

Reactive Rectification System and High-Octane Component Production

Method

Field of the Invention

This invention applies to the petrochemical and oil-refining industries, namely, to
5 production methods for high-octane gasoline components.

Background of Invention

Until recently, benzene has been widely used as a car-fuel component to increase the fuel
octane number. In particular, a benzene-containing reformat was used as a high-octane
component in truck and aircraft motor gasolines; it was produced by catalytic reforming of
10 straight-run gasoline fractions.

However, nowadays, the benzene concentration in the gasoline shall be reduced for the
sake of environmental safety but it entails the problem of keeping antiknock properties, namely, a
high octane number. The benzene concentration can be reduced in the reformat or in its fractions
by hydrogenating benzene to obtain cyclohexane but cyclohexane is a low-octane substance and is
15 unsuitable as a motor-fuel component. Methylcyclopentane, its isomer, could be more beneficial.

There is a production method for high-octane gasoline components from oil raw materials
(US Patent No. 5,830,345) where the gasoline-enriched fraction of this raw material, which
contains C5 through C7 paraffins, is hydrogenated and isomerized by using a dual functional
catalyst in a reactive rectification process. However, when the same reaction zone is used to
20 hydrogenate benzene and to isomerize cyclohexane and paraffins C5 through C7 concurrently, it
results in competition among all raw-material components for interaction with the catalyst and,
therefore, in incomplete reactions and in a failure to increase the octane number as desired.

In a similar situation, a different method (WO 2006/088528) uses two separate catalysts
instead of the dual functional catalyst, namely, the hydrogenation catalyst and the isomerization
25 catalyst. However, there is still competition among cyclohexane and paraffins C5 through C7 for
interaction with the hydrogenation catalyst, and it results in incomplete transformation. In
addition, a higher molecular weight of cyclohexane prevents it from delivery to the isomerization
catalyst located in the rectification column above the hydrogenation catalyst; it reduces the
cyclohexane ability to get isomerized to methylcyclopentane and, consequently, prevents from
30 getting an octane number desired.

Summary of the Invention

Thus, there is still a problem to produce high-octane gasoline components with reduced benzene concentration and minimal octane loss and there is a problem to develop processes which would allow to use raw-material components as efficiently as possible and to reduce production expenditures for high-octane gasoline components.

This problem is solved by providing a reactive rectification system which is used for production of high-octane gasoline components, which system contains a rectification column with a feeding zone and a hydrogen-containing gas supply zone, and has at least three reaction zones, at least one which is a benzene hydroisomerization zone, at least one of the other ones is a hexane isomerization zone, and at least one of the remaining ones is the pentane isomerization zone. The benzene hydroisomerization zone is located lower than the other reaction zones and is in the lower part of the column while the hexane isomerization zone is located higher than the feeding zone but lower than the pentane isomerization zone. The system also has one side output which is above the hexane isomerization zone but lower than the pentane isomerization zone.

It is feasible to have all of the three reaction zones inside the rectification column.

An implementation of this system has four distillation zones, so all reaction zones are separated by distillation zones.

It is feasible to have the feeding zone above the benzene hydroisomerization zone.

It is preferable to have a dedicated hydrogen supply zone for each reaction zone in the system.

The catalyst in the lower hydroisomerization zone can be zeolite covered with a Group VIII metal.

The catalyst of the upper isomerization zones can be a Group IV metal oxide covered with a Group VIII metal and promoted by sulfate and/or tungstate ions.

A method for producing is also provided to obtain high-octane gasoline components where the feeding flow is directed into the feeding area of the reactive rectification column, which column is a part of the reactive rectification system, which system contains at least three reaction zones, at least one of which is a benzene hydroisomerization zone located right in the column, at least one of the other ones is a hexane isomerization zone, and at least one of the remaining zones is a pentane isomerization zone. Benzene is hydroisomerized in the benzene hydroisomerization zone located in the lower part of the column and under all the other reaction zones. Hexanes are isomerized in the hexane isomerization zone located above the feeding zone but lower than the pentane isomerization zone. Pentane is isomerized in the pentane isomerization zone. Isohexanes are recovered from the column side output located above the hexane isomerization zone but under

the pentane isomerization zone, isopentanes are recovered from the column top, and cyclopentanes are recovered from the column bottom.

It is feasible to have such a feeding-flow temperature that the flow is a vapor-liquid one where benzene is mostly in the liquid phase.

5 It is preferable to direct the feeding flow into the column distillation zone located between the isomerization and hydroisomerization zones and it is desirable to split the feeding flow at the column input into two flows, one of which is descending and contains benzene and components with a higher molecular weight while the other flow is ascending and contains components whose molecular weight is lower than that of benzene.

10 According to one embodiment of the invention, paraffins C4 through C6 move from the feeding flow into the isomerization reaction zone located above the feeding-flow entry point while aromatics, naphthenes, paraffins C7, and heavier hydrocarbons enter the hydroisomerization reaction zone located under the feeding-flow entry point.

In another embodiment of the invention, isomerization reactions take place in reaction zones outside the column while the mixture of products gets back into the column.

It is feasible to mix hydrocarbons and hydrogen right in the reaction zone and to supply hydrogen to each zone separately.

According to this invention, the feeding flow usually consists of the C4 through C8 hydrocarbon fraction which contains benzene at a concentration between 0 and 30 percent (w/w).

20 Benzene can be hydroisomerized by using a catalyst which is zeolite covered with a Group VIII metal.

Isomerization can be done by using a catalyst which is a Group IV metal oxide covered with a Group VIII metal and promoted by sulfate and/or tungstate ions.

It is feasible to have a hydrogen-to-hydrocarbon molar ratio between 0.01 and 5 to 1; a preferable value is between 0.01 and 3 to 1; a more preferable value is between 0.1 and 3 to 1; even more preferable one is between 0.08 and 1.5 to 1.

It is feasible to have an overpressure in the column between 10 and 40 atm in excess (a more preferable value is between 30 and 35 atm in excess).

It is feasible to have a tower temperature between 80°C and 350°C (preferably, between 80°C and 300°C; even more preferably, between 150°C and 280°C).

In an embodiment of invention, the temperature at the column top is between 80°C and 220°C (preferably, between 150°C and 200°C) while the temperature at the column bottom is between 120°C and 350°C (preferably, between 220°C and 280°C).

35 The authors of this invention have suddenly discovered that the raw-material component-competition problem for the reaction can be solved by using at least three reaction zones, one of

which is used for benzene hydrogenation and isomerization while the other two zones are used for paraffin isomerization.

The benzene hydrogenation zone in known state-of-the-art rectification systems was usually located at the upper part of column above the raw-material feeding zone. The authors of this invention have suggested to arrange it as low as possible, preferably even lower than the raw-material feeding zone to employ the exothermal effect of the hydrogenation reaction efficiently for liquid evaporation in the reaction zone and, thus, to reduce the energy consumption for the reactive rectification column boiler and the energy consumption for the reactive rectification system at large.

According to this invention, it is preferable to supply the raw materials into the column in a vapor-liquid state where benzene is mostly in the liquid phase. On one side, it allows to reduce expenditures for raw-material heating (the benzene was in the gaseous phase in the state-of-the-art systems to ensure its ascending up the column but it requires more heating). On the other side, it allows to get more benefits from the exothermal effect of the hydrogenation reaction in the reaction zone located under the raw-material feeding zone where liquid benzene enters.

The authors have suddenly discovered that when C7 paraffins from the benzene fraction are added into the raw-material flow under the process conditions, they are isomerized into high-octane components which increase the octane number of the bottom product.

It was also suddenly discovered that under the process conditions, there is a C7 hydrocarbon disproportionation reaction in the lower reaction zone where C6 and C8 high-octane components appear, which increase the octane number of the bottom product.

The side reaction in the process suggested (the cracking which results in light hydrocarbons C3 through C4) is minimized because end products are removed from the reaction zone prior to the light-hydrocarbon formation.

Brief Description of the Drawings

Fig.1 illustrates the reactive rectification process setup where all reaction zones are within the reactive rectification column.

Fig. 2 illustrates the reactive rectification process setup where at least one isomerization reaction zone is outside the reactive rectification column.

Fig. 3 illustrates the reactive rectification process setup where at least two isomerization reaction zones are outside the reactive rectification column.

Detailed Description of the Invention

This invention relates to the production process which is a single reactive rectification process.

The term "reactive rectification process" is used to describe a combined process where catalytic and distillation reactions take place in the column concurrently. "Reaction distillation", "catalytic distillation" or any other term can be used to describe the process if such a term describes a combined process where catalytic and distillation reactions take place in the column concurrently.

The reactive rectification process combines catalytic reactors and distillation zones in a single column, i.e. ensures a combination of chemical reaction with separation of the reaction mixture in the same apparatus and offers benefits from the kinetic, thermodynamic, and energy-saving prospective.

The raw material in the invention method is a light straight-run naphta along with the reformat fraction which includes mainly benzene and other components with similar boiling points. In general, the raw materials are preliminary distilled water-free petroleum products (in particular, straight-run light gasoline) and catalytic-reforming products (in particular, light reformat which contains mainly benzene and other components with similar boiling points). The feeding flow usually consists of C4 through C8 or C5 through C8 hydrocarbons which can contain up to 30 percent of benzene (w/w). The raw materials (feeding flow) include saturated and unsaturated normal paraffins and their isomers, cycloparaffins, and aromatics.

The benzene from the raw materials is hydrogenized while the other hydrocarbons go through reactions which ensure a higher octane number, in particular, through the isomerization reaction.

Benzene is hydrogenized and the resultant cyclohexane is isomerized in the "benzene hydroisomerization zone". It is a zone for hydroisomerization of hydrocarbons which contain mainly six or more carbon atoms, including saturated and unsaturated normal paraffins and their isomers, cycloparaffins, and aromatics, in particular, benzene.

Two other reaction zones are for isomerization of hydrocarbons which contain mainly between five and eight carbon atoms, including saturated and unsaturated normal paraffins and their isomers, cycloparaffins, and aromatics. These two isomerization zones can be outside of the column, so a corresponding phase is directed into them from the distillation zone while the isomerization product comes back into the column. Two isomerization zones are located at different levels. Therefore, different starting materials get into such zones due to mass-transfer processes. Products in the lower isomerization zone are mainly isohexanes. Therefore, the lower isomerization zone is called the "hexane isomerization zone". Products in the upper isomerization zone are mainly isopentanes. Therefore, the upper isomerization zone is called the "pentane isomerization zone".

The applicant has also discovered that two and even three reaction zones can be located right in the rectification column.

Thus, according to the invention, the reactive rectification process mainly includes at least four distillation and three reaction zones. At least one reaction zone is inside the reactive rectification column. The other reaction zones are mainly inside the reactive rectification column but they can be placed outside of it and made as stand-alone units with relevant support equipment (known to any average specialist); thus, they are still a part of the reactive rectification process.

As it is known to any person skilled in the art, distillation zones with non-stop fractionation can include rectification separation plates, non-structured mass-transfer attachment, and a structured mass-transfer attachment.

The process uses a hydrogen-containing gas which is any suitable gas which contains hydrogen. Such a gas may also contain hydrocarbons, in particular, C1 through C3. The reforming gas can be used as hydrogen-containing gas. Hydrogen is consumed in the benzene-hydrogenation reaction but it is not consumed in isomerization reactions although it is required to maintain the catalyst stability and potency. Hydrogen is supplied into the column bottom part, preferably, into the bottom of each reaction zone.

General Process Diagram

The raw materials are delivered into the reactive rectification column in the raw-material feeding zone.

Hydrogenation and isomerization reactions take place at least in three reaction zones.

The gas flow at the column output contains isomerization reaction products, including mainly isopentane as well as the hydrogen-containing gas and hydrocarbons which contain between two and four carbon atoms and produced during the cracking reaction in the reaction zones, including two isomerization and one hydroisomerization reaction zones.

The gas flow at the column-top output enters the condenser from where it enters the distillate-collection container as liquid and vapors to provide a liquid distillate used to provide the reflux in the reactive rectification column and to collect the distillate product flow. The vapor phase consists of uncondensed hydrocarbons and leaves the distillate collection container to leave the reactive rectification system. The liquid phase flows from the distillation-collection container as the reflux of the reactive rectification column and as the distillate collection product, respectively.

There is a side product output in the reactive rectification column, in the distillation zone between the isomerization reaction zones. Such a side output is mainly used to recover high-octane components with five between seven carbon atoms, including such hydrocarbons as isopentane, methylpentanes, dimethylpentanes, and other hydrocarbons, in general, isomers, as well as methylcyclopentane.

The liquid product is delivered from the reactive rectification column bottom into the reactive rectification column boiler. The boiler together with hydroisomerization reaction zone or alone provides the necessary vapor flow on the bottom of the reactive rectification column. The boiler also maintains stable operating conditions in the reactive rectification column. The vapor flow from the boiler returns mainly into the reactive rectification column bottom while the liquid flow leaves the reactive rectification system as the bottom product. The bottom products consist of hydrocarbons which contain mainly six or more carbon atoms, including cyclohexane and methylcyclopentane; in general, methylcyclopentane concentration is higher than that of cyclohexane.

Reactive Rectification Process Conditions

In general, the following values are applied for the reactive rectification process operating conditions. The pressure is between 1 and 40 absolute bars in the reactive rectification column, preferably, in a range between 20 and 35 absolute bars.

In general, the temperature at the reactive rectification column top is between 80°C and 220°C, preferably, between 120°C and 200°C. In general, the temperature at the reactive rectification column bottom is between 120°C and 350°C, preferably, between 200°C and 280°C. In general, the hydrogen-to-raw-material molar ratio is between 0.01 and 5; a more preferable value is between 0.01 and 3; even more preferable one is between 0.08 and 1.5.

The operating conditions for the reaction zones inside the reactive rectification column depend on the process parameters in the reactive rectification column and on the best process parameters for the isomerization and/or hydrogenation and/or hydroisomerization reactions and are in a range between the parameter values for the top and bottom of the reactive rectification column.

In general, the following values are applied to the operating conditions in the reaction zones outside the reactive rectification column (if used). The pressure is between 1 and 60 absolute bars, preferably, in a range between 5 and 35 absolute bars. In general, the temperature is between 60°C and 400°C; a more preferable value is between 100°C and 300°C. In general, the hydrogen-to-raw-material molar ratio is between 0.01 and 5; a more preferable value is between 0.01 and 3; even more preferable one is between 0.08 and 1.5.

Reaction Zones: Structural Description

The reaction-zones inside the reactive rectification column have a structure which is mainly designed for the catalytic reaction purposes but it also allows distillation.

The structure of the reaction zone involves "a fluid flow which has the same direction as the hydrogen-containing gas flow ascending through the catalyst layer".

The catalyst in the reaction zone is in pipes and/or in containers located on a mesh installed to support the catalyst and to deliver the hydrogen-containing gas into the reaction zone.

The liquid flows down from a higher distillation zone into the reaction zone through the reaction-zone distributor. The liquid inside the reaction zone moves in the same direction as the
 5 hydrogen-containing gas flow ascending through the catalyst layer.

The vapor phase enters the reaction zone from a lower distillation zone. The vapor phase moves through pipes and/or containers adjacent to the pipes and/or containers filled with the catalyst. The liquid can flow down from the pipes and/or containers filled with the catalyst through the pipes and/or containers where the vapor phase ascends. Such pipes and/or containers
 10 (where the vapor phase ascends) can be hollow or filled with a non-reactive mass-transfer packing material (either structured or unstructured one) to improve the mass-transfer process as known to any average expert.

The hydrogen-containing gas is delivered to the reaction zone via a pipeline which preferably connects to the floor of the reaction zone. The hydrogen-containing gas is distributed
 15 and delivered into the pipes and/or containers filled with the catalyst through a dedicated distributor and/or distribution header preferably located on the floor of the reaction zone.

The reaction zones outside the reactive rectification column have a structure based on application of the most advanced and common methods, solutions for stand-alone apparatuses with relevant support equipment used for isomerization and/or hydrogenation and/or
 20 hydroisomerization reactions known to any average specialist.

Catalysts for Reactive Rectification Process: Description

Group VIII metal catalysts are used in the hydroisomerization reaction zones. The methods known to any average specialist are employed to apply such catalysts onto their carriers such as active aluminum oxide, beta-zeolite, pentasils (such as ZSM-5) or mordenite. Such
 25 carriers can be modified by such halogens as F and/or Cl or different elements.

The process employs catalysts based on the artificial and/or natural mordenite in a mixture with active aluminum oxide, modified with halogens Cl and/or F, and covered with such Group VIII metals as Ni, Pt, and Pd.

The isomerization reaction zones inside the reactive rectification column have Group VIII
 30 metal catalysts applied on such carriers as $ZrO_2/SO_4(SO_3)$, ZrO_2/W_2O_3 , so called "solid superacids". Solid and/or applied heteropolyacids can be used as catalysts. Such catalysts are promoted by Mn, Fe, Cl and/or F halogens, and other elements.

It is allowed to use most conventional contemporary isomerization catalysts known to any average specialist in the isomerization reaction zones outside the reactive rectification column.

Examples

Example 1. The reactive rectification process where all reaction zones are within the reactive rectification column (please refer to Fig. 1).

The raw materials are delivered into reactive rectification column (3) via line (1).

5 The reactive rectification column consists of three reaction zones (4), (5), and (6) located between the distillation zones inside reactive rectification column (3).

Reaction zones (4) and (5) are situated mainly closer to the reactive rectification column (3) top and middle parts, respectively. The hydrocarbon-isomerization catalyst is loaded into reaction zones (4) and (5).

10 Reaction zone (6) is located mainly closer to the reactive rectification column (3) bottom. The hydroisomerization catalyst is loaded into reaction zone (6). Benzene is hydroisomerized to cyclohexane and methylcyclopentane (mainly, to methylcyclopentane).

The hydrogen-containing gas is supplied to the reaction zones via lines (2c), (2b), and (2a) mainly into the floor of reaction zones (4), (5), and (6), respectively.

15 The gas flow from line (11) at the column-top output contains isomerization products, mainly isopentane.

The gas flow from line (11) at the column-top output enters condenser (12) from where it goes into distillate-collection container (14) via line (13) as a liquid and vapors. The vapor phase consists of uncondensed hydrocarbons and leaves distillate-collection container (14) via line (15)
20 to leave the reactive rectification system. The liquid phase from container (14) enters lines (16) and (17) as the reactive rectification column (3) reflux and as the distillate-collection product, respectively.

There is a side product output line (18) in the reactive rectification column, in the distillation zone between isomerization reaction zones (4) and (5). The side product output line is
25 used to remove such components as isopentane, methylpentanes, dimethylbutanes, and methylcyclopentane.

The liquid product is delivered from the reactive rectification column (3) bottom into reactive rectification column boiler (8) via line (7). Boiler (8) together with hydroisomerization reaction zone (6) or alone provides the necessary vapor flow on the bottom of reactive
30 rectification column (3). Boiler (8) also maintains stable operating conditions in the reactive rectification column as known to any average specialist. The vapor flow from boiler (8) returns into the reactive rectification column (3) bottom while the liquid flow leaves the reactive rectification system via line (10) as the bottom product. Bottom product (10) consists of hydrocarbons, including cyclohexane and methylcyclopentane; the methylcyclopentane
35 concentration is higher than that of cyclohexane.

Example 2. The reactive rectification process where one isomerization reaction zone is outside the reactive rectification column (please refer to Fig. 2).

The reactive rectification process in Fig. 2 is set up in a similar way as the reactive
5 rectification process in Fig. 1 with the following differences:

The liquid and/or vapor phases flow from the distillation zone located mainly closer to the reactive rectification column (3) top into isomerization reaction zone (4) via line (19). Isomerization reaction zone (4) is made as a stand-alone apparatus with relevant support equipment as known to any average specialist; thus, it is still a part of the reactive rectification
10 system. Isomerization reaction products in the liquid and/or vapor phase return to reactive rectification column (3) via line (20). The hydrogen-containing gas is supplied mainly to the reaction-zone top (4) via line (2c) or is mixed with the liquid and/or vapor flow of line (19) and jointly enters mainly the reaction-zone top (4).

Example 3. The reactive rectification process where two isomerization reaction zones are outside the reactive rectification column (please refer to Fig. 3).

The reactive rectification process in Fig. 3 is set up in a similar way as the reactive rectification process in Fig. 2 with the following differences:

The liquid and/or vapor phase enters isomerization reaction zone (5) from the distillation zone located mainly between the raw-material input into the reactive rectification column (3) via
20 line (1) and side product-collection line (18). Isomerization reaction zone (5) is made as a stand-alone apparatus with relevant support equipment as known to any average specialist; thus, it is still a part of the reactive rectification system. Isomerization reaction products in the liquid and/or vapor phase return to reactive rectification column (3) via line (22). The hydrogen-containing gas
25 is supplied mainly to the reaction-zone top (5) via line (2b) or is mixed with the liquid and/or vapor flow of line (21) and jointly enters mainly the reaction-zone top (5).

Example 4. The reactive rectification process where all reaction zones are within the reactive rectification column (please refer to Fig. 1).

30 The raw-material flow (the model mixture) has a composition shown in Table 1 and was supplied to the column with three reactors and 4 distillation zones under the following conditions:

Pressure: 25 atm

Column-top temperature: 1,700°C

Column-bottom temperature: 2,450°C

35 Raw-material volume flow rate: 3 h⁻¹

Hydrogen-to-raw-material molar ratio: 3:1

It resulted in products whose composition is shown in Table 2.

Table 1. Raw-Material Composition

Component	Concentration, % (w/w)
n-pentane	35
n-hexane	30
Benzene	25
n-heptane	10

5

Table 2. Product Composition and Yield Rates

Component	Top Collection Output, % (w/w)	Side Collection Output, % (w/w)	Bottom Product, % (w/w)
Total C3 through C4	3.8	-	-
Isopentane	93.0	1.0	-
n-pentane	3.2	2.0	-
2,3 dimethylbutane	-	60.0	-
2,3-dimethylbutane	-	19.0	-
2-,3-methylpentanes	-	15.0	-
n-hexane	-	3.0	3.74
Benzene	-	-	0.1
Cyclohexane	-	-	28.5
Methylcyclopentane	-	-	42.8
I-C7	-	-	17.0
n-C7	-	-	3.0
Total C8	-	-	4.86
Yield rate, % (w/w)	36,4	30,0	34.6

What is claimed is:

1. A reactive rectification system which is used for production of high-octane gasoline components and which: i) contains a rectification column with a feeding zone and a hydrogen-containing gas supply zone; and ii) has at least three reaction zones, at least one which is a benzene hydroisomerization zone, at least one of the other ones is a hexane isomerization zone, and at least one of the remaining ones is the pentane isomerization zone, wherein the benzene hydroisomerization zone is located lower than the other reaction zones and is in the lower part of the column while the hexane isomerization zone is located higher than the feeding zone but lower than the pentane isomerization zone; and iii) the system has also one side output which is located above the hexane isomerization zone but lower than the pentane isomerization zone.
2. The system according to claim 1 where all of the three reaction zones are within the rectification column.
3. The system according to claim 2 with four distillation zones where all reaction zones are separated by distillation zones.
4. The system according to claim 1 where the feeding zone is located higher than the benzene-hydroisomerization zone.
5. The system according to claim 1 where each reaction zone has a dedicated hydrogen-supply zone.
6. The system according to claim 1 where the catalyst of the lower hydroisomerization zone is zeolite covered with a Group VIII metal.
7. The system according to claim 1 where the catalyst of the upper isomerization zones is a Group IV metal oxide covered with a Group VIII metal and promoted by sulfate and/or tungstate ions.
8. A method for producing high-octane gasoline components comprising directing the feeding flow into the feeding zone of the reactive rectification column, which column is a part of the reactive rectification system, which system contains at least three reaction zones, at least one

of which is a benzene hydroisomerization zone, at least one of the other ones is a hexane isomerization zone, and at least one of the remaining zones is a pentane isomerization zone; hydroisomerizing benzene in the benzene hydroisomerization zone located in the lower part of the column and under all the other reaction zones; isomerizing hexanes in the hexane isomerization zone located above the feeding zone but lower than the pentane isomerization zone; isomerizing pentane in the pentane isomerization zone; recovering isohexanes from the column side output located above the hexane isomerization zone but under the pentane isomerization zone; recovering isopentanes from the column top; and recovering cyclopentanes from the column bottom.

9. The method according to claim 8 where the feeding-flow temperature is such that the flow is a vapor-liquid one where benzene is mostly in the liquid phase.

10. The method according to claim 9 where the feeding flow is directed into the column distillation zone located between the isomerization and hydroisomerization zones.

11. The method according to claim 10 where the feeding flow is split at the column input into two flows, one of which is descending and contains benzene and components with a higher molecular weight while the other flow is ascending and contains components whose molecular weight is lower than that of benzene.

12. The method according to claim 10 where paraffins C4 through C6 get from the feeding flow into the isomerization reaction zone above the feeding-flow entry point while aromatics, naphthenes, paraffins C7, and heavier hydrocarbons enter the hydroisomerization reaction zone under the feeding-flow entry point.

13. The method according to claim 8 where isomerization reactions are conducted in reaction zones outside the column while the mixture of products gets back into the column.

14. The method according to claim 8 where hydrocarbons and hydrogen are mixed right in the reaction zone and hydrogen is supplied to each zone separately.

15. The method according to claim 8 where the feeding flow consists of the C4 through C8 hydrocarbon fraction which contains benzene at a concentration between 0 and 30 percent (w/w).

16. The method according to claim 8 where benzene is hydroisomerized by using a catalyst which is zeolite covered with a Group VIII metal.

5 17. The method according to claim 8 where isomerization is done by using a catalyst which is a Group IV metal oxide covered with a Group VIII metal and promoted by sulfate and/or tungstate ions.

10 18. The method according to claim 8 where a hydrogen-to-hydrocarbon molar ratio is between 0.01 and 5; and i) a preferable value is between 0.01 and 3; and ii) a more preferable value is between 0.1 and 3; and iii) even more preferable one is between 0.08 and 1.5.

15 19. The method according to claim 8 where the overpressure in the column is between 10 and 40 atm in excess and a more preferable value is between 30 and 35 atm in excess.

20 20. The method according to claim 8 where the column temperature is between 80°C and 350°C; and i) the preferable value is between 80°C and 300°C; and ii) even more preferable value is between 150°C and 280°C.

20 21. The method according to claim 8 where the temperature at the column top is between 80°C and 220°C (preferably, between 150°C and 200°C) while the temperature at the column bottom is between 120°C and 350°C (preferably, between 220°C and 280°C).