Abstract: The invention relates to a process and an apparatus for producing gasoline components from C₅-C₁₀ unsaturated cyclic and acyclic hydrocarbons in a single step in the presence of a catalyst system comprising a dewaxing catalyst. The components obtained by the process are suitable for gasoline components as such or as an additive in gasoline compositions, and in cosmetics or pharmaceutical products.
Process and apparatus for producing hydrocarbons

Field of the invention

[0001] The present invention relates to a process and an apparatus for producing hydrocarbons. More particularly, the invention relates to a conversion of terpenes to hydrocarbon compounds which are useful as gasoline components or gasoline fuel as such.

Background of the invention

[0002] There is an increasing interest on the use of hydrocarbon components of biological origin from renewable sources in fuels to replace the fossil starting materials. The use thereof is highly desirable for environmental reasons. There is a lot of literature relating to production of fuel composition from biological starting materials like vegetable oils, such as tall oil.

[0003] US 2004/0230085 A1 discloses a process for producing hydrocarbon components from wood-based tall oil by a two-step procedure in which a fatty acid fraction of tall oil (TOFA) is subjected to a hydrodeoxygenation step to hydrogenate TOFA in the presence of a desulphurization catalyst and then to an isomerization step to branch the hydrocarbon chain. The products obtained from the isomerization are predominantly i-paraffins which are suitable for use as components in diesel fuels. The hydrocarbon chain lengths suitable for diesel components are typically in the range of C₉-C₂₀.

[0004] US 2009/0020089 A1 discloses a fuel composition comprising at least a tetramethylcyclohexane and optionally an aromatic isoprenoid compound, and a monocyclic and acyclic hydrocarbon component. The fuel composition can be of petrol fuel grade, for example. The tetramethylcyclohexane is produced by hydrogenation of pinene in the presence of a hydrogenation catalyst. Pinene and the starting materials for the optional components included in the fuel composition are produced by microbiological methods using a host cell.

[0005] Tall oil is retrieved from the kraft pulping process of coniferous wood as a by-product. From the same process, also crude turpentine is extracted as a by-product. Chemical compositions of said substances differ from each other to a significant extent. Tall oil is mainly composed of fatty acids and resin acids with a chain length varying between C₁₂ to C₁₈, and fused ring systems as abietic acids and sitosterols while the crude turpentine comprises an oil mixture of terpenes derived from pitch. Terpenes are a wide range
of volatile hydrocarbons having a chemical formula of C₁₀H₁₆, including typically unsaturated mono- and bicyclic hydrocarbons. Crude turpentine, which contains terpenes, is formed in the kraft pulping process and is generally referred to as crude sulphate turpentine (CST). The main terpene components included in the CST are α-pinene, β-pinene and Δ-3-carene. The major component is typically α-pinene.

![Chemical structures of α-pinene, β-pinene, and Δ-3-carene]

**[0006]** The unsaturated bicyclic terpenes included in the turpentine having the formulas given above are too reactive as such for use as fuel components. Also, the high sulphur content of the turpentine prevents using it for fuel application.

**[0007]** Processes for converting terpenes to cymenes are previously known. In these processes, different types of catalysts are used for the conversion. For example, alkali metal carbonate catalysts, catalysts comprising noble metals or rare earth metals on a zeolite support and a palladium catalyst supported on activated carbon or alumina have been used.

**[0008]** CST comprising a large amount of terpene isomers also contains a relatively high amount of sulphur, up to 6%, as a contaminant. In order to be able to utilize the CST for further applications sulphur has to be removed from it. In EP 0267833 A1 sulphur is removed from the terpenes included in the crude turpentine through hydrogenation in the presence of a catalyst of cobalt and molybdenum oxides on an inorganic support. It is desired that any chemical transformation of the terpenes is avoided during the hydrodesulphurization procedure.

**[0009]** At present, the crude sulphate turpentine is processed for use as a solvent or odorants in pharmaceutical and cosmetic industry. However, a wide range of utilization of the turpentine is restricted because of the high level of sulphur, and no cost efficient processes for desulphurization and refining the turpentine are now present. Accordingly, a large amount of the crude sulphate turpentine is now burned without further processing.
Brief description of the invention

[0010] It has now been found that C₅-C₁₀ unsaturated cyclic and acyclic hydrocarbons can be converted to suitable gasoline components by a one-step process by using a conventional dewaxing catalyst. The components obtained in the process of the invention can be used as fuel components as such or as fuel additives in the gasoline fuel compositions. A part of the produced components can also be utilized in other products, such as in cosmetics or pharmaceutical products. The hydrocarbon components received from the process has a carbon number typical for gasoline fuel components, varying from C₄ to C₁₀.

[0011] In a specific embodiment of the invention, crude sulphate turpentine is used as a starting material. The crude sulphate turpentine may also comprise distillation bottoms products from turpentine distillation. As stated above, the high sulphur content of the turpentine prevents using it for fuel application. It was surprisingly found that it is possible to produce fuel components from crude sulphate turpentine by using only one catalyst in a single-step process, the catalyst being able to both crack hydrocarbons and remove sulphur from the CST. It is an advantage of the process that there is no need of any pretreatment procedure in order to remove sulphur from the CST prior to its further processing. In an embodiment, the invention thus provides a simple, efficient and economical process for the treatment of the crude sulphate turpentine to provide a product that is usable for fuel applications.

[0012] The invention provides a simple, efficient and economical process for converting C₅-C₁₀ unsaturated hydrocarbons to gasoline components which can be either used as such or blended to gasoline to produce a gasoline composition that is in compliance with the EN 228:2008 gasoline standard. Specifically, the proportions of the components in the product can be adjusted in a controlled manner by converting the aromatics further to toluene to the desired extent.

[0013] It is thus an object of the present invention to provide a process and an apparatus for producing gasoline components. The object of the invention is achieved by what is stated in the independent claims.

[0014] Another object of the invention is to provide a use of the gasoline components obtained by the process of the invention as fuel additives in the gasoline fuel compositions, or as a gasoline fuel as such.
Brief description of the drawings

[0015] Figure 1 shows an embodiment of an apparatus of the invention comprising one reactor where a catalyst system is packed in one layer in the reactor.

[0016] Figure 2 shows an embodiment of an apparatus of the invention comprising one reactor where a catalyst system is packed in two separate layers in the reactor.

[0017] Figure 3 shows an embodiment of an apparatus of the invention comprising two reactors where a catalyst system is packed in one layer in each reactor.

[0018] Figure 4 shows an embodiment of an apparatus of the invention comprising a reactor and a hydrogen sulphide separator.

Detailed description of the invention

[0019] An object of the invention is to provide a process for producing gasoline components, wherein a feed of C₅-C₉ unsaturated cyclic and acyclic hydrocarbons is subjected to a single step of hydroprocessing in the presence of hydrogen gas and a catalyst system comprising a dewaxing catalyst to form a mixture of gasoline components.

[0020] C₅-C₁₀ unsaturated cyclic and acyclic hydrocarbons constituting the starting material for the process of the present invention can be obtained from any suitable source. The hydrocarbons can contain heteroatoms and minor amounts of heavier hydrocarbons as a contaminant. In an embodiment of the invention, the hydrocarbon feed is composed of C₁₀H₁₆ terpenes. In an embodiment of the invention, the terpene feed is substantially composed of crude turpentine. In the present invention, the crude turpentine is to be understood to be one of wood origin. In a specific embodiment of the invention, the crude turpentine is obtained from kraft pulping process of coniferous wood as crude sulphate turpentine which is predominantly composed of volatile unsaturated C₁₀H₁₆ terpene isomers derived from pitch. The crude turpentine of this origin is also referred to as crude sulphate turpentine (CST). Due to the process chemicals used in kraft process, sulphur is included in the crude turpentine as a contaminant, amounting typically to up to 6% by weight. Also turpentine distillation bottoms can be used as terpene feed.

[0021] In another embodiment of the invention, the crude turpentine is derived from mechanical pulping of wood, like from grinding and pressure
grinding, thermomechanical pulping, or chemimechanical pulping. From these processes, turpentine can be retrieved in gaseous form, provided that the process is equipped with gas collecting means. Also from chipping of wood or saw mills turpentine can be recovered in gaseous form.

[0022] In a further embodiment of the invention, also a mixture of various crude turpentines can be used as a crude turpentine feed. In still further embodiment of the invention, the terpene feed can be composed of one or more terpene compounds like a-pinene which is/are isolated from a terpene mixture, such as from the crude sulphate turpentine. In a further embodiment, the feed can be composed of terpenoils.

[0023] In another embodiment of the invention, sulphur-containing C5 to C10 hydrocarbon streams from wood processing industry, or side streams of wood processing industry can be used as a crude turpentine feed.

[0024] In an embodiment of the invention, gasoline components are produced by a single-step of hydroprocessing by using a conventional dewaxing catalyst (hereinafter also referred to as HW catalyst) known in the art. The HW catalyst is a catalyst capable of hydrodeoxygenating, isomerising and cracking the hydrocarbons that come in contact with it. In an embodiment of the invention, NiW on a support selected from Al2O3, zeolite, zeolite-Al2O3, and Al2O3-SiO2 is used as a dewaxing catalyst. In a specific embodiment, NiW on an Al2O3 support is used.

[0025] In the following, the invention will be further illustrated in light of the crude sulphate turpentine (CST) as a starting material, while it is to be understood that the invention is not limited to this embodiment. As stated above, CST is mainly composed of an oil mixture of terpenes derived form pitch. Terpenes are a wide range of volatile hydrocarbons having a chemical formula of C10H16, including typically a-pinene, β-pinene and Δ-3-carene. The major component is typically a-pinene.

[0026] The dewaxing catalyst used in the present invention has a capability of hydrogenating the olefinic bonds of the terpene compounds included in CST, opening at least one of the bicyclic rings, and cracking the propene side chains of cymene and other hydrocarbon chains in a single step. As used herein, the term "a single step" means that the hydroprocessing is carried out in one reactor and the catalyst system is arranged therein as a fixed bed.

[0027] In the present invention, the cracking can also be called dewaxing. Specifically, 1-isopropyl-4-methylbenzene, also called cymene, can be
decomposed to toluene. In addition, the dewaxing catalyst is advantageously capable of simultaneously removing undesirable sulphur compounds present in the CST, like dimethyl sulphide, dimethyl disulphide and methyl mercaptane, by converting the organic sulphur compounds to gaseous hydrogen sulphide. Sulphur removal is generally called hydrodesulphurization (HDS). Thus, in the present invention, CST undergoes a single step in which the above chemical transformation reactions are simultaneously taken place.

[0028] In this step, light gaseous hydrocarbons, like methane, are also formed. Generally, gaseous compounds including hydrogen sulphide, methane and H₂ formed in the reactions can be easily discarded from the process and separated from each other, if desired.

[0029] It is characteristic of the dewaxing catalyst that it needs sulphur for maintaining the catalytic activity of the catalyst. Advantageously, when the hydrocarbon feed comprises CST, hydrogen disulphide needed for catalytic activity of the dewaxing catalyst is thus simultaneously provided from the sulphur compounds inherently present in CST. Gaseous hydrogen sulphide can be easily discarded from the mixture of the gasoline components, if necessary.

[0030] It may be necessary to supply supplementary sulphur to the process to maintain the catalytic activity of the catalyst. Supplementary sulphur can be supplied in gaseous form like hydrogen sulphide, or it can be any material that produces hydrogen sulphide in the process, like organic sulphur compounds, such as dimethyl disulphide. In an embodiment of the invention, supplementary sulphur is provided by recirculating the H₂S-containing gas retrieved from the mixture of gasoline components produced by the process of the invention. The amount of supplementary sulphur depends on the amount of sulphur in the CST. Generally, the H₂ feed/H₂S relation must be maintained over about 0.0001. This means that an added amount of sulphur is in the range of about 100 to about 200 ppm. Sulphur can be fed to the initial crude turpentine feed, for example, or to the hydroprocessing step.

[0031] In one embodiment of the invention, the catalyst system further comprises a hydrodesulphurization (HDS) catalyst. The catalyst can be any conventional HDS catalyst known in the art. It is to be noted that any catalysts conventionally used for removal of heteroatoms from the organic compounds can be used in the process of the invention. Heteroatoms are typically sulphur, oxygen and nitrogen. Particularly, catalysts which are typically re-
ferred to as hydrodeoxygenation (HDO) catalysts in the art can be used in the process. HDO catalysts are especially intended for oxygen removal but are usable for sulphur and nitrogen removal as well. In a preferred embodiment of the invention, the HDS catalyst is arranged upstream of the dewaxing catalyst. In this embodiment, the HDS catalyst acts as a pre-hydrogenation catalyst to provide aromatic hydrocarbons that are further converted to toluene to the desired extent in the presence of a dewaxing catalyst.

[0032] In the present invention, the HDS catalyst is selected from a group consisting of NiO/MoO3, CoO/MoO3 and a mixture of NiO/MoO3 and CoO/MoO3 on a support selected from Al2O3 and Al2O3-SiO2. In a specific embodiment of the invention, NiO/MoO3 on the Al2O3 support is used.

[0033] Like the dewaxing catalyst, the HDS catalyst needs sulphur to maintain its catalytic activity. The HDS catalyst has no cracking properties but has a capability of hydrogenating the olefinic bonds of the terpene compounds, opening at least one of the bicyclic rings and converting organic sulphur compounds to hydrogen sulphide.

[0034] The amount of hydrogen gas needed to hydrogenate the olefinic bonds of the terpene structure is determined by the amount of the turpentine feed. A suitable amount of hydrogen can be determined by a man having ordinary skills in the art. Typically, the relation H2 feed/turpentine feed is in the range of about 200 to about 1500 NI/l, preferably about 250 to about 1000 NI/l (NI = normal litre).

[0035] If desired, any gasoline component can be isolated from the mixture received in the process of the invention.

[0036] In an embodiment of the invention, the mixture of hydrodesulphurized gasoline components is subjected to a hydrogen sulphide removal step to remove any residual hydrogen sulphide from the mixture.

[0037] Terpenic compounds present in the CST undergo a number of chemical reactions including hydrogenation, isomerization, dehydrogenation, hydrogenolysis and C-C bond cleavage and cracking. Favour of the various reactions is influenced by the reactions conditions, especially temperature and feeding speed (WHVS) of the CST to the reaction. Various reactions of the initial components of the CST, i.e. α-pinene and Δ-3-carene, can be described, for example, as follows:
[0038] Compounds obtained in the process of the invention can be classified in unsaturated non-terpenic hydrocarbons, terpenes, acyclic, poly-cyclic, monocyclic and aromatic hydrocarbons. Further, when propyl group breaks off from aromatics (o-, m- and p-cymene), toluene is formed according to the following:

\[
\begin{align*}
\text{H}_3\text{C} & \quad + \quad \text{H}_2 \\
\text{H}_3\text{C} & \quad \text{CH}_3 \\
\text{CH}_3 & \quad \text{CH}_3 \\
\end{align*}
\]

[0039] This reaction is especially favorable when using the combination of HDS + HW catalyst arrangement.

[0040] If no ring opening takes place completely in the hydroprocessing step, bicyclic C10 compounds can also be formed, the structure of which corresponds to that of the starting compounds except that the olefinic bonds are reduced. It has been recognized that when operating at lower tem-
temperatures, ring opening of the initial compounds is reduced and the relative amount of the bicyclic compounds is increased. The proportions of the components in the product can thus be influenced by controlling the temperature through the catalytic bed. The temperature in the step of hydrogenation/cracking can vary from about 200°C to about 450°C, preferably about 275°C to about 375°C. When operating at temperatures, over about 330°C, there is a tendency that the amount of toluene is increased. This is because the content of the aromatic hydrocarbons, especially cymenes, like 1-propyl-4-methylbenzene, also called p-cymene, is increased. P-cymene can be further converted to toluene in the process of the invention.

[0041] Conversion of p-cymene to toluene can be accomplished completely or partly, depending on the desired properties of the gasoline product to be produced, and controlled by adjustment of temperature and/or WHHSV.

[0042] The composition of the mixture of the gasoline components can be influenced by controlling the temperature and/or WHVS. Also the catalyst type has an influence on the proportions of the components. For example, if only one catalyst layer comprising a HW catalyst is used, the amount of toluene can be increased by keeping the temperature high, e.g. over about 330°C, and WHVS low, e.g. under about 5. If the WHVS is increased and the temperature is still kept high, the amount of toluene is decreased and the product comprises more cymene. If a two layer catalyst system is used, where the first layer downstream of the turpentine feed inlet is a HDS catalyst and the second layer is a HW catalyst, keeping the temperature high and WHVS low will result to a situation, where HDS layer produces cymene and the HW layer converts it to toluene.

[0043] Advantageously, toluene has a high octane number (RON = 121, MON = 107). In addition, toluene has a favourable steam pressure for providing a standard gasoline fuel. If desired, an octane enhancer such as ethanol can be added to the product obtained by the process of the invention.

[0044] Production of p-cymene and/or toluene can also be increased by means of recirculation where a mixture of the gasoline components obtained in the process is circulated back to the turpentine feed and/or to the step of hydrogenation and cracking. Especially, if only a HW catalyst is used, it is possible to obtain a high yield of toluene at lower process temperatures by means of recirculation of the mixture. On the other hand, in an embodiment,
where a HDS catalyst is used for pre-hydrogenation, recirculation of the mixture provides a high yield of paracymene at lower temperatures. P-cymene is then is cracked to toluene by means of the HW catalyst.

[0045] Reaction realized by a dewaxing and a hydrodesulphurization catalyst is highly exothermic reaction in which temperature can rise to a level which is detrimental to the catalytic activity of the catalyst and/or product quality. In some cases, it may be necessary to control the temperature variations. Recirculation of the product provides an efficient means for constraining the exothermic reaction whereby the recycled product stream acts as an inert media lowering the temperature of the bed in a controlled manner. In an embodiment of the invention, the gasoline components obtained in the process are circulated back to the initial turpentine feed and/or to the ongoing step of hydroprocessing.

[0046] The pressure in the process can vary from about 10 to about 150 bar, preferably from about 20 to about 70 bar. More preferably, the process of the invention is performed at a pressure of about 25 to about 50 bar.

[0047] The hydroprocessing step can be effected either in a single catalyst layer or in two or more catalyst layers of a catalyst system. The one or more catalyst layers can be arranged in a single reactor or in several reactors as described in more detail below. When two or more catalyst layers are employed, a catalyst system comprising a HDS and HW catalysts can be divided so that the first catalyst layer, lying upstream of the subsequent layers, includes a HDS catalyst material but no dewaxing catalyst material, and the subsequent layer(s) comprise(s) only dewaxing catalyst material.

[0048] After the step of hydroprocessing, sulphur is retrieved in the form of gaseous hydrogen sulphide which can be easily discarded from the product, i.e. the mixture of gasoline components. Further, light gaseous hydrocarbons, like methane, are formed and can be easily removed from the process, if desired. The sulphur content of the product mixture can be reduced to a level of 10 ppm at most, the level being within the range stipulated for gasoline fuels. However, in some cases it may be necessary to remove the residual hydrogen sulphide from the product in order to achieve the above sulphur level. This can be accomplished by various methods, like stripping, flashing or bubbling with inert gas, for example nitrogen gas. If desired, hydrogen sulphide retrieved can be led to the reactor for maintaining the catalytic activity of the catalyst.
Moreover, if appropriate, a pre-treatment step can be accomplished prior to the hydroprocessing step. The pre-treatment step can include one or several of the following procedures: distillation, filtration and cleaning of the CST.

As the product obtained by the process of the invention, a high quality hydrocarbon component, useful as a gasoline component, is obtained. In addition, the product can be used as a fuel additive in the conventional gasoline compositions. The invention thus further provides a use of the gasoline components prepared by the process of the invention as additives in the gasoline compositions, or as gasoline fuel as such.

Another object of the invention is to provide an apparatus for producing gasoline components. The apparatus of the invention is adapted to realize an embodiment of the process of the invention. The apparatus comprises

- at least one reactor 1 comprising at least one catalyst layer 3 of a catalyst system comprising a dewaxing catalyst
- hydrocarbon inlet pipe 9
- hydrogen feed pipe 5, 50, 50'
- product outlet pipe 10, 15 for recovering a mixture of gasoline components.

With reference to Fig. 1, crude sulphate turpentine and H₂ are fed to a reactor 1 including a catalyst layer 3 of a catalyst system comprising a dewaxing catalyst for hydrodesulphurization and cracking of the CST. The reactor is for example in a form of a separate tank or a tubular reactor. CST and H₂ are supplied via terpene feed pipe 4 and hydrogen feed pipe 5, respectively. In the Fig. 1, CST and H₂ are combined and fed together via terpene inlet pipe 9 to the reactor 1. In an embodiment of the invention, inlet pipe 9 is omitted and the feed pipes 4 and 5 enter separately the reactor 1.

The catalyst bed comprising the catalyst system can be packed in one or more layers 3, 3'. Also, one or more of the catalyst layers can be diluted with an appropriate medium. The diluting material can be for example the passive material used in passive layers described below, or another catalyst suitable for hydroprocessing. Also, it is possible to form the diluted catalyst by mixing HW catalyst material with HDS catalyst material. In an embodiment, where several catalyst layers are used in the reactor, the first layer downstream of the turpentine feed is diluted while the remaining layers are un-
diluted. If the first layer downstream of the turpentine feed is diluted, it acts as a pre-hydrogenation catalyst. In Fig. 1, the catalyst system is packed in one layer 3. Preferably, the catalyst layer is undiluted in the embodiment illustrated in Fig. 1.

[0054] H₂ feed can be supplied to reactor 1 downstream to the turpentine feed. H₂ feed can also be supplied to reactor 1 via H₂ feed pipe 50 at one or more locations between the terpene inlet pipe 9 and the product outlet pipe 10, preferably at one or more locations in the catalyst bed 3, to control reaction conditions of the exothermic reaction. These H₂ feed inlets are denoted by reference numbers 6, 7 and 8.

[0055] H₂ can also be fed upstream to the turpentine feed, i.e. the H₂ and turpentine feed are countercurrent to each other (not shown in Fig. 1).

[0056] Catalytic hydrodesulphurization and other reactions, i.e. ring opening, saturation of olefinic bonds, and cracking reaction, are carried out in a catalyst layer 3 packed in the reactor 1. Product is recovered from the reactor 1 via product outlet pipe 10. At least a portion of the product, i.e. a mixture of the gasoline components, can be circulated back to the reactor 1 through recirculation pipe 100 as shown by the dotted line. In the recirculation, the product can be combined with the initial CST and H₂ feeds into a single feed flow and supplied to the reactor 1 through the terpene inlet pipe 9 as shown in the Figure. The recirculation pipe 100 can also be arranged to the reactor 1 separately from the terpene inlet pipe 9. The product can also be supplied to the reactor 1 at one or more locations between the terpene inlet pipe 9 and the product outlet pipe 10, preferably at one or more locations in the catalyst bed 3 via inlets 6, 7 and 8.

[0057] Moreover, at least a portion of the product can be supplied via pipe 101 to a separating reactor 17 for isolating any component from the mixture of the gasoline components. One of more of the isolated components can be recovered via pipe 18.

[0058] Also, passive layers 11 and 12 comprising suitable passive or inert material, such as Al₂O₃, SiC or glass beads can be arranged in the reactor 1. Their task is to act as guard beds against harmful substances in the feed. When a passive layer is arranged in the reactor 1 as the first layer to receive the feed via inlet pipe 9, upstream of the catalyst layer, it also acts as a preheating layer for the feed. It also enhances the even distribution of the feed to the catalyst. In Fig. 1, a first passive layer 11 is arranged upstream of the
catalyst layer 3, and a second passive layer 12 is arranged downstream of the catalyst layer 3.

[0059] In an embodiment of the invention, a dewaxing catalyst and HDS catalyst constituting a catalyst system are mixed together and packed in one layer 3.

[0060] If appropriate, supplementary sulphur from an outer source is supplied via sulphur feed pipe 16 to the reactor 1 through inlets 6, 7, 8, and/or 9. Supplementary sulphur can also be fed to the turpentine feed. Supplementary sulphur fed via pipe 16 can be any compound that produces hydrogen sulphide in the process, like organic sulphur compounds, such as dimethyl disulphide.

[0061] The crude turpentine is pumped to the reactor 1 at a desired speed. Feed rate WHSV (weight hourly spatial velocity) of the turpentine feed is proportional to an amount of the catalyst and is calculated according to the following equation:

$$\text{WHSV}[\text{h}^{-1}] = \frac{V_{\text{feed}[m^3/h]}}{m_{\text{catalyst}[g]}}$$

[0062] wherein $V_{\text{feed}[m^3/h]}$ means a pumping velocity of the crude turpentine feed, and $m_{\text{catalyst}[g]}$ means an amount of the catalyst.

[0063] In an embodiment where only one catalyst layer comprising HW catalyst is used, the WHSV is typically in the range from about 2 to about 8, preferably not higher than about 5. In an embodiment, where there are at least two catalyst layers, the WHSV is typically in the range from about 0.5 to about 6, preferably in the range from about 1 to about 4. In an embodiment of the invention, WHSV is about 1 to about 1.5. In an embodiment, where there are two catalyst layers, several combinations of catalyst types are possible. The both catalyst layers may comprise HW catalyst, the first catalyst layer being diluted and the second catalyst layer being undiluted. It is also possible that the first catalyst layer comprises HDS catalyst and the second catalyst layer comprises HW catalyst.

[0064] In an embodiment of the invention, when there are several catalyst layers, the operating parameters have to be adjusted accordingly to obtain the optimal product composition. For example, if a first catalyst layer 3’ is a HDS catalyst and a second catalyst layer 3 is a HW catalyst, as for example in an embodiment illustrated in Fig. 2, the amount of H₂ feed to the catalyst layers
is adjusted according to the layer, whose \( \text{H}_2 \) demand is higher, that is, HW catalyst. Another way to is to lead more recirculated hydrogen to the HW catalyst layer.

[0065] The proportions of the gasoline components in the product mixture can be influenced by adjustment of WHSV. HDS and HW catalysts have different optimal WHVS values. For HDS catalyst, the WHVS/\( \text{V}_{\text{feed}} \) relation is lower than for HW catalyst. Since there is no means to control the feed velocity between the catalyst layers, the only possibility is to adjust the amount the catalyst material packed in the bed. In practice this means that the amount of HW catalyst has to be smaller than the amount of HDS catalyst.

[0066] The amount of hydrogen feed is proportional to the amount of the turpentine feed and the composition of the catalyst system. For example, a catalyst system comprising both HDS and HW catalysts in separate layers, the relation \( \text{H}_2 \) feed/turpentine feed is higher than for a system comprising only HW catalyst. Typically, the relation \( \text{H}_2 \) feed/turpentine feed is in the range from about 200 to about 1 500 Nl/l, for example about 250 to about 550 Nl/l (Nl = normal litre).

[0067] Figure 2 shows another embodiment of an apparatus of the invention where a catalyst system is packed in two separate layers, a first catalyst layer 3' and a second catalyst layer 3, in a reactor 1. The first catalyst layer 3' is arranged upstream of the second catalyst layer 3. In an embodiment, HDS catalyst is packed in the first catalyst layer 3', and HW catalyst in the second catalyst layer 3. The HDS catalyst layer 3' is preferably diluted. In this embodiment, the HDS catalyst acts as a pre-hydrogenation catalyst. Further, an intermediate insulating layer 13 is disposed between the two catalyst layers to prevent the layers to mix with each other and to facilitate the operating of the first and second catalyst layers in different temperatures. As an intermediate layer the same material can be used as in the passive layers. A passive layer 11 is arranged upstream of the first catalyst layer 3'.

[0068] The \( \text{H}_2 \) feed can be supplied to the reactor 1 either downstream to the turpentine feed, or the \( \text{H}_2 \) feed can be supplied to the reactor 1 via \( \text{H}_2 \) feed pipe 50 at one or more locations denoted by reference numbers 6, 7 and 8. When appropriate, the \( \text{H}_2 \) feed can be divided so that a part of the \( \text{H}_2 \) feed is supplied to the first catalyst layer 3' and a part of it is supplied to the second catalyst layer 3, as shown in Figure 2.
As in an embodiment illustrated in Fig. 1, external sulphur can be supplied via sulphur feed pipe 16 to the reactor 1, if appropriate. Also, external sulphur feed can be divided so that a part of the external sulphur feed is supplied to the first catalyst layer 3' and a part of it is supplied to the second catalyst layer 3.

The catalyst materials used in the catalyst layers 3' and 3 must be activated before they are effective. The activation comprises several steps, of which one is treating the catalyst with activating sulphur compound, for example dimethyl disulphide. The activation of catalysts is common knowledge in the art and will thus not be discussed here in detail.

Product recovered via product outlet pipe 10 can be further led to a separating reactor 17 in a similar manner as shown in Figure 1 (not shown in Figure 2).

Fig. 3 shows an embodiment of the invention, where a catalyst system is packed in two separate catalyst layers, a first catalyst layer 3' and a second catalyst layer 3, which layers 3' and 3 are disposed in separate reactors, a first reactor 1' and a second reactor 1, respectively. The first reactor 1' is arranged upstream of the second reactor 1. In an embodiment of the invention, the first catalyst layer 3' includes diluted HDS catalyst, whereas the second catalyst layer 3 includes undiluted HW catalyst. Passive layers 11' and 12', and 11 and 12 are arranged in the first and second reactors 1' and 1, respectively.

Crude sulphate turpentine is fed to the first reactor 1'. The product obtained from the first reactor 1' is recovered via pipe 10' and supplied to the second reactor 1. The product is recovered via product outlet pipe 10 from the second reactor.

H₂ feed is supplied to both reactors 1' and 1. H₂ feed can be supplied either downstream to the turpentine feed, or the H₂ feed can be supplied to the reactors 1' and 1 via H₂ feed pipes 50' and 50, at one or more locations denoted by reference numbers 6', 7' and 8', and 6, 7 and 8, respectively.

In another embodiment of the invention, both first and second catalyst layers 3' and 3' comprise diluted catalyst material. The catalyst layers may be arranged in the same reactor, as in the embodiment shown in Figure 2, or they may be arranged in separate reactors, as illustrated in the embodiment shown in Figure 3.
[0076] At least a portion of the product, i.e. mixture of gasoline components, can be circulated back to the first reactor 1' through recirculation pipe 100 as shown by the dotted line in the Figure 3. The recirculated product can be combined with the initial CST and H$_2$ feeds into a single feed flow and supplied to the first reactor V through the terpene inlet pipe 9 as shown in the Figure. The recirculation pipe 100 can also be arranged to the first reactor V separately from the terpene inlet pipe 9. The product can also be supplied to the first reactor V at one or more locations between the terpene inlet pipe 9 and the pipe 10', preferably at one or more locations in the catalyst layer 3' via inlets 6', 7' and 8'.

[0077] If appropriate, external sulphur is supplied via sulphur feed pipe 16 to the first reactor V through inlets 6', 7', 8' and/or 9, and/or to the second reactor 1 through inlets 6, 7, and/or 8. Supplementary sulphur can be fed to the turpentine feed and/or H$_2$ feed.

[0078] Product recovered via product outlet pipe 10 can be further led to a separating reactor 17 in a similar manner as shown in Figure 1 (not shown in Figure 3).

[0079] Fig. 4 shows an embodiment of the apparatus of the invention, where the product recovered from the catalytic hydrodesulphurization and cracking of the CST in a liquid form is fed from the reactor 1 via pipe 10 to a H$_2$S removal reactor 2. In the H$_2$S removal reactor 2, gaseous compounds composing predominantly of hydrogen sulphide, hydrogen and methane are removed from the product via pipe 14. This can be accomplished for example by stripping, flashing or bubbling with inert gas, such as nitrogen.

[0080] When supplementary sulphur supply is desired, at least part of the gaseous compounds recovered from the reactor 2 can be recirculated back to reactor 1 via H$_2$S recirculation pipe 140 as shown in Fig. 4 by a dotted line. Supplementary sulphur can also be supplied to the reactor 1 from an outer source via sulphur feed pipe 16 through inlets 6, 7, 8 and/or 9. Supplementary sulphur can also be fed to the turpentine feed. Supplementary sulphur fed via pipe 16 can be any compound that produces hydrogen sulphide in the process, like organic sulphur compounds, such as dimethyl disulphide.

[0081] The gasoline grade product that has been treated in the H$_2$S removal reactor 2 is recovered via pipe 15. As in the embodiment illustrated in the Fig. 1, at least a portion of the product can be supplied to a separating reactor 17 for isolating any component from the mixture of the gasoline com-
ponents. Also, recirculation of the product obtained in the process of the invention via product recirculation pipe 100 can be accomplished in a similar manner as in Figure 1 in an embodiment illustrated in Figure 4 (not shown).

[0082] Gaseous compounds can also be led to a gas treatment system (not shown in Fig. 4). In the gas treatment system, gaseous compounds recovered from the H₂S reactor are treated. Unreacted hydrogen is cleaned from hydrogen sulphide and methane by means of membrane technique, for example. The cleaned hydrogen is pressurized and can be recycled into the reactor 1 (not shown). The recovered hydrogen sulphide can be recycled to pulp mills chemical recovery cycle and converted to elementary sulphur by Claus process.

[0083] The following examples are presented for further illustration of the invention without limiting the invention thereto.

Example 1

[0084] Crude turpentine obtained from kraft pulping process, i.e. CST, was used as a crude turpentine feed. The crude turpentine comprised 50-60% a-pinene, 20-30% of Δ-carene, the rest being other terpenes. The sulphur content was about 1.5%.

[0085] The catalyst system comprised NiW as a dewaxing catalyst. No hydrodesulphurization catalyst was present.

Table 1

<table>
<thead>
<tr>
<th>Pumping of feed (V_{feed}) (g/h)</th>
<th>48</th>
</tr>
</thead>
<tbody>
<tr>
<td>Catalysts</td>
<td>NiW (10 g)</td>
</tr>
<tr>
<td>Reaction pressure (bar)</td>
<td>48</td>
</tr>
<tr>
<td>H₂ (l/h)</td>
<td>25</td>
</tr>
<tr>
<td>WHSV (h⁻¹)</td>
<td>4.9</td>
</tr>
<tr>
<td>Temperature of bed (°C)</td>
<td>365</td>
</tr>
<tr>
<td>H₂ feed/turpentine feed (NI/l)</td>
<td>440</td>
</tr>
</tbody>
</table>

[0086] The composition of the product is shown in Table 2.
Table 2 shows that it is obtained a composition that is suitable for use as gasoline fuel component, having a content of the aromatics in compliance with the EN228 gasoline standard. The composition of the fuel component presented in Table 2 can also be used as an octane number enhancer of the gasoline fuel.

Example 2

The same turpentine feed as in Example 1 was used. The process parameters and the composition of the product are summarized in Tables 3 and 4, respectively.

Table 3

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pumping of feed ($V_{\text{feed}}$) (g/h)</td>
<td>28</td>
</tr>
<tr>
<td>Catalysts</td>
<td>NiW (10 g)</td>
</tr>
<tr>
<td>Reaction pressure (bar)</td>
<td>47</td>
</tr>
<tr>
<td>$H_2$ (l/h)</td>
<td>20</td>
</tr>
<tr>
<td>WHSV ($h^{-1}$)</td>
<td>2.8</td>
</tr>
<tr>
<td>Temperature of bed ($^\circ$C)</td>
<td>330</td>
</tr>
<tr>
<td>$H_2$ feed/turpentine feed (NI/l)</td>
<td>607</td>
</tr>
</tbody>
</table>

The composition of the product is shown in Table 4.
The Example shows that the proportions of the components in the gasoline mixture can be influenced by varying the temperature and WHSV in the process. Table 4 shows that it is obtained a composition that is suitable for use as gasoline fuel component, having a content of the aromatics in compliance with the EN228 gasoline standard.

Example 3

The same turpentine feed as in Example 1 was used in this Example. The catalyst system comprised NiW, and NiMo/Al2O3 as a hydrodesulphurization catalyst. The two catalysts were packed in separate layers in one single reactor where NiW layer was disposed downstream of the HDS catalyst layer, i.e. a layer comprising NiMo/Al2O3. A guard bed of Al2O3 was disposed upstream of the HDS catalyst layer whereby the CST feed entered first the guard bed prior to the HDS layer. Al2O3 intermediate layer was disposed between the catalyst layers. SiC layer was placed downstream of the NiW layer, i.e. at the bottom of the reactor towards the outlet for the product recovery.

The process parameters are summarized in Table 3 below.

Table 5

<table>
<thead>
<tr>
<th>Pumping of feed (V_{feed}) (g/h)</th>
<th>59</th>
</tr>
</thead>
<tbody>
<tr>
<td>Catalysts</td>
<td>NiMo/Al2O3 (21 g) + NiW (6 g)</td>
</tr>
<tr>
<td>Reaction pressure (bar)</td>
<td>47</td>
</tr>
<tr>
<td>H2 (l/h)</td>
<td>20</td>
</tr>
<tr>
<td>WHSV (h^{-1}) (NiMo/Al2O3)</td>
<td>5.9</td>
</tr>
<tr>
<td>Temperature of bed (NiMo/Al2O3) (°C)</td>
<td>390</td>
</tr>
<tr>
<td>Temperature of bed (NiW) (°C)</td>
<td>380</td>
</tr>
<tr>
<td>H2 feed/turpentine feed (Ni/l)</td>
<td>290</td>
</tr>
</tbody>
</table>
The composition of the product is shown in Table 6.

Table 6

<table>
<thead>
<tr>
<th>Component</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Liquid yield (%)</td>
<td>78-81</td>
</tr>
<tr>
<td>Heterocycles (%)</td>
<td>17.1</td>
</tr>
<tr>
<td>Monocycles (%)</td>
<td>22.1</td>
</tr>
<tr>
<td>Acycles (%)</td>
<td>8.8</td>
</tr>
<tr>
<td>Aromatics (cymenes) (%)</td>
<td>2.0</td>
</tr>
<tr>
<td>Toluene (%)</td>
<td>25.6</td>
</tr>
<tr>
<td>Others (C₆, C₇, C₁₀) (%)</td>
<td>24.2</td>
</tr>
</tbody>
</table>

In Example 3, the HDS catalyst first converts the terpene compounds of CST to hydrocarbons that are further converted to gasoline components. Table 6 shows that by using a small amount of a dewaxing catalyst the composition of the resulting fuel components can be varied. Table 6 further shows that by using a combination of different catalysts it is possible to obtain a composition that is suitable for use as gasoline fuel component, having a content of the aromatics in compliance with the EN228 gasoline standard.
Claims

1. A process for producing gasoline components, wherein:
a feed of C₅-C₁₀ unsaturated cyclic and acyclic hydrocarbons is subjected to a single step of hydroprocessing in the presence of hydrogen gas and a catalyst system comprising a dewaxing catalyst to form a mixture of gasoline components.

2. The process of claim 1 wherein the hydrocarbon feed is substantially composed of terpenes.

3. The process of claim 1 or 2 wherein the hydrocarbon feed is substantially composed of crude sulphate turpentine derived from kraft pulping of wood.

4. The process of any of the preceding claims wherein the catalyst system is a fixed-bed system and the dewaxing catalyst is NiW on a support selected from Al₂O₃, zeolite, zeolite-Al₂O₃, and Al₂O₃-SiO₂, preferably NiW on an Al₂O₃ support.

5. The process of any of the preceding claims wherein the catalyst system further comprises a hydrodesulphurization catalyst.

6. The process of claim 5 wherein the hydrodesulphurization catalyst is selected from the group consisting of NiO/MoO₃, CoO/MoO₃ and a mixture thereof on a support selected from Al₂O₃ and Al₂O₃-SiO₂, preferably NiO/MoO₃ on an Al₂O₃ support.

7. The process of any of the preceding claims wherein a sulphur feed is optionally fed to the step of hydroprocessing.

8. The process of any of the preceding claims wherein at least a portion of the mixture of gasoline components is circulated back to the hydrocarbon feed and/or to the step of hydroprocessing.

9. The process of any of the preceding claims wherein the mixture of gasoline components is subjected to a hydrogen sulphide removal step to remove any residual hydrogen sulphide from the mixture.

10. The process of claim 9 wherein the residual hydrogen sulphide is removed by stripping, flashing or bubbling with inert gas.

11. The process of any of the preceding claims wherein the step of hydroprocessing is carried out at a temperature range from about 200°C to about 450°C, preferably from about 275°C to about 375°C.
12. The process of any of the preceding claims wherein the step of hydroprocessing is carried out at a pressure of about 10 to about 150 bar, preferably at a pressure of about 20 to about 70 bar, more preferably at about 25 to about 50 bar.

13. The process of any of the preceding claims wherein the ratio of \( \text{H}_2 \) feed to sulphur feed is maintained over about 0.0001.

14. The process of any of the preceding claims wherein the ratio of \( \text{H}_2 \) feed to the hydrocarbon feed is in the range from about 200 to about 1500 Nl/l, preferably in the range from about 250 to 1000 Nl/l.

15. The process of any of the preceding claims wherein the pumping speed WHSV of the hydrocarbon feed, measured in accordance with the following equation:

\[
\text{WHSV} \left( \text{h}^{-1} \right) = \frac{V_{\text{feed}[g/l]}}{m_{\text{catalyst}[g]}}
\]

wherein \( V_{\text{feed}[g/l]} \) means a pumping velocity of the hydrocarbon feed, and \( m_{\text{catalyst}[g]} \) means an amount of the catalyst; is in the range from about 2 to about 8, preferably not higher than about 5, when the catalyst system is arranged in one catalyst layer, or is in the range from about 0.5 to about 6, preferably from about 1 to 4, more preferably about 1 to 1.5, when the catalyst system is arranged in at least two catalyst layers.

16. The process of any of the preceding claims wherein the mixture of gasoline components comprising toluene is obtained.

17. The process of any of the preceding claims wherein any component is isolated from the mixture of gasoline components.

18. An apparatus for producing gasoline components from a feed of C5-C1 unsaturated cyclic and acyclic hydrocarbons, comprising
- at least one reactor (1) comprising at least one catalyst layer (3) of a catalyst system comprising a dewaxing catalyst
  - hydrocarbon inlet pipe (9)
  - hydrogen feed pipe (5, 50, 50')
  - product outlet pipe (10, 15) for recovering a mixture of the gasoline components.
19. The apparatus of claim 18 wherein the catalyst system further comprises a hydrodesulphurization catalyst.

20. The apparatus of claim 18 or 19 wherein the apparatus comprises only one reactor (1) which comprises a first catalyst layer (3') and a second catalyst layer (3), the first catalyst layer (3') lying upstream of the second catalyst layer (3).

21. The apparatus of claim 20 wherein the first catalyst layer (3') is composed of a hydrodesulphurization catalyst and the second catalyst layer (3) is composed of a dewaxing catalyst.

22. The apparatus of claim 20 or 21 wherein a first passive layer (11) is arranged upstream of the first catalyst layer (3'), a second passive layer (12) is arranged downstream of the second catalyst layer (3), and an intermediate layer (13) is disposed between the first and second catalyst layers (3', 3).

23. The apparatus of any of claims 20 to 22 wherein the apparatus comprises a product recirculation pipe (100) for recirculating the mixture of the gasoline components to the reactor (1).

24. The apparatus of any of claims 20 to 23 wherein the apparatus comprises a H₂S removal reactor (2) for hydrogen sulphide removal and a H₂S recirculation pipe 140 for feeding gaseous compounds recovered from the H₂S removal reactor (2) to the reactor (1).

25. The apparatus of claim 18 or 19 wherein the apparatus comprises two reactors (1', 1), a first reactor (1') comprising a first catalyst layer (3'), and a second reactor (1) comprising a second catalyst layer (3), the first reactor (1') lying upstream of the second reactor (1).

26. The apparatus of claim 25 wherein the first catalyst layer (3') comprises a hydrodesulphurization catalyst and the second catalyst layer (3) comprises a dewaxing catalyst.

27. The apparatus of claim 25 or 26 wherein the apparatus comprises a product recirculation pipe (100) for recirculating the mixture of the gasoline components to the first reactor (1').

28. The apparatus of any of claims 18 to 27 wherein the apparatus comprises a sulphur feed pipe (16) for supplying external sulphur to the at least one reactor (1, 1').

29. The apparatus of any of claims 18 to 28 wherein the apparatus comprises a separating reactor (17) for isolating any component from the mixture of the gasoline components.
30. A use of gasoline components prepared by the process of any of claims 1 to 17 as a gasoline or as an additive in gasoline compositions.

31. A use of gasoline components prepared by the process of any of claims 1 to 17 in cosmetics or pharmaceutical products.

32. Use of a dewaxing catalyst in a process for forming a mixture of gasoline components in a single step of hydroprocessing of a feed of C₅-Ci₀ unsaturated cyclic and acyclic hydrocarbons.