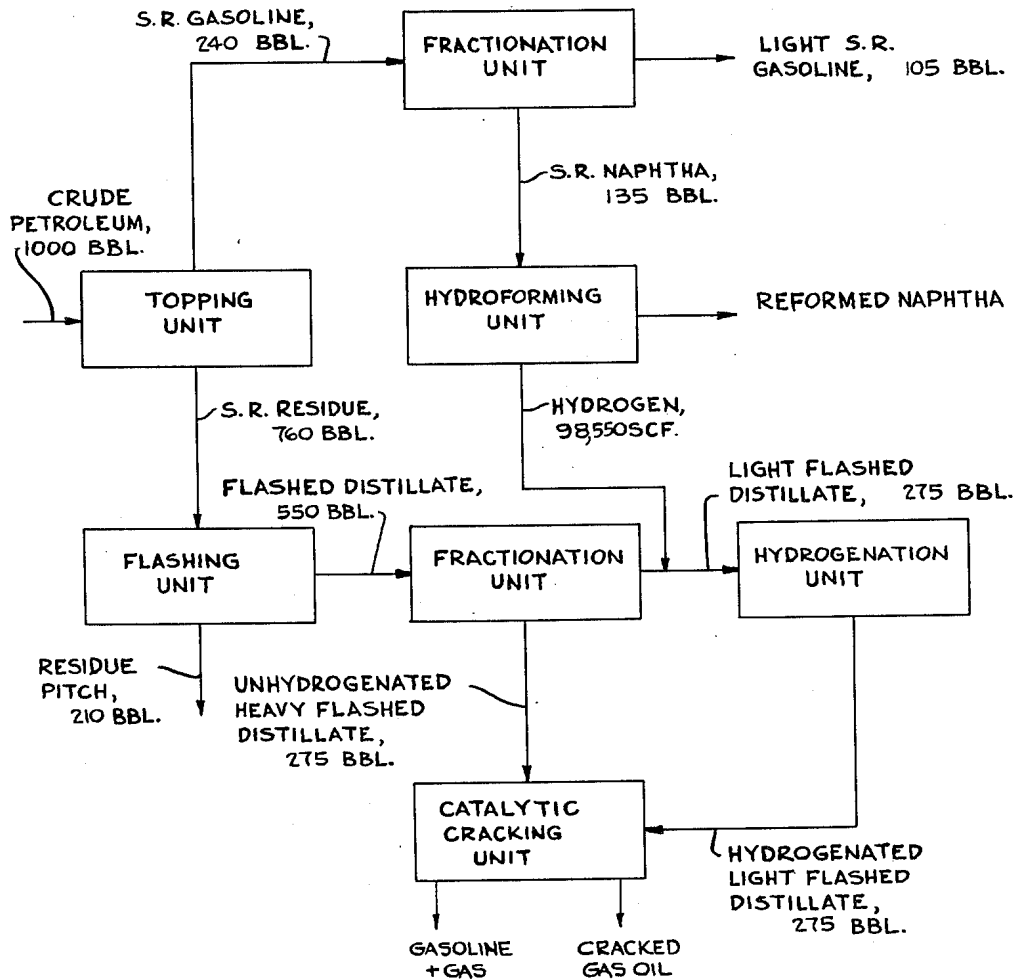


FIG. I

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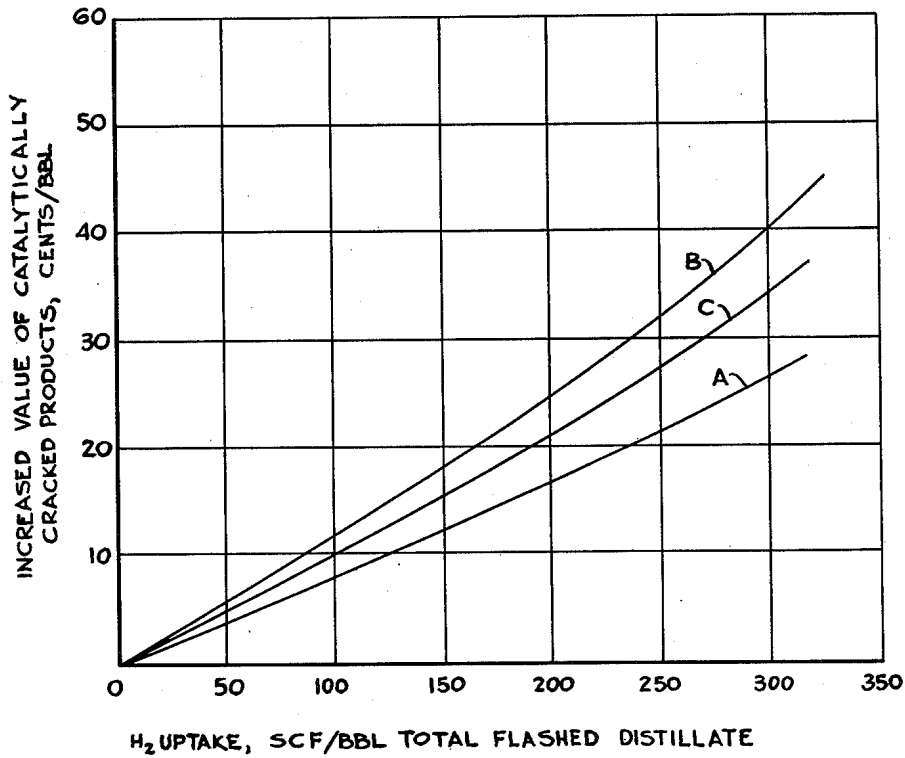


FIG. II

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**PRODUCTION OF LIGHTER HYDROCARBONS FROM PETROLEUM OILS INVOLVING HYDROGENATION AND CATALYTIC CRACKING**

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5 Claims. (Cl. 196-49)

This invention relates to the conversion of petroleum oils heavier than gasoline into gasoline and related lighter products by a process involving hydrogenation and catalytic cracking.

In describing our invention, we use the expression "catalytic gasoline and related lighter products" to designate light liquid hydrocarbon fractions boiling below about 430° F. obtained by catalytically cracking petroleum oils heavier than gasoline and the normally gaseous products including C<sub>1</sub>-C<sub>4</sub> hydrocarbons normally obtained in minor amounts by such cracking. We use the expression "petroleum oils heavier than gasoline" to designate fractions of virgin petroleum boiling essentially above 430° F. including so-called reduced crude obtained by topping petroleum. The term "gas oil" is used to designate distillate oils boiling above 430° F. but devoid of any appreciable amounts of tars or other extremely high boiling materials which cannot be distilled in commercial practice without decomposition. The term "thermal gas oil" is used to designate distillate oils boiling in the gas oil range but containing hydrocarbons produced by non-catalytic cracking of higher boiling oils; such oils are obtained upon heating virgin oils to decomposition temperatures and have a different composition and character than virgin petroleum oils of the same boiling range. The term "catalytic cracking" is used to designate the process of converting higher boiling hydrocarbon oils into lower boiling hydrocarbon oils by treating them in the vapor phase with a solid catalyst which promotes cracking. By "hydrogenation" we refer to the process of reacting hydrogen with an oil with a substantial uptake of hydrogen and without any material lowering of the average molecular weight of the oil; if an appreciable lowering of the molecular weight of the oil takes place, we refer to the process as "hydrocracking" rather than "hydrogenation."

The process known as catalytic cracking is one of the most important processes used in the refining of petroleum, and its importance is steadily increasing. This importance is due to the fact that by catalytic cracking, the higher boiling part of the petroleum may be converted in good yields to gasoline and related lighter by-products of better quality than possible by the previously used processes. The situation is such that it is to the advantage of refiners to process as much as possible of the higher boiling petroleum constituents by catalytic cracking. The most desirable practice on this basis would, therefore, be to subject to catalytic cracking the total reduced crude remaining after removing the straight-run gasoline from the petroleum by conventional topping operations. Certain prior patents have suggested the catalytic cracking of such reduced crudes and such operation has, in fact, been tried. This operation is possible but is generally considered impractical due to the fact that feed stocks such as reduced crude which contain considerable amounts of asphaltic constituents and a certain amount of ash constituents produce inordinate amounts of carbonaceous deposits ("coke") on the cracking catalyst and ruin the

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cracking catalyst by contamination with ash constituents. Rather than to attempt to catalytically crack reduced crude it is, therefore, the goal of the refiner to produce from the reduced crude the maximum amount of relatively clean feed stock for catalytic cracking. Such feed stock is generally obtained from the reduced crude by flashing, viscosity breaking, and/or deasphaltizing. Thus, for instance, by flashing, about half of the reduced crude may be obtained as a distillate fraction, called flashed distillate, which is a quite satisfactory feed stock for the catalytic cracking operation. If the residue from such operation is viscosity broken and vacuum flashed or deasphaltized, a further amount of material may be obtained thereby increasing the yield of suitable clean oil up to around 80% of the reduced crude. As the percentage of the reduced crude taken as feed stock is increased, the quality as a catalytic cracking feed stock steadily declines and this is generally known and recognized.

It is generally known and recognized that catalytic cracking feed stocks may be improved by subjecting them to a suitable hydrogenation treatment. The uptake of hydrogen in such treatment depends upon the severity of the hydrogenation conditions. Thus, under relatively low pressures and high space velocities, relatively small amounts of hydrogen, e. g., less than 100 s. c. f./bbl., may be reacted with the oil. As the pressure and/or contact time are increased the hydrogen uptake increases until the oil is completely hydrogenated. This requires a hydrogen uptake of the order of 700 s. c. f./bbl. It is known that the improvement as a catalytic cracking feed stock increases as the depth of hydrogenation is increased. In practice, however, it is not possible to hydrogenate the catalytic cracking feed stock to any appreciable extent because of the high cost of the hydrogenation process and the high cost of the large amounts of hydrogen required. Most refineries have small amounts of hydrogen available from the reforming of naphthas or related operations but the improvement obtainable upon hydrogenating the catalytic cracking feed stock with the available amounts of hydrogen generally do not warrant such hydrogenation. For this reason, hydrogenation of catalytic cracking feed stock is not used commercially except possibly under some very special circumstances.

The present invention is based on the discovery that the total product values produced by catalytically cracking hydrogenated feed stocks is much improved if the limited supply of hydrogen (usually by-product hydrogen) is used to hydrogenate certain portions of the feed quite deeply rather than in hydrogenating a broader range fraction less deeply. This is contrary to the previously supposed situation.

We are not prepared at this time to explain why this should be so. We have found it to be so by analyses of the products obtained upon catalytically cracking selected fractions of the feed stock hydrogenated to different degrees. Looking at the matter in the light of a typical case, a refinery receives a crude petroleum or mixture of petroleum from different fields. These petroleum contain in a favorable case, at most about 25% straight-run gasoline which is removed in the so-called topping columns leaving a remainder of 75% as a so-called reduced crude. In an optimum case, the refiner is able by flashing, viscosity breaking, and further vacuum flashing or deasphaltizing, to obtain about 70% of the reduced crude as a catalytic cracking feed stock, leaving an asphaltic residue of approximately 30%. The naphtha portion of the straight-run gasoline separated in the topping operation (ca. 50%) has a poor octane number and is hydroformed (which is essentially a dehydrogenation process) with the production of at most about 500 to 700 cubic feet of hydrogen per barrel. This

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hydrogen, based on the catalytic cracking feed stock, corresponds to approximately around 150 cubic feet per barrel. In practice, all of this hydrogen cannot be reacted with the flashed distillate. However, assuming 100% utilization of the available hydrogen, the catalytic cracking feed stock would be up-graded by the hydrogenation and the value of the products obtained upon catalytically cracking the hydrogenated feed would be improved.

The magnitude of this improvement in value of the catalytically cracked products, versus the hydrogen consumption in the hydrogenation step, is shown for a typical case in curve A in the graph shown in Figure II of the accompanying drawing. The increase in value of the catalytically cracked products is shown on the ordinate and the amount of hydrogen uptake in the hydrogenation is shown on the abscissa. The values assigned to the products are shown in Table I, as follows:

Table I

Product:	Value—\$
10 lb. RVP, 430° F. E. P. gasoline	4.62/bbl.
Gas oil	3.23/bbl.
Excess C <sub>4</sub>	5.04/bbl.
Propane	1.51/bbl.
Propylene	1.51/bbl.
Gas	0.17/MM B. t. u.
Coke	0.17/MM B. t. u.

These values are typical of those currently prevailing in a refinery in California. They may vary slightly from place to place and from time to time, but such variation does not alter the general conclusions. It is seen that the value of the catalytically cracked products increases with the hydrogen uptake over the range shown.

If now the total hydrogen available at by-product hydrogen cost, is reacted with only the lower boiling half of the catalytic cracking feed stock instead of with the whole, the value of the products produced upon catalytically cracking the mixture of the more deeply hydrogenated part with the unhydrogenated heavier part is as shown in curve B of the graph. Not only is the product value greatly increased but the cost of the hydrogenation plant may be reduced due to the smaller quantity of oil treated.

As pointed out above, the quality of the catalytic cracking feed stock declines as the percentage of the reduced crude taken is increased. If the feed stock is separated into equal fractions of increasing average boiling point, it is found that the quality of the fractions as a catalytic cracking feed stock decreases as the boiling point is increased. One would, therefore, except that, in order to obtain the maximum improvement with a limited hydrogenation of a portion of the feed rather than the whole, one should hydrogenate the heavier portion. For the purpose of comparison, the product values are shown in curve C in the graph for the case in which all of the available hydrogen is used to hydrogenate the heavier 50% of the same feed stock. It is seen that this alternative, contrary to expectation, is much less favorable in spite of the fact that the higher boiling 50% of the feed contributes the most towards coke make in the catalytic cracking operation.

Figure I of the attached drawing is a flow diagram illustrating the process. The process of the invention will be described in more detail with reference to a specific example. This example, which is typical of the situation confronted by refineries, is for the case of a refinery in Southern California processing California petroleum. For ease of consideration, the quantities given are those per 1000 barrels of crude intake. Referring to Figure I, 1000 barrels of desalted crude is charged to the topping section wherein it is topped to produce 240 barrels of straight-run gasoline and 760 barrels of straight-run residue. The straight-run gasoline is fractionated in the fractionation section to produce 105 barrels of light

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straight-run gasoline which requires no further treating other than a caustic wash, and 135 barrels of straight-run naphtha (ASTM boiling range 200–400° F.) which has an F-1 clear octane number of 57. This straight-run naphtha is passed into the reforming section wherein it is platformed to an octane number of 89 with the production of 730 s. c. f. of hydrogen per barrel of oil. The platforming operation is carried out under the following conditions:

Table II

Catalyst:	Pt./HF treated alumina
Average reactor pressure	p. s. i. g. 700
Average reactor temperature	° F. 800–920
Liquid hourly space velocity	3.0
H <sub>2</sub> /Feed mole ratio	6.0

The reformed naphtha is used for blending without further treatment.

The straight-run residue from the topping section is passed to the flashing section where it is vacuum flashed to produce 550 barrels of flashed distillate having the properties listed below in Table III and 210 barrels of pitch which is either thermally cracked, coked, or blended to fuel oil. The flashed distillate is passed to the fractionation unit wherein it is separated into 275 barrels of lower boiling flashed distillate and 275 barrels of higher boiling flashed distillate having the properties listed in Table III.

Table III

	Total Flashed Distillate	Light Flashed Distillate	Heavy Flashed Distillate
Gravity, ° API	23.1	27.0	18.4
Molecular Weight	341	282	425
Kinematic Viscosity at 100° F, Centistokes	50		
Percent w. Sulfur	1.3	1.0	1.6
Ramsbottom Carbon Residue, Percent w	0.7	0.1	1.3

The lower boiling flashed distillate fraction is passed to the hydrogenation unit wherein it is hydrogenated with the product gas from the platforming unit. The available hydrogen is 179 s. c. f. per barrel of total flashed distillate. The hydrogenation is effected under the conditions given in Table IV whereby the hydrogen uptake is 284 cubic feet per barrel of the light flashed distillate.

Table IV

Catalyst:	Tungsten nickel sulfide
Temperature	° F. 710
Pressure	p. s. i. g. 750
Liquid hourly space velocity	0.5
H <sub>2</sub> /Feed mole ratio	3.0

The unhydrogenated heavy flashed distillate and the hydrogenated light flashed distillate are combined and passed to the catalytic cracking unit wherein they are cracked in the conventional manner with a synthetic silica alumina composite catalyst under the following conditions:

Table V

Catalyst:	Synthetic silica-alumina
Temperature	° F. 930
Pressure	atm. ca 1
Liquid hourly velocity	0.68

The increase in the values of the products based on the above typical relative values of the individual product is 17¢ per barrel, compared to 11¢ per barrel for the case where the total distillate is hydrogenated with the same hydrogen consumption.

From the above, it will be seen that our invention is based upon the application of the unexpected finding that, in the utilization of by-product hydrogen to improve clean feed stock for catalytic cracking, it is ad-

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vantageous to react the available hydrogen with a part of the flashed distillate under relatively severe conditions and with a high hydrogen uptake per barrel of feed hydrogenated than to use the available hydrogen to treat the total feed at the same hydrogen consumption. While some improvement over hydrogenating the whole feed may be obtained by reacting the available hydrogen with a portion of the whole feed, or in the alternative, reacting the available hydrogen with only the higher boiling portion of the feed, an unexpected larger improvement in the product values is obtained if the available hydrogen is reacted with the lower boiling part of the total feed. An alternative application of the principle of the invention is to utilize the available hydrogen from the dehydrogenation of the straight-run naphtha in the hydrogenation of the lowest and part of the highest boiling portion of the catalytic cracking feed stock, leaving the middle portion unhydrogenated. This alternative, although more complicated from the feed preparation standpoint, has the additional advantage of allowing the desired increased product values to be obtained with a somewhat greater reduction in the coke make.

In general, the lower and higher boiling portions of the total feed may be separated by fractional distillation, but other methods may be used. For instance, it is possible and practicable to effect the separation by flash distilling the residue in two operations under different flashing conditions, in which case the material obtained from the first flashing operation is lower boiling than the material obtained by the second or subsequent flashing operation. Also, the lighter fraction may be obtained by a conventional flashing operation and the residue from this flashing operation may be subjected to a conventional desphalting treatment to produce a clean, substantially ash free heavier fraction. Especially when the hydrogenated portion of the feed is the lighter boiling part, the hydrogenated portion and the unhydrogenated portion are combined and catalytically cracked together, although they may be introduced into the catalytic cracking unit at the same or different feed points.

It is found that the hydrogen uptake per barrel of material hydrogenated is preferably between about 200 and 400 s. c. f. per barrel but hydrogen uptakes as low as 100 s. c. f. and up to about 700 s. c. f. per barrel can be used to some advantage. The split between the portion of the feed to be hydrogenated and the portion not to be hydrogenated therefore is preferably not arbitrarily set at 50:50 but is preferably adjusted such that the amount of material to be hydrogenated will consume the available hydrogen from the naphtha with hydrogen uptakes in the stated range.

In all cases where the hydrogen used is produced in the catalytic reforming of the straight-run gas or naphtha, the process of the invention provides a better and more profitable way of utilizing the by-product hydrogen from such reforming, since the available hydrogen in such cases is only sufficient to provide a relatively small hydrogen uptake based on the gas oil used as catalytic cracking feed stock.

We claim as our invention:

1. In the production of gasoline and related lighter products from petroleum involving the catalytic cracking of non-residual virgin petroleum oil boiling above gasoline, the improvement which comprises splitting said virgin oil destined for catalytic cracking into two portions A and B, the split being made such that portion A is between 1 and 7 barrels per 700 s. c. f. of the available hydrogen and comprises the lower boiling constituents of said oil, portion B being the remainder, catalytically and, non-destructively hydrogenating said portion A to a hydrogen uptake within 100-700 s. c. f. per barrel with an available supply of hydrogen which is insufficient to completely non-destructively hydrogenate the total amount of said oil and is limited in amount to a value in s. c. f.

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per barrel of total oil less than the value of said uptake, and catalytically cracking the thus hydrogenated portion A together with the remaining unhydrogenated portion B to produce gasoline and related by-products.

2. In the production of gasoline and related lighter products from petroleum involving the catalytic cracking of non-residual oil boiling above gasoline, the improvement which comprises fractionating petroleum to separate a straight-run gasoline fraction, a straight-run naphtha fraction and straight-run residue, catalytically reforming the straight-run naphtha fraction to produce a reformed naphtha and a product gas rich in hydrogen, separating from the straight-run residue a clean virgin oil boiling above gasoline as catalytic cracking feed stock, said oil being incapable of being completely non-destructively hydrogenated by said hydrogen, splitting said virgin oil destined for catalytic cracking into two portions A and B, the split being made so that portion A is between one and two barrels per 400 s. c. f. of the available hydrogen and comprises the lower boiling constituents of said oil, portion B being the remainder, catalytically and non-destructively hydrogenating said portion A with said hydrogen to a hydrogen uptake within 200 and 400 s. c. f. per barrel, and catalytically cracking the thus hydrogenated portion A simultaneously with the remaining unhydrogenated portion B to produce gasoline and related by-products.

3. In the production of gasoline and related lighter products from petroleum involving the catalytic cracking of non-residual petroleum oil boiling above gasoline and wherein the supply of hydrogen is limited to that obtained from the reforming of a straight-run naphtha taken from the same crude oil as said petroleum oil, the improvement which comprises flashing straight-run residue to produce a flashed distillate and a residue pitch, splitting the flashed distillate into a higher boiling virgin fraction and a lower boiling virgin fraction, the split being made so that the amount of low boiling fraction is between one and two barrels per 400 s. c. f. of the available hydrogen, catalytically and non-destructively hydrogenating the lower boiling fraction with the hydrogen to a hydrogen uptake within 200 and 400 s. c. f. per barrel, and catalytically cracking the hydrogenated portion combined with the remaining unhydrogenated portion to produce gasoline and related lighter products.

4. In the production of gasoline from petroleum involving separating from a petroleum a virgin flashed distillate, hydrogenating said flashed distillate and catalytically cracking the hydrogenated flashed distillate, and wherein the amount of hydrogen available is not enough to hydrogenate said flashed distillate to a hydrogen uptake above about 150 s. c. f. per barrel, the improvement which comprises splitting the virgin flashed distillate into a lower boiling fraction and a higher boiling fraction, the split being made so that the amount of lower boiling fraction is between 1 and 2 barrels per 400 s. c. f. of the available hydrogen, catalytically and non-destructively hydrogenating the lower boiling fraction to a hydrogen uptake between 200 and 400 s. c. f. per barrel, combining the hydrogenated lower boiling flashed distillate with the unhydrogenated higher boiling flashed distillate and subjecting the mixture to catalytic cracking.

5. The process according to claim 1 in which the portion of oil hydrogenated is composed of the lowest and the highest boiling constituents of the total virgin oil subjected to catalytic cracking.

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