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(54) Process for production of high quality gasoline with low aromatic content

(57) A two-stage process for production of high-octane gasoline from a hydrocarbon stream comprising C_4-C_{12} hydrocarbon mixtures of paraffins, optionally including cycloalkanes, aromatics and olefins is disclosed. During the first step linear molecules are activated and converted predominantly to mono-branched isomers. Present cyclic molecules and olefins are hydrogenated, but conversion must be sufficiently low to avoid ring opening. Only such (low) amount of multi-branched isomers is formed in the first reaction zone that extent of cracking is still acceptable. Concentration of multi-branched isomers is consecutively increased in the second step. Reaction of mono-branched isomers requires lower activation energy than cracking and isomerisation of linear molecules. Monomethyl-paraffins readily react to their multi-branched counterparts with a high selectivity under mild reaction conditions with catalysts having a Hammet acidity value lower than -10 at temperature of maximum 100°C and at least 50°C lower than in the first step. These conditions effectively isomerise hydrocarbon molecules containing tertiary carbon, while other feed components are little effected. The combination of both steps utilising different catalysts and conditions is essential to achieve a high selectivity. Both reaction steps can be combined with separation of low octane number paraffin molecules by a suitable separation process.

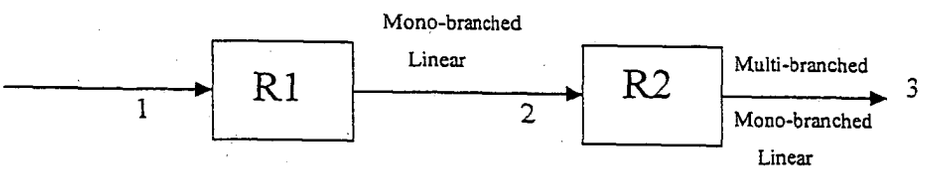

FIG. 1

EP 1 357 167 A1

Description

BACKGROUND OF THE INVENTION

[0001] The present invention relates to a process for the production of high quality gasoline with reduced content of aromatic compounds. In particular, the invention is a catalytic two stage isomerisation process of C_4-C_{12} paraffinic hydrocarbons to multi-branched hydrocarbons.

[0002] Multi-branched paraffins are ideal gasoline blending components possessing high octane numbers. For environmental reasons there is also a need to find substitutes for aromatic components in gasoline. Therefore, there is an incentive to develop a process for increasing octane number of the C_4-C_{12} cuts. While C_5/C_6 paraffin isomerisation is a common refinery process, commercialisation of processes including higher fractions (C_{7+} hydrocarbons) meets significant difficulties given by high degree of cracking to gas and low octane number of the once-through products. The present invention relates to a catalytic process, where combinations of given steps allow sufficient yields of products with high octane numbers also for the C_{7+} hydrocarbon fraction. The process can thus convert the complete C_4-C_{12} cut, or it can solely be designed for the C_{7+} fraction.

[0003] The C_{7+} fraction is difficult to isomerise because of several reasons. Unlike the C_5/C_6 paraffins, mono-branched C_{7+} isomers possess too low octane number. Octane number is around 50 for methylhexanes, and linear molecules have RON equal to zero or even negative when blended with other hydrocarbons. Only multi-branched paraffins are valuable blending components, but their concentration is limited by thermodynamics. A maximum of 40% of multi-branched C_7 isomers can be formed by passing n-heptane once-through over an isomerisation catalyst at 230°C. This number increases to 50% at 150°C. All mono-branched and linear isomers have to be removed from the product and recycled with close to 100% selectivity. Although separation of linear isomers is a common technology, no efficient and economical process to separate mono-branched from multi-branched isomers is operational.

[0004] Still another difficulty is that C_7 and longer paraffin molecules are very susceptible to cracking. Unlike their shorter counterparts, heptane and longer molecules can crack fully via tertiary carbenium ion, thus their cracking requires relatively low activation energy. The reaction intermediate is identical for both isomerisation and cracking paths, therefore it is very difficult to separate both reactions.

[0005] Currently, C_{7+} hydrocarbon fractions are converted in the refinery scheme by catalytic reforming. This process is particularly inefficient for C_7 and C_8 isomers with liquid yields only around 80% to obtain gasoline with RON=90. Moreover, the large part of the product consists of aromatics of which the maximum fraction in the gasoline is limited by environmental legislation.

[0006] C_{7+} isomerisation must be able to offer yields and octane numbers comparable with catalytic reforming. This is, however, a very difficult task. The typical reaction temperature for the C_5/C_6 zeolite catalyst is around 230°C. Due to thermodynamics only a maximum yield of 40% can be reached at this temperature. Simple calculation reveals that not more than 7% of paraffins can be cracked during the reaction to achieve liquid yields comparable with reforming. Performance of known solid catalysts is far behind these basic requirements. For example, in Handbook of Heterogeneous Catalysis (Eds. G. Ertl, H. Knözinger and J. Weitkamp, Wiley-VCH, Weinheim, 1997, p. 2003) it is shown that the solid catalyst can approach 85% of equilibrium in hexane isomerisation with only 2.1% of cracking. When only 59% of n-heptane are converted on the same catalyst cracking is as high as 55.3%. Zeolite Beta belongs to the most selective C_7 isomerisation zeolite-based catalysts (U.S. Patent Nos. 5,233,121 and 5,095,169), but still the maximum achievable yields are around 25% only. U.S. Patent No. 5,648,589 describes use of $Pt/WO_3/ZrO_2$ catalyst in n-heptane isomerisation. Although n-heptane conversion is only about 60% (mainly to mono-branched products), as much as 8% of heptane is cracked. Even the most active solid catalysts do not reach sufficient selectivity. For example FR Patent No. 2,771,307 describes the use of a catalyst based on $AlCl_3$ in n-heptane isomerisation at 110°C. Although the branched isomers represent only 73% of the C_7 paraffin fraction (with this conversion vast majority of the products are still mono-branched isomers) cracking is already 7%.

[0007] As formation of multi-branched isomers is thermodynamically more favoured at low temperatures, the situation improves by utilising liquid catalysts at temperatures below 100°C. However, the liquid catalysts, most typically presented by SbF_5/triflic acid, still do not possess sufficient selectivities even under high hydrogen pressures. For example U.S. Patent No. 3,839,489 describes heptane isomerisation at room temperature with a yield of multi-branched isomers 33.5%, but with 53.5% cracking. Commercial application of these catalysts is moreover very difficult due to inevitable corrosion and very difficult regeneration.

[0008] Still another problem with C_{7+} isomerisation is separation. Any percentage of n-heptane present in the product decreases its octane number by one point, so the separation must be very efficient. Due to low once-through yields of multi-branched products, large recycles are expected. Distillation or reactive distillation (U.S. Patent No. 5,948,948) sometimes used in separation of C_5/C_6 isomers is difficult to apply to the separation of hydrocarbons with carbon number greater than 6 as the number of possible isomers increases sharply and boiling points get much closer. Pressure swing adsorption is commonly applied to separate linear paraffins, but when applied to separate mono-branched prod-

ucts, selectivities close to 100% are very difficult to obtain. For example U.S. Patent No. 4,956,521 describes a C_5/C_6 isomerisation process that includes separation of the product stream by PSA using silicalite and Ca-A zeolites as adsorbents. Another possibility for separation is zeolite membranes. Use of zeolite membranes for a broad spectrum of possible applications was described in U.S. Patent No. 5,069,794, among others very generally also for paraffin isomer separation. Still another possibility is using chromatography separation on various adsorbents. The separation proceeds by passing the hydrocarbon mixture through the column filled with molecular sieve and the separated streams of products are withdrawn in the end of the column. U.S. Patent Nos. 5,770,783 and 5,744,684 describe a process based on reactive chromatography, where the molecular sieve is mixed with the isomerisation catalyst to combine the separation and reaction step. Simulated moving bed is a similar option as described in U.S. Patent No. 6,348,637.

[0009] It is common to use a two-reactor concept in C_5/C_6 isomerisation. The first reactor typically operates at high temperature to achieve high space velocities, while the second reactor is operating at much lower temperature to achieve thermodynamically more favourable product composition. This configuration is used for example in the Penex Process (UOP). The purpose of this configuration is mainly to limit the catalyst and reactor volume. The same or better selectivity can be obtained by simply increasing the reactor volume and operating at the temperature used in the second reaction zone. If the selectivity is the main issue this configuration is not sufficient and substantially different catalysts and conditions must be used as shown in this invention.

[0010] A two reactor configuration is also disclosed in EP 653,400 A. This application describes a process for preparation of multi-branched paraffins from a feed consisting of linear paraffins of at least 5 carbon atoms. The process comprises two molecular sieve units, in which mono-branched isomers are produced on shape selective 10-membered ring molecular sieve, while multi-branched isomers should be produced in the next stage on zeolite with large pores to avoid cracking. No experimental data are, however, presented.

[0011] Isomerisation by two separate steps, i.e. to produce mono-branched isomers in the first stage and to convert these to valuable products in the second stage, was also studied by E. Benazzi et al. (IFP, Europacat 5, Limerick 2001). The conclusion of this study was negative as no selectivity improvement was observed, when two zeolitic catalysts in a series were used. Again substantially different catalysts and conditions must be used.

DETAILED DESCRIPTION OF THE INVENTION

[0012] The general object of this invention is to provide increased octane numbers of a C_4-C_9 hydrocarbon mixture through isomerisation in a multi-stage process without substantial cracking of produced multi-branched hydrocarbons. "Multi-Branched Isomers" as used herein before and in the following description means compounds containing more than one carbon atom having bond to at least three other neighbouring carbon atoms. Mono-branched isomers are defined as compounds containing just one such atom.

[0013] The general embodiment of the invention is a combination of two catalytic steps. In a first step, linear paraffins are activated by being selectively converted to predominantly mono-branched isomers at high temperatures (typically around 200°C) on solid catalysts. Mono-branched isomers are further converted in a second step under much milder conditions typically at temperature 100°C lower, preferably in presence of a liquid catalyst. The milder conditions, which are essential to suppress cracking, can be applied since mono-branched isomers are significantly more reactive than n-paraffins. They are readily converted under conditions, when n-paraffin reaction is still slow. Although the catalytic system in the second stage is not limited to liquids, these materials are more attractive than solid catalysts, since they are stronger acids and their acid strength is more uniform. Since the liquids can be easier handled than solids, they are also easier to reactivate.

[0014] The main intermediate for heptane cracking is 2,4-dimethylpentane carbenium ion, which is also the basic isomerisation intermediate. Isomerisation starting from mono-branched isomers requires only tertiary carbenium ion, which has low energy of formation. Both cracking and n-heptane activation need the more energetically demanding secondary ion. Cracking and heptane isomerisation are thus almost inseparable under normal conditions, where selectivities are too poor. It is possible, however, to use the subtle differences in activation energies by dividing the process into two steps. Handbook of Heterogeneous Catalysis (Eds. G. Ertl, H. Knözinger and J. Weitkamp, Wiley-VCH, Weinheim, 1997, p. 1140) gives a difference in enthalpy of formations between tertiary and secondary carbenium ions approximately 15 kJ/mole. The following examples show that at low (e.g. ambient) temperatures it is possible to find a combination of conditions and a catalyst, which is able to activate mono-branched isomers, while linear molecules remain almost intact and cracking to gas is very slow. Such combination is for example a liquid catalyst with a Hammet acidity of about -14 and reaction temperature of about 50°C at ambient pressure under inert atmosphere. Decreasing the acid strength would require increasing reaction temperature and otherwise. The basic assumption is that the catalyst possesses sites of homogeneous acid strength. This condition is better fulfilled on liquid than on solid catalysts. Selectivity and activity of the catalyst is also improved in the presence of compounds containing tertiary carbon like methylcyclohexane and isobutane. There are also several other factors influencing the isomerisation reaction known to the person skilled in the art like for example hydrogen pressure (decreasing activity but increasing selectivity), the way of

contacting catalyst and feed (inefficient contact will require higher reaction temperature), etc.

[0015] There are two options to perform the first isomerisation step to mono-branched isomers selectively. The first choice is use shape selective molecular sieve as a catalyst, which does not allow formation of bulky (multi-branched) cracking intermediate. The other option is to operate at such conversion that concentration of multi-branched isomers is relatively far from thermodynamic equilibrium and thus cracking is limited. The second option is based on the simple fact that mono-branched isomers are necessary and first step on the way to multi-branched isomers. It is almost always possible to stop the reaction in the stage, when some mono-branched isomers (typically at least 50%) are formed with almost no reaction to multi-branched isomers and cracking. Some catalysts and conditions are more efficient for this application as described below.

[0016] In the second step, from mono to multi-branched isomers, mild reaction conditions (combination of the reaction temperature below 100°C and corresponding uniform acid strength for example 50°C and H_0 = -14) are chosen to avoid formation of secondary ion. Although reaction of linear molecules and cracking proceed very slowly, isomerisation reaction of mono-branched isomers too high octane product is still fast.

[0017] The multi-stage process consists of the following steps:

1. Reactor section for formation of mono-branched isomers and saturation of aromatics with a very low extent of ring opening, preferentially using a solid catalyst.
2. Optional separation section for recycles of non-converted linear molecules.
3. Reactor section for conversion of mono-branched isomers to multi-branched isomers, preferentially using a liquid catalyst or a supported liquid phase catalyst. This step might include recovery and reactivation of the catalyst.
4. Separation section for concentration of multi-branched isomers and cycloalkanes using e.g. distillation, molecular sieve membranes, simulated moving bed or pressure swing adsorption.

[0018] In the first isomerisation step, mono-branched paraffins are prepared from linear molecules on shape selective molecular sieves. These acidic molecular sieves do not allow further (double and triple) branching due to steric reasons. They possess pores of which the minor axis has a minimum width of 4 Å and the major axis has a maximum width of 7 Å and the average value of the both axes should be in the range from 4.5 to 6.5 Å. The material should not contain any cavities which diameter is larger than 8 Å. The molecular sieves can be any of the following structural type: AEL (for example SAPO-11, MeAPO-11), AFO (for example SAPO-41 or MeAPO-41), FER (for example ferrierite, FU-9 or ZSM-35), MFS (for example ZSM-57), MTT (for example ZSM-23, EU-13 or ISI-4), MWW (for example MCM-22 or ITQ-1) and TON (for example Theta-1, ZSM-22, ISI-1 or NU-10). The preferred material is the AFO type. The catalyst (in acidic form) would further typically contain a binder (alumina for example) and noble metal with loading of 0.05 to 1 wt%. The noble metal is typically Pt or Pd or a mixture thereof, which are most suitable to achieve sufficient selectivity and to suppress deactivation. The reaction proceeds in presence of hydrogen with hydrogen to hydrocarbon ratio between 0.1 to 5, at the temperature range 150°C to 400°C with a total pressure varying between 1 and 40 bar and liquid hourly space velocity LHSV between 0.1 to 30 h^{-1}. The preferred conditions are temperatures between 250°C-300°C, LHSV = 0.5-5 h^{-1}, pressure between 5-15 bar and a hydrogen:hydrocarbon ratio between 1 and 3.

[0019] The C_4/C_{10} hydrocarbon streams contain typically a significant fraction of aromatics, which content is strictly limited by legislation (especially in the case of benzene). During the first step the aromatic compounds are hydrogenated, but ring opening of cycloalkanes formed is limited to minimum by shape selective properties of the catalyst. The shape selective properties mean that there is not enough space (pore diameter) around the active sites to form intermediate leading to this reaction. This is important not only to keep high octane number of the product, but also for a proper function of the liquid catalyst during the second isomerisation step.

[0020] Another possibility in the first step is to use a non-shape selective catalyst, and to operate sufficiently far from thermodynamic equilibrium between mono and multi-branched isomers. The multi-branched isomers crack much faster than their mono-branched counterparts, and if their concentration is sufficiently low cracking can be limited. Mono-branched isomers are by definition the first products of isomerisation of linear molecules. The reaction can always be stopped in such stage, when extent of following reactions (isomerisation to multi-branched isomers and cracking) is low so that cracking is below 5%. The typical examples of suitable catalysts are materials based on tungsten oxide or tungsten containing compounds both supported or unsupported. Tungsten oxide catalysts supported on zirconia, hafnia, titania or SnO_2 are of main interest. However, in principle all oxides of group VI elements supported on group IV oxides are potential candidates for the application (using current IUPAC nomenclature for the periodic table of elements). Yet another group of materials applicable are heteropoly acids consisting of Keggin ion structures. The most typical examples are phosphotungstic and silicotungstic acids. Friedel-Crafts catalysts based on $AlCl_3$ can also be used for this application.

[0021] Similarly to shape selective materials the other group of catalysts also requires the presence of 0.05 to 1 wt% of noble metal. The noble metal is typically Pt or Pd or a mixture thereof. The reaction proceeds in the presence of hydrogen with a hydrogen to hydrocarbon ratio between 0.1 to 5 at the temperature range 150°C to 300°C with total

pressure varying between 1 and 40 bar, and liquid space velocity LHSV between 0.1 to 30 h^{-1}. The preferred conditions are temperatures between 130°C-250°C, LHSV=0.5-5 h^{-1}, pressure between 5-15 bar and a hydrogen:hydrocarbon ratio between 1 and 3.

[0022] The purpose of the second reaction step is to increase the concentration of multi-branched isomers under conditions without cracking. This can be done by tuning reaction conditions and catalyst most significantly influenced by varying the reaction temperature and the catalyst acid strength. Materials especially suitable for the second step are liquid super acids. There might be various liquid catalysts used for example a range of fluorinated alkanesulfonic acids, HF, sulphuric acid, etc., optionally promoted with strong Lewis acids like SbF_5. The other preferred materials are ionic liquids, i.e. complexes of group III halogenides with quarternary amines. An example of such a material is a mixture of trimethylammonium hydrochloride and aluminium chloride in ratio 1:2. Advantage of these materials is their non-miscibility with the hydrocarbon phase, their very low viscosity, their low vapour pressure and their non-dangerous handling as concern corrosion.

[0023] The total process scheme is based on the combination of two reaction steps described in the above paragraphs and at least one separation step. All these steps can be combined in various ways. The simplest process is shown schematically in Fig. 1. R1 is the isomerisation unit operating with the solid catalyst and R2 is the second isomerisation step. The hydrocarbon feedstock is passed via line 1 to the first isomerisation unit R1. The effluent from R1 comprising predominantly linear and mono-branched isomers is passed via line 2 to the second isomerisation unit R2. The effluent from R2 consists mainly of multi-branched high-octane number isomers and cycloalkanes.

[0024] A further embodiment of the process is illustrated in Fig. 2. The hydrocarbon feedstock is passed via line 1 to the isomerisation units R1 and R2. The effluent from unit R2 is passed via line 3 to a separator S1. The effluent from separator S1 containing linear paraffins is recycled to reactor R1. The product stream 5 consists mainly of multi-branched isomers and cycloalkanes.

[0025] The process sequence as described in Fig. 1 and Fig. 2 is also illustrated in Fig. 3. The effluent from reactor R1 is passed via line 2 to the separation unit S1. In separation unit S1 linear paraffins are separated from mono-branched paraffins and are recycled back to R1. The mono-branched paraffins are fed to reactor R2 for further isomerisation to multi-branched paraffins.

[0026] Another embodiment of the process is illustrated in Fig. 4. Compared to the process in Fig. 3, this process comprises of an extra separator S2 after reactor R2. The separation unit S2 separates mono-branched isomers from multi-branched isomers. The mono-branched isomers are recycled to reactor R2.

[0027] Still another embodiment is to transfer separator S1 behind reactor R2 with separator S2 present or not present or using a separator, which separates linear and mono-branched isomers in one step and recycles them into one of the reactors.

[0028] For each of the versions of the process of the invention separation is accomplished in the liquid or gas phase using e.g. zeolite membranes, adsorption or distillation. ZSM-5 membranes or PSA based on zeolite A can be successfully applied to remove linear molecules. Adsorbents with larger pores have to be used to perform separation of multi-branched isomers and cyclic compounds by PSA. The example of such adsorbent is a non-acidic form of the AFO molecular sieve. Moving bed or simulated moving bed can be economically more feasible with less efficient adsorbents like silicalite, since they allow larger amount of theoretical separation steps than PSA.

Example 1

[0029] In order to illustrate the invention an example is now given to describe a process configuration capable of producing high RON gasoline with a high liquid yield.

[0030] Zirconium oxide is prepared by adding diluted ammonia to a water solution of zirconyl nitrate and adjusting pH to 11. The mixture is refluxed for 4 days. The white solid is filtered and dried overnight at 120°C. 30 wt% of ammonium metatugstate is added to the zirconia support by incipient wetness impregnation and the sample is calcined for 3 hours at 750°C. 0.3% Pd is introduced to the catalyst by cation exchange and the catalyst is calcined at 350°C before being put into the reactor.

[0031] The feed used in the reaction is a C_7 cut consisting of 32 wt% cycloparaffins, 3 wt% toluene and 65% of heptanes. The detail composition is shown in Table 1. The reaction is performed in a fixed bed reactor at 190°C with LHSV=1 h^{-1} at the total pressure 6 bar, and the feed consisting of a hydrocarbons:hydrogen mixture with the ratio of 1:2. The detail feed and product compositions are shown in Table 1.

Table 1

Feed and product compositions referring to the first reaction step		
	Feed [wt%]	**Product [wt%]**
Propane	-	0.7
Isobutane	-	0.9
Isopentane	-	-
Isohexanes	-	-
2,2-dimethylpentane	-	4.0
2,4-dimethylpentane	0.6	4.5
2,2,3-trimethylbutane	-	0.5
3,3-dimethylpentane	-	1.0
2-methylhexane	13.5	17.2
2,3-dimethylpentane	0.5	4.4
3-methylhexane	11.4	15.9
3-ethylpentane	1.2	1.1
n-heptane	37.6	15.5
Cycloheptanes	32.2	34.2
Toluene	3	-
RON - calculated	49.5	64.8

[0032] The product is cooled down and hydrogen and light products are removed. The feed is contacted with the liquid catalyst in a stirred autoclave at 0°C for 1 hour under inert atmosphere. The catalyst is ionic liquid consisting of trimethylammonium hydrochloride and aluminium chloride in the ratio 1:2 to which 10 molar% of anhydrous $CuCl_2$ is added. The volume ratio between the catalyst and the hydrocarbon phase is 1:1. The feed and product composition is shown in Table 2. The hydrocarbon fraction is easily separated from the liquid catalyst and sent to the caustic treatment to remove ppm levels of HCl.

Table 2

Feed and product compositions referring to the second reaction step		
	Feed [wt%]	**Product [wt%]**
Propane	-	-
Isobutane	0.1	0.2
Isopentane	-	-
Isohexanes	-	-
2,2-dimethylpentane	4.0	4.1
2,4-dimethylpentane	4.5	11.0
2,2,3-trimethylbutane	0.5	1.2
3,3-dimethylpentane	1.0	1.1
2-methylhexane	17.4	16.1
2,3-dimethylpentane	4.5	5.0
3-methylhexane	16.1	10.3

Table 2 (continued)

Feed and product compositions referring to the second reaction step		
	Feed [wt%]	**Product [wt%]**
3-ethylpentane	1.2	0.2
n-heptane	15.8	15.7
Cycloheptanes	34.9	34.8
Toluene	-	-
C_{7+}		0.3
RON-calculated	61.6	66.4

[0033] 25 g of adsorbent (APO-41) is pre-heated to 150°C under hydrogen atmosphere. 5 ml of the feed (Table 3) is pumped into the adsorber, and when the mixture is equilibrated pressure increases to 2.2 bar. 15 ml/min hydrogen flow is sent through the adsorber keeping the pressure at the constant level and the product is condensed and collected for the first 8 minutes. The composition of the product is shown in Table 3. The temperature in the reactor is increased to 250°C and desorbed hydrocarbon together with hydrogen are sent directly to the first reactor. The adsorbent is cooled down and prepared for the next cycle. As the adsorbent possesses weak acid sites besides separation methyl shift from 2,4-DMP and 2-MH to 2,3-DMP and 3-MH occurs, which is beneficial for a higher octane number of the product.

Table 3

Separation step - composition of recycle and product streams		
	Recycle	**Product**
Propane	-	-
Isobutane	-	0.9
Isopentane	-	-
Isohexanes	-	-
2,2-dimethylpentane	1.6	13.1
2,4-dimethylpentane	8.0	12.6
2,2,3-trimethylbutane	0.4	4.2
3,3-dimethylpentanes	0.5	3.3
2-methylhexane	17.8	-
2,3-dimethylpentane	4.3	16.8
3-methylhexane	15.8	-
3-ethylpentane	0.1	0.1
n-heptane	20.0	-
Cycloheptanes	31.1	48.6
Toluene	-	-
C_{7+}	0.2	0.5
Fraction of feed	78.6	21.4
RON - calculated	59.6	93.2

[0034] The once-through yield is 22.9% the calculated research octane number of the product is 93.2 and the liquid (C_{5+}) yield of the whole process configuration is 93%.

Claims

1. A process for production of high-octane gasoline from a hydrocarbon feed stream comprising of C_4-C_{12} hydrocarbon cuts or intermediate cuts of linear paraffins and naphtenes, aromates and olefins comprising

   two isomerisation steps in series by subjecting the feedstock in a first isomerisation step to a first isomerisation reaction in presence of a first catalyst in form of a solid acid containing noble metal being effective in converting the linear paraffins to mono-branched isomers and saturation of aromatics to saturated cyclic hydrocarbons; and

   in a second isomerisation step increasing concentration of multi-branched isomers in effluent from the first step by converting the mono-branched isomers contained in the effluent to the multi-branched isomers in presence of a second catalyst having a Hammet acidity value lower than -10, and at reaction temperature of up to 100°C and at least 50°C lower than the temperature in the first step.

2. Process of claim 1, further comprising a first separation step for separation of the linear paraffins contained in the effluent from the first isomerisation step and/or a second separation step for separation of the linear paraffins and mono-branched isomers contained in the effluent from the second isomerisation step.

3. Process according to claim 1, wherein the first catalyst comprises a solid, shape selective molecular sieve, and/or a mesoporous, acidic catalyst and the second catalyst comprises a liquid super acid.

4. Process according to claim 1, wherein the first catalyst comprises an acidic, shape selective molecular sieve with a pore diameter of 4 to 7 Å, further containing at least one noble metal of palladium and platinum in an amount of 0.01 to 5 wt%.

5. Process of claim 3, wherein the mesoporous, acidic catalyst is tungsten oxide supported on zirconia, titania, hafnia or tin oxide with a tungsten content of between 5 to 50 wt%.

6. Process of claim 1, wherein the first isomerisation step is carried out at a temperature of between 100°C and 400°C in presence of hydrogen under total pressures between 1 to 40 bar with hydrogen to hydrocarbon ratio between 1 to 10.

7. Process of claim 1, wherein the second isomerisation catalyst comprises any fluorinated alkanesulphonic acid, hydrofluoric acid; sulphuric acid or mixtures thereof and/or an ionic liquid based on complexes of metal halogenides with quaternary ammonium salts.

8. Process of claim 3, wherein the liquid catalyst is grafted on inorganic solid support.

9. Process wherein the effluent from the first isomerisation reactor is passed directly to the liquid isomerisation process.

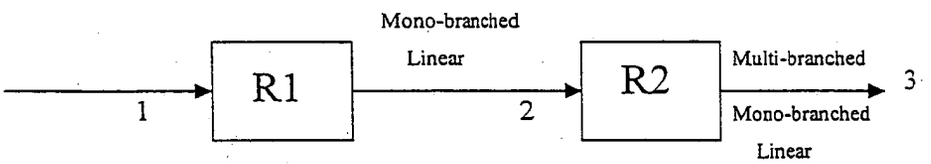
Mono-branched
Linear
R1
R2
Multi-branched
Mono-branched
Linear
1
2
3

FIG. 1

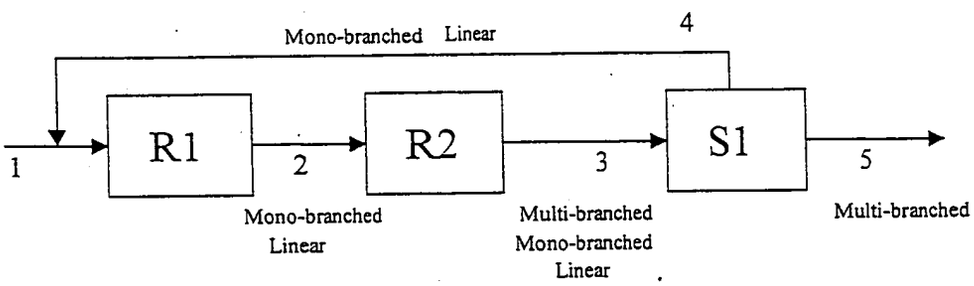
Mono-branched Linear
4
R1
R2
S1
1
2
3
5
Mono-branched
Linear
Multi-branched
Mono-branched
Linear
Multi-branched

FIG. 2

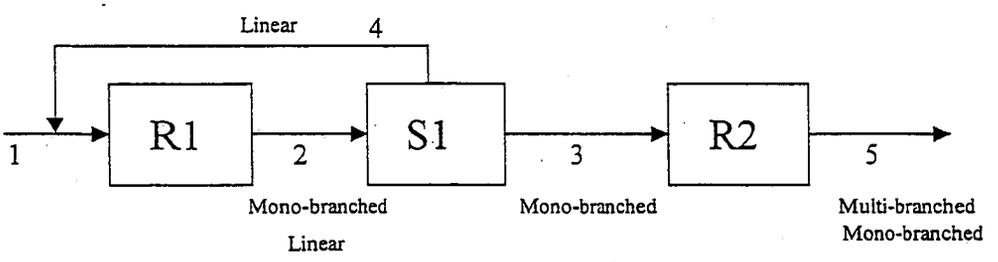
Linear
4
R1
S1
R2
1
2
3
5
Mono-branched
Linear
Mono-branched
Multi-branched
Mono-branched

FIG. 3

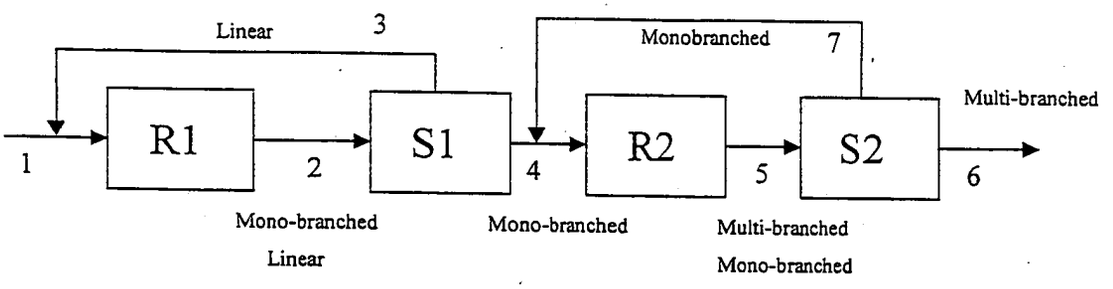
Linear
3
Monobranched
7
Multi-branched
R1
S1
R2
S2
1
2
4
5
6
Mono-branched
Linear
Mono-branched
Multi-branched
Mono-branched

FIG. 4

European Patent Office

EUROPEAN SEARCH REPORT

Application Number
EP 03 00 6545

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