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(54) Process for producing middle distillates

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Procédé de production de distillats moyens

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Description**PROCESS FOR PRODUCING MIDDLE DISTILLATES**

5 **[0001]** The present invention relates to a process for producing middle distillates. The process produces hydrogen, gasoline and middle distillate from a heavy naphtha and an olefinic stream.

BACKGROUND OF THE INVENTION

10 **[0002]** Currently, there is an imbalance between the demand and the production of diesel fuel and gasoline in the European market. As a result of the decrease in the demand for gasoline in the European market, many catalytic reforming units are out of service most of the time.

[0003] Catalytic reforming units are catalytic units with several reactors in series, where a straight run naphtha or a conversion naphtha, such as, for example, an FCC (Fluid Catalytic Cracking) naphtha, undergoes naphthene dehydrogenation, paraffin isomerisation and paraffin dehydrocyclisation reactions, in order to improve the properties of said naphthas as fuels and, more specifically, increase their octane number for gasolines.

15 **[0004]** There are several patents and commercial processes, from the companies Axens and UOP, for example, which describe this industrial process in depth, such as, for example, patent US 4431522.

[0005] On the other hand, the literature discloses different processes for obtaining middle distillates. For example, patent WO 00/39253 discloses the improvement of the cetane number of FCC heavy naphthas or FCC light gas oil, by directly alkylating them with olefinic streams, in the presence of a solid acid catalyst. Patent US 4594143 discloses the alkylation of Jet-fuel (150°C-260°C) with an olefinic stream, to produce a diesel fuel fraction, using a solid acid catalyst. Patent US 290460 discloses the production of alkyl aromatics with a high octane number in the gasoline distillation range, starting from aromatic and olefinic streams. In patent US 791639, diesel fuel is produced from the alkylation of a direct distillation naphtha with a high aromatic content and FCC naphthas with an acid catalyst such as aluminum chloride.

20 **[0006]** Patent WO 00/39253 discloses a process for obtaining diesel fuel by the alkylation of a heavy naphtha stream or a distillate containing more than 40% by weight of aromatics with a second stream that contains olefins, in the presence of a solid acid catalyst. Said patent does not mention that the aromatic-rich stream may be obtained by reforming the heavy naphtha nor the naphthene content of said stream.

30 **[0007]** Patent WO 2008/043066 discloses a process for the production of middle distillates, such as kerosene and diesel fuel. The process includes a step where the paraffinic naphtha is converted into benzene and olefins, and the benzene and the olefins are made react, in order to obtain alkylbenzenes. The process described uses a Sn/Pt catalyst to perform the first step. In said step, the production of aromatics is practically limited to benzene, since the rest of the C7+ paraffins are basically converted into olefins.

35 **[0008]** Patents US 5380425 and US 5273644 disclose processes comprising reforming and alkylation. Both processes introduce a benzene-containing effluent to the alkylation step.

Patent US 4594144 discloses a process for reforming and alkylation, with intermediate extraction of aromatic compounds

40 **[0009]** On the other hand, it is worth noting that there is a growing need for hydrogen, largely due to the toughening of environmental legislation in the field of fuels. Producing fuels with less than 10 ppm of sulfur entails a great increase in hydrogen consumption, and this consumption may increase even further if, in upcoming years, the sulfur content in other fuels, such as aviation jet fuel and heating gas oils, is reduced. Moreover, the minimum biocomponent content in fuels could also make it necessary to process or co-process oils or fats in hydrosulfurisation (HDS) units, to obtain diesel fuel of bio-renewable origin, with the consequent increase in hydrogen consumption.

45 **[0010]** Taking into consideration all of the above, economical options are needed which make it possible to produce middle distillates from naphthas or olefinic streams and which, as far as possible, make it possible to re-adapt existing industrial units, thereby minimising the investment. Processes are needed which are flexible in regards to the feeding thereof, capable of processing combinations of different streams depending on the situation at a given time, and contribute to the production of hydrogen.

DESCRIPTION OF THE INVENTION

50 **[0011]** The present invention relates to a process to produce hydrogen, gasoline and a middle distillate which can be used for the blending of middle distillates dedicated to fuels. Although the process can be implemented from scratch, it can be also implemented by modifying an existing catalytic reforming plant, by using one of the multiple reforming reactors for the dehydrogenation of naphthenes and the remaining reactors to carry out an alkylation process.

[0012] Surprisingly, when the naphthas undergo a dehydrogenation reaction prior to the alkylation step with an olefinic stream, better yield of middle distillate is obtained in the overall process.

[0013] The process as herein disclosed produces hydrogen, gasoline and a middle distillate. The process can also produce a LPG fraction. Another advantage of the process is that it can be used as raw material olefinic streams and straight run naphthas, whose current destination is the production of gasoline or the chemical industry. In addition, hydrogen is obtained, which is currently a necessary and expensive chemical and refineries may present a deficit of it.

[0014] Moreover, the possibility of adapting a catalytic reforming plant for the production of a middle distillate from an aromatic and/or a naphthenic stream and an olefinic stream, entails a reduction of the costs. Furthermore, the catalyst of the process can be regenerated in situ by burning the coke formed during the process with air.

[0015] Therefore, in a first aspect, a process for producing hydrogen, gasoline and a middle distillate is provided according to claim 1.

[0016] Preferred heavy naphtha to be used in step (i) is an hydrocarbon stream with a content of at least 20% w/w of naphthenes plus aromatics, and with a distillation range between 75°C to 200°C, preferably between 90°C to 140 °C. Specific examples of suitable naphtha for the process as herein disclosed are straight-run naphtha, heart cut FCC naphtha, aromatic concentrates, coker naphtha, visbreaker naphtha, steam cracker naphtha or mixtures thereof. Preferably the naphtha is straight-run. C6+ heavy naphtha is also preferred. A C6+ heavy naphtha is a heavy naphtha that consists essentially of molecules with 6 or more carbon atoms.

[0017] The dehydrogenation of the heavy naphtha of step (i) is carried out at typical temperature higher than 250°C, preferably between 250°C and 650°C, more preferably between 350°C and 650°C and more preferably between 480°C and 530 °C. The pressure of the system in this step is typically between 1 and 80 bar, and preferably between 3 and 30 bar.

[0018] The aromatic compounds are typically produced in the dehydrogenation of heavy naphtha in the presence of at least one reforming catalyst of step (i). In addition, the content of naphthenes is typically reduced after the dehydrogenation of heavy naphtha in the presence of at least one reforming catalyst of step (i). In the step (ii) excellent results are obtained when the amount of naphthenes is as low as possible and the amount of aromatic compounds is as high as possible. Normally, at least a 20% by weight of the stream of naphtha used in step (ii) are aromatics and less than a 1 % by weight of the stream of naphtha used in step (ii) are naphthenes.

[0019] In the process as herein disclosed, a reforming catalyst is used in step (i). It will be understood by those having skill in the art that there may be more than one reforming catalyst in step (i). Examples of useful reforming catalysts used in step (i) as herein disclosed include Pt, Re, Ir, Ge, Sn or mixtures thereof supported over alumina. The reforming catalyst could be preferably selected from RG-582 and RG-682 of Axens or R62, R86, R56 and R98 of UOP or mixtures thereof.

[0020] In a preferred embodiment of the invention, at least 90% of the hydrogen produced at the stage of dehydrogenation is separated between steps (i) and (ii) or between steps (ii) and (iii). Preferably, essentially all the hydrogen produced at the stage of dehydrogenation is separated between steps (i) and (ii) or between steps (ii) and (iii). Even more preferably, more than 99 % of the hydrogen produced is separated.

[0021] When the step (i) is completed, an alkylation step (ii) is carried out. In this step, the olefins are alkylated with the aromatic compounds produced in step (i) or oligomerised by reacting among them, giving rise to a new hydrocarbon stream, which is rich in compounds with a distillation range of 150+ (products that distillate at temperature above 150°C according to standard ASTM D86). The alkylation of aromatic compounds with olefinic streams, using a solid acid catalyst such as zeolites, acidic resins or supported phosphoric acid, to produce alkylaromatics and oligomers, is studied in the literature. For example, the production of specific compounds such as ethylbenzene, cyclohexylbenzene or cumene is described in the patents WO 96202148, US 6730625 and US 4992606 respectively. The stream from step (i), rich in aromatic compounds (dehydrogenated naphtha), is mixed in the presence of a solid acid catalyst, with a stream rich in olefins. Solid acid catalysts useful for the process as herein disclosed are zeolites, acid resins, supported phosphoric acid, aluminosilicates, or mixtures thereof.

[0022] In a preferred embodiment the solid acid catalyst is a zeolite. Preferred zeolites are beta, mordenite, ferrierite, ZSM-5, faujasite (type Y or X) or mixtures thereof. More preferably the zeolite is a beta zeolite. And more preferably, the zeolite is beta zeolite with a SiO₂/Al₂O₃ ratio of 25, which will be called hereafter "Beta 25".

[0023] In one embodiment, the solid acid catalyst is an ITQ catalyst, synthesized at Instituto Tecnológico Químico (ITQ) at Valencia (Spain). The preferred ITQ catalysts are ITQ-39, ITQ-30, ITQ-2 or mixtures thereof.

[0024] In another embodiment, the solid acid catalyst is a MCM catalyst. The preferred MCM catalysts are MCM-5, MCM-22, MCM-36, MCM-49, MCM-56 or mixtures thereof. More preferably, the MCM catalyst is MCM-5 catalyst.

[0025] In one embodiment, the solid acid catalyst is an acid resin. The preferred acid resins are selected from Acid Resins manufactured by Purolite, or the AMBERLYSTTM manufactured by Rohm and Haas and supported Nafion resin manufactured by Dupont and mixtures thereof.

[0026] Nafion refers to a sulfonated tetrafluoroethylene based fluoropolymercopolymer. Preferred Nafion for the present invention are Nafion NR50, NR40, R1000 and R1100.

[0027] Preferably the acid resin is Purolite CT-275, Amberlyst A-15, A-35, A-36, A-46 or mixtures thereof. More preferably the acid resin is Purolite CT-275.

[0028] Since in both sections of reactions the deactivation of the catalyst is due to the formation of coke or coke

precursors on the surface thereof, it may be required to periodically regenerate the catalyst. The three typical processes to regenerate the alkylation catalyst are: hydrogen stripping, gasoline/naphtha washing and combustion with air. In the dehydrogenation section, the catalyst regeneration is normally held at intervals of at least six months after stopping the unit, and air is introduced to burn the coke. In the alkylation section, as the catalyst deactivation is normally faster, the process contemplates having two (even three) reactors in parallel or in series with a facility such that while one is in normal operation, the other is regenerating the catalyst. The zeolite catalyst regeneration may be performed by washing with a stream of hydrocarbon as disclosed in the patent WO 01/83408 or by a stripping with hydrogen as disclosed in the patent EP 0679437 or by burning the coke with air.

[0029] The adequate temperature to carry out step (ii) depend on the solid acid catalyst used, preferably the temperature is between 80°C and 350°C, more preferably between 200 and 300°C. The pressure of the system is normally between 2 and 120 bars, and preferably between 30 and 60 bars.

[0030] In another preferred embodiment of the process as herein disclosed, the olefinic stream is selected from ethylene; propylene; butene, preferably FCC butene; pentene, preferably FCC or Cracker pentene; olefinic LPG; heart cut FCC naphtha; coker naphtha; FCC light naphtha and mixtures thereof. More preferably the olefinic stream of step (ii) is selected from the group consisting of propylene, butene, pentene, FCC light naphtha, and mixtures thereof.

[0031] In another preferred embodiment of the process as herein disclosed, the fraction obtained in step (iii) also comprises LPG. LPG are mixtures of C3 and C4 hydrocarbons which are predominantly propane, propylene, n-butane, butylenes, iso-butane and isobutylene.

[0032] The production of the middle distillate fraction is typically between 10 and 70% weight/weight of the initial mixture of compounds obtained in step (ii). The fraction rich in gasoline is typically between 30 and 90% weight/weight of the initial mixture of compounds obtained in step (ii). The fraction rich in LPG is typically less than 45% of the mixture of compounds obtained in step (ii).

[0033] The separation of the middle distillate and other fraction rich in gasoline may be carried out by distillation.

[0034] Preferably the heavy naphtha of step (i) comprises less than 0.5 ppm of sulphur and less than 0.5 ppm of nitrogen.

[0035] Preferably the olefinic stream which feeds step (ii) comprises less than 1 ppm of nitrogen. The elimination of nitrogen can be carried out by treatment with acid resins for example. Surprisingly, it has been noticed that contents of nitrogen higher than 1 ppm in the olefinic stream of step (ii) may inhibit the formation of middle distillates by alkylation reactions.

[0036] Optionally, after the alkylation section, the obtained product may need to be fractionated into gasoline (150-, which are products that distillate at temperature below 150°C according to standard ASTM D86) and middle distillate (150+), preferably by distillation.

DEFINITIONS

[0037] LHSV: Liquid Hourly Space Velocity (units: h^{-1}). It is calculated as volumetric flowrate divided by the volumen of the catalyst in the reactors, and it is equivalent to the inverse of the residence time.

[0038] WHSV: Weight hourly space velocity (units: h^{-1}). It is calculated as mass flowrate divided by mass of catalyst in the reactors.

[0039] ASTM D86: This test method covers the atmospheric distillation of petroleum products using a laboratory batch distillation unit to determine quantitatively the boiling range characteristics of such products.

[0040] PIONA: Method of analysing chemical components by means of chromatography. The compounds are grouped into families (Paraffins, Isoparaffins, Olefins, Naphthenes and Aromatics).

[0041] The "octane number", sometimes called "octane rating", is a scale that measures the anti-knock capacity of the fuel (such as gasoline) when it is compressed inside an engine cylinder. Although commercially a single Octane Number is usually mentioned, the technical specifications of different countries include two values, which measure the behaviour of gasoline in two different situations:

- R.O.N. *Research Octane Number* - This is the one that is usually shown in gas stations. It represents, approximately, the behaviour in the city: Low regime with numerous accelerations.
- M.O.N. *Motor Octane Number* - Octane rating tested in a static engine. It is intended to reproduce the situation in roadways, high regime and regular driving.

[0042] The "cetane number or rating" is related to the time that elapses between the injection of fuel and the beginning of the combustion thereof, called "Ignition interval". High-quality combustion takes place when there is a fast ignition, followed by total, uniform burning of the fuel. In sum, it is an indicator of the efficiency of the reaction that takes place in internal combustion engines.

[0043] This number is calculated from the density and the boiling point of the hydrocarbons that make up the basis of the fuel. The calculation method has always been strictly standardised, and for quite a long time a two-variable equation

was used to determine it (ASTM D976); currently, a more precise correlation (ASTM D4737) is applied, which operates with four variables.

[0044] FCC (Fluid Catalytic Cracking): This is a process for converting the heavy hydrocarbons present in vacuum gas oils, which makes it possible to produce gasoline and, consequently, increase the yield of this fuel in refineries, by reducing the production of residual products. The FCC process is based on the decomposition or breakdown of high-molecular-weight molecules; this reaction is promoted by a zeolite-based solid catalyst in pulverised form, which is incorporated into the load hydrocarbons in a tubular-type reactor with an upward flow. At the reactor outlet, the catalyst is separated from the reaction products by means of cyclones, and the coke that is generated and adhered thereto due to the high reaction temperatures is burnt in a special equipment prior to being re-circulated into the reactor; the energy released during the burning is used to provide part of the heating to the load stream.

[0045] "Coker": this process consists of heating a residual oil feed to its thermal cracking temperature in a furnace with multiple parallel passes. This cracks the heavy, long chain hydrocarbon molecules of the residual oil into coker gas oil and petroleum coke.

[0046] "Coke": Products of condensation reactions that deactivate the catalyst by blocking the active centers of the catalyst.

[0047] "Straight run naphtha": Direct distillation naphtha, which has not undergone any catalytic conversion process.

[0048] "Heart cut FCC naphtha": Naphtha produced in an FCC process with a distillation range of between 80°C-150°C.

[0049] "Reformate": Naphtha produced in a catalytic reforming process. Its boiling range is between 75°C-170°C and it is basically composed of aromatics and isoparaffins.

[0050] "Dehydrogenation": Process whereby a hydrocarbon molecule loses one or more Hydrogen molecules. When it is applied to the production of aromatic compounds, each hydrocarbon molecule loses 3 hydrogen molecules.

[0051] "Alkylation": Chemical process whereby an aromatic compound and an olefin react to form an alkyl aromatic compound.

[0052] "LPG": Liquefied petroleum gas is a flammable mixture of hydrocarbon gases used as a fuel in heating appliances and vehicles. It consists of hydrocarbon molecules of 3 and 4 carbon atoms.

[0053] In petroleum engineering, "full range naphtha" is defined as the fraction of hydrocarbons in petroleum boiling between 30 °C and 200 °C. It consists of a complex mixture of hydrocarbon molecules generally having between 5 and 12 carbon atoms. It typically constitutes 15-30% of crude oil, by weight. "Light naphtha" is the fraction boiling between 30 °C and 90 °C and consists of molecules with 5-6 carbon atoms. "Heavy naphtha" boils between 90 °C and 200 °C and consists of molecules with C6+, preferably 6-12 carbons.

[0054] The term "gasoline" refers to any liquid fuel that can be used to operate a spark ignition internal combustion engine. Gasoline typically contains a mixture of C5 to C10 hydrocarbons having a boiling range of about 70 °C to 160 °C (ASTM D86).

[0055] The term "partially recycled" refers to a stream of at least 90%(v) with respect to the fraction rich in gasoline obtained in step (ii).

[0056] The term "middle distillate" refers to a hydrocarbon fraction, wherein the hydrocarbons consist essentially of hydrocarbons typically having a carbon chain length of 10 to 25 (designated C₁₀-C₂₅). The middle distillate fraction typically has a boiling point in the range of 150 °C to 430 °C (ASTM D86) and preferably 175 °C to 350 °C (ASTM D86). The middle distillate hydrocarbons are those typically used as kerosene and/or diesel fuels. It should be noted that since distillation does not provide an absolute cut off at a specific chain length, the various distillate fractions may contain insignificant amounts of hydrocarbons having a slightly lower or slightly higher carbon chain lengths. The cut off point in the distillation slightly varies depending on the intended use and the desired properties of the middle distillate. Thus, a distillate fraction comprising a wider range of hydrocarbons such as C₉ to C₂₆ or a narrower range of hydrocarbons such as C₁₄ to C₁₈ should also be understood as a middle distillate fraction.

[0057] "Light fraction" refers to a hydrocarbon fraction, wherein the hydrocarbon chain length is 1 to 4 (designated C₁-C₄). The light fraction also includes other gaseous components such as hydrogen, depending on the process from which the light fraction derives.

[0058] The term "kerosene" refers to a hydrocarbon fraction with a boiling point of 150°C to 220°C. It is part of the called Middle distillate.

[0059] The term "diesel" refers to a hydrocarbon fraction with a boiling point of 220°C to 380°C. It is part of the called Middle distillate.

[0060] As used herein, "reforming catalyst" refers to a dehydrogenation catalyst and requires a metal to provide the dehydrogenating activity, preferably dispersed on a support material. Examples of these metals include platinum and palladium, although several metals may be present at the same time, such as, for example, platinum-rhenium, platinum-germanium or platinum-tin. If cyclisation and/or isomerisation activity are required in the catalyst, as in the case of the catalytic reforming process catalyst, it is preferred that the metal or metals be dispersed on an acid support, such as, for example, alumina, chlorided alumina or a zeolite. The reforming catalysts may be prepared by using any suitable techniques. Example of those catalysts are well known in the art, as for example in the patents US 4124491 and CA

1080689.

[0061] By the term "acid catalyst" is meant a substance which has the ability to donate protons as defined by Bronsted, or a substance which can form a covalent bond with an atom, molecule or ion that has an unshared electron pair as defined by Lewis, or a substance which presents both Bronsted and Lewis acid sites. Any known acid catalyst can be used for the process as herein disclosed.

[0062] As defined here, "a zeolitic catalyst or zeolite" refers to a microporous aluminosilicate with a three-dimensional channel system. It is generally acidic and may present numerous different structures, known as topologies. Their small pore size, of molecular dimensions, gives zeolites the property of being molecular sieves, i.e. useful in the separation of molecules with different sizes. Moreover, these acidity and morphological properties provide catalytic activity in numerous reactions, such as cracking, isomerisation, dewaxing or NO_x decomposition. They present shape selectivity, which means that the dimension of their channels allows for certain chemical reactions to take place in the interior thereof and prevents others from taking place. Examples of zeolites are faujasite (X and Y), beta, mordenite, ferrierite, ZSM-5 and MCM-22. Example of zeolite applications may be found in patents EP 0550120 and US 4740292.

[0063] The "ITQ catalysts" are zeolitic catalysts that have been developed by the Instituto Tecnológico Químico at Valencia (Spain).

[0064] The "MCM catalysts" are known in the art, and can be obtained from, for example, ExxonMobil Catalyst Technologies LLC (Baytown, TX). MCM type catalysts, including synthesis details, are described in, for example, the patents U.S. 7198711, US 5639931, US 5296428, US 5146029 and U.S. Application 2006/0194998.

[0065] "Acid resin" is understood to mean a matrix made of an organic polymer. The structure presents pores wherein ions may be exchanged, which makes them capable of being used in purification and separation. The most typical resins are based on a cross-linked polystyrene matrix, which is obtained by adding another compound, such as, for example, divinylbenzene, to styrene during the polymerisation process. By substituting protons from the surface thereof with other organic groups, it is possible to functionalise the resins, such that they may be acidic or basic. For example, acid resins have sulfonic acid groups inside them. Examples of resins are CT-275, manufactured by Purolite, or A-15, A-35 and A-36, manufactured by Rohm and Haas. As an application example, they are used industrially for the production of ethers, as described in patents US 4423251 and US 4540831.

DESCRIPTION OF THE FIGURES

[0066]

FIG. 1.- Represents a block diagram of a process as herein disclosed in which all the steps and conditions of the process are showed. **(A)** Naphtha stream with one or more components with Parafinic, Olefinic, Aromatic or naphthene content (E.g.: Straight Run Naphtha); **(B)** Naphthene dehydrogenation section; **(C)** Pressure: 1-80 bar; Temperature: 480-530 °C; LHSV: 3-10 h⁻¹; **(D)** hydrogen production: 100-150 Nm³/m³ feed; **(E)** Fractionation column; **(F)** Light naphtha rich in benzene; **(G)** Heavy naphtha fraction free from benzene; **(H)** Olefinic stream (e.g.: Light FCC naphtha, olefinic LPG, coker naphtha, pentenes); **(I)** Alkylation section; **(J)** Pressure: 2-120 bar; Temperature: 100-350 °C; LHSV: 0,5- 10 h⁻¹; **(K)** Liquid product from alkylation section; **(L)** Fractionation column; **(M)** Gasoline; **(N)** Kerosene and/or diesel; and **(P)** recycled gasoline stream.

FIG. 2.- Represents the yield drop with time (t (hours)) on stream for products with a boiling point above 150°C (middle distillate), as a consequence of the catalyst deactivation in the alkylation step. Wherein: t(h) is time on stream (hours); Yield% is Middle distillate net yield, %wt; and ■ represents fresh catalyst.

FIG. 3.- Represents the regeneration of the catalyst used in step (ii) by burning of the coke with air. Wherein: t(h) is time on stream (hours); Yield% is Middle distillate net yield, %wt (fresh catalyst vs. regenerated catalyst); and □ represents a fresh catalyst; • represents a regenerated catalyst.

EXAMPLES

[0067] The following examples illustrate the process for obtaining the middle distillates as disclosed herein and are not intended to limit the scope of the invention set in the claims.

TYPICAL EMBODIMENT OF THE PROCESS

[0068] The following tables (Tables 1 and 2) list the typical compositions of the major streams that are obtained throughout the typical process described in Figure 1.

[0069] Thus, stream **(A)**, rich in naphthenes and aromatics, feeds section **(B)** (dehydrogenation section), to obtain a hydrogen-rich gaseous stream **(D)**. Subsequently, the naphtha produced in the dehydrogenation section may be fractionated in order to reduce its benzene content. Jointly with an olefin-rich stream **(H)**, the naphtha stream without benzene

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(G) feeds the alkylation section (I). The product of the alkylation section (K) is fractionated, to obtain two differentiated streams, a gasoline stream (M), which may be partially recycled (P) as a feed for the naphthene alkylation section (I), and a middle distillate stream (kerosene + diesel fuel) (N).

Table 1

Stream (see Fig. 1)	S, ppm weight	N, ppm weight	Naphthenes, % by weight	Aromatics, % by weight	Olefins, % by weight	Initial Boiling Point °C	Final Boiling Point °C
Feed (A)	0.5	0.5	40	15	0	85	180
Output from dehydrogenation section (B)	0.5	0.5	1	52	0	50	180
Stream Rich in aromatics (G)	0.5	0.5	1	84	0	80	180
Stream rich in olefins (H)	10	1	0	0	80	20	50
Output from alkylation (K)	<10	1	1	60	20	52	342

Table 2

Stream (see fig. 1)	S, ppm weight	N, ppm weight	Initial Boiling Point °C	Final Boiling Point °C	Gross yield, % by weight
Gasoline (M)	<10	1	52	149	65
Middle Distillate (N)	<10	1	155	342	35

Properties of the products obtained in the typical embodiment

[0070] Below we list the main properties of the two primary products obtained in the process described (Tables 3 and 4).

Table 3

GASOLINE	
Density (g/cc)	0.7855
PIONA (wt. %)	
N-Paraffins	9.07
I-Paraffins	33.64
Naphthenes	1.86
Aromatics	55.02
Olefins	0.41
Benzene, wt. %	0.97
Sulfur (ppm)	<10
CALC. RON	94.6
CALC. MON	86

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(continued)

ASTM D86, v. %	
1%	52.6
5%	90.2
10%	101.8
30%	113.6
50%	119.7
70%	127.7
90%	138.3
95%	141.0
99%	149

Table 4

MIDDLE DISTILLATE	
Density (g/cc)	0.8835
Cetane Number (ASTM D4737-96A)	29
Sulfur (ppm)	<10
IP-391/2000 STANDARD ANALYSIS	
Total aromatics (wt. %):	90-100
ASTM D86 (v. %)	
1%	155.0
5%	162.0
10%	169.3
30%	171.8
50%	178.3
70%	245.9
90%	299.9
95%	319.2
99%	342.5

Process yields for different olefinic feeds to the process

[0071] Below we show the yields obtained in middle distillates (hydrocarbons with a boiling range between 150°C-360°C) as a function of the starting olefinic streams that are fed to the process alkylation section (Table 5).

[0072] The methodology followed to obtain the results shown in Table 5 was:

Feeding a typical heavy naphtha feed stream to the process (F1), which would correspond to stream (A) of the process diagram. This stream was fed to a reactor loaded with an RG-582 catalyst from Axens, at a Pressure of 20 kg/cm² and a temperature of 500°C. The product was fractionated by eliminating the benzene-rich light fraction and the hydrogen, and the heavy fraction, rich in aromatics heavier than benzene, which would correspond to stream (G), was fed, jointly with an olefinic stream (F2) with variable compositions for each of the examples, which would correspond to stream (H) of the process diagram, to a pilot plant with an upward-flow piston reactor, loaded with Beta 25 as the catalyst. The operating conditions of this reactor are summarised as: Temperature: 250°C, WHSV: 1 h⁻¹ and Pressure: 30 kg/cm².

[0073] The product obtained in each of the experiments was fractionated, separating and calculating the middle distillate yield obtained.

Table 5

	Example 1		Example 2		Example 3		Example 4	
Middle distillate gross yield in weight	55%		62%		33%		28%	
	F1	F2	F1	F2	F1	F2	F1	F2
Aromatics ¹	15	0	15	0	15	0	15	3,5
Total olefins ¹	0	100	0	100	0	77	0	53
Olefins C3 ¹	0	100	0	0	0	0	0	0
Olefins C4 ¹	0	0	0	100	0	14	0	3
Olefins C5 ¹	0	0	0	0	0	60	0	24
Olefins C6 ¹	0	0	0	0	0	3	0	19
Olefins C7 ¹	-	-	-	-	-	-	0	7
Naftenes ¹	40	0	40	0	40	1,7	40	6
Paraffins	Rest Up to 100	0	Rest Up to 100	0	Rest Up to 100	Rest Up to 100	Rest Up to 100	Rest Up to 100
N, ppm	0,5	0	0,5	0	0,5	0	0,5	1
S, ppm	0,5	0	0,5	0	0,5	0	0,5	13
1: % weight								

[0074] F1 corresponds to the heavy naphtha stream and F2 corresponds to the olefinic stream.

EFFECT OF THE AROMATICS AND NAPHTHENE CONTENT IN THE ALKYLATION SECTION

[0075] The two tables shown below (Tables 6 and 7) attempt to illustrate the effect of the % of aromatics and the % of naphthenes in the feed that is supplied to the alkylation section on the middle distillate yield of the product.

[0076] The methodology followed to obtain the results shown in the following tables was to feed a mixture of refinery streams in variable percentages into a pilot plant with an upward-flow piston reactor, loaded with Beta 25 as the catalyst, such that the resulting feed had different concentrations of aromatics and naphthenes. The product obtained in each of the experiments was fractionated, separating and calculating the middle distillate yield obtained. The operating conditions are summarised as: Temperature: 250°C, WHSV: 1 h⁻¹ and Pressure: 30 bar.

[0077] As may be seen in the table, as the naphthene content increases, lower yields are obtained, which seems to indicate an inhibitory effect of the naphthenes in the catalyst.

[0078] The opposite occurs in regards to the aromatics content: when the aromatics content increases, greater middle distillate yields are obtained.

Table 6.- Effect of the naphthene content at the inlet to the alkylation section

Type of feed to the Alkylation section	Naphthene content at the inlet to the alkylation section following the dehydrogenation step (weight %)	Middle distillate yield (weight %)
85% Reformate Naptha + 15% Heart Cut Naphtha	3%	12%
50% Reformate Naptha + 10% Heart Cut Naphtha + 40% Straight Run Naphtha	15%	4%

(continued)

Type of feed to the Alkylation section	Naphthene content at the inlet to the alkylation section following the dehydrogenation step (weight %)	Middle distillate yield (weight %)
78% Straight Run Naphtha + 22% Heart Cut Naphtha	30%	2%

Table 7.- Effect of the aromatics content at the inlet to the alkylation section

Type of feed to the Alkylation section	Aromatics content at the inlet to the Alkylation section following the naphthene dehydrogenation step (weight %)	Middle distillate yield (weight %)
85% Straight Run Naphtha + 15% Heart Cut Naphtha	15%	2%
85% Reformate Naphtha + 15% Heart Cut Naphtha	51%	12%

Claims

1. A process for producing hydrogen, gasoline and middle distillate, comprising at least the following steps:

- (i) dehydrogenation of a heavy naphtha in the presence of at least one reforming catalyst, to obtain a stream of dehydrogenated naphtha;
- (ii) alkylation of the stream of dehydrogenated naphtha rich in aromatic compounds heavier than benzene obtained in step (i) with an olefinic stream in the presence of a solid acid catalyst; and
- (iii) separation of the mixture of compounds obtained in step (ii) in at least a middle distillate fraction and a fraction rich in gasoline;
- (iv) the fraction rich in gasoline obtained in step (iii) is partially recycled to the olefinic stream to the inlet of alkylation of step (ii);

and wherein a total or partial separation of hydrogen produced in step (i) is carried out between steps (i) and (ii) or between steps (ii) and (iii) in order to obtain a stream of hydrogen, and which comprises separation of light naphtha rich in benzene and heavy naphtha rich in aromatics compounds heavier than benzene between steps (i) and (ii).

2. The process according to the preceding claim, wherein the heavy naphtha used in step (i) is a hydrocarbon stream with a content of at least 20% w/w of naphthenes plus aromatics, and with a distillation range between 75°C to 200 °C, preferably between 90°C to 140 °C.

3. The process according to any one of the preceding claims, wherein the heavy naphtha used in step (i) is selected from the group consisting of: straight run naphtha, heart cut FCC naphtha, aromatic concentrates, coker naphtha or mixtures thereof, preferably the naphtha is straight run naphtha.

4. The process according to any one of the preceding claims, wherein the dehydrogenation of the heavy naphtha of step (i) is carried out at a temperature between 250 °C and 650°C, preferably between 350 °C and 650 °C, more preferably between 480 and 530 °C.

5. The process according to any one of the preceding claims, wherein the dehydrogenation of the heavy naphtha of step (i) is carried out at a pressure between 1 and 80 bar, preferably between 3 and 30 bar.

6. The process according to any one of the preceding claims, wherein at least 90% of the hydrogen produced at the stage of dehydrogenation is separated between steps (i) and (ii) or between steps (ii) and (iii).

7. The process according to any one of the preceding claims, wherein the alkylation of the dehydrogenated naphtha stream obtained in step (ii) with a olefinic stream is carried out in the presence of a solid acid catalyst selected from the group consisting of zeolites, acid resins, supported phosphoric acid, aluminosilicates, Nafion or mixtures thereof, preferably the solid acid catalyst is ITQ catalyst, MCM catalyst, Beta 25 catalyst, A-35 resin or Purolite CT-275.
8. The process according to any one of the preceding claims, wherein the alkylation of the stream of naphtha obtained in step (ii) is carried out at a temperature between 80°C and 350 °C, preferably between 200°C and 300°C.
9. The process according to any one of the preceding claims, wherein the alkylation of the stream of naphtha obtained in step (ii) is carried out to a pressure between 2 to 120 bar, preferably between 30 to 60 bar.
10. The process according to any one of the preceding claims, wherein the olefinic stream of step (ii) is selected from the group consisting of ethylene, propylene, butene, pentene, olefinic LPG, heart cut FCC naphtha, coker naphtha, FCC light naphtha, or mixtures thereof.
11. The process according to any one of the preceding claims, wherein the middle distillate fraction obtained is between 10 and 70% weight/weight of the initial mixture of compounds obtained in step (ii).
12. The process according to any one of the preceding claims, wherein the fraction rich in gasoline is between 30 and 90% weight/weight of the initial mixture of compounds obtained in step (ii).
13. The process according to any one of the preceding claims, wherein the olefinic stream which feeds step (ii) comprises less than 1 ppm of nitrogen.
14. The process according to any one of the preceding claims, wherein the content of naphthenes are reduced after the dehydrogenation of a heavy naphtha in the presence of at least one reforming catalyst of step (i), preferably the content of naphthenes is below 1 % by weight.

Patentansprüche

1. Verfahren zur Herstellung von Wasserstoff, Benzin und Mitteldestillaten, das mindestens folgende Schritte umfasst:
 - (i) Dehydrierung eines schweren Naphthas in Anwesenheit von mindestens einem Reformierungskatalysator zur Gewinnung eines Stroms dehydrierten Naphthas;
 - (ii) Alkylierung des in Schritt (i) erhaltenen Stroms dehydrierten Naphthas, das reich an aromatischen Verbindungen ist, die schwerer sind als Benzol, mit einem olefinischen Strom in Anwesenheit eines sauren Feststoffkatalysators, und
 - (iii) Auftrennung der in Schritt (ii) erhaltenen Mischung von Verbindungen in mindestens eine Mitteldestillatfraktion und eine benzinreiche Fraktion;
 - (iv) die in Schritt (iii) erhaltene benzinreiche Fraktion wird teilweise in den olefinischen Strom zur Einleitung in die Alkylierung von Schritt (ii) zurückgeführt;

und wobei eine vollständige oder teilweise Trennung des in Schritt (i) erhaltenen Wasserstoffs zwischen den Schritten (i) und (ii) oder zwischen den Schritten (ii) und (iii) ausgeführt wird, um einen Wasserstoffstrom zu erhalten, und das die Trennung des benzolreichen leichten Naphthas und des schweren Naphthas, das reich an aromatischen Verbindungen ist, die schwerer sind als Benzol, zwischen den Schritten (i) und (ii) umfasst.
2. Verfahren nach dem vorhergehenden Anspruch, wobei das in Schritt (i) verwendete schwere Naphtha ein Kohlenwasserstoffstrom mit einem Gehalt an Naphthenen plus Aromaten von mindestens 20 Gew.-% und einem Destillationsbereich von 75°C bis 200°C, vorzugsweise von 90°C bis 140°C ist.
3. Verfahren nach irgendeinem der vorhergehenden Ansprüche, wobei das in Schritt (i) verwendete schwere Naphtha ausgewählt wird aus der Gruppe bestehend aus: Straight-Run-Naphtha, Heart-Cut-FCC-Naphtha, aromatischen Konzentraten, Kokereinaphtha oder Mischungen davon, wobei das Naphtha vorzugsweise Straight-Run-Naphtha ist.
4. Verfahren nach irgendeinem der vorhergehenden Ansprüche, wobei die Dehydrierung des schweren Naphthas in Schritt (i) bei einer Temperatur von 250°C bis 650°C, vorzugsweise von 350 bis 650°C, besonders bevorzugt von

480 bis 530°C durchgeführt wird.

- 5 5. Verfahren nach irgendeinem der vorhergehenden Ansprüche, wobei die Dehydrierung des schweren Naphthas in Schritt (i) unter einem Druck von 1 bis 80 bar, vorzugsweise von 3 bis 30 bar durchgeführt wird.
6. Verfahren nach irgendeinem der vorhergehenden Ansprüche, wobei mindestens 90 % des in der Dehydrierungsstufe hergestellten Wasserstoffs zwischen den Schritten (i) und (ii) oder zwischen den Schritten (ii) und (iii) abgetrennt wird.
- 10 7. Verfahren nach irgendeinem der vorhergehenden Ansprüche, wobei die Alkylierung des in Schritt (ii) erhaltenen Stroms dehydrierten Naphthas mit einem olefinischen Strom in Anwesenheit eines sauren Feststoffkatalysators durchgeführt wird, der ausgewählt wird aus der Gruppe bestehend aus Zeolithen, sauren Harzen, geträgerter Phosphorsäure, Aluminiumsilikaten, Nafion oder Mischungen davon, wobei der saure Feststoffkatalysator vorzugsweise ein ITQ-Katalysator, MCM-Katalysator, Beta 25 Katalysator, A-35-Harz oder Purolite CT-275 ist.
- 15 8. Verfahren nach irgendeinem der vorhergehenden Ansprüche, wobei die Alkylierung des in Schritt (ii) erhaltenen Naphthastroms bei einer Temperatur von 80°C bis 350°C, vorzugsweise von 200°C bis 300°C durchgeführt wird.
9. Verfahren nach irgendeinem der vorhergehenden Ansprüche, wobei die Alkylierung des in Schritt (ii) erhaltenen Naphthastroms unter einem Druck von 2 bis 120 bar, vorzugsweise von 30 bis 60 bar durchgeführt wird.
- 20 10. Verfahren nach irgendeinem der vorhergehenden Ansprüche, wobei der olefinische Strom aus Schritt (ii) ausgewählt wird aus der Gruppe bestehend aus Ethylen, Propylen, Buten, Penten, olefinischem verflüssigtem Petroleumgas (LPG), Heart-Cut-FCC-Naphtha, Kokereinaphtha, leichtem FCC-Naphtha oder Mischungen davon.
- 25 11. Verfahren nach irgendeinem der vorhergehenden Ansprüche, wobei die erhaltene Mitteldestillatfraktion zwischen 10 und 70 Gew.-% der ursprünglichen, in Schritt (ii) erhaltenen Mischung von Verbindungen ausmacht.
12. Verfahren nach irgendeinem der vorhergehenden Ansprüche, wobei die benzinreiche Fraktion zwischen 30 und 90 Gew.-% der ursprünglichen, in Schritt (ii) erhaltenen Mischung von Verbindungen ausmacht.
- 30 13. Verfahren nach irgendeinem der vorhergehenden Ansprüche, wobei der olefinische Strom, der in Schritt (ii) eingespeist wird, weniger als 1 ppm Stickstoff umfasst.
- 35 14. Verfahren nach irgendeinem der vorhergehenden Ansprüche, wobei der Gehalt an Naphthenen nach der Dehydrierung eines schweren Naphthas in Anwesenheit von mindestens einem Reformierungskatalysator in Schritt (i) reduziert ist, wobei der Gehalt an Naphthenen vorzugsweise unter 1 Gew.-% liegt.

Revendications

- 40 1. Un procédé pour produire de l'hydrogène, de l'essence et du distillat moyen, comprenant au moins les étapes suivantes :
 - 45 (i) déshydrogénation d'un naphta lourd en présence d'au moins un catalyseur de reformage, pour obtenir un flux de naphta déshydrogéné ;
 - (ii) alkylation du flux de naphta déshydrogéné riche en composés aromatiques plus lourds que le benzène obtenu au cours de l'étape (i) avec un flux oléfinique en présence d'un catalyseur acide solide ; et
 - (iii) séparation du mélange de composés obtenu au cours de l'étape (ii) dans au moins une fraction de distillat moyen et une fraction riche en essence ;
 - 50 (iv) la fraction riche en essence obtenue au cours de l'étape (iii) est partiellement recyclée vers le flux oléfinique à l'entrée d'alkylation de l'étape (ii) ;

et dans lequel une séparation totale ou partielle de l'hydrogène produit au cours de l'étape (i) est réalisée entre les étapes (i) et (ii) ou entre les étapes (ii) et (iii) afin d'obtenir un flux d'hydrogène, et qui comprend la séparation du

- 55 naphta léger riche en benzène et du naphta lourd riche en composés aromatiques plus lourds que le benzène entre les étapes (i) et (ii).
- 2. Le procédé selon la revendication précédente, dans lequel le naphta lourd utilisé au cours de l'étape (i) est un flux

d'hydrocarbure avec une teneur d'au moins 20% p/p en naphtènes plus aromatiques, et avec une gamme de distillation comprise entre 75°C et 200°C, de préférence entre 90°C et 140°C.

3. Le procédé selon n'importe laquelle des revendications précédentes, dans lequel le naphta lourd utilisé au cours de l'étape (i) est sélectionné dans le groupe composé de : naphta de distillation directe, naphta fraction de coeur par craquage catalytique fluide, concentrés d'aromatiques, naphta de cokéfaction ou leurs mélanges, le naphta est de préférence du naphta de distillation directe.
4. Le procédé selon n'importe laquelle des revendications précédentes, dans lequel la déshydrogénation du naphta lourd de l'étape (i) est réalisée à une température comprise entre 250°C et 650°C, de préférence entre 350°C et 650°C et de préférence encore entre 480 et 530°C.
5. Le procédé selon n'importe laquelle des revendications précédentes, dans lequel la déshydrogénation du naphta lourd de l'étape (i) est réalisée à une pression comprise entre 1 et 80 bar, de préférence entre 3 et 30 bar.
6. Le procédé selon n'importe laquelle des revendications précédentes, dans lequel au moins 90% de l'hydrogène produit au cours de l'étape de déshydrogénation est séparé entre les étapes (i) et (ii) ou entre les étapes (ii) et (iii).
7. Le procédé selon n'importe laquelle des revendications précédentes, dans lequel l'alkylation du flux de naphta déshydrogéné obtenue au cours de l'étape (ii) avec un flux oléfinique est réalisée en présence d'un catalyseur acide solide sélectionné dans le groupe composé de zéolithes, résines acides, acide phosphorique supporté, aluminosilicates, Nafion ou leurs mélanges, le catalyseur acide solide est de préférence un catalyseur ITQ, un catalyseur MCM, un catalyseur bêta 25, une résine A-35 ou Purolite CT-275.
8. Le procédé selon n'importe laquelle des revendications précédentes, dans lequel l'alkylation du flux de naphta obtenue au cours de l'étape (ii) est réalisée à une température comprise entre 80°C et 350°C, de préférence entre 200°C et 300°C.
9. Le procédé selon n'importe laquelle des revendications précédentes, dans lequel l'alkylation du flux de naphta obtenue au cours de l'étape (ii) est réalisée à une pression comprise entre 2 et 120 bar, de préférence entre 30 et 60 bar.
10. Le procédé selon n'importe laquelle des revendications précédentes, dans lequel le flux oléfinique de l'étape (ii) est sélectionné dans le groupe composé d'éthylène, propylène, butène, pentène, GPL oléfiniques, naphta fraction de coeur par craquage catalytique fluide, naphta de cokéfaction, naphta léger par craquage catalytique fluide, ou leurs mélanges.
11. Le procédé selon n'importe laquelle des revendications précédentes, dans lequel la fraction de distillat moyen obtenue est comprise en 10 et 70% poids/poids du mélange initial de composés obtenu au cours de l'étape (ii).
12. Le procédé selon n'importe laquelle des revendications précédentes, dans lequel la fraction riche en essence est comprise en 30 et 90% poids/poids du mélange initial de composés obtenu au cours de l'étape (ii).
13. Le procédé selon n'importe laquelle des revendications précédentes, dans lequel le flux oléfinique qui alimente l'étape (ii) comprend moins de 1 ppm d'azote.
14. Le procédé selon n'importe laquelle des revendications précédentes, dans lequel la teneur en naphtènes est réduite après la déshydrogénation d'un naphta lourd en présence d'au moins un catalyseur de reformage de l'étape (i), de préférence la teneur en naphtènes est inférieure à 1 % en poids.

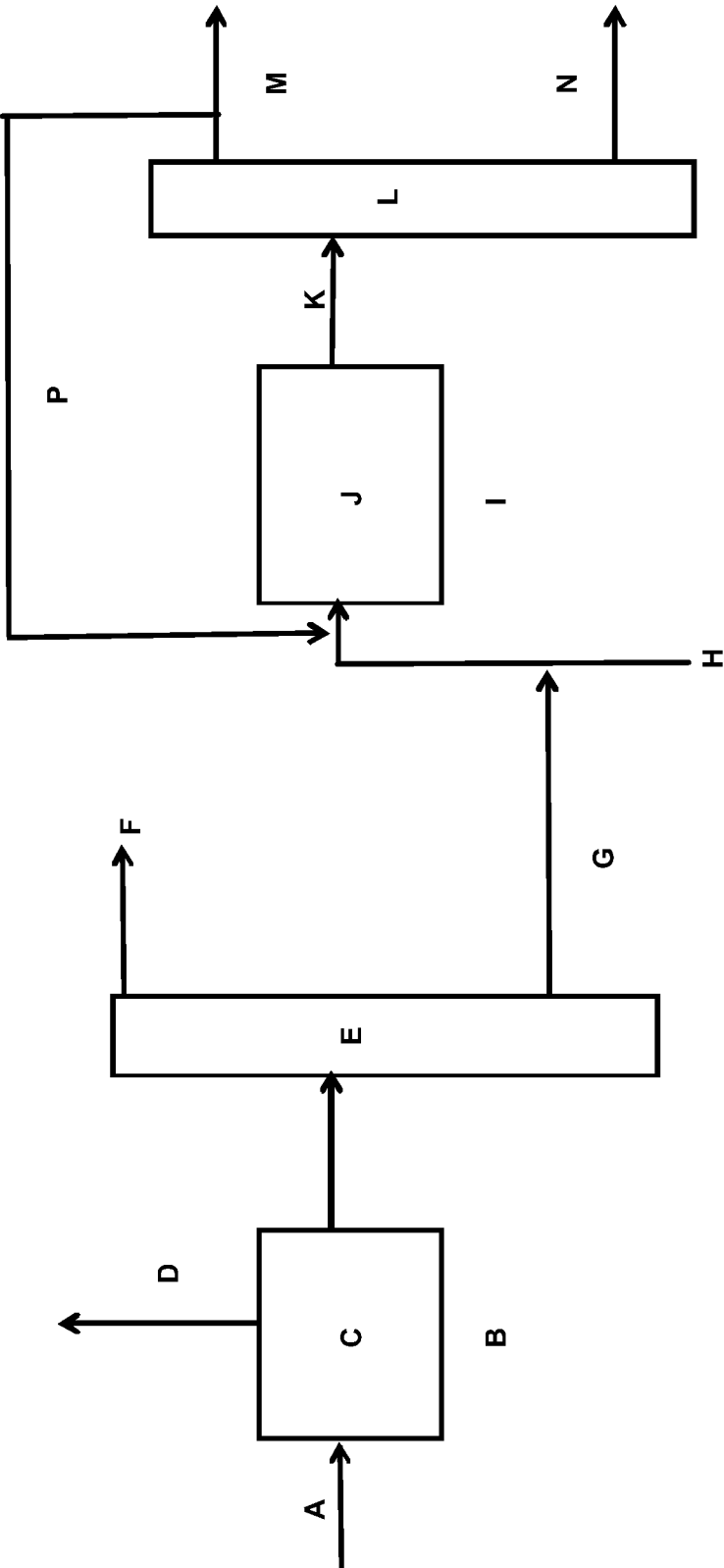


FIG. 1

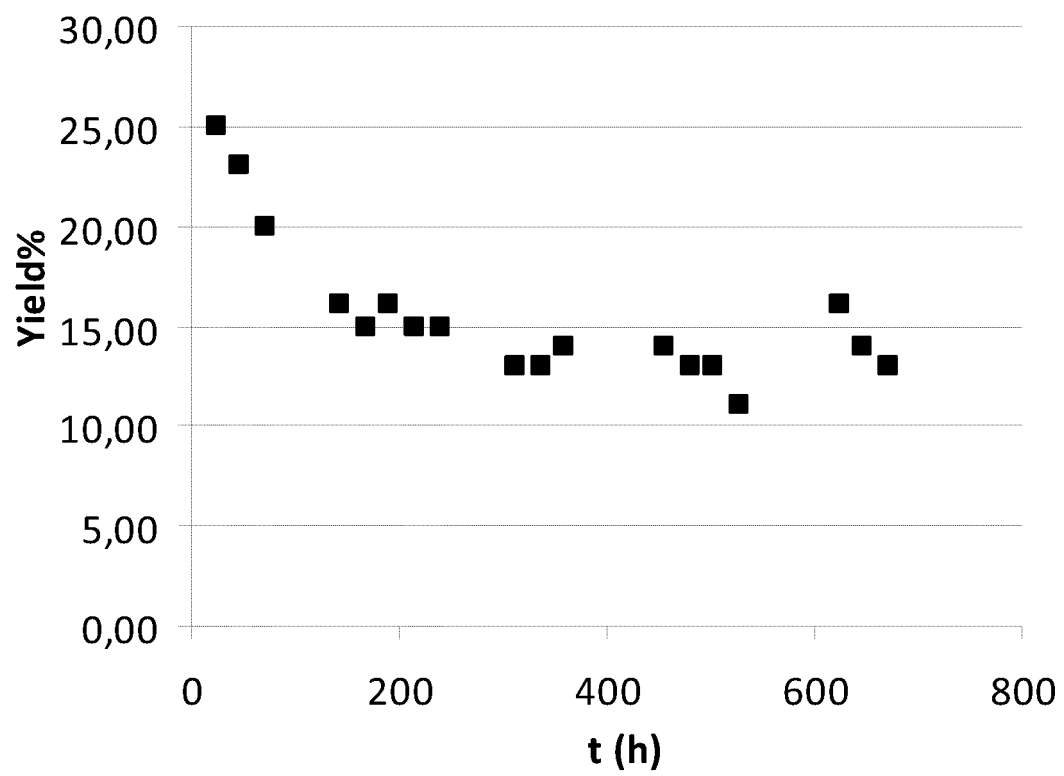


FIG.2

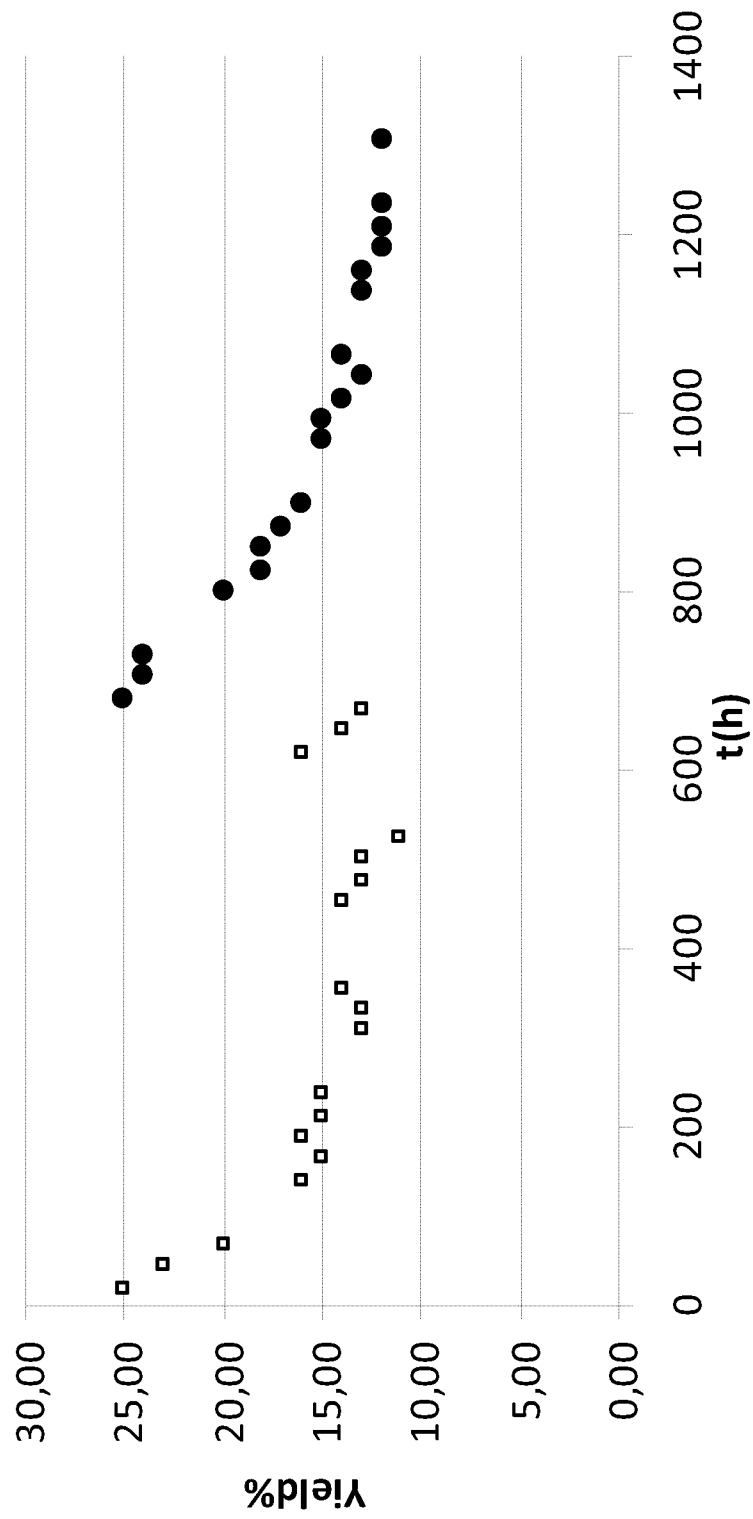


FIG. 3

REFERENCES CITED IN THE DESCRIPTION

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