

[54] CATALYTIC CRACKING PROCESS

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[22] Filed: **Apr. 14, 1972**

[21] Appl. No.: **244,249**

[57] **ABSTRACT**

Process for preparing high clear octane gasoline is provided comprising:

[52] U.S. Cl..... **208/70, 208/80, 208/93, 208/141**
[51] Int. Cl..... **C10g 37/10**
[58] Field of Search 208/70, 80, 65, 93, 141

- catalytically cracking a hydrocarbon feed stream at high conversion levels for the production of a $C_5/430^\circ\text{F}$. fraction;
- fractionating said $C_5/430^\circ\text{F}$. fraction to obtain a light fraction, e.g., a $C_5/180^\circ\text{F}$. fraction, an intermediate fraction, e.g., a $180^\circ/270^\circ\text{F}$. fraction, and a heavy fraction, e.g., a $270^\circ/430^\circ\text{F}$. fraction;
- reforming at least a portion of said intermediate fraction over a reforming catalyst to obtain a high octane reformat; and,
- blending said reformat with said light and heavy fractions to obtain a high clear octane gasoline.

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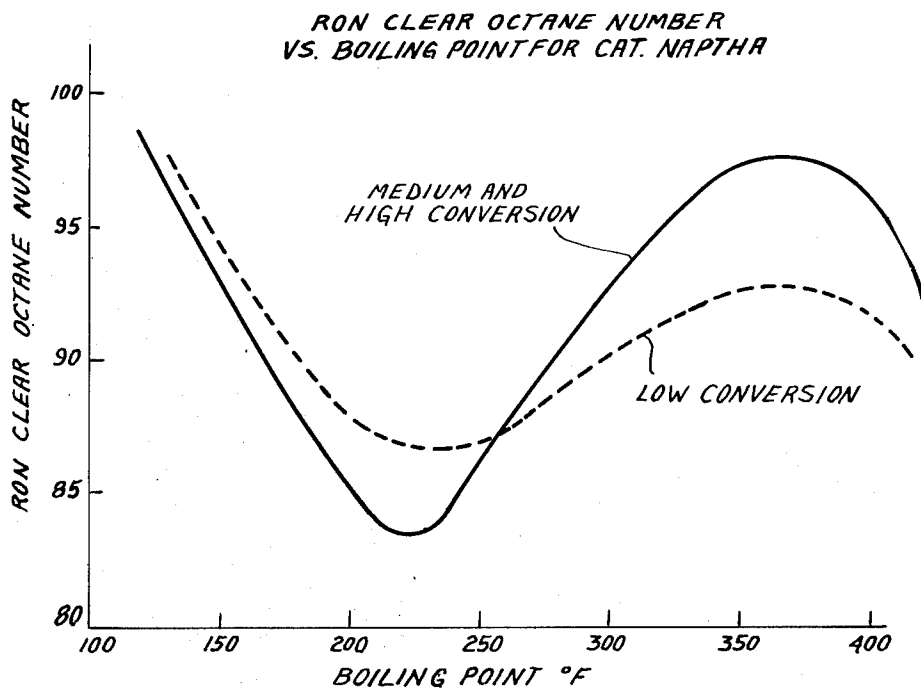
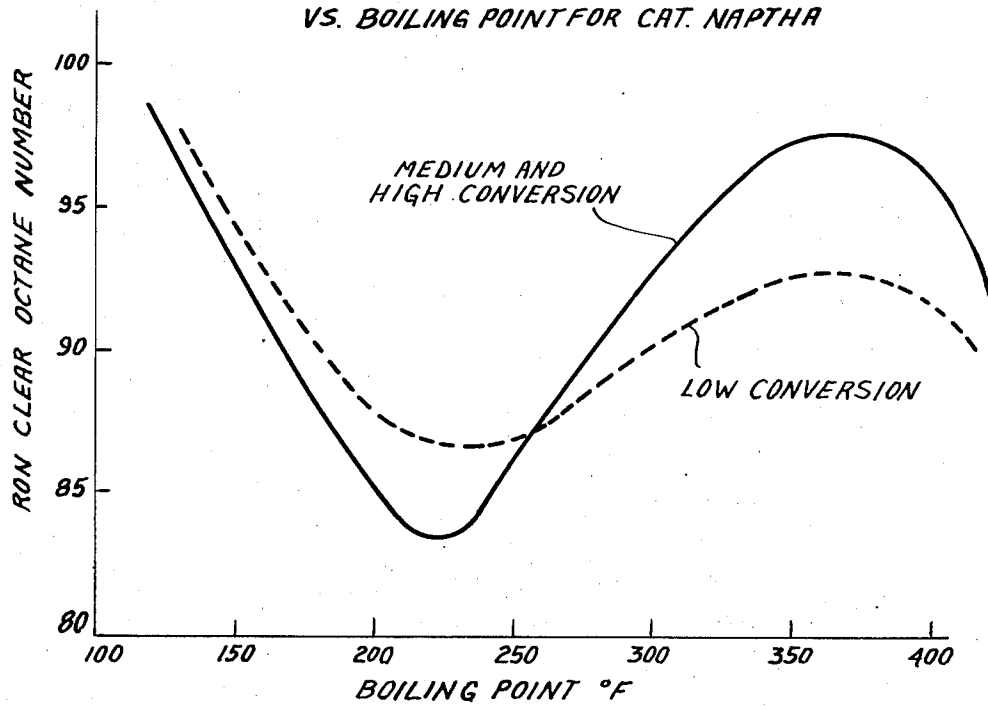
15 Claims, 2 Drawing Figures

Fig. 1.

RON CLEAR OCTANE NUMBER
VS. BOILING POINT FOR CAT. NAPHTHA



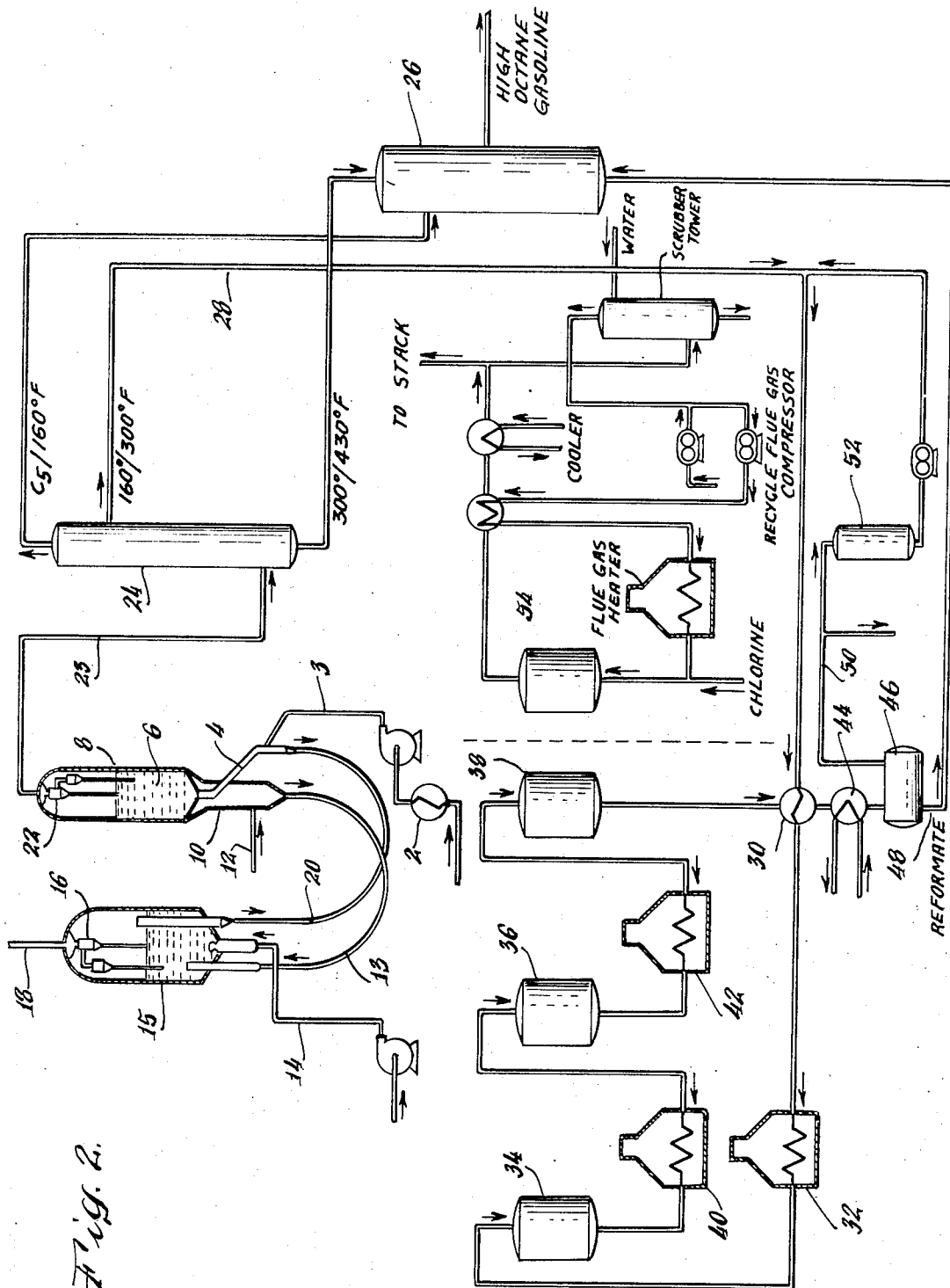


Fig. 2.

CATALYTIC CRACKING PROCESS

This invention relates to an improved catalytic cracking process. More particularly, this invention relates to a catalytic cracking process in combination with naphtha reforming to provide a high yield of high clear octane gasoline.

The demand imposed upon the automotive industry to redesign automobile engines to utilize a 91 RON clear gasoline has concomitantly imposed restrictions upon refiners to provide such fuel economically. Catalytic cracking normally provides a large share of the refiners total naphtha pool, but catalytically cracked naphtha is generally insufficient in clear octane number ratings to meet the 91 rating objective.

It is well known that the octane number of catalytically cracked naphtha is dependent upon a number of variables, for example, feedstock quality and composition, conversion level or cracking severity, catalyst type and composition and cracking temperature. For a given feedstock and catalyst, catalytic cracking operations can be controlled to obtain the maximum C₈/430°F. naphtha yield. Beyond this point further increases in cracking severity or conversion do not result in further increases in naphtha yield. In addition to the high yield of naphtha obtainable at these conditions, several key compositional effects occur which make the naphtha particularly amenable to the production of high clear octane mogas. The aromatic content of the naphtha increases with severity which improves naphtha octane. This is due to the refractory nature of aromatic rings and secondary cracking or reactions of the acyclics in the naphtha. Advantageously, however, the naphthenic content of the naphtha is not reduced at high severity. Thus, the naphthenic content can be easily reformed to high clear octane aromatics at low reformer severities. Additionally, the olefin content of the naphtha is greatly reduced at high severities. This is advantageous since olefins are potential atmospheric pollutants. Moreover, low olefin content permits reforming without prior hydrotreating, providing a sulfur tolerant reforming catalyst is employed.

It is an object of the present invention to employ these compositional effects in a combined high severity catalytic cracking-mild naphtha reforming process to provide a high yield of high clear octane gasoline.

It is another object of the present invention to provide a high yield of high clear octane gasoline without hydrofining by reforming a low octane naphtha heart-cut fraction with a sulfur tolerant catalyst.

It is still another object of the present invention to provide a process for preparing unleaded gasoline of high octane number by cracking a gas oil at high conversion levels, separating the relatively low octane intermediate fraction, particularly a 180°-270°F. fraction therefrom, reforming at least a portion of said fraction under mild conditions and blending the reformat back into the cat-cracked naphtha. The final gasoline so obtained is low in olefins with a high content of aromatics and isoparaffins and exhibits low potential for polluting air when burned.

These as well as other objects are accomplished by the present invention wherein a process is provided for preparing high clear octane gasoline comprising:

a. catalytically cracking a hydrocarbon feedstream in a cracking zone at high conversion levels for the production of a C₈/430°F. fraction;

b. fractionating said C₈/430°F. fraction to obtain a light fraction, particularly a C₅/180°F. fraction, an intermediate fraction, particularly a 180°/270°F. fraction and a heavy fraction, particularly a 270°/430°F. fraction;

c. reforming at least a portion of said intermediate fraction in a reforming zone over a reforming catalyst to obtain a high octane reformat; and,

d. blending said reformat with said light and heavy fractions to obtain a high clear octane gasoline.

The present invention will be more completely understood by reference to the drawing wherein:

FIG. 1 is a graphical representation of the variation in RON clear octane number versus boiling point for a catalytically cracked naphtha;

FIG. 2 is a schematic flow diagram illustrating one embodiment of the present invention.

It has been found in accordance with the present invention that the light and heavy fractions of a cat-naphtha, i.e., the C₅/180°F. and the 270°/430°F. fractions which constitute about 30-40 volume percent and 25-30 volume percent, respectively, of the total naphtha are of high octane; whereas, in sharp contrast, the intermediate portion (180°/270°F) is of very low octane. The light fraction is largely isopentane and C₅ olefins and the heavy fraction are largely aromatics, all being of fairly high octane. The intermediate portion, however, has been found to contain major amounts of naphthenes, a low octane material, per se, but one which can be readily reformed to aromatics. Thus, in accordance with the present invention, an intermediate fraction can be easily reformed even at very mild conditions to obtain a high octane product. It has also been found that the intermediate fraction must be separated from the light fraction of the total cat-naphtha prior to reforming since reforming of the light fraction will produce C₄'s and gas, thereby lowering C₅⁺ liquid yield.

It can be seen from FIG. 1 that a total catalytically cracked naphtha shows a very dramatic and surprising minimum in the octane versus boiling point curve in the range of about 180°/270°F., regardless of the degree of conversion, corresponding generally to the C₇ to C₉ molecular weight range among the cracked products. Moreover, it has been found that at high conversion levels (to 430°F.-), i.e., about 50-90 percent, depending upon the particular feed employed, the olefin content of the 180°/270°F. fraction is drastically reduced. This can be seen in Table I below which shows data obtained using a 650°-1,050°F. gas oil operating at 925°F. at various 430°F.- conversion levels with, in one instance, a 25 percent alumina-75% SiO₂ amorphous gel catalyst (A) and in another, a zeolite catalyst comprising 10% Mg-faujasite embedded in 90% silica gel (B).

TABLE I

Catalyst	A			B		
	65	76	81	53	72	90
Conversion (430°F.-)	65	76	81	53	72	90
Composition of Approx. C ₇ -C ₉ Cut						
Paraf. + Naph.	23	39	44	39	50	59
Olefins	58	24	11	38	30	9
Aromatics	19	37	45	23	20	32

The data show that as conversion increases above about 75 percent, there is a marked reduction in olefin content in this C₇ to C₉ fraction, a marked increase in aromatics and a rather large amount of saturates. Although not wishing to be bound by any theory or mechanism, it is currently believed that the relatively low clear octane numbers of this C₇-C₉ fraction result from the high proportion of naphthenes and paraffins present. In accordance with the present invention, this low octane fraction can be upgraded by reforming said fraction and subsequently reblending the reformate with the other high octane fractions from the cat-cracker to produce high quality gasoline.

Referring now to FIG. 2, there is illustrated a schematic arrangement of one method for conducting the process of the present invention. The feedstock which is preferably a low sulfur-containing feedstock such as, for example, a virgin gas oil feed, typically material boiling between 600°-1,050°F. FVT is preheated to somewhat below cracking temperatures in heater 2 and is then transferred to riser cracker 4 via line 3 and then to the dense bed of catalyst 6 contained within the fluid catalytic cracker shown generally as 8.

The preferred catalysts for use in the catalytic cracking unit are of the crystalline aluminosilicate zeolite types. In general, the chemical formula of the anhydrous crystalline zeolites employed in the present invention expressed in terms of moles may be represented as:



wherein Me is selected from the group consisting of metal cations, hydrogen and ammonia, *n* is its valence and *x* is a number above 3, e.g., 4 to 14, preferably 4.5 to 6.5. The zeolites include synthetic crystalline aluminosilicates, naturally occurring crystalline aluminosilicates and treated clays in which a substantial portion of the clay has been converted to crystalline zeolite. Synthetic materials include faujasites and mordenites. Natural materials are erionite, analcite, faujasite, Phillipsite, clinoptilolite, chabazite, gmelinite, mordenite and mixtures thereof containing or treated to contain 5-95 percent crystalline aluminosilicate having an ordered structure. All or a portion of the cations of the zeolites such as sodium cations can be replaced with hydrogen ions, ammonium ions or metal cations such as rare earths, manganese, cobalt, zinc and other metals of Group I to VIII of the Periodic Table. The catalyst can be one of the matrix types, i.e., one in which the zeolite crystals are coated with or encapsulated in a silica-alumina gel, silica gel, clay or mixtures thereof. Matrix catalysts contain 5-60 percent, preferably 5 to 20 percent crystalline zeolite. The catalyst is generally particulate in nature. The catalyst particles can be in the form of powder, granules, spray dried microspheres, or the like and may be of a size within the range of from about 5 to about 250 microns. The catalyst particles should be sufficiently uniform in particle size to permit easy handling and avoid any tendency to classify in the circulating catalyst system.

Hot, regenerated catalyst is admixed with the feed in the riser cracker 4 wherein it completes preheating of the charged feedstock which was partially preheated in heater 2. As the catalyst is mixed with the oil in the riser cracker 4, the oil is flash vaporized and forms a suspended fluidized catalyst-hydrocarbon mixtures

which is forced through the riser cracker 4 into the dense bed of catalyst 6 maintained within the reactor. In the reactor, the catalyst settles to a finite level and forms a fluidized bed, the depth of which regulates the time of reaction and can be varied to provide the desired degree of cracking. This bed is maintained in a fluid, turbulent condition by the entering feed vapors which continuously pass upwardly, thereby effecting contact of oil with catalyst and producing a substantially uniform temperature in the range of about 700°-1,200°F. and preferably 800°-1,000°F. with increasing temperature favoring cracking or conversion of feed to lower boiling products. The liquid hourly space velocity ranges between about 0.5-20 V/Hr./V, and preferably ranges from 1-8 V/Hr./V. The catalyst:oil ratio ranges between about 2:1 and 20:1 and can vary depending upon the type of process employed, e.g., a transfer line reactor or a riser cracker-dense bed, and upon the nature of the catalyst system, i.e., whether a fluid, moving bed or fixed bed is employed. Generally, higher catalyst:oil ratios reduce the extent of catalyst deactivation from coke production and increase the conversion of the feed to lower boiling products. The approximate pressure can range from sub-atmospheric to several atmospheres. Preferably, the pressure ranges from about 5-100 psig, and more preferably 5-20 psig. Increasing the pressure generally reduces the octane quality of the gasoline product and increases the production of coke at a given conversion level.

As cracking progresses, coke forms on the catalyst and reduces its activity. The spent catalyst laden with coke is continuously and automatically withdrawn through the stripping zone 10 at the bottom of the reactor where the absorbed and entrained feed vapors are stripped from the catalyst by countercurrent contact with a stripping gas admitted to the stripping zone through line 12. The stripped catalyst is passed via line 13 into regenerator 15. En route, the catalyst is picked up by a stream of air charged through line 14 and is carried into the regenerator wherein the carbon is burned off the catalyst at temperatures of about 1,100°F. or higher. The entrained catalyst is removed via cyclone 16 and flue gas exits via stack 18. The hot regenerated catalyst leaves the bottom of the regenerator taking with it much of the heat of combustion and is recycled via line 20 to the catalytic cracking unit.

The cracked products together with the stripping gas pass through cyclone 22 which collects entrained catalyst and returns it to the dense bed. Upon leaving cyclone 22, vapors pass from the reactor to fractionator 24 via line 23 which separates the catalytically cracked naphtha into three streams: a light fraction boiling in the C₅-180°F. range, an intermediate fraction locking in the 180°-270°F. range and a heavy fraction boiling in the 270°-430°F. range. The light fraction and the heavy fraction are sent directly to blending tank 26; whereas, the intermediate fraction can be fed directly to a reforming unit through line 28 wherein it is mixed with recycle gas and partially preheated by indirect heat exchange with the product stream in heat exchanger 30. Final preheat is obtained in the preheat furnace 32. The temperature to which the feed and recycle are heated in this furnace depends upon the condition of the catalyst. With a fresh or freshly regenerated catalyst, reactor inlet temperatures may be as low as 825°F. As coke is laid down on the catalyst, its activ-

ity decreases requiring a higher inlet temperature to maintain the same octane product. Thus, temperature is slowly raised over the on-stream period to maintain constant octane. The maximum reactor inlet temperature is set by rapid catalyst deactivation. This is generally in the range of about 1,000°F. Generally, temperatures in the reforming reactors range between 825°F. and 975°F. Preferably, however, reforming temperatures range between 925°F. to 975°F.

The reactants generally pass through at least one and generally several reforming reactors 34, 36 and 38 at space velocities ranging between about 1 to 5 W/Hr./W, at pressures between about 100–1,000 psig, preferably 200–800 psig, and at hydrogen rates between about 4,000–12,000 SCF/B.

The reforming reaction is largely an endothermic reaction. This heat of reaction is in the order of 200 to 350 BTU/lb., depending on the type of feed. Since the individual fixed bed reactors operate adiabatically, the high endothermicity of the reforming reactions, particularly in the lead reactors, results in a large temperature drop. As temperature falls, the reforming reaction rate decreases. Thus, to maintain a relatively high rate of reaction and keep catalyst requirements at a minimum, intermediate reheat furnaces 40 and 42 are required between each of the reactors.

After passage through the reactors, the reactants are cooled by heat exchange with the feed stream in heat exchanger 30. Final cooling is obtained in condenser 44. The gas-liquid stream then passes into a high pressure separator 46 from which unstabilized reformate is withdrawn through line 48 and the major portion of the gas is removed via line 50, dried in dryer 52 and then recycled. The excess gas, called "make" or "tail" gas, then flows to an absorber (not shown) for recovery of C₄ and heavier hydrocarbons. The reformate passes via line 48 to blending tank 26 wherein it is blended with both the light fraction and the heavy fraction from fractionator 24 to form a high octane gasoline product.

When regeneration of the catalyst in a reforming reactor is necessary, a swing reactor 54 is manifolded to the reforming system to replace the reactor which is to be regenerated. When a reactor is to be regenerated, it is taken off stream and replaced by the swing reactor 54. The reactor to be regenerated is first purged with recycle gas and then with flue gas from an inert gas generator. After purging, flue gas is circulated through the regeneration equipment and air is added. Flame front temperatures are limited to about 1,000°F. After the carbon burns, oxygen content of the flue gas is generally increased to about 6 percent and the catalyst is dried, chlorine treated and purged before it is replaced on stream.

Conventional reforming catalysts can be employed, for example, deposits of activated alumina with minor proportions of platinum, palladium, rhodium, molybdenum oxide, vanadium oxide or chromium oxide can be employed. Preferably, the catalysts comprise activated alumina containing minor proportions of halogen such as chlorine, fluorine and the like and minor proportions, for example, from about 0.05 percent to about 1 percent, of platinum. Platinum supported on steam activated silica or silica-alumina can also be employed. Because of the relative mildness of the reforming reaction, other catalysts which are sulfur-tolerant and can be employed to advantage comprise mixtures of Group VI and iron group metals, e.g., cobalt molybdate sup-

ported on activated alumina, bauxite or other clays. Such catalysts generally contain from about 2 percent to about 8 percent by weight CoO, and between from about 4 percent to about 20% MoO₃. Additionally, sulfided platinum or molybdenum can be employed.

Employing the process of the present invention, gasoline having research clear octane values of 95 and higher can be readily achieved. Thus, for example, the naphthene content of a 180°/270°F. mid-boiling naphtha cut obtained by cracking a South Louisiana gas oil over an equilibrium zeolite catalyst (comprising a mixture of a zeolite in a matrix of silica-alumina plus clay) to an 80 volume percent 430°F. conversion is about 30%. The octane improvement in this cut obtained by reforming at low severity to convert naphthenes to aromatics in accordance with the present invention is about 7 RON numbers, or an increase from 88 to 95 RON. Aromatic content thereby increased from approximately 20 percent to about 50 percent by volume.

Other modifications of the present invention will occur to those skilled in the art upon a reading of the present disclosure. For example, although reforming of the catalytically cracked low octane fraction, e.g., a 180°/270°F. fraction is described herein, this fraction can instead be blended with regular reformer feed with the reformate product again blended with the light and heavy cat cracked naphtha fractions to accomplish the purposes of the present invention.

Also, instead of passing the entire catalytically cracked low octane, or 180°/270°F. fraction, to the reformer, it can be extracted to remove the aromatics which can be directly blended with the light and heavy fractions. In this manner, only the raffinate is sent to reforming. The reformate is then blended with the light and heavy fractions and the aromatic extract.

These as well as other modifications are intended to be included within the scope of this invention.

What is claimed is:

1. Process for preparing high clear octane gasoline comprising:

- a. catalytically cracking a hydrocarbon feed stream at conversion levels ranging from about 50–90% (to 430°F.) for the production of a C₅/430°F. fraction;
- b. fractionating said C₅/430°F. fraction to obtain a light C₅/180°F. fraction, an intermediate 180°/270°F. fraction of low octane and a 270°/430°F. heavy fraction;
- c. reforming said intermediate fraction by direct passage, without a diluent, over a reforming catalyst to obtain a higher octane reformate; and,
- d. blending said reformate with said light and heavy fractions to obtain a high clear octane gasoline.

2. Process for preparing high clear octane gasoline comprising:

- a. catalytically cracking a hydrocarbon feed stream at conversion levels ranging from about 75–90 percent (to 430°F.) for the production of a C₅/430°F. fraction;
- b. fractionating said C₅/430°F. fraction to obtain a light C₅/180°F. fraction, an intermediate 180°/270°F. fraction, and a 270°/430°F. heavy fraction;
- c. reforming at least a portion of said intermediate fraction over a reforming catalyst by direct pas-

sage, without a diluent, to obtain a high octane reformat; and,

d. blending said reformat with said light and heavy fractions to obtain a high clear octane gasoline.

3. Process as defined in claim 1 wherein the intermediate fraction is extracted to form an aromatic extract and a raffinate, the aromatic extract is blended with said light and heavy fractions, the raffinate is reformed over a reforming catalyst to obtain a high octane reformat, and said reformat is blended with said light and heavy fractions and said aromatic extract to obtain a high clear octane gasoline.

4. Process as defined in claim 1 wherein catalytic cracking is effected at temperatures ranging from 700° to about 1,200°F.

5. Process as defined in claim 1 wherein the liquid hourly space velocity within the cracking zone ranges between about 0.5 and 20 V/Hr./V.

6. Process as defined in claim 1 wherein the catalyst:oil ratio ranges between about 2.1 and 20:1.

7. Process as defined in claim 1 wherein the pressure within the cracking zone ranged from about 5 to about 100 psig.

8. Process as defined in claim 1 wherein the catalyst employed in the cracking zone comprises a crystalline aluminosilicate zeolite.

9. Process as defined in claim 1 wherein the temperature within the reforming zone ranges between about 825°F. and 1,000°F.

10. Process as defined in claim 1 wherein the space velocity of the reactants in the reforming zone ranges between about 1 to 5 W/Hr./W.

11. Process as defined in claim 1 wherein the pressure within the reforming zone ranges between about 100 to 1,000 psig.

12. Process as defined in claim 1 wherein the hydrogen rate to the reformer zone ranges between about 4,000 to 12,000 SCF/B.

13. Process as defined in claim 1 wherein the catalyst employed in the reforming zone comprises activated alumina with from about 0.05% to about 1% of platinum and from about 0.05 percent to about 1 percent of a halogen.

14. Process as defined in claim 1 wherein the catalyst employed in the reforming zone comprises a mixture of Group VI and iron group metals supported on activated alumina.

15. Process as defined in claim 1 wherein the intermediate fraction is blended with reformer feed prior to reforming.

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