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(54) METHOD FOR PRODUCING COMPONENTS FOR ENGINE FUELS

(57) The present invention relates to the production of high octane components of motor fuels, aromatic hydrocarbons, and hydrogen from gasoline fractions of petroleum and gas condensate origin and C_1-C_4 hydrocarbon gases. The invention may be useful in petroleum processing and gas processing industries.

The present invention solves the problem of raising the effectiveness of the process by increasing the yield of a high octane component to 95-98 percent by weight as calculated for the amount of gasoline fraction fed for processing, by reducing substantially the conversion of the feedstock into inferior hydrocarbon gases.

Gasoline fractions are processed under typical conditions of catalytic reforming. The products are separated into gaseous products (hydrogen and C_1-C_4 hydrocarbon gases) and liquid high octane products. Gaseous products are directed for separation to a zone of hydrogenation of aromatic hydrocarbons, wherein binding of hydrogen is effected through the incorporation thereof into the composition of forming hydrocarbons of the cyclohexane series, and separation from C_1-C_4 hydrocarbon gases. C_1-C_4 hydrocarbon gases continuously circulate from the hydrogenation zone to the reforming zone and back, with the hydrogen concentration and pressure being constant, and are not removed from the process. Cyclohexane hydrocarbons are directed to a catalytic dehydrogenation reaction vessel to produce: pure hydrogen which is removed from the process as a target product, and aromatic hydrocarbons which are recycled to the hydrogenation reaction vessel for blending with gaseous reforming products.

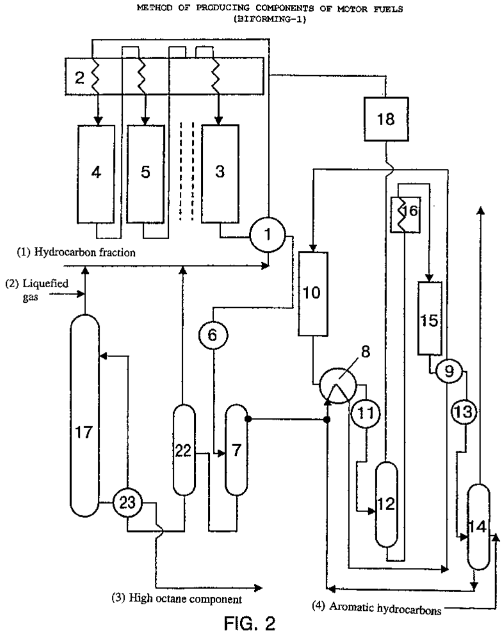

FIG. 2

Fig. 2. Flowchart of the process of producing components of motor fuels
(1) Hydrocarbon fraction; (2) Liquefied gas; (3) High octane component;
(4) Aromatic hydrocarbons

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Description

[0001] The present invention relates to the production of high octane components of motor fuels, aromatic hydrocarbons, and hydrogen from gasoline fractions of petroleum and gas condensate origin and C_1-C_4 hydrocarbon gases. The present invention may find application in petroleum processing and gas processing industries.

Description of the Related Art

[0002] Known the art is a method of processing gasoline fractions of petroleum and gas condensate, which boil out within the temperature range of 62°C to 190°C, into high octane components of motor fuels, aromatic hydrocarbons and hydrogen by catalytic reforming on catalysts containing platinum, chlorine and promoters on inorganic oxide carriers based on alumina (G.P. Antos, A.M. Aitani, and J.M. Parera / Catalytic Naphtha Reforming, Science and Technology, Marcel Dekker, Inc., 1995).

[0003] Also known is a process of catalytic reforming of gasolines, in which natural gas whose main component is methane is fed to the reforming zone (US Patent No. 3806447, C10G 35/06, 1974).

[0004] A disadvantage of this process is that adding gas to the reforming zone does not influence the selectivity of the process, but only contributes to improving the stability of the catalyst operation. The yield of the target product - a high octane component and aromatic hydrocarbons - as a rule does not exceed 75-85 percent by weight on conversion to the amount of gasoline fractions to be processed. Correspondingly, from 15 to 25% of the initial costly feed are converted to less valuable C_1-C_4 hydrocarbon gases. This lowers the effectiveness of the process and tells negatively on its economic characteristics.

[0005] The prior art most relevant in the technical essence and the obtained result to the herein-proposed process of producing high octane components of motor fuels and hydrogen is a process of reforming gasoline fractions with a two-step separation of the reaction products (US Patent No. 4615793, C10G 35/06, 1986). In the first step of the separation, at an elevated pressure and low temperature (Fig. 1), gas enriched with hydrogen is stripped from the reaction products, part of this gas is removed from the process, and the rest is recycled to the process. In the second step, at a higher temperature, hydrogen-depleted hydrocarbon gas containing predominantly C_2-C_5 saturated hydrocarbons is stripped from the reaction products and recycled to the reforming zone for blending with the feedstock. Disadvantages of this prior art process are a low effectiveness of stripping hydrogen and hydrocarbon gases by separation techniques along with a substantial power intensity of the process, caused by the necessity of compressing the hydrocarbon gas from the second-step separator to the value of pressure in the reforming zone. Furthermore, this process does not eliminate to a considerable extent the conversion of the feedstock into C_1-C_4 hydrocarbon gases, whereby the yield of the end product (high octane component) is on the level of 75-85 percent by weight, and the economic characteristics of the process are appreciably lowered.

Brief summary of the invention

[0006] It is an object of the present invention to increase the effectiveness of the process by increasing the yield of the high octane component to 95-98 percent by weight as calculated for the amount of the gasoline fraction supplied for processing, by reducing substantially the conversion of the feedstock into inferior light hydrocarbon gases.

[0007] Said object is accomplished by the provision of a process of producing high octane components of motor fuels, comprising reforming in the presence of a platinum-containing catalyst, followed by separating liquid high octane products from gaseous products (hydrogen and C_1-C_4 hydrocarbon gases) and recycling C_1-C_4 hydrocarbon gases to the reforming zone. The obtained gaseous products of reforming are subjected to separation by binding hydrogen when contacting thereof with aromatic hydrocarbons in a catalytic hydrogenation zone, whereafter the hydrogenation products are separated and C_1-C_4 hydrocarbon gases are recycled to the reforming zone. C_1-C_4 hydrocarbon gases continuously recirculate in a closed system from the hydrogenation zone to the reforming zone and back without being removed from the process. It is possible to supply an additional amount of C_1-C_4 hydrocarbon gases from an external source to the recirculating gas flow. The rate of binding hydrogen in the hydrogenation zone is maintained equal to the rate of hydrogen evolution in the reforming zone. The process in the hydrogenation zone is carried out at a pressure of at least 0.3 MPa and a temperature of 50-300°C on a catalyst containing Group VIII metal(s). The hydrogenation products are separated into cyclohexane hydrocarbons and C_1-C_4 hydrocarbon gases by the method of medium-temperature separation of phases. Bound hydrogen in the form of cyclohexane hydrocarbons are removed from the process. Cyclohexane hydrocarbons are directed to the catalytic dehydrogenation zone with subsequent separation of the dehydrogenation products into aromatic hydrocarbons, which are then recycled to the hydrogenation zone, and hydrogen. The process in the dehydrogenation zone is carried out at a temperature of 300-500°C on a catalyst containing Group VIII metal(s). C_1-C_4 hydrocarbon gases dissolved in liquid reforming products are separated and recycled to the reforming zone for blending with liquid feedstock. The reforming zone comprises one reaction vessel or a system of several reaction vessels.

[0008] The authors of the invention suggested to call this process **Biforming-1** as a trademark.

[0009] The schematic flow sheet of the process is shown in Fig. 2.

[0010] The feedstock of the process are straight-run gasoline fractions of petroleum or gas condensate origin, boiling out within the temperature range of 62°C to 190°C, with sulfur content not over 0.0001 percent by weight. The feedstock is heated in a heat exchanger 1 by the reaction products, blended with a flow of C_1-C_4 hydrocarbon gases recycled from the hydrogenation zone, and then heated in a multiple zone furnace 2 to the reforming temperature in a reaction vessel 3 (where $n \geq 1$). In the reaction vessels a complex of catalytic reforming reactions is carried out on platinum-containing catalysts. The reaction gives aliphatic hydrocarbons (having predominantly an iso-structure), aromatic hydrocarbons, hydrogen, and C_1-C_4 hydrocarbon gases. The reaction products give off their heat in the heat exchanger 1, become cooled in a cooler 6 and come to a separator 7. In the separator gaseous reaction products are separated from liquid ones. Liquid products from the separator 7 come to a low-pressure separator 22, wherein additional separation of light hydrocarbon gases, predominantly of C_1-C_4, takes place. The liquid high octane product from the separator 22 through a heat exchanger 23 comes to a column 17, wherein final separation of dissolved gases is effected by precise fractionation. The liquid product from the bottom of the column 17 is removed from the process through the heat exchanger 23. Gaseous products from the separator 22 and column 17 are recycled for blending with the reforming feedstock. Gaseous reaction products comprise a mixture of hydrogen (75-85 vol.%) and light hydrocarbon gases from 1 to 4. Gaseous reaction products are heated in heat exchangers 8 and 9, blended with a flow of aromatic hydrocarbons, and fed to a catalytic hydrogenation reaction vessel 10. In this reaction vessel there takes place the reaction of hydrogenation of aromatic hydrocarbons

$$C_6H_5R + 3H_2 + C_1\text{-}C_4 = C_6H_{11}R + C_1\text{-}C_4 \qquad (1)$$

where $R = H, CH_3, C_2H_5$, etc.

[0011] Here at a temperature of 50-300°C and a pressure of at least 0.3 MPa there occurs binding of hydrogen with its passing into the composition of high-molecular hydrocarbons of the cyclohexane series. C_1-C_4 hydrocarbon gases do not enter into the reaction, and thereby their effective and complete separation from hydrogen is accomplished. The reaction runs with a large evolution of heat, therefore the reaction products are cooled first in the heat exchanger 8, then in a cooler 11, and then fed to a separator 12, where C_1-C_4 hydrocarbon gases are separated from liquid hydrocarbons of the cyclohexane series, containing bound hydrogen in their composition. The hydrocarbon gases are recycled to the reforming zone for blending with gasoline fractions. The liquid hydrocarbons of the cyclohexane series are heated to a temperature of 300-500°C and directed to a reaction vessel 15 containing a heterogeneous catalyst for the selective dehydrogenation of naphthene hydrocarbons. In the reaction vessel 15 there takes place evolution of bound hydrogen in the reaction of catalytic dehydrogenation of hydrocarbons of the cyclohexane series:

$$C_6H_{11}R = C_6H_5R + 3H_2, \qquad (2)$$

where $R = H, CH_3^+, C_2H_5^+$, etc.

[0012] The reaction runs with a high speed and with selectivity close to 100%, which provides the possibility of obtaining hydrogen with a high degree of purity (> 95 mol.%). The reaction products are cooled in the heat exchanger 9, then in cooler 13, and fed to a separator 14. In this separator pure hydrogen is separated from aromatic hydrocarbons that are formed according to reaction (2). This hydrogen is removed from the process as an end product. Liquid aromatic hydrocarbons are heated in the heat exchanger 9, blended with the hydrogen-containing gas from the separator 12, and recycled to the process (reaction vessel 10) for binding and separating hydrogen from C_1-C_4 hydrocarbon gases. The process is carried out continuously by effecting as complex of the above-described operations in the reaction vessels 3, 10 and 15. Additional evolution of C_1-C_4 hydrocarbon gases dissolved in liquid high octane products of reforming, and also in liquid cyclohexane hydrocarbons, with subsequent recycling thereof to the reforming zone for blending with liquid feedstock, makes it possible to effect recirculation of C_1-C_4 hydrocarbon gases in full scope.

[0013] An essential distinctive feature of the proposed method of processing is the separation of gaseous reforming products into C_1-C_4 hydrocarbon gases and pure hydrogen.

[0014] It is also an essential distinctive feature of the proposed method of processing that the separation is carried out by contacting with aromatic hydrocarbons in the catalytic hydrogenation zone. Hydrogen becomes bound, separated from C_1-C_4 hydrocarbon gases, and passes into the composition of the forming hydrocarbons of the cyclohexane series.

[0015] In the known processes of catalytic reforming of gasolines, excess hydrogen-containing gas is removed from the process. This technique is an objective necessity, because under the process conditions, as a result of the occurring cracking and aromatization reactions, there evolves a large amount of hydrogen and light hydrocarbon gases, this being accompanied by a large increase in the volume of the reaction products, compared with the volume of the feedstock components supplied to the reforming reaction zone. The removal of excess amounts of the forming gases from the process is a necessary technique for maintaining constant and optimal pressure in the reforming system. In the proposed process this condition is insured by effective removal of hydrogen from the process by the technically simple and economical technique of binding hydrogen under the conditions of catalytic hydrogenation of aromatic hydrocarbons, with hydrogen molecules entering into the composition of hydrocarbons of the cyclohexane series.

[0016] Constancy of hydrogen concentration by maintaining the equality of the rates of hydrogen binding in the hydrogenation zone and of hydrogen evolution in the reforming zone is one of the distinctive features of the proposed method of processing. The rate of removing hydrogen from the reforming zone must be such as to compensate for the increase in the gas volumes in the reforming reaction zone. Usually, the amount of forming hydrogen is from 1.5 to 3.0 percent by weight of the amount of processed gasoline. Consequently, the catalyst operation conditions in the hydrogenation reaction vessel must insure binding said amount of hydrogen. This is achieved owing to the conditions of running the reaction (pressure, temperature), type of the catalyst (metals of Group VIII), and rate of feeding aromatic hydrocarbons to the hydrogenation reaction vessel 10. Optimal conditions for carrying out this operation are temperature of 50 to 300°C and pressure in the reaction vessel 10 of at least 0.3 MPa. The best catalysts are applied catalysts from Group VIII metals (platinum, palladium, rhodium, etc). The rate of supplying toluene is calculated from the formula:

$$\Pi_a = \frac{H_2}{3} \bullet M_a,$$

where

Π_a is the rate of supplying aromatic hydrocarbons to the reaction vessel 10 (g/hr);
H_2 is the amount of hydrogen evolving in the reforming (mole/hr);
3 is the stoichiometry of the reaction of hydrogenation of aromatic hydrocarbons;
M_a is the molecular weight of aromatic hydrocarbons.

[0017] For carrying out this reaction, it is most preferable to use aromatic hydrocarbons which have low volatility of vapors at temperatures of 15-30°C: this insures complete separation of their hydrogenation products from C_1-C_4 hydrocarbon gases at elevated pressures in the C_2 separator. To such hydrocarbons there belong aromatic hydrocarbons with the number of carbon atoms greater than seven (toluene, xylenes, aromatic hydrocarbons C_9 and higher). The chemical composition of the catalysts and the conditions of carrying out the process are presented in the Table. If the above-stated condition is not insured (see Example 5 in the Table), the pressure in the reforming system grows. The rate of this process is the higher, the greater the difference between the rate of hydrogen evolution in the reforming zone and the rate of hydrogen binding in the hydrogenation reaction vessel Γ is. In the given case, the necessary condition for the trouble-free carrying out of the process is the removal of excess part of hydrogen-containing gas. The main principle of the proposed process, which consists in complete recycling of the forming hydrocarbon gases to the reforming zone, with the hydrogen concentration and the pressure in the reforming system maintained constant, is violated. With the given technique, two essential effects are achieved, each of which to a considerable extent depends on the value of partial pressure of C_1-C_4 hydrocarbon gases in the reforming zone.

[0018] The value of the partial pressure of an individual component or of a group of components of a complicated mixture of reagents is determined from the equation:

$$P_i = P_o \bullet C_i,$$

where

P_i is the partial pressure of the component, atm;
P_o is the overall pressure in the reaction zone, atm;
C_i is the concentration of the component in the mixture, vol.%.

[0019] Under typical conditions of the catalytic reforming of gasolines, the hydrogen-containing gas contains 70-80 vol.% of hydrogen and 20-30 vol.% of hydrocarbon gases. Consequently, the partial pressure of hydrocarbon gases in the reaction zone of typical reforming is 20-30% of the overall process pressure, or 0.2-0.3 P_o. In the proposed process of producing high octane components of motor fuels, with the condition of equality of the rate of hydrogen absorption in the reaction vessel 10 to the rate of hydrogen formation in the reaction vessel 3 fulfilled, a real opportunity is provided for increasing the partial pressure of C_1-C_4 hydrocarbon gases in the reaction zone, equal to 0.3-0.95 P_o.

[0020] Under the given conditions, in the reforming reaction vessels, under the effect of the high concentration and partial pressure of C_1-C_4 hydrocarbon gases, the rate of the reactions of cracking and hydrogenolysis of the components of the reforming feedstock substantially lowers, down to complete termination thereof, and the formation of light hydrocarbon gases stops. At the same time, the rate of the reactions of isomerization and aromatization of paraffin hydrocarbons, i.e., of the target reactions which are the main source of increasing the octane number of the end product, increases. In view of these reasons, the proposed process insures the attainment of the yield of the end product (high octane gasoline and aromatic hydrocarbons) equal to 93-98 percent by weight as calculated for the amount of straight-run low octane gasoline fed for processing. In other words, in terms of this characteristic, the effectiveness of the proposed process excels the effectiveness of the known analogs by 10-20 percent by weight and approaches the theoretically possible level (100% as calculated for the supplied feedstock). The significance of said effect is such that the resource saving result attained in the present process for the feedstock is equivalent to additionally involving up to 20 percent by weight of petroleum feedstock for processing by the known methods.

[0021] A distinctive feature of the proposed method of processing is also that C_1-C_4 hydrocarbon gases formed as a by-product are not removed from the process, but continuously recirculate in the closed system from the hydrogenation zone to the reforming zone and back.

[0022] Secondary conversions of light hydrocarbon gases lead to the formation of liquid high octane components of motor fuels, that are hydrocarbons having five and more carbon atoms in the molecule. This is favored by the high partial pressure of hydrocarbon gases and their active recirculation through the catalyst bed in the reaction vessels 3 according to the scheme:

$3 \rightarrow 7 \rightarrow 10 \rightarrow 12 \rightarrow 3.$

Such conditions promote conjugated adsorption of the C_1-C_4 molecules of gas and of the molecules of the gasoline fraction components on the catalyst active sites of the same nature. Conditions are thus created for building light hydrocarbon molecules into the composition of compounds of a higher molecular structure. If the rate of the given reaction becomes higher than the rate of formation of C_1-C_4 hydrocarbon gases, then there occurs a drop of pressure in the system of the recirculating gas, the concentration of hydrogen therein remaining constant.

[0023] In the proposed process this effect is compensated for by supplying to the flow of the recirculating C_1-C_4 hydrocarbon gas a light hydrocarbon gas from an external source (C_1-C_4 hydrocarbon gas from natural gas deposits, dry gas from petroleum processing plants, etc.). The loss of C_1-C_4 gases owing to their conversion into liquid components of motor fuels is thus compensated for, and prerequisites are provided for additional formation of the end product. The attained level of the yield of reforming gasoline due to this effect is 95-98 percent by weight, as calculated for low octane gasoline fed for processing. This is equivalent to additionally involving another 5-7 percent by weight of liquid petroleum feedstock for processing by the known methods. Hence, maintaining constant pressure in the system by supplying to the recirculating flow the required amount of C_1-C_4 hydrocarbon gases from an external source is one more distinctive feature of the proposed method of processing.

[0024] Another distinctive feature of the proposed method of processing is the production of high-purity hydrogen by bringing hydrogen to the bound state, i.e., by incorporating it into the composition of the molecules of cyclohexane hydrocarbons that are formed in the hydrogenation zone and subsequent treating them in the catalytic dehydrogenation zone to release pure hydrogen. The dehydrogenation reaction proceeds in according to the equation:

$$C_6H_{11}R = C_6H_5R + 3H_2$$

in the presence of metallic catalysts from Group VIII metals. The reaction is carried out at high space velocities of feeding liquid hydrocarbons of the cyclohexane series (10-50 hr^{-1}) and temperatures within the range of 300-500°C. The use of industrial platinum catalysts, for instance, of a reforming catalyst, for carrying out the reaction, provides for the selectivity of the process, close to 100%. This circumstance constitutes the basis for obtaining high-purity hydrogen (> 99.0 mol.%). The reaction is run in the reaction vessel 15 (Fig. 2). This reaction vessel is supplied with hydrocarbons of the cyclohexane series from the separator 12, said hydrocarbons being preheated in a one zone furnace 16 to the reaction temperature. The reaction products are aromatic hydrocarbons and hydrogen, which are successively cooled in the heat exchanger 9 and cooler 13 and come to the separator 14. In the separator 14 high-purity hydrogen is separated from liquid aromatic hydrocarbons. Gaseous hydrogen is removed from the process as the end product. Aromatic hydrocarbons are recycled to the reaction vessel 10 for binding and separating reforming hydrogen from C_1-C_4 hydrocarbon gases.

[0025] It should be noted that the above-cited distinctive features of the proposed process provide for attaining a considerable technical result over the known methods only with the proviso that the entire combination of the steps constituting the essence of the proposed method are carried out. Excluding at least one of the above-cited steps leads to unbalance of the material flows and to lowering the effectiveness of the process as a whole.

[0026] The feedstock of the process are hydrocarbon fractions containing from 5 to 12 carbon atoms in the molecules of the components and boiling out within the range of temperatures from 65 to 190°C. Natural gas containing 95 vol. % of methane and hydrocarbon gas from a petroleum processing plant, containing 5 vol.% of ethane, 55 vol.% of propane, and 40 vol.% of butanes were used as the hydrocarbon gases.

[0027] Experiments according to the known method were carried out on a catalytic setup with reaction vessels of isothermal type, with the catalyst charge volume of 100 cm^3 (the setup is shown diagrammatically in Fig. 1) (US Patent No. 4615793, C10G 35/06, 1986).

[0028] The proposed method of processing fractions of liquid hydrocarbons and C_1-C_4 hydrocarbon gases is carried out on equipment which is shown diagrammatically in Fig. 2. In the reforming zone a system of one reactor and of three reactors is used.

[0029] Presented hereinbelow as Examples are data relevant to the main characteristics of the known method (Examples 1, 6) and of the proposed method (Examples 2, 3, 4, 7, 8). Example 5 is given for comparison.

[0030] ***Example 1*** illustrates the known method of catalytic reforming of gasoline fractions.

[0031] The setup is illustrated diagrammatically in Fig. 1. In the reforming unit one reaction vessel is used with the 100 cm^3 volume of the reaction zone. The process is carried out under catalytic reforming conditions.

[0032] The feedstock of a gasoline fraction with a 105-190°C, having a density of 0.743 kg/l, is supplied to a reforming reaction vessel 4 with the velocity of 150 ml/hr. In the course of the reaction there are formed hydrogen, a light hydrocarbon gas, and liquid hydrocarbons (catalyzate), which are cooled first in a heat-exchanger 1, then in a cooler 6, and after that are supplied for separation to a first-step separator 7. Owing to an increase in the volume of the reaction products, caused by vigorous evolution of hydrogen and light hydrocarbon gases, the pressure in the reforming system increases to 2.2 MPa. At that moment removal of the hydrogen-containing gas from the process is started through the separator, said gas containing 75 vol.% of hydrogen and 25 vol.% of light hydrocarbon gases which constitute a mixture of methane, ethane and propane. Liquid reaction products are condensed in the lower portion of the separator 7, and they are directed to a second-step separator 12. The pressure in the separator 12 is 0.3-0.8 MPa and is balanced by the conditions in a stripping column 17. In the second-step separator dissolved hydrogen and hydrocarbon gases are separated, extracted by a circulation compressor 18, and supplied for blending with the feedstock and further to the reforming reaction vessel. The process is carried out continuously for 100 hours. The conditions and main parameters of the process are presented in the Table.

[0033] The yield of the reaction products, in percent by weight, is as follows: high octane component, 79.2; dry hydrocarbon gas from the separator 7, 14.8; liquefied C_3-C_4 gases, 4.0; hydrogen, 2.0. The motor octane number of the reforming gasoline is 83 M.O.N. The content of aromatic hydrocarbons is 61.1 percent by weight.

[0034] ***Example 2*** illustrates the proposed method of producing motor fuels and hydrogen.

[0035] The process is carried out in a reforming setup which is illustrated diagrammatically in Fig. 2. In the reforming unit a reaction vessel is used with the 100 cm^3 volume of the reaction zone. The reaction vessel, as in Example 1, is charged with a polymetallic reforming catalyst, containing, in percent by weight: platinum, 0.25; rhenium, 0.3; chlorine, 0.1; carrier (aluminum hydroxysulfate), the balance. The reactors 10 and 15 are charged with the same catalyst, in the amount of 25 g each. Before the process is started, the catalysts in each reactor are reduced with hydrogen at 500°C, at the pressure of 1.0 MPa, and the hydrogen circulation rate of 10 nl/l_{cat} per hour.

[0036] The feedstock of a hydrocarbon fraction with a 62-190°C, having a density of 0.743 kg/l, is supplied to the reforming reaction vessel 4 with the velocity of 150 ml/hr. The reaction products from the reaction vessel 4 are cooled to a temperature of 15-30°C and fed to the high-pressure separator 7. Hydrogen (80 vol.%) and hydrocarbon gases (20 vol.%) from the separator 7 are fed for blending with a flow of toluene, which is supplied from the separator 14 with the velocity of 62.3 ml/hr. The mixture is heated to 250°C and fed to hydrogenation reaction vessel 10, wherein hydrogen is bound in the course of toluene hydrogenation, giving methylcyclohexane. The reaction is endothermic, so that the temperature over the bed increases by 25-35°C. The reaction products are cooled down to 15-30°C and fed to the separator 12. In this separator, owing to a great difference in the boiling points of methylcyclohexane and C_1-C_4 hydrocarbon gases their separation takes place. The hydrocarbon gases and a part of unreacted hydrogen are extracted by the compressor 18 and recycled to the reforming reaction zone. The conditions in the reaction vessel 5 are maintained such that the rate of binding and stripping hydrogen from the hydrogen-containing gas should be somewhat (1.1 to 1.3 times) higher in the beginning of the process and then equal to the rate of hydrogen formation in the reforming zone. Thereby the possibility is provided for a complete recycle of the entire amount of hydrocarbon gases to the reforming zone, with the hydrogen concentration and pressure in the system being constant. The optimal concentration range of the hydrogen-containing gas fed from the separator 12 to the reforming zone is from 20 to 50 vol.%. This insures an increase in the partial pressure of the hydrocarbon gas at the inlet of the reforming reaction vessel to 0.5-0.8 P_o, where P_o is the total pressure in the system. This condition is decisive for attaining the necessary effectiveness of the process. Under the effect of high concentration in the reaction zone, the hydrocarbon gases are adsorbed on the active sites of the catalyst, this providing for realization of two fundamentally important effects. In the first place, the rate of the reaction of cracking of the reforming feedstock components lowers considerably, down to complete termination, this being the main cause of an increase in the selectivity of the process and of an increase in the yield of liquid catalyzate. In the second place, intensive recirculation of hydrocarbon gases according to the scheme 12 - 18 - 4 - 7 - 12 provides prerequisites for secondary conversions of the hydrocarbon gases with the formation of liquid high octane (aromatic) hydrocarbons. So, the fundamental difference of the proposed process, consisting in that the hydrocarbon gas formed under the reforming conditions is not removed from the process as a inferior by-product, is realized. The hydrocarbon gas circulates in the closed system via the reforming zone and, suppressing the hydrocracking of the feedstock components, becomes incorporated into the composition of liquid high octane hydrocarbons. The yield of stable catalyzate increases from 79.2 to 92.5%, compared to the known methods of reforming, while the yield of gases decreases: the yield of dry gas, from 14.8 to 3.2%; and the yield of liquid hydrocarbon gas, from 4.0 to 1.5%. The factor responsible for the appearance of these gases as products of the process is their dissolution in the liquid product in the separator 7. In addition to these effects, an increase is observed in the selectivity of the target reactions. The content of aromatic hydrocarbons in the catalyzate increases from 62 to 69.3 percent by weight; the motor octane number increases from 83 to 89 M.O.N.; the yield of hydrogen increases from 2.0 to 2.8 percent by weight (see the Table).

[0037] Methylcyclohexane containing bound hydrogen in its composition is heated to the temperature of 500°C in the furnace 16 and fed to the dehydrogenation reaction vessel 15. In this reaction vessel methylcyclohexane is dehydrogenated to toluene and hydrogen that are formed in the mole ratio of 1:3. The reaction products are cooled down to 15-30°C and fed to the separator 14, wherein toluene is condensed and hydrogen is stripped therefrom. The purity of hydrogen is 97 mol.%. Liquid toluene is recycled for blending with the hydrogen-containing gas and further to the hydrogenation reaction vessel 10 for binding hydrogen from the reforming reaction zone.

[0038] ***Example 3*** illustrates the proposed method of carrying out the process.

[0039] The process is carried out as described in Example 2. The difference is as follows. The reforming reaction vessel 4 is charged with a polymetallic catalyst, comprising the following components, in percent by weight: platinum, 0.35; tin, 0.25; chlorine, 1.5; alumina, the balance.

[0040] The hydrogenation reactor vessel 10 and the dehydrogenation reaction vessels are charged with a catalyst having the following chemical composition, in percent by weight: platinum, 0.1; palladium, 0.5; alumina, the balance.

[0041] The temperature in the reaction vessel 4 is 490°C; in the reaction vessel 10, 150°C; in the reaction vessel 15, 400°C. The process pressure is 2.5 MPa. The rate of feeding toluene to the hydrogenation reaction vessel 10 is 67.3 ml/h.

[0042] For producing an additional amount of high octane gasoline, straight-run gasoline and a propane-butane fraction are fed to the reforming system in the amount of 5 percent by weight as calculated for the fed gasoline.

[0043] The main characteristics of the process are presented in the Table. The yield of high octane liquid catalyzate is 98.4 percent by weight as calculated for the feedstock. The yield of dry and liquid gas is 1.8 and 0.4%, respectively. The content of aromatic hydrocarbons in the catalyzate is 70 percent by weight; the octane number is 90 M.O.N. The yield of hydrogen having purity of 98.5 vol.% is 2.9 percent by weight. So, carrying out the proposed process under the above-described conditions has insured an increase in the yield of liquid catalyzate from 79.2 to 98.4%, i.e., by 19.2%. This is equivalent to involving into processing by the known methods an additional amount of gasoline exceeding 20-23 percent by weight for producing the same amount of the end product.

[0044] ***Example 4.*** The process is carried out as described in Example 2, the difference being in that the reforming reaction vessel 4 is charged with 70 g of a catalyst having the following chemical composition in percent by weight: platinum, 0.35; iridium, 0.35; chlorine, 1.3; alumina, the balance.

[0045] The dehydrogenation reaction vessel 15 is charged with a catalyst having the following chemical composition in percent by weight: palladium, 1.5; alumina, the balance.

[0046] The temperature in the reaction vessel 10 is 50°C; in the reaction vessel 15, 300°C. The process pressure is 0.3 MPa. The rate of feeding toluene to the reaction vessel 10 is 61 ml/h.

[0047] Constancy of pressure in the reforming zone is compensated for by pumping into the liquid feedstock a hydrocarbon gas from a petroleum processing plant, containing in percent by weight: ethane, 5; propane, 55; butanes, 40.

[0048] The main characteristics of the process are presented in the Table. The yield of high octane liquid catalyzate is 98.5 percent by weight as calculated for the supplied feedstock. The yield of hydrogen is 3.1 percent by weight; the purity of hydrogen is 99.0 vol.%. The octane number of the catalyzate is 87 M.O.N. The content of aromatic hydrocarbons is 67.8%.

[0049] ***Example 5*** (comparative)

[0050] The process is carried out as described in Example 4. The difference is as follows. The temperature in the reaction vessel 10 is maintained equal to 40°C; in the reaction vessel 15 the temperature is maintained equal to 250°C. The initial pressure in the system is ~ 0.2 MPa. These conditions do not insure complete binding of hydrogen evolving in the reforming zone. For these reasons there was a constant increase in the process pressure from 0.2 to 3.0 MPa.

To prevent pressure growth, it was necessary to remove part of hydrogen and of C_1-C_4 hydrocarbon gases from the process.

[0051] The main characteristics of the process are presented in the Table.

[0052] From these characteristics it follows that the temperature of 40°C and pressure of 0.2 MPa do not insure effective binding of hydrogen and its removal from the process.

[0053] The yield of liquid catalyzate is 84.2 percent by weight. The yield of hydrogen is 1.5 percent by weight.

[0054] ***Example 6*** illustrates the known method of producing high octane motor fuel by the reforming of petroleum fractions (for comparison).

[0055] The process is carried out as described in Example 1, the difference being in that the reforming system comprises three series-connected reaction vessels. The first reaction vessel is charged with 10 g of a platinum-rhenium catalyst, the second reaction vessel is charged with 20 g, and the third reaction vessel is charged with 40 g of the same catalyst. The total catalyst charge in the reforming zone is, as in Example 1, 70 g of the catalyst. The pressure in the system is 1.5 MPa.

[0056] The feedstock for the process is a hydrocarbon fraction of gasoline boiling in the temperature range of 65-105°C; the feedstock density is 0.695 kg/l.

[0057] The process characteristics are presented in the Table.

[0058] The yield of liquid catalyzate is 81.6 percent by weight. The octane number is 73 M.O.N.; the content of aromatic hydrocarbons is 42%.

[0059] ***Example 7*** illustrates the proposed method of carrying out the process. The reforming unit comprises three reaction vessels, as in Example 6, with a similar charge of the same catalyst.

[0060] The hydrogenation reaction vessel 10 is charged with a catalyst containing the following components in percent by weight: platinum, 0.2; rhodium, 0.25; carrier (alumina), the balance.

[0061] The dehydrogenation reaction vessel 15 is charged with a catalyst having the following chemical composition in percent by weight: platinum, 0.35; alumina, the balance.

[0062] The temperature in the reaction vessel 10 is maintained equal to 200°C; the temperature in the dehydrogenation reaction vessel 15 is maintained equal to 450°C. The process pressure is 1.5 MPa. The hydrogenation reaction vessel is fed with orthoxylene with the rate of 55.6 g/h. Dissolved C_3-C_5 hydrocarbon gases are separated from the high octane product of reforming (from the reforming zone) and from cyclohexane hydrocarbons (from the separator 12) in stabilization columns and directed to blending with the liquid reforming feedstock.

[0063] The conditions and main characteristics of the process are presented in the Table.

[0064] The yield of liquid high octane catalyzate is 97.4 percent by weight. The yield of hydrogen is 3 percent by weight. The octane number is 78 M.O.N., the content of aromatic hydrocarbons is 53 percent by weight.

[0065] ***Example 8*** illustrates the proposed method.

[0066] The process is carried out as described in Example 7. The difference is as follows.

[0067] The hydrogenation reaction vessel 10 is charged with a catalyst containing the following components in percent by weight: palladium, 3.0; porous silica, the balance.

[0068] The dehydrogenation reaction vessel 15 is charged with a catalyst containing the following components in percent by weight: platinum, 0.5; silica, the balance.

[0069] The temperature in the reaction vessel 10 is 300°C; the temperature in the reaction vessel 15 is 500°C. The process pressure is 2.5 MPa. The rate of feeding para-xylene to the reaction vessel 10 is 51.1 g/h. The conditions and characteristics of the process are presented in the Table.

[0070] The yield of liquid catalyzate is 97.2 percent by weight. The octane number is 76 M.O.N., the content of aromatic hydrocarbons is 50.9 percent by weight.

[0071] So, the proposed method of producing high octane gasolines insures a substantial increase in the yield of the target ;product and high-purity hydrogen, compared with the known methods.

Table

Characteristics of the method of producing components of motor fuels

Examples	Catalysts			Temperature			P, MPa	Feedstock, fractional composition, °C	Supplied, percent by weight		Produced, percent by weight					Catalyzate C_5+	
	3	10	15	3	10	15			Gasoline	Hydrocarbon gas	High octane component of aromatic hydrocarbons	Dry C_1-C_2 gas	Liquid C_3-C_4 gases	H_2	Total	Octane number, M.O.N.	Content of aromatic hydrocarbons, %
1. For comparison	N = 1 Pt+Re+Cl /Al_2O_3	-	-	495	-	-	2.2	105-190	100	-	79.2	14.8	4.0	2.0	100	83	62.1
2. Proposed	N = 1 Pt+Re+Cl /Al_2O_3	Pt+Re+Cl /Al_2O_3	Pt+Re+Cl /Al_2O_3	495	250	500	2.2	105-190	100	-	92.5	3.2	1.5	2.8	100	89	69.3
3. Proposed	N = 1 Pt+Sn+Cl /Al_2O_3	Pt+Pd/ Al_2O_3	Pt+Pd/ Al_2O_3	490	150	400	2.5	105-190	100	3.5	98.4	1.8	0.4	2.9	103.5	90	70.1
4. Proposed	N = 1 Pt+Ir+Cl /Al_2O_3	Pt+Pd/ Al_2O_3	Pd/Al_2O_3	490	50	300	0.3	105-190	100	5.0	98.5	2.5	0.9	3.1	105	87	67.8
5. For comparison	N = 1 Pt+Re+Cl /Al_2O_3	Pt+Pd/ Al_2O_3	Pd/Al_2O_3	490	40	250	0.2-3.0	105-190	100	-	84.2	12.1	2.2	1.5	100	85	64.5
6. For comparison	N = 3 Pt+Re+Cl /Al_2O_3	-	-	498	-	-	1.5	65-105	100	-	81.6	12.8	3.5	2.1	100	73	42
7. Proposed	N = 3 Pt+Re+Cl /Al_2O_3	Pt+Rh/ SiO_2	Pt/Al_2O_3	498	200	450	1.5	65-105	100	5.0	97.4	3.2	1.4	3.0	105	78	53
8. Proposed	N = 3 Pt+Re+Cl /Al_2O_3	Pd/SiO_2	Pd/SiO_2	498	300	500	2.5	65-105	100	5.0	97.2	3.9	1.1	2.8	105	76	50.9

Claims

1. A method of producing components of motor fuels, comprising reforming in the presence of a platinum-containing catalyst, followed by separating liquid high octane products from gaseous products (hydrogen and C_1-C_4 hydrocarbon gases) and recycling C_1-C_4 hydrocarbon gases to a reforming zone, wherein the reforming gaseous products are subjected to separation by binding hydrogen upon contact thereof with aromatic hydrocarbons in a catalytic hydrogenation zone, whereafter the hydrogenation products are separated, and C_1-C_4 hydrocarbon gases are recycled to the reforming zone.

2. The method according to claim 1, wherein C_1-C_4 hydrocarbon gases continuously recirculate in a closed system from the hydrogenation zone to the reforming zone and back, without being removed from the process.

3. The method according to claim 2, wherein an additional amount of C_1-C_4 hydrocarbon gases is fed from an external source into the recirculating gas flow.

4. The method according to claim 1, wherein the rate of binding hydrogen in the hydrogenation zone is equal to the rate of hydrogen evolution in the reforming zone.

5. The method according to claim 1, wherein the process in the hydrogenation zone is carried out at a pressure of at least 0.3 MPa and at a temperature of 50-300°C on a catalyst containing Group VIII metal(s).

6. The method according to claim 1, wherein the hydrogenation products are separated into cyclohexane hydrocarbons and C_1-C_4 hydrocarbon gases by the method of medium-temperature separation of phases.

7. The method according to claim 1, wherein bound hydrogen in the form of cyclohexane hydrocarbons is removed from the process.

8. The method according to claim 1, wherein cyclohexane hydrocarbons are directed to a catalytic dehydrogenation zone, the dehydrogenation products being subsequently separated into aromatic hydrocarbons, to be recycled to the hydrogenation zone. And hydrogen.

9. The method according to claim 8, wherein the process in the dehydrogenation zone is carried out at a temperature of 300-500°C on a catalyst containing Group VIII metal(s).

10. The method according to claim 1, wherein C_1-C_4 hydrocarbon gases dissolved in liquid reforming products are separated and then recycled to the reforming zone for blending with liquid feedstock.

11. The method according to claim 1, wherein C_1-C_4 hydrocarbon gases dissolved in liquid reforming products are separated and recycled to the reforming zone for blending with liquid feedstock.

12. The method according to claim 1, wherein the reforming zone comprises one reaction vessel or a system of several reaction vessels.

METHOD OF PRODUCING COMPONENTS OF MOTOR FUELS
(BIFORMING-1)

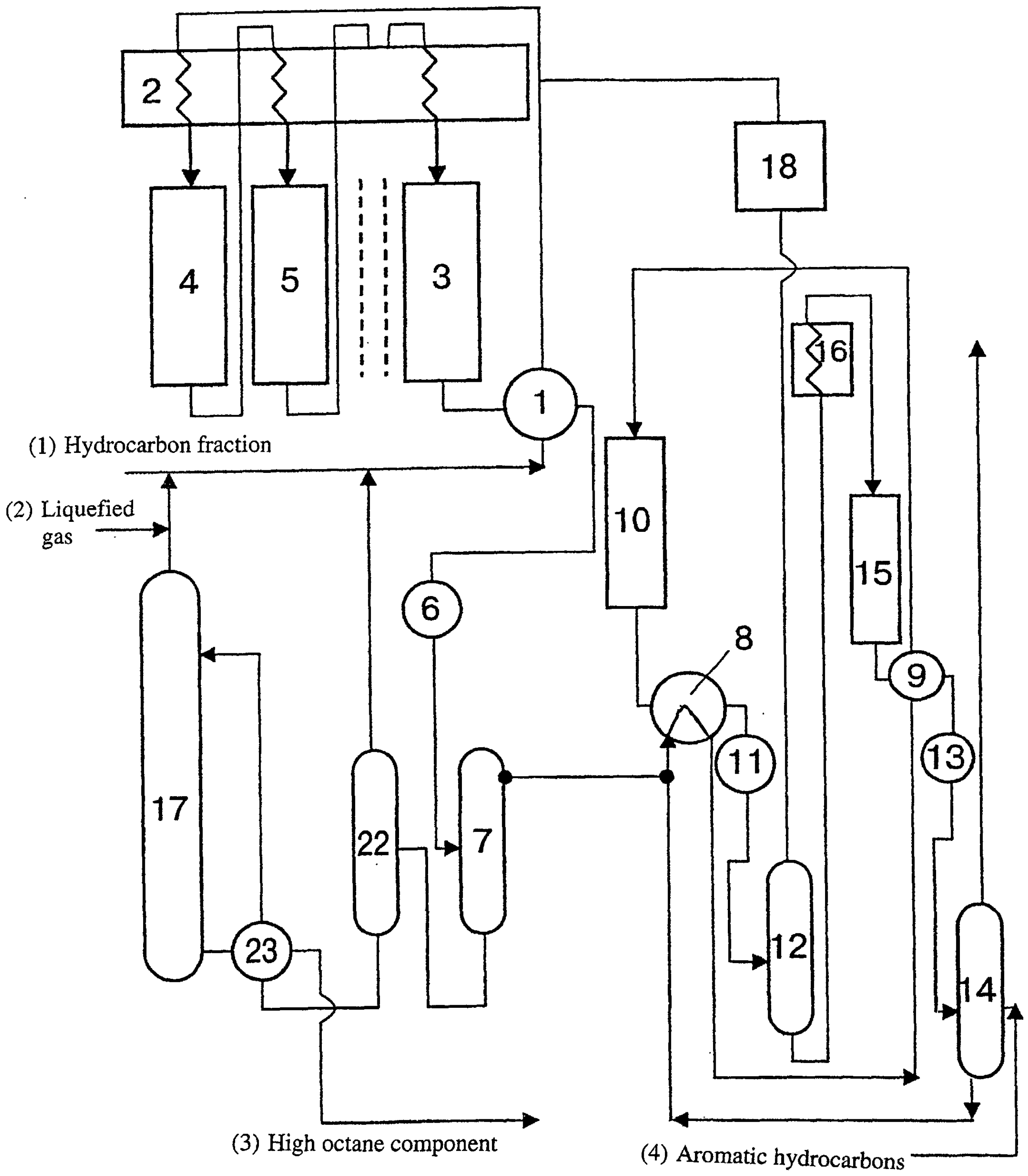

FIG. 2

Fig. 2. Flowchart of the process of producing components of motor fuels
(1) Hydrocarbon fraction; (2) Liquefied gas; (3) High octane component;
(4) Aromatic hydrocarbons

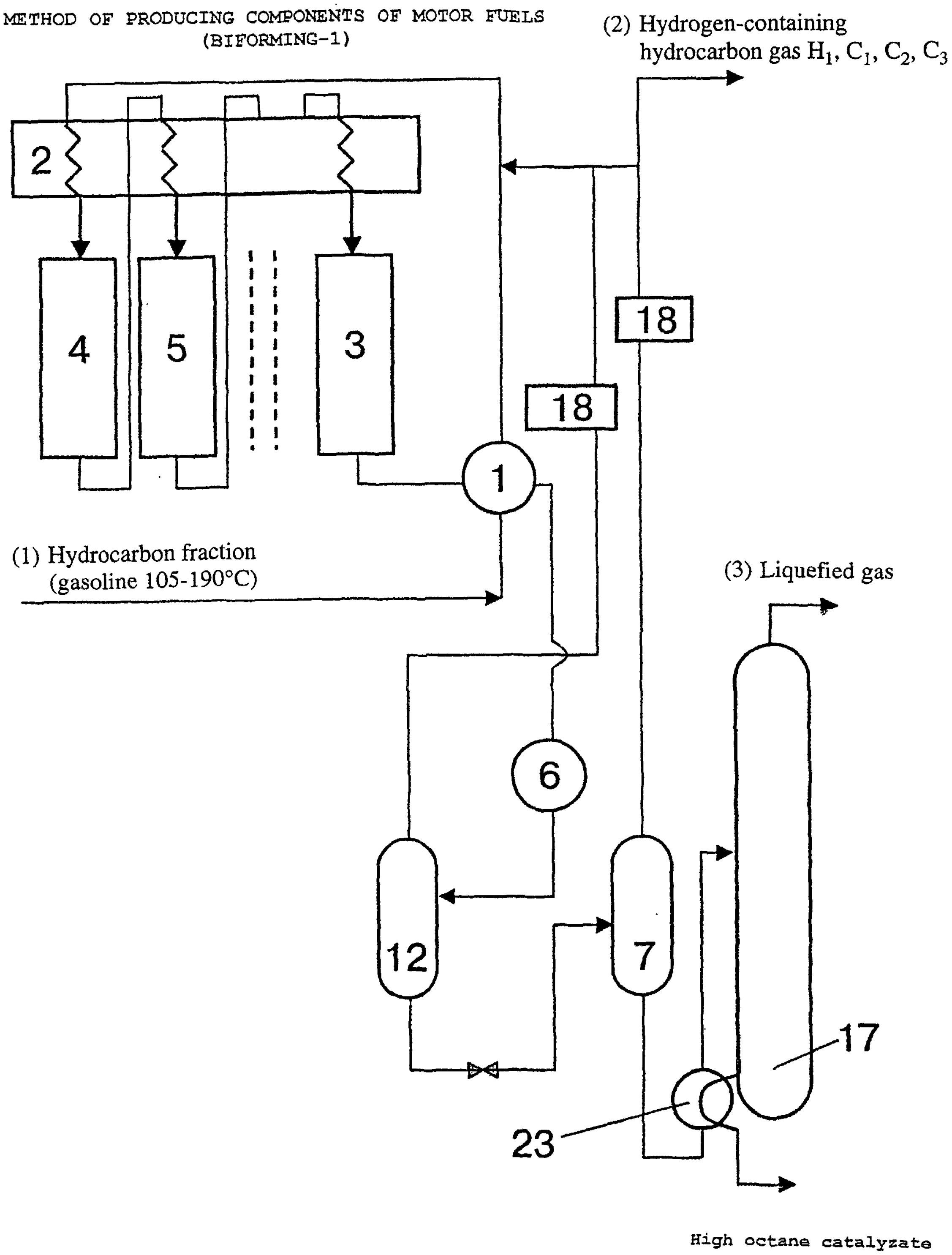

FIG. 1

Fig. 1. Flowchart of the known method of producing components of motor fuels (US Patent No. 4613793, C10G 35/06, 1986)
(1) Hydrocarbon fraction (gasoline 105–190°C); (2) Hydrogen-containing hydrocarbon gas H_1, C_1, C_2, C_3; (3) Liquefied gas

INTERNATIONAL SEARCH REPORT

International application No.
PCT/RU 00/00145

A. CLASSIFICATION OF SUBJECT MATTER
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According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
IPC 7 C10G 35/04, 35/06, 59/02, 63/00, 63/02

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	US 4615793 A (CHEVRON RESEARCH COMPANY) 07 October 1986 (07 10 86), the abstract, column 2 lines 32-57, the claims	1-12
A	US 5370786 A (UOP) 06 December 1994, the abstract, the drawing, column 5, lines 67-68 ; column 6, lines 1-38, the claims	1-12
A	RU 2124553 C1 (FALKEVICH Genrikh Semenovich) 10 January 1999 (10.01.99) the abstract, columns 8-12	1-12

■ Further documents are listed in the continuation of box C. ■ Patent family members are listed in annex.

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Name and mailing address of the R U	Authorized officer Telephone No.

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