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[54] PRODUCTION OF MOTOR FUEL-BLENDING COMPONENTS

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[58] **Field of Search** .....208/62, 57, 87; 260/666 P

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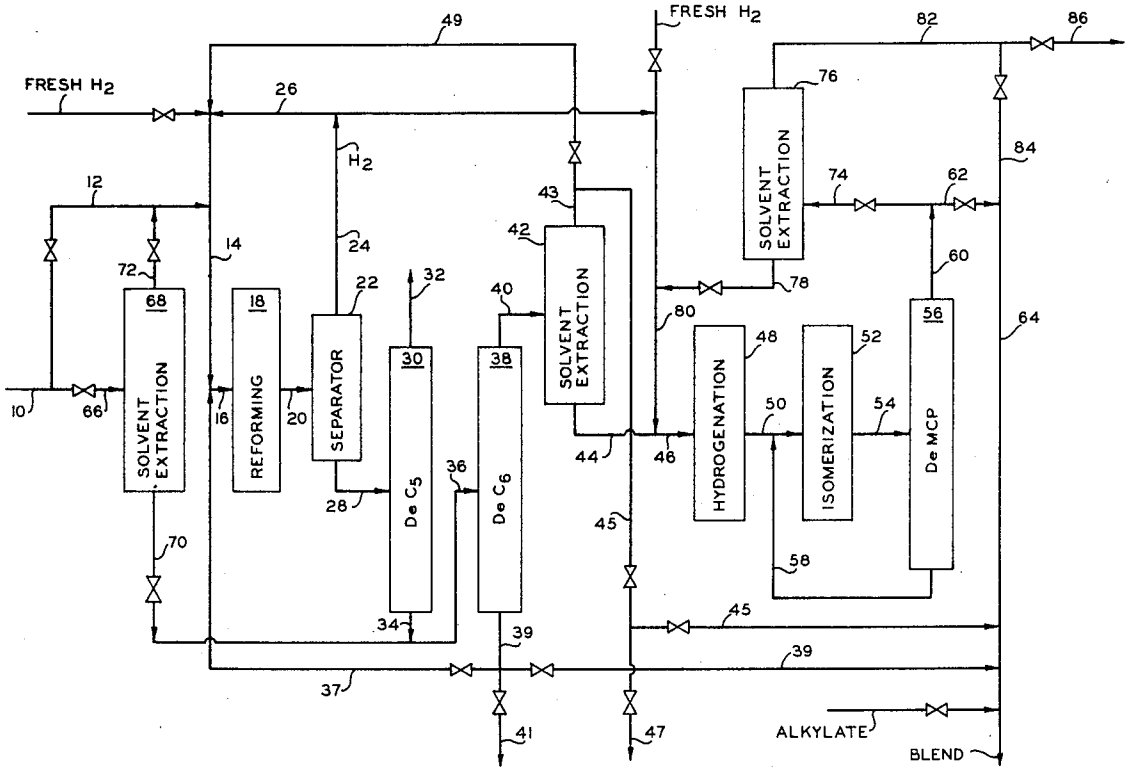
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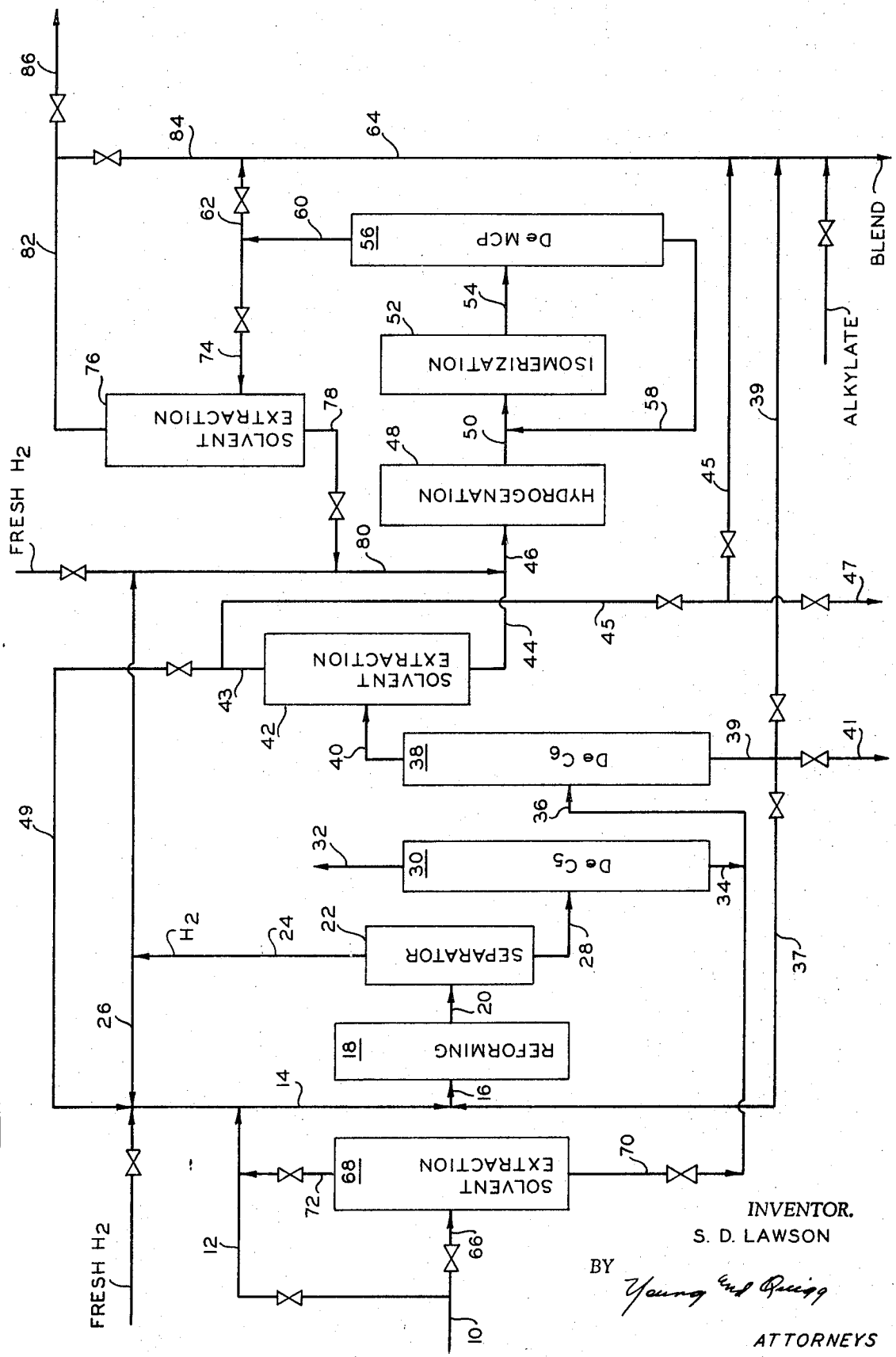
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[57] **ABSTRACT**

Motor fuel-blending components are produced by a combination of steps comprising naphtha reforming, hydrogenation of aromatics, e.g., benzene, separated from the reformate, and isomerization of cyclohexane to methylcyclopentane.

14 Claims, 1 Drawing Figure





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PRODUCTION OF MOTOR FUEL-BLENDING COMPONENTS

This invention relates to the production of motor fuel-blending components.

Aromatics such as benzene have long been used in limited but significant quantities as components of motor fuel. Said aromatics have been desirable because of their relatively high antiknock properties as compared to some of the other hydrocarbon components normally used. However, from other standpoints said aromatics are undesirable. For example, upon prolonged exposure thereto, benzene has certain toxic effects, such as causing a skin rash, etc. This has limited the amount of benzene, and is likely to prevent the use of benzene to produce so-called "lead-free" motor fuels, discussed below. In recent years it has also been learned that benzene is a substantial contributor to air pollution when present in motor fuels in significant quantities. Thus, from several standpoints, it is more desirable to reduce the amount of, or eliminate, the benzene used in motor fuel blends.

C_5 hydrocarbons such as isopentane have also been used in motor fuel blends, Because of their greater volatility, said C_5 hydrocarbons also contribute significantly to air pollution. Thus, it is also desirable to reduce the amount of, or eliminate, the C_5 hydrocarbons used in motor fuel blends.

Recently there have been proposals to eliminate, or at least reduce the amount of, antiknock materials, such as tetraethyllead used in motor fuels. This complicates the problems of removing benzene and C_5 hydrocarbons such as isopentane, both of which have good antiknock properties, from motor fuel. Thus, it is desirable when benzene and C_5 hydrocarbons are to be reduced in quantity or eliminated from motor fuels, that they be replaced with components having good antiknock properties.

The present invention provides a solution for the above problems. In accordance with the present invention, there is provided a combination of steps whereby aromatics such as benzene, and C_5 hydrocarbons, are eliminated and replaced with methylcyclopentane.

An object of this invention is to provide a process for producing blending components which are suitable for use in blending improved motor fuels meeting proposed environment requirement as well as motor operating requirements. Another object of this invention is to provide a process for producing methylcyclopentane which can be used, if desired, to replace benzene and C_5 hydrocarbons in motor fuel blends. Other aspects, objects, and advantages of the invention will be apparent to those skilled in the art in view of this disclosure.

Thus, according to the invention, there is provided a process for producing blending components, suitable for use in blending an improved motor fuel, which process comprises, in combination, the steps of: (*a*) reforming a hydrocarbon naphtha feedstock to produce a reformate stream comprising C_5 and heavier paraffinic, naphthenic, and aromatic hydrocarbons; (*b*) fractionating said stream of hydrocarbons produced in step (*a*) to recover therefrom a first stream comprising C_6 hydrocarbons, and a second stream comprising C_7 hydrocarbons; (*c*) solvent extracting said stream of C_6 hydrocarbons from step (*b*) to produce an aromatic extract stream comprising benzene, and a raffinate stream comprising paraffinic and naphthenic hydrocarbons; (*d*) hydrogenating said extract stream from step (*c*) to produce a stream comprising cyclohexane; and (*e*) isomerizing said stream comprising cyclohexane from step (*e*) to produce a stream comprising methylcyclopentane as a product of the process.

A number of advantages are obtained or realized in the practice of the invention. For example, benzene with its undesirable toxicity and air pollution problems can be eliminated from motor fuel blends. The C_5 hydrocarbons with their volatility and air pollution problems can also be eliminated. In converting benzene to methylcyclopentane there is approximately a 27 percent increase in volume. This volume increase more than offsets the volume of the replaced benzene and C_5 hydrocarbons and, to a large extent, offsets the somewhat lower antiknock properties of the methylcyclopentane. Said lower antiknock properties can be compensated for by using components having high antiknock properties, such as alkylate, in the final motor fuel blend.

The drawing is a diagrammatic flow sheet illustrating various embodiments of the invention. It will be understood that many valves, control equipment, and other equipment not necessary for explaining the invention have been omitted for the sake of brevity. It should also be understood that the various operating conditions set forth for the various processing steps and separation steps are given by way of example only and should not be construed as limiting on the invention.

Referring now to the drawing, the invention will be more fully explained. In one embodiment of the invention, a low end point straight run naphtha, such as obtained from the distillation of crude oils or from natural gasolines, is introduced via conduits **10**, **12**, **14**, and **16** into reforming zone **18**. Preferably, said naphtha can have a boiling range of about 100 to about 300, more preferably about 180° to about 300° F. Typically, said naphtha can contain from 0 to about 2 volume percent C_5 and lighter hydrocarbons, from about 10 to about 20 volume percent C_6 hydrocarbons, from about 40 to about 60 volume percent C_7 hydrocarbons, and from about 25 to about 35 volume percent C_8 and heavier hydrocarbons. Typically, said hydrocarbons will comprise, in volume percent, from about 35 to about 55 percent paraffinic hydrocarbons, from about 40 to about 50 percent naphthenic hydrocarbons, and from about 5 to about 15 percent aromatic hydrocarbons. Said reforming zone **18** comprises a conventional reforming unit and any conventional operating conditions known to the art can be employed therein. Typically, said operating conditions can include a temperature within the range of from about 700° to about 1,000° F., preferably 800° to 950° F., a pressure within the range of from about 350 up to about 1,000, preferably about 200 to about 600 p.s.i.g., and can use from about 0.5 to about 20 mols of hydrogen per mol of feedstock charged thereto. Preferably, the amount of hydrogen will be within the range of 1 to 6 mols per mol of feedstock. Any suitable catalyst known to the art can be employed. One presently preferred catalyst is a platinum-type reforming catalyst, e.g., aluminum impregnated with between 0.1 and 5 weight percent platinum, preferably 0.1 to 1 weight percent platinum, and containing fluorine as a promoter. One such process is known as the Platforming process.

Reformate from reforming zone **18** is withdrawn via conduit **20**, passed into separator **22**, from which stream of hydrogen is withdrawn via conduit **24**. At least a portion of said hydrogen can be recycled to reforming zone **18** via conduits **26** and **14**. Liquid reformate is withdrawn from separator **22** via conduit **28** and introduced into depentanizer **30**. A stream of C_5 and lighter hydrocarbons is removed overhead from said depentanizer via conduit **32** and removed from the system. Typical operating conditions for said column **30** would be a pressure of about 70 p.s.i.g., a top tower temperature of about 195° F., and a bottom tower temperature of about 290° F. The depentanized reformate is withdrawn from column **30** via conduit **34** and passed via conduit **36** into dehexanizer column **38**. Said dehexanizer column **38** can be operated under any suitable conditions for removing overhead therefrom a stream comprising C_6 hydrocarbons. Typical operating conditions for said column would be a pressure of about 45 p.s.i.g., a top tower temperature of about 230° F., and a bottom tower temperature of about 295° F. An overhead stream comprising C_6 hydrocarbons is removed from column **38** via conduit **40** and passed into solvent extraction zone **42**.

Said solvent extraction zone **42** can comprise any suitable process and means known to the art for recovering aromatic hydrocarbons, e.g., benzene, from said C_6 hydrocarbon stream. Any suitable solvent can be used in said solvent extraction zone. Examples of such solvents are sulfolane and triethylene glycol, with the latter solvent being a presently preferred solvent. Typical operating conditions in said solvent extraction zone would include a pressure of about 135 p.s.i.g., a temperature within the range of about 220° to about 300° F.,

and a solvent to hydrocarbon volume ratio within the range of about 3 to about 5. An aromatic extract comprising benzene is withdrawn from solvent extraction zone **42** via conduit **44** and passed via conduit **46** into hydrogenation zone **48**.

Said hydrogenation zone **48** can comprise any suitable process and apparatus known to the art for the hydrogenation of aromatics such as benzene to the corresponding naphthenes, such as cyclohexane. Any suitable catalyst can be employed in said hydrogenation zone. Examples of such catalysts are nickel on alumina and nickel on kieselguhr. One presently preferred catalyst is a nickel on kieselguhr catalyst containing from about 20 to about 55 percent nickel. Typical operating conditions in said hydrogenation zone include a temperature within the range of about 370° to about 550° F., a pressure within the range of about 400 to about 600 p.s.i.g., a liquid hourly space velocity within the range of about 1 to about 3 liquid volumes of feedstock per volume of catalyst per hour, and a hydrogen to benzene mol ratio within the range of about 4 to about 15. A stream comprising cyclohexane is withdrawn from hydrogenation zone **48** via conduit **50** and passed into isomerization zone **52**.

Said isomerization zone **52** can comprise any suitable process and apparatus for isomerizing cyclohexane to methylcyclopentane. Any suitable catalyst can be employed in said isomerization zone. In one presently preferred process the catalyst employed is the so-called Penex catalyst which is a platinum on alumina catalyst, promoted with fluorine. Any other suitable catalyst such as those described in U.S. Pat. No. 3,260,762, issued July 12, 1966, to J. T. Cabbage, can be employed. Typical operating conditions in said isomerization zone can include a temperature within the range of about 650° to about 750° F., a pressure within the range of about 400 to about 550 p.s.i.g., and a liquid hourly space velocity within the range of about 1.5 to 3 volumes per volume of catalyst per hour. A stream comprising methylcyclopentane is withdrawn from isomerization zone **52** via conduit **54** and passed into demethylcyclopentanizer column **56**. Typical operating conditions in said column **56** can includes a pressure of about 40 p.s.i.g., a top tower temperature of about 230° F., and a bottom tower temperature of about 270° F. A stream comprising unconverted cyclohexane is withdrawn from column **56** via conduit **58** and recycled to said isomerization zone **52**. A stream comprising methylcyclopentane is withdrawn from column **56** via conduit **60**, and can be removed from the system via conduits **62** and **64** as a product of the process.

In another embodiment of the invention, the raffinate comprising nonaromatic C_6 hydrocarbons removed from solvent extraction zone **42** via conduit **43** can be passed, at least in part, via conduit **45** and removed from the system via conduit **47**. Still another embodiment of the invention, said raffinate can be passed via conduit **45** into conduit **64** for blending with said methylcyclopentane product in the production of motor fuels. In still another embodiment of the invention, said raffinate in conduit **43** can be passed via conduit **49** into conduit **14** for recycle to reforming zone **18** as a portion of the feedstock thereto.

In one operation of dehexanizer column **38**, a stream comprising C_7 hydrocarbons can be withdrawn from said column via conduit **39**. In another embodiment of the invention, said C_7 hydrocarbons can be removed from the system, if desired, via conduit **41**. In still another embodiment of the invention, said C_7 hydrocarbons, if desired, can be passed via conduit **39** into conduit **64** for blending with said methylcyclopentane product in the production of motor fuels. In still another embodiment of the invention, said C_7 hydrocarbons in conduit **39** can, if desired, be passed via conduit **37** into conduit **16** for recycle to reforming zone **18** as a portion of the feedstock thereto.

When the feedstock in conduit **10** contains an appreciable amount of aromatics, it will usually be desirable to remove said aromatics from said feedstock before reforming same. Thus, in another embodiment of the invention, said feedstock in conduit **10**, at least in part, can be introduced via conduit **66** into solvent extraction zone **68**. Said solvent extraction zone **68** can comprise any suitable process and apparatus such as described above for solvent extraction zone **42**. An aromatic extract comprising benzene is removed from solvent extraction zone **68** via conduit **70** and passed into conduit **36** for introduction into dehexanizer column **38**. A raffinate comprising paraffinic and naphthenic hydrocarbons is withdrawn from extraction zone **68** via conduit **72** and passed via conduits **12**, **14**, and **16** into reforming zone **18** as at least a portion of the feedstock thereto. This embodiment of the invention has the additional advantage that the aromatics such as benzene contained in the naphtha feedstock are not subjected to reforming conditions, and are instead passed ultimately to solvent extraction zone **42**. By thus removing the benzene from the naphtha feedstock, hydrogenating same, and isomerizing the resulting cyclohexane to methylcyclopentane, the production of methylcyclopentane is maximized.

In one presently preferred embodiment of the invention wherein it is desired to produce the maximum amount of methylcyclopentane, all of the raffinate from solvent extraction zone **42** is recycled via conduits **43** and **49**, and **14** to reforming zone **18** as a portion of the feedstock thereto. Similarly, all of the stream in conduit **39** comprising C_7 hydrocarbons is passed via conduits **37** and **16** into reforming zone **18** as a portion of the feedstock thereto. This embodiment of the invention has the advantage of maximizing the production of benzene in reforming zone **18** and thus maximizing the ultimate production of methylcyclopentane.

In some instances, a small amount of benzene may be produced in isomerization zone **52**. In such instances, and in accordance with the invention, the methylcyclopentane stream in conduit **60** can be passed via conduit **74** into solvent extraction zone **76** which can be a zone like solvent-extraction zone **42**. An extract stream comprising benzene is withdrawn from said zone **76** via conduit **78** and passed via conduits **80** and **46** into hydrogenation zone **48** for hydrogenation as described above. A raffinate stream comprising essentially pure methylcyclopentane is withdrawn from zone **76** via conduit **82**. Said pure methylcyclopentane can be passed via conduit **84** into conduit **64** for use as previously described, or can be removed from the system via conduit **86**.

The following calculated example will serve to further illustrate the invention.

EXAMPLE

In this illustrative embodiment a depentanized light straight run naphtha having a boiling range of about 180° to about 300° F. is charged to a reforming zone such as zone **18** described above in the drawing. Said naphtha contains about 16.3 volume percent C_6 hydrocarbons, about 52.2 volume percent C_7 hydrocarbons, and about 31.5 volume percent C_8 and heavier hydrocarbons. Said hydrocarbons have a composition of about 47.9 percent paraffinic, about 45.3 percent naphthenic, and about 6.8 percent aromatic. In said reforming zone said naphtha is reformed in conventional manner employing the above-described Platforming catalyst. Operating conditions in the reforming zone include a pressure of about 350 p.s.i.g., a temperature of about 940° F., a hydrogen to hydrocarbon mol ratio of about 7, and a liquid hourly space velocity of about 2 volumes per volume of catalyst per hour.

The resulting reformate is then processed as indicated in the drawing with the recovery of a stream of C_6 hydrocarbons in conduit **40**. Said C_6 hydrocarbon stream is then solvent extracted in conventional manner in solvent-extraction zone **42** using triethylene glycol solvent. Operating conditions in said solvent-extraction zone include a pressure of about 137 p.s.i.g., a temperature of about 250° F., a solvent to hydrocarbon ratio of about 4.

The extract from said solvent-extraction zone is charged to a hydrogenation zone **48** wherein benzene is hydrogenated in a conventional manner using a nickel on kieselguhr catalyst. Operating conditions in said hydrogenation zone include a

pressure of about 500 p.s.i.g., a temperature of about 400° F., a hydrogen to benzene mol ratio of about 5, and a liquid hourly space velocity of about 2.4 volumes of feed per volume of catalyst per hour.

The cyclohexane effluent stream from hydrogenation zone **48** is charged to isomerization zone **52** and therein isomerized in conventional manner using the above-described conventional platinum on alumina catalyst (Penex catalyst) to produce methylcyclopentane. Operating conditions in said isomerization zone include a pressure of about 500 p.s.i.g., a temperature of about 750° F., a liquid hourly space velocity of about 2 volumes of charge per volume of catalyst per hour. The isomerizate in conduit **54** is charged to column **56** and the methylcyclopentane product recovered therefrom via conduit **60** as described above in connection with the drawing.

Table I below sets forth the stream quantities and compositions of same for the principal streams.

TABLE I

Fresh Feed (10) to Reformer (18)	
Barrels per day	13,500
Gravity, °API at 60° F.	60
Octane No., RON, clear	69
Feed (40) to Extraction Zone (42)	
Barrels per day	5,300
Composition, Vol. %	
Aromatics (benzene)	15.0
Naphthenes	14.0
Paraffins	71.0
Feed (44) to Hydrogenation (48)	
Barrels per day	800
Benzene, vol. %	99.95
Feed to Isomerization Zone (52)	
Barrels per day, fresh feed (50)	970
Barrels per day, recycle (58)	230
Barrels per day, Total	1,200
Cyclohexane, vol. %	99.0
Methylcyclopentane, vol. %	1.0
Product MCP (60)	
Barrels per day	1,015
Octane No., RON, clear	91.3

Referring to the above Table I, it will be noted that 1,015 barrels per day of methylcyclopentane having a research octane number (clear) of 91.3 are produced from 800 barrels per day of benzene. This represents a volume increase of 27 percent of the valuable methylcyclopentane-blending component over benzene.

While the invention has been described above with particular reference to benzene as the aromatic hydrocarbon being converted, the invention is not so limited. For example, in naphtha streams from some sources toluene will sometimes be present along with benzene, at least in small amounts. It is within the scope of the invention to adjust operating conditions in column **38** to remove the toluene overhead with the benzene. In such instances the toluene would then be processed along with the benzene. Said toluene will hydrogenate to methylcyclohexane, which will isomerize to ethylcyclopentane and various dimethylcyclopentanes.

While certain embodiments of the invention have been described for illustrative purposes, the invention is not limited thereto. Various other modifications or embodiments of the invention will be apparent to those skilled in the art in view of this disclosure. Such modifications or embodiments are within the spirit and scope of the disclosure.

I claim:

1. A process for producing blending components, suitable for use in blending an improved motor fuel, which process comprises, in combination, the steps of:

a. reforming a hydrocarbon naphtha feedstock to produce a reformate stream comprising C_5 and heavier paraffinic, naphthenic, and aromatic hydrocarbons;

b. fractionating said stream of hydrocarbons produced in step (a) to recover therefrom a first stream comprising C_6 hydrocarbons, and a second stream comprising C_7 hydrocarbons;

c. solvent extracting said stream of C_6 hydrocarbons from step (b) to produce an aromatic extract stream comprising benzene, and a raffinate stream comprising paraffinic and naphthenic hydrocarbons;

d. hydrogenating said extract stream from step (c) to produce a stream comprising cyclohexane; and

e. isomerizing said stream comprising cyclohexane from step (d) to produce a stream comprising methylcyclopentane as a product of the process.

2. A process in accordance with claim **1** wherein: at least a portion of said raffinate produced in step (c) is recovered as another product of the process; and at least a portion of said stream comprising C_7 hydrocarbons from step (b) is also recovered as another product of the process.

3. A process in accordance with claim **1** wherein at least a portion of said stream of C_7 hydrocarbons of step (b) is blended with said methylcyclopentane of step (e) as a product of the process.

4. A process in accordance with claim **1** wherein at least a portion of said raffinate produced in step (c) is blended with said methylcyclopentane of step (e) as a product of the process.

5. A process in accordance with claim **1** wherein at least a portion of said stream of C_7 hydrocarbons of step (b) is recycled to said step (a) as a portion of said feedstock.

6. A process in accordance with claim **1** wherein at least a portion of said raffinate produced in step (c) is recycled to said step (a) as a portion of said feedstock.

7. A process in accordance with claim **1** wherein:

said methylcyclopentane stream of step (e) is solvent extracted to recover therefrom a second aromatic extract comprising benzene, and a second raffinate consisting essentially of purified methylcyclopentane which is recovered as a product of the process; and

said second aromatic extract is passed to said hydrogenation of step (d).

8. A process according to claim **1** wherein:

said stream comprising C_7 hydrocarbons of step (b) is recycled to step (a) as a portion of said feedstock; and

said raffinate produced in step (c) is recycled to step (a) as a portion of said feedstock.

9. A process according to claim **8** wherein:

said methylcyclopentane stream of step (e) is solvent extracted to recover therefrom a second aromatic extract comprising benzene, and a second raffinate consisting essentially of purified methylcyclopentane which is recovered as a product of the process; and

said second aromatic extract is passed to said hydrogenation of step (d).

10. A process according to claim **1** wherein:

prior to said step (a), said naphtha feedstock is solvent extracted to produce an aromatic extract comprising benzene, and a raffinate comprising paraffinic and naphthenic hydrocarbons;

said last-mentioned aromatic extract is passed to said fractionation of step (b); and

said last-mentioned raffinate is passed to said step (a) as said feedstock.

11. A process according to claim **10** wherein:

said stream comprising C_7 hydrocarbons of step (b) is recycled to step (a) as a portion of said feedstock; and

said raffinate produced in step (c) is recycled to step (a) as a portion of said feedstock.

12. A process according to claim **11** wherein:

said methylcyclopentane stream of step (e) is solvent extracted to recover therefrom a second aromatic extract

comprising benzene, and a second raffinate consisting essentially of purified methylcyclopentane which is recovered as a product of the process; and

said second aromatic extract is passed to said hydrogenation of step (d).

13. A process in accordance with claim 12 wherein:

prior to said step (b), a stream of hydrogen is separated from said reformate stream; and

at least a portion of said hydrogen is passed to said hydrogenation of step (e) as at least a portion of the hydrogen used therein.

14. A process in accordance with claim 13 wherein a portion of said separated hydrogen is returned to said reforming operation of step (a).

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