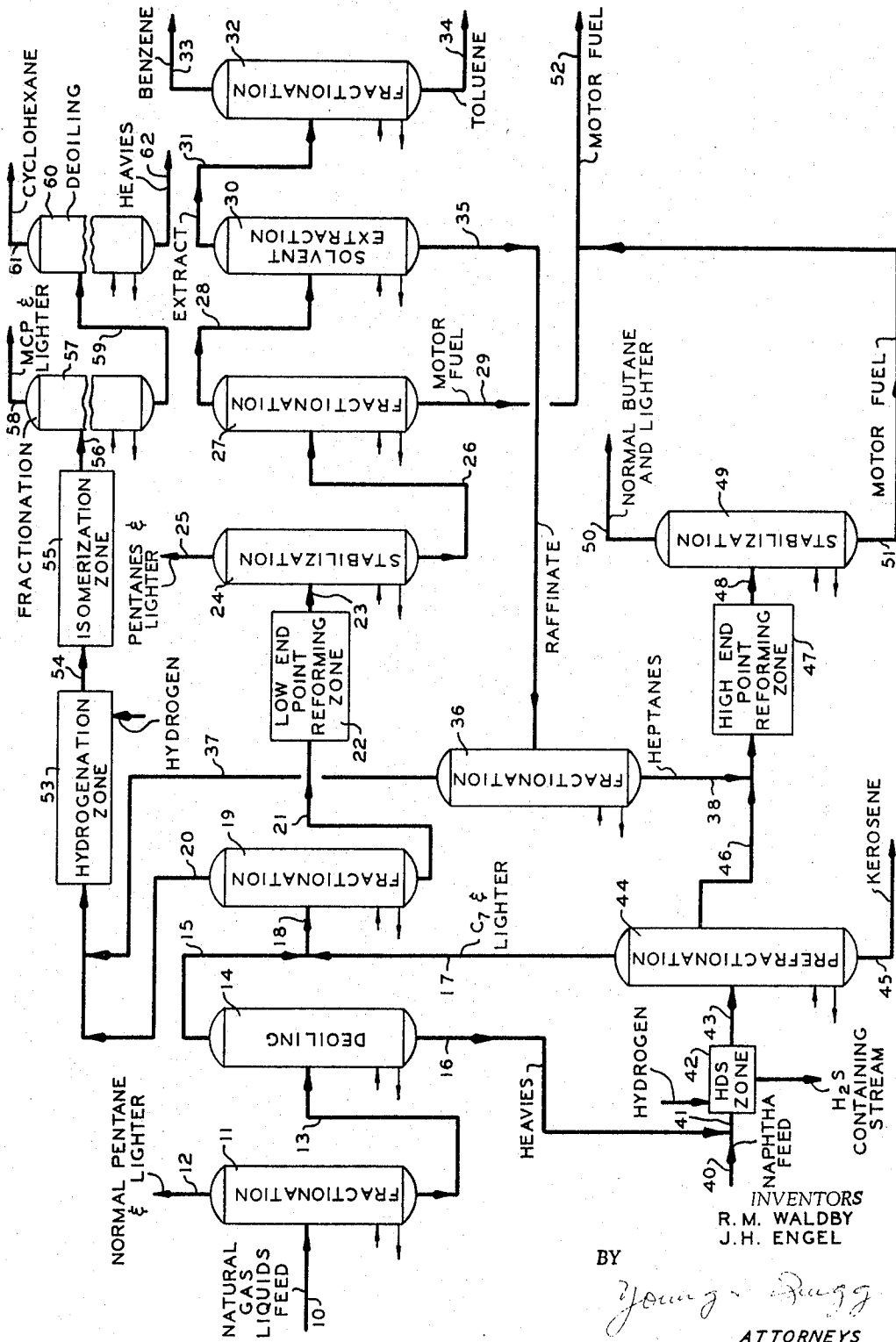


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DEHYDROCYCLIZATION PROCESS FOR PRODUCING A HIGH  
OCTANE GASOLINE AND AROMATICS  
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**DEHYDROCYCLIZATION PROCESS FOR PRODUCING A HIGH OCTANE GASOLINE AND AROMATICS**

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This invention relates broadly to the treatment of hydrocarbon mixtures. In another aspect, this invention relates to process and apparatus for upgrading gasoline hydrocarbon mixtures. In another aspect, this invention relates to a novel combination of steps comprising reforming, fractionation, solvent extraction, hydrogenation and isomerization. In still another aspect, the invention relates to process and apparatus for producing high yields of benzene, toluene, cyclohexane, and gasoline hydrocarbon mixtures (motor fuels) from commonly available process streams.

Because of the rapid and relatively recent growth of the petrochemical industry, demand for certain bulk chemicals of relatively high purity has increased to the point where it is more economically attractive to produce these chemicals than others which were in former demand. Among these chemicals of present demand are benzene, toluene and cyclohexane. As known to the art, these chemicals are valuable, for example, as solvents, reaction media and polymer starting materials. There is a substantial need in the art for processes and apparatus suitable for producing increasing quantities of these named chemicals from commonly available process, e.g., refinery streams.

In a refining situation wherein such factors as the high cost of crude petroleum oils and upward trends in the quality of gasoline-type motor fuels are present, it is essential from an economic standpoint that consideration be given to upgrading the several gasoline components that have inferior performance characteristics. The C<sub>2</sub> and heavier, normally gaseous olefins can be polymerized or alkylated to produce blending stocks of high octane number. The virgin naphtha fraction containing heptane and higher boiling hydrocarbons, having an end boiling point of about 400° F., normally is subjected to catalytic reforming to provide an aromatic blending material having an improved octane number. The fuel requirements of high-output, high-speed, spark-ignited internal combustion engines with high compression ratios make it necessary to refine more selectively the various liquid hydrocarbon constitutes boiling in the gasoline range. Thus, it can be seen that there is a distinct need in the industry for improved processes whereby low quality or low octane gasoline fractions are upgraded to meet present day product specifications.

The present invention provides a novel, integrated refining process for upgrading various hydrocarbon mixtures, especially gasoline fractions, derived from naphtha-containing streams.

Accordingly, it is an object of this invention to provide process and apparatus for producing increased quantities of benzene, toluene, cyclohexane and gasoline hydrocarbon mixtures.

Another object of this invention is to provide a novel combination of steps whereby commonly available refinery streams can be processed to produce increased quantities of relatively high purity benzene, toluene, cyclohexane, and high octane gasoline hydrocarbons.

A further object of this invention is to provide a novel integrated refining process for upgrading naphtha streams whereby a gasoline stock having excellent road perfor-

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mance and containing a desirable content of aromatic hydrocarbons is produced.

Other aspects, objects, and the several advantages of the invention will become apparent to one skilled in the art upon a study of this disclosure, drawing, and the appended claims.

According to the invention there is provided process and apparatus for upgrading hydrocarbons which comprises reforming a feed stream in a first reforming zone to produce a reformate stream, recovering from the said reformate stream a paraffin-containing stream, and reforming a second feed stream along with said paraffin-containing stream in a second reforming zone to produce a second reformate stream, and recovering an upgraded gasoline hydrocarbon product from the second reformate.

In one embodiment, the present process comprises separately reforming a light naphtha and a heavy naphtha, recovering a C<sub>7</sub> paraffinic fraction from the reformate from the light naphtha reforming, and charging the paraffinic fraction along with the heavy naphtha to a heavy naphtha reformer to produce additional aromatics, e.g., toluene thus, upgrading the gasoline hydrocarbon product recovered from the heavy naphtha reformate.

According to another embodiment of the invention, there is provided process and apparatus for upgrading hydrocarbons, e.g., light naphthas and heavy naphthas, which process comprises reforming a light naphtha stream in a first reforming zone to produce a first reformate stream, solvent extracting said first reformate stream to produce an extract stream comprising benzene and toluene and a raffinate stream comprising paraffins and naphtheness, separating said extract stream into a high purity benzene product stream and a high purity toluene product stream, separating said raffinate stream into a paraffin-containing stream and a naphthene-containing stream, hydrogenating and isomerizing said naphthene containing stream, separating from the thus hydrogenated and isomerized stream a high purity cyclohexane product, reforming a heavy naphtha stream together with the paraffin-containing stream recovered from said first reformate in a second reforming zone to produce a second reformate stream, the paraffins in the feed stream to the second reforming zone being dehydrocyclized to toluene, and recovering from said second reformate stream an upgraded motor fuel (gasoline hydrocarbon mixture).

For a more complete understanding of the invention, reference is now made to the accompanying drawing which represents in schematic detail a presently preferred form of the invention.

Referring now to the drawing, a feed stream comprising natural gas liquids is passed to fractionator 11 by way of line 10. Feed stream 10 is separated in fractionator 11 into a normal pentane and lighter stream removed overhead by way of line 12 and a bottoms stream removed by way of line 13. Stream 12 can be further separated, if desired. Residual stream 13 is deoiled in column 14, with the heavy ends being removed by way of line 16 and an overhead fraction (heart cut of feed 10) removed by way of line 15, which is passed by way of line 18 to fractionation zone 19. The feed stream in line 18 passed to fractionator 19 is separated into an overhead stream comprising methylcyclopentane and lighter materials (but including some benzene) removed by line 20 and a bottoms fraction comprising light naphtha removed by line 21, the latter stream being passed as feed to low end-point reforming zone 22. The light naphtha stream in line 21 is comprised principally of cyclohexane, 2,2-dimethylpentane, and 2,4-dimethylpentane, and other seven carbon hydrocarbons.

Low end-point reforming zone 22 is operated, as known in the art, to convert paraffins and naphthenes present

in the feed to aromatics and higher octane isomers, and can comprise Platforming, Ultraforming, Houdriforming, or other known reforming operations. The low end-point reforming operation can be operated in the temperature range of 700 to 1000° F., preferably from about 800 to about 950° F., and a pressure range of 0 to 1000 p.s.i.g., preferably 200 to 600 p.s.i.g. The hydrogen used is usually 0.5 to 20 mols per mol of feed, preferably 1 to 6. The catalyst is ordinarily a platinum-type reforming catalyst, that is, alumina impregnated with between 0.1 and 5 weight percent platinum, preferably 0.1 to 1 weight percent, and containing fluorine and/or chlorine.

The reformate formed in low end-point reforming zone 22 is passed by way of line 23 to stabilization zone 24. In stabilization zone 24, excess hydrogen resulting from the reforming and lighter fractions of the reformate, for example pentanes and lighter hydrocarbons, are removed by way of line 25. The resulting bottoms stream comprising a mixture of C<sub>6</sub> and heavier paraffins, naphthenes, and aromatics is passed by way of line 26 to fractionation zone 27 wherein a bottoms stream comprising C<sub>8</sub> and heavier hydrocarbons (motor fuel) is removed by way of line 29. The latter stream can be utilized as a gasoline product or, for example, as a blending stock. The remaining stream taken overhead from fractionator 27 by way of line 28 comprises C<sub>6</sub> and C<sub>7</sub> paraffins, naphthenes and aromatics, and is passed to solvent extraction zone 30. Solvent extraction zone 30 can comprise one of the many known processes for selective separation of hydrocarbon types, such as extraction with liquid SO<sub>2</sub> or glycol-type solvents. The aromatic extract stream thus produced is passed by way of line 31 to fractionation zone 32 and is there separated into a high purity benzene product stream removed by way of line 33 and a high purity toluene stream removed by way of line 34.

According to the invention, the raffinate stream removed from solvent extraction zone 30 by way of line 35 is passed to fractionation zone 36. This stream comprises C<sub>6</sub> and C<sub>7</sub> paraffins and naphthenes and is separated in fractionator 36 to produce an overhead fraction comprising methylcyclopentane and lighter materials removed by line 37 and a bottoms stream comprising C<sub>7</sub> paraffins removed by way of line 38. The bottoms stream removed from fractionator 36 is a low octane gasoline stream principally comprised of normal heptane and isoheptanes. It is normal practice to utilize this stream as a gasoline blending stock. However, according to the invention, this stream is passed to a high end-point reforming zone (zone 47), which is described hereinbelow, to dehydrocyclize the C<sub>7</sub> paraffins to toluene and upgrade the resulting gasoline product recovered from the reformate.

A high end-point naphtha stream is passed by way of lines 40 and 41 to hydrodesulfurization unit 42 to remove sulfur in the feed. The residual or heavy materials removed from the base of deoiling zone 14 by line 16 is also combined with the high end-point naphtha feed in line 40. Hydrodesulfurization zone 42 is operated, as known in the art, to desulfurize hydrocarbon fractions in the presence of hydrogen and employing well known catalysts such as a cobalt-molybdate type desulfurization catalyst. The desulfurized hydrocarbon effluent removed from zone 42 is passed by way of line 43 to fractionation zone 44 wherein an overhead fraction comprising C<sub>7</sub> and lighter hydrocarbons is passed by way of line 17 to fractionation zone 19 previously described. A bottoms fraction comprising kerosene is removed from zone 44 by way of line 45. A high end-point heart cut naphtha fraction to be reformed is removed from fractionation zone 44 by way of line 46 and passed along with the C<sub>7</sub> paraffins recycled from the low end-point reforming zone in line 38 to a high end-point reforming zone 47.

The high end-point reforming zone 47 is operated, as known in the art, to convert paraffins and naphthenes present in the feed to aromatics and can comprise Plat-

forming, Ultraforming, Houdriforming, or other known reforming operations. The high end-point reforming zone is ordinarily operated in the temperature range of 700 to 1000° F., preferably at about 800 to 950° F., and in a pressure range of 0 to 1000 p.s.i.g., preferably 300 to 700 p.s.i.g. The hydrogen used is usually 1 to 20 mols per mol of feed, preferably 2 to 10. The catalyst is the same as described with respect to the low end-point reforming zone.

The reformate removed by line 48 from reforming zone 47 is passed to stabilization zone 49. The reformate contains toluene formed in zone 47 from 2,2-dimethylpentane, 2,4-dimethylpentane and other C<sub>7</sub>'s recycled by way of line 38 from reforming zone 22 effluent. An overhead fraction comprising C<sub>4</sub> hydrocarbons and lighter materials is removed overhead from zone 49 by way of line 50. A high octane gasoline product stream is removed as bottoms from zone 49 by way of line 51. As illustrated in the drawing, the gasoline fraction removed from the base of fractionator 27 and the base of stabilizing zone 49 can be combined and passed to further processing, as desired, by way of line 52.

An overhead fraction comprising methylcyclopentane and some cyclohexane is removed overhead from fractionator 36 by way of line 37. The fraction in line 37 and the C<sub>6</sub> hydrocarbon fraction removed overhead from fractionation zone 19 by way of line 20 are passed to hydrogenation zone 53. The feed passed to hydrogenation zone 53 is hydrogenated so as to effect saturation of residual unsaturation in the stream and results primarily in the formation of cyclohexane from benzene. The resulting stream is passed by way of line 54 to isomerization zone 55 wherein generally normal paraffins are isomerized to isoparaffins, and alkyl naphthenes such as methylcyclopentane are isomerized to unsubstituted naphthenes such as cyclohexane. The isomerized stream is passed by way of line 56 to fractionation zone 57, wherein methylcyclopentane and lighter (isohexanes and normal hexane) is passed overhead by way of line 58 to further processing as desired. The bottoms from fractionation zone 57 is passed by way of line 59 to deoiling zone 60, wherein a high purity cyclohexane product is separated overhead and passed to further utility by way of line 61. The heavy fraction, which can be used as a gasoline blending stock, is recovered from the base of column 60 by way of line 62.

Benzene hydrogenation in zone 53 is effected at temperatures ordinarily ranging from 370 to 500° F., and at pressures ranging from 400 to 500 p.s.i.g., and hydrogen-to-aromatics mol ratios in the range of 5:1 to 12:1. The catalyst ordinarily used is a nickel hydrogenation catalyst, e.g., nickel on kieselguhr, the nickel content ranging from 20 to 55 weight percent nickel. However, other catalysts and other conditions can be used when desired.

The isomerization process in zone 55 is ordinarily effected at a temperature ranging from 80 to 170° F., preferably from 100 to 150° F. The pressures used are 160 to 200 p.s.i.g., preferably 170 to 190 p.s.i.g. The catalyst ordinarily used is an aluminum chloride complex promoted by hydrochloric acid.

The solvent extraction and fractionation steps illustrated in the drawing are operated as known in the art to make the disclosed separations. With regard to the description of the drawing, for simplicity and ease of understanding, only essential major processing equipment and flow lines have been shown. Conventional pumps, heat exchangers, overhead accumulators, tanks, etc. that are not shown are understood to be used throughout where required.

A better understanding of the invention will be obtained upon reference to the following illustrative example which should not be interpreted as being unduly limitative of the invention.

## EXAMPLE

In a commercial operation, a typical operation as set out in the table hereinbelow, in accordance with the drawing, a low end-point  $C_7$  hydrocarbon portion is subjected to catalytic reforming in a low end-point reforming zone. The feed to the low end-point reforming zone is comprised principally of cyclohexane, 2,2-dimethylpentane, 2,4-dimethylpentane, and the like. The reformate from the low end-point reforming zone is subjected to a series of separations as described in connection with the drawing to separate out a stream comprising pentanes and lighter materials, a gasoline hydrocarbon fraction, an extract comprising benzene and toluene, and a raffinate comprising methylcyclopentane, cyclohexane, and  $C_7$  hydrocarbons.

The raffinate stream is subjected to fractionation to separate overhead methylcyclopentane and cyclohexane. A  $C_7$  stream is recovered as bottoms.

The high end-point naphtha feed comprising  $C_8$  hydrocarbons to 400° end point is passed as feed to a high end-point catalytic reforming zone. The bottoms from fractionator 36 are combined with the high end-point naphtha feed and passed to reforming zone 47. The total gasoline fraction is recovered in line 51 from the reformate from zone 47.

TABLE.—TYPICAL OPERATION  
[Liquid volume percents]

Stream Number	10	15	17	20	37	21	29	61	33	34	35	51	38 <sup>1</sup>	46					
	Feed	De-oiler overhead	Pre-fract. overhead	Fract. overhead	Fract. overhead	Feed to low end point reformer	Motor fuel	Cyclohexane product	Benzene product	Toluene product	Raffinate	Motor fuel	Fract. bottoms	Heart-cut					
Components:																			
Normal pentane and lighter		0.2	20.5	0.7															
Isohexanes		10.7		24.6	11.3							2.0							
Normal hexane		15.4		49.2	11.0							2.0	0.1						
Methylcyclopentane		6.1		18.3	52.5			0.2	0.2		10.4		1.6						
2,2-dimethylpentane		0.9	79.5	0.3	14.3			0.7			7.0		5.5						
2,4-dimethylpentane																			
2,2,3-trimethylbutane																			
Benzene		2.1		6.3	0.8				99.8	0.9	0.1			Trace					
Cyclohexane		5.5		0.6	2.7			98.7			1.4		1.2	0.1					
Isoheptanes		11.4			7.0			0.4			53.1		62.8	0.4					
Normal heptane		8.9			0.1						13.1		15.7	0.5					
Dimethylcyclopentane		4.0			0.3						6.2		7.4	0.2					
Toluene		3.5							Trace	99.1	2.1		2.6	0.2					
Isooctanes and heavier		31.3									2.6		3.1	98.6					
Total		100.0	100.0	100.0	100.0			100.0	100.0	100.0	100.0		100.0	100.0					
Total flow, bbl./day	38,500	21,400	1,200	7,150	720	15,450	5,400	2,000	700	600	4,150	13,400	3,430	12,000					
Research octane, 3 cc. TEL							99.0					96.5	81.5						
Purity, vol. percent								98.7	99.8	99.1									

<sup>1</sup> Conventionally yielded as gasoline product or product blend component.

It will be observed from the example and the table that by conventionally yielding gasoline stream 38 directly to product or to product blending, there are 3,430 barrels per day of gasoline, but the octane (research octane number with 3 cc. TEL) is but 81.5. However, when operating in accordance with this invention, the 3,430 barrels per day yields 2,744 barrels per day of 92.0 octane gasoline (research octane number with 3 cc. TEL). Approximately 20 percent of the stream 38 is processed to normal butane and lighter hydrocarbons in this upgrading step. This 2,744 barrels per day of high octane gasoline is included in the total (stream 51) reformed gasoline of 13,400 barrels per day of 96.5 octane gasoline.

Thus, it can be seen that a substantial upgrading in the octane value of a reformed gasoline product is obtained according to the invention as well as yielding high purity benzene, high purity toluene and high purity cyclohexane product streams.

Having thus described the invention by providing a specific example thereof, it is to be understood that no undue limits or restrictions are to be drawn by reason thereof and that many variations and modifications thereof are within the scope of the invention.

We claim:

1. A process for upgrading a plurality of hydrocarbon mixtures which comprises the steps of:

- (1) in a first reforming zone, reforming a feed comprising a low end-point reforming feed containing paraffins, naphthenes, and aromatics;
- (2) separating the reformate of step (1) into a  $C_4$  and lighter product stream, a gasoline product, and a  $C_6$ -containing stream;
- (3) separating by solvent extraction the  $C_6$ -containing stream of step (2) into a benzene and toluene-containing extract product stream and a paraffin and naphthene-containing raffinate stream;
- (4) separating the raffinate stream of step (3) into a methylcyclopentane and lighter stream and a  $C_7$  and heavier paraffin-containing stream;
- (5) in a second reforming zone reforming a feed comprising a high end-point reforming feed containing paraffins, naphthenes, and aromatics;
- (6) admixing the  $C_7$  and heavier paraffin-containing stream obtained in step (4) with the feed passed to said second reforming zone to make additional aromatics from said  $C_7$  paraffin-containing stream by dehydrocyclization; and

(7) separating the reformate of step (5) into a  $C_4$  and lighter product stream and an upgraded gasoline product.

2. A process for upgrading a plurality of hydrocarbon mixtures which comprises the steps of:

- (1) in a first reforming zone reforming a feed comprising a low end-point reforming feed containing paraffins, naphthenes, and aromatics;
- (2) separating the reformate of step (1) into a  $C_4$  and lighter product stream, a gasoline product stream, a benzene and toluene-containing stream, a methylcyclopentane and lighter stream, and a  $C_7$  and heavier paraffin-containing stream;
- (3) in a second reforming zone reforming a high end-point reforming feed stream containing paraffins, naphthenes and aromatics having admixed therewith said  $C_7$  paraffin stream obtained in step (2); and
- (4) separating from the reformate of step (3) an upgraded gasoline product.

3. A process for upgrading a plurality of hydrocarbon mixtures which comprises the steps of:

- (1) separating a natural gas liquids feed stream into a  $C_5$  and lower light product stream, a heavy ( $C_8$ )

- fraction, a C<sub>6</sub> product stream, and a C<sub>7</sub> fraction comprising paraffins, naphthenes, and aromatics;
- (2) in a first reforming zone reforming a feed comprising said C<sub>7</sub> fraction in a low end-point reforming zone;
- (3) separating the reformate of step (2) into a C<sub>4</sub> and lighter product stream, a gasoline product, and a C<sub>6</sub>-containing stream;
- (4) separating by solvent extraction the C<sub>6</sub>-containing stream of step (3) into a benzene and toluene-containing extract product stream and a paraffin and naphthene-containing raffinate stream;
- (5) separating the raffinate stream from step (4) into a methylcyclopentane and lighter stream and a C<sub>7</sub> and heavier paraffin-containing stream;
- (6) subjecting the naphtha-containing feed together with heavies of step (1) to hydrodesulfurization;
- (7) separating the effluent from step (6) into a C<sub>7</sub> and lighter stream, a kerosene fraction, and a high end-point reforming feed stream;
- (8) providing said high end-point reforming feed stream of step (7) with the C<sub>7</sub> paraffin stream contained in step (5);
- (9) in a second reforming zone reforming the combined stream of step (8) in a high end-point reforming zone; and
- (10) separating the reformate of step (9) into a C<sub>4</sub> and lighter product stream and an upgraded gasoline product stream.
4. The process of claim 3 characterized in that the C<sub>6</sub> fraction contained in step (1) and the methylcyclopentane-containing stream contained in step (5) are subjected to hydrogenation and isomerization to form cyclohexane.
5. The process of claim 3 characterized in that the gasoline fraction contained in step (3) and the gasoline fraction contained in step (10) are combined as a high octane motor fuel blend.
6. In a process for catalytic reforming wherein a C<sub>7</sub> hydrocarbon-containing fraction separated from natural gas liquid is passed into a first reforming zone under reforming conditions in the presence of hydrogen to produce a

- first effluent containing hydrogen, light hydrocarbons and gasoline hydrocarbons, said effluent being separated into a first stream containing C<sub>4</sub> and lighter materials, a second stream containing gasoline hydrocarbons, a third stream containing aromatic hydrocarbons, a fourth stream containing methylcyclopentane and cyclohexane, and a fifth stream containing C<sub>7</sub> paraffins, the improvement which comprises passing a high end-point naphtha fraction together with said fifth stream to a second reforming zone under reforming conditions in the presence of hydrogen to produce a second effluent containing hydrogen, light hydrocarbons and gasoline hydrocarbons, and separating from said second effluent a C<sub>4</sub> and lighter and a high-quality gasoline hydrocarbon fraction.
7. A refining process for upgrading gasoline hydrocarbon fractions which comprises the steps of:
- (1) reforming a heptane-containing stream to yield benzene, toluene, naphthenes and paraffins;
- (2) separating from said reforming special octanes and heavier as motor fuel, benzene, toluene, methylcyclopentane-containing stream and a C<sub>7</sub> paraffin stream substantially free of aromatics, passing the methylcyclopentane-containing stream to hydrogenation and isomerization to form cyclohexane;
- (3) purging said C<sub>7</sub> paraffins along with a high end-point naphtha feed to high end-point reforming zone to dehydrocyclize C<sub>7</sub>'s into additional toluene and upgrade the reformate; and
- (4) separate from the reformate from said second reforming a high quality motor gasoline product.

## References Cited by the Examiner

## UNITED STATES PATENTS

2,005,770	10/1961	Lutz	208—140
3,013,088	12/1961	Merryfield	208—79
3,121,676	2/1964	Skraba	208—79

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