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MENETELMÄ KORKEAMMAN KUIN 300 °C:N KIEHUMISLÄMPÖTILAN JA MATALAMMAN TAI YHTÄ SUUREN KUIN -40 °C:N JÄHMETTYMISPISTEEN OMAAVIEN HIILIVETYLIUOTTIMIEN SAAMISEKSI

METHOD FOR OBTAINING HYDROCARBON SOLVENTS HAVING A BOILING TEMPERATURE HIGHER THAN 300 °C AND A POUR POINT LOWER THAN OR EQUAL TO - 40 °C

METHOD FOR OBTAINING HYDROCARBON SOLVENTS HAVING A BOILING TEMPERATURE HIGHER THAN 300 °C AND A POUR POINT LOWER THAN OR EQUAL TO - 40 °C

The subject of the present invention is a method for producing hydrocarbon solvents devoid of aromatic compounds and of sulfur, with boiling temperature greater than or equal to 300°C and final boiling temperature less than or equal to 500°C and the pour point of which is strongly lowered down to -40°C and less. Such method is particularly suitable for the processing of gas oil fractions obtained by distilling and refining crude oil. The present invention further relates to products obtained by the method and finally the application of said products as solvent, in particular in cold environments requiring a very low pour point. The solvents can be used as drilling fluids, lubricants for industry including the automobile industry, metalwork, as entering into the composition of phytosanitary products, inks and extension oils for sealants putty, and as viscosity thickeners for formulations based on resin and pastes based on polyvinyl chloride (PVC).

The chemical nature and the composition of fluids known to a person skilled in the art vary considerably depending on the application envisaged and the raw material of the products. Thereby, certain are derived from oil, and other come from chemistry via polymerization and/or olefin oligomerization. For products derived from oil, the distillation interval measured as per ASTM D-86 or ASTM D 2887 (choice depending upon the initial or final boiling point needed below 270°C or above 400°C), the pour point as per ASTM D 5950 (with reference to ASTM D97 3-points), the viscosity, the specific gravity, the sulfur and aromatic content, the specific gravity, the aniline point measured as per ASTM D-611, the method of production of the hydrocarbons, in particular the nature of the raw material distilled in fractions and the flash point are important characteristics that allow said products to be distinguished and to adapt said products to the different applications considered.

Such hydrocarbon fluids often have narrow boiling point ranges between the Initial Boiling Point (IBP) and the Final Boiling Point (FBP). Said ranges are chosen depending on the application considered. The narrowness of said ranges provides a precise ignition point and/or flash point. Same are important safety parameters. A narrow range of fractions also serves to obtain a better defined viscosity, a better stability of same and evaporation characteristics suitable for the applications requiring a drying step lasting a controlled time: said range also favors obtaining hydrocarbon fractions with better defined

surface tension, the aniline point and the solvent power of which are more precise. However, said features are not always the only ones to take into account and others could take priority depending on the targeted applications.

To be applied as solvents in different applications, said fluids should be purified. The purification typically consists of hydrosulfuration steps (and/or hydrocracking) and/or hydrogenation for reducing the sulfur content, the nitrogen content and/or for eliminating aromatic hydrocarbons, olefins and/or un-saturated rings by transforming said compounds into naphthenes. Hydrocarbon fluids thereby purified are mainly aliphatic, containing normal paraffins, isoparaffins and naphthenes. For said type of dearomatized fluid, the hydrocarbon product that has been desulfurized and/or had nitrogen eliminated from same, can be hydrogenated to saturate all the aromatic hydrocarbons present. Hydrogenation can also be carried out before the final fractionation.

The users have firstly searched essentially hydrocarbon fluids containing low concentrations of aromatic hydrocarbons and extremely low sulfur contents, the fractions of which have higher initial boiling points, in order to take into account environmental conditions or safety.

It is possible to process gas oils coming from the direct distillation the final boiling point (FBP) of which is 320°C to obtain dearomatized products the pour point of which is less than or equal to 0°C. The processing of distillation fractions with higher final boiling points, e.g. higher than 350°C is also easy but does not allow sufficiently low pour points to be achieved in the heavy fraction, greater than 330°C after dearomatization. Furthermore, the content of aromatic hydrocarbons, in particular polyaromatics, is higher. The presence of such compounds in the hydrocarbons has harmful effects on hydrogenation catalysts the service life and the performance of which is limited. Sometimes, a supplementary hydrogenation processing is needed to decrease again the sulfur content in such products. Thereby, the processing of such fractions in particular burdens the economics of hydrogenation processes by considerably increasing the consumption of hydrogen and the renewal costs of the catalyst that deactivates rapidly.

Furthermore, the hydrocarbon fluids should now exhibit a good compromise between high viscosity and good cold properties, i.e. a very low pour point, e.g. less than -25°C and even lower than -30°C, a high solvent power, in particular for printing ink applications requiring the dissolving of resins, but also viscous or solid compounds entering into the composition of drilling fluids. The hydrocarbon fluids used as extension oils for the manufacture of silicone-based sealants should also exhibit good compatibility with silicone-based polymers and also the ability to lower the viscosity of certain polymers

like the PVCs when same are used in the manufacture of PVC pastes or Plastisols. The hydrocarbon fluids also entering into the composition of phytosanitary products should also have a viscosity and a degree of purity compatible with toxicity and phyto-toxicity constraints implied in such use. US 2003 211949 A1 deals with a fluid having a pour-point equal to -40 °C. US 6517704 B1 deals with a process for obtaining hydrocarbon solvents comprising a hydro-paraffining step and a hydro-dearomatization step.

It is also known how to obtain such fluids from compounds coming from vacuum distillation, in particular vacuum or vapor-cracked gas oils that can then be subject to other processes like catalytic cracking coupled with a hydrogenation (hydro-desulfurization, hydro-dearomatization) as described in the patent EP1447437 or again hydrocracking coupled with a hydrogenation, such as described in the patents WO03/074634 and WO03/074635. The hydrocracking or catalytic cracking processes favor the concentration of aromatics, in particular polycyclic aromatics in the 200 to 450°C fractions leaving said units, the aromatics transforming into naphthenic compounds, more particularly polycyclic naphthenic compounds, by aromatic ring hydrogenation.

However, the requirements of new less toxic and less volatile fluids with moderately high viscosity have led the claimant to use deparaffined hydrocarbons for the application thereof as solvents which is described in the patent application WO2010/103245. The fluids are obtained from hydro-paraffining units from different fractions of gas oils coming from other refining units and by distilling said fluids to produce hydro-paraffined fluids at appropriate fraction intervals, possibly after same have been subject to purification processing for eliminating sulfur and aromatic hydrocarbons. Said hydro-paraffined fluids should have the same characteristics of purity as the fluids required for products coming from crude oil, like sulfur content measured by ASTM D5453 less than 10 ppm and a low concentration of aromatic compounds, much less than 300 ppm. Furthermore, said characteristics are identical or not better than the characteristics of products coming from oil. Said products have a final boiling point (FBP) greater than 300°C.

However, all the criteria are not met over all the fractions and in particular on fractions with Initial Boiling Points (IBP) greater than 300°C. Indeed, while meeting characteristics in sulfur content, flash point, aromatics and aniline point, said fractions have a very high pour point, greater than -10°C and even 0°C which makes same unusable in a cold environment at temperatures less than -25°C and even less at - 30°C. Said fractions are particularly sought for drilling applications, inks and sealant type materials.

To solve such problem, the Applicant decided to implement a special hydroparaffining method consisting of improving the pour point of the initial boiling point (IBP) fractions greater than or equal to 300°C determined by ASTM D 86 independently of the other fractions.

Amongst the hydroparaffining methods, there are two methods, one favoring the transformation of paraffins into isoparaffins by a very isomerizing method with very little cracking of normal paraffins and the other based on the soft cracking of processes hydrocarbons, more particularly normal paraffins.

The hydroparaffining method favoring the isomerization of olefins is done in the presence of a zeolite-based isomerization catalyst, e.g. a ZSM5 supporting transition metals or a ZSM48 supporting platinum/palladium type metals at a temperature varying from 200 to 500°C under a hydrogen pressure varying from 25 to 200 bar. The hydrofinishing method is also obtained under hydrogen pressure in the presence of a catalyst on a metal oxide base supporting nickel, molybdenum, cobalt, palladium, tungsten or pairs of said metals.

Said very intensive hydroparaffining methods are used for the preparation of Diesel or hydroparaffined oils from heavy hydrocarbon fractions coming from the vacuum distillate catalytic cracking units (FCC (Fluid Catalytic Cracking)), such as the LCO (Light Cycle Oil) or oil residues (slurry) or again hydrocracked gas oils, leading to lower points without for all that achieving pour points less than -25°C, in particular on fractions above 300°C like said described e.g. in the patent applications and patents WO2009/154324, WO2009/011479, EP665283, US6517704 or again US6340430. It should be noted that said processing is done on large interval fractions corresponding to desired, traditional oil and Diesel grades. So-called naphthenic hydrocarbon fractions are obtained but the aromatic concentration of same is greater than 0.1% by weight, or even greater than 10% by weight (as per the analytical method IP391: determination by HPLC). The so-called “hydrofinishing” processing used after hydroparaffining does not serve to convert aromatics into naphthenic compounds. In said methods, “isomerizing” hydroparaffining in the presence of platinum/palladium-based catalysts on a zeolite/alumina support, is preferred over hydroparaffining with cracking.

The hydroparaffining method favoring soft cracking of normal, long-chain paraffins present in the load, is described in the patents US4781906, US4842717 and US5997727. Said method aims at the lowering, like said other method, of the pour point of gas oils by the processing of the whole gas oil fraction in the presence of a silicate-based catalyst possible supporting nickel and/or a nickel/tungsten pair under hydrogen at a temperature

varying from 350 to 450°C and a pressure of from 1 to 80 bar. Said method was applied more particularly to a gas oil fraction with a boiling temperature above 300°C for a fraction interval exceeding 100°C and the lowering of the pour point did not serve to achieve a temperature less than or equal to -25°C, the pour point being only close to 0°C.

The present invention aims at lowering the pour point to a temperature less than or equal to -40°C for solvents coming from gas oil (GO) fractions with initial boiling point greater than or equal to 300°C and a final boiling temperature less than or equal to 500°C, determined as per the standard ASTM D 86, by implementing a method serving in an integrated manner to produce dearomatized solvents with a boiling temperature greater than 300°C, from less than a 100°C fraction interval and containing less than 500 ppm of aromatics, desulfurized to less than 10 ppm of sulfur and the solvent power of which measured by the aniline point thereof being improved. The invention also aims to integrate said method into a method of preparing all fractions usable as solvents, with boiling temperature comprised between 200 and 500°C and fraction interval less than 100°C.

In the present description of the invention, the boiling temperatures, initial and final distillation points of the fractions, are measured as per the standard ASTM D86.

The subject matter of the present invention is a method for obtaining hydrocarbon solvents, with sulfur concentration less than 10 ppm, concentration of aromatics less than 500 ppm, initial boiling temperature greater than or equal to 300°C and final boiling temperature less than or equal to 500°C, determined as per ASTM D86, for a fraction interval of more than 100°C and a pour point less than -40°C, as per the standard ASTM D5950, the method being as per claim 1. [NF1]

By fraction 300°C+, is meant fractions distilling above 300°C as per the standard ASTM D 86.

Such a method has the advantage of preparing heavy hydrocarbon fractions with initial boiling temperatures greater than 300°C, called 300°C+, but also simultaneously preparing other fractions with initial boiling temperature less than 300°C, meeting the specifications of hydrocarbon solvents without aromatics and without sulfur. Said result is obtained by integrating known methods into a new chain serving to separate and mix the streams before and after processing.

A load consisting of a gas oil fraction obtained by all refining methods refers, in particular, to a fraction chosen amongst atmospheric distillation gas oils, vacuum distillation gas oils, hydrocracked gas oils, catalytic cracking gas oils, viscoreduction gas oils, coking gas oils, gas oils coming from gas deposits, deasphalted gas oils, gas oils

coming from hydroprocessing of heavy fractions (Atmospheric residue and vacuum distillation gas oil or VGO), gas oils with a sulfur content greater than 15 ppm being necessarily desulfurized by hydroprocessing and/or hydrocracking prior to processing as per the method of the invention. If said load comes from a plurality of gas oil fractions referenced in the list above, said load still remains within the framework of the invention.

The hydrocarbon fraction with boiling temperature greater than or equal to 300°C is obtained by separation of the gas oil fraction into two fractions, a light fraction (CI) with final boiling temperature less than 300°C and at least one heavy fraction (CL) with initial boiling temperature greater than or equal to 300°C, each fraction presenting an interval of boiling temperature between 300°C and 500°C and a distillation interval preferentially less than 85°C.

The step of deparaffining processing the so-called heavy fraction (CL) comprises at least one first soft cracking section in the presence of a silicate based catalyst, chosen amongst the silicates with silica/alumina ratio greater than 200 comprising 0 to 10% by weight of at least one metal from group VIII and possibly from 0 to 10% by weight of a metal from group VI, and a second hydrogenation of olefins section in the presence of a catalyst which is an alumina supporting a metal pair chosen amongst the pairs cobalt/molybdenum, nickel/tungsten, cobalt/tungsten and nickel/molybdenum.

So as to inhibit coking of the load and the effluents so produced, nor even the isomerization of the olefins formed, the paraffining step comprises at least two soft cracking sections alternated with two sections of hydrogenation of the olefins formed during said crackings, the deparaffining catalyst being chosen amongst the silicates with a silica/alumina ratio greater than 200, said silicates supporting nickel alone or a nickel/tungsten pair and the olefin hydrogenation catalyst being an alumina supporting a metal pair chosen amongst the pairs cobalt/molybdenum, nickel/tungsten, cobalt/tungsten and nickel/molybdenum. The first cracking section serves to crack the products without causing the formation of coke, the hydrogenation section, serving to saturate the olefins produced, without secondary isomerization reaction, the second cracking section serving to continue the cracking whereas the last hydrogenation section is a finishing section for the saturation of the olefins.

The deparaffining step is performed under hydrogen pressure, at a temperature varying from 150 to 450°C under a total pressure varying from 10 to 400 bar, preferably at a temperature varying from 280 to 380°C and a pressure varying from 20 to 200 bar.

The deparaffined effluent obtained at the deparaffining step is sent to an additional separation step placed before the dehydrogenation step. This additional effluent is

separated into at least two effluents, a hydrocarbon fraction of C1 to C4 (hydrocarbons comprising 1 to 4 carbon atoms) and a deparaffined fraction (or CDP), at least a part thereof distilled above 300°C and presenting a pour point less than or equal to -40°C. Said action remains within the framework of the invention if the separated fractions were more numerous and do not correspond exactly to the fractions specified below.

The deparaffined effluent is separated into two fractions, three fractions or four deparaffined fractions:

- a C1 to C4 hydrocarbon fraction and a hydrocarbon fraction with more than 5 carbon atoms (or C5+),

- or a C1 to C4 hydrocarbon fraction and two hydrocarbon fractions, one distilling C5 at 150°C (or C5-150 corresponding to a gasoline fraction) and the other distilling above 150°C (or 150°C+),

- or a C1 to C4 hydrocarbon fraction and three hydrocarbon fractions, one distilling C5 at 150°C (or C5-150), the second distilling from 150 to 300°C (or 150-300 corresponding to a light diesel fraction) and the third distilling above 300°C (or 300°C+),

With regard to the 300°C+ fraction, said could be one or a plurality of fractions distilling above 300°C (or 300°C+),

At the outlet of the additional separation step, the deparaffined fraction with the highest initial boiling temperature of the deparaffined effluent is sent to the hydrodearomatization step, said step comprising one or a plurality of hydrodearomatization sections.

For example, if the deparaffined effluent is separated into two fractions only, the hydrocarbon fraction with more than 5 atoms of carbon (or C5+) is sent to the hydrodearomatization step. If the deparaffined effluent is separated into three fractions, the fraction distilling above 150°C (or 150°C+) is sent to the hydrodearomatization step. Finally, if the deparaffined effluent is separated into four fractions, the fraction distilling above 300°C (or 300°C+) is sent to the hydrodearomatization step. If appropriate, the light fraction (CI) coming from the separation of the gas oil fraction into two fractions, is mixed in all or part with the deparaffined fraction sent to the hydrodearomatization step.

However, in a variant of said method, the fractions (C5-150) and (150-300) could be dearomatized in the hydrodearomatization unit alone or in a mixture with all or part of the other separation fractions in said additional separation step.

In a variant of the method according to the invention, the heavy fraction (CL) coming from the separation of the gas oil fraction into at least two fractions, can be sent for a part at least, to the deparaffining step, the other part being mixed with the

deparaffined fraction recovered at the outlet of the separation step of the deparaffined effluent and sent to the hydrodearomatization step. Such variant serves in particular for adjusting the temperature of the pour point of said fraction. Preferably, all of the heavy fraction (CL) is sent to the deparaffining step.

At the outlet of the last atmospheric distillation step, the 300°C+ fraction with a pour point less than -40°C, is completely recovered for applications envisaged or at least partially, a part at least being recycled in a deparaffined fraction sent to the hydrodearomatization step, the recycling serving advantageously for lowering again the concentration of aromatics of said fraction.

In one embodiment of the method of the invention, the deparaffining and hydrodearomatization steps are carried out in the same tank or in different tanks. Preferably, said steps are conducted at the same pressure varying from 60 to 200 bar, under a hydrogen atmosphere, at a temperature varying from 150 to 450°C, preferably varying from 280 to 380°C for the deparaffining method and at a temperature varying from 80 to 250°C for the hydrodearomatization step, the temperature of the effluent being adjusted before the hydrodearomatization step by injection of at least one liquid or gaseous compound with a temperature lower than the deparaffined effluent by at least 50°C.

For said temperature adjustment, the liquid or gaseous compound is chosen from amongst hydrogen, the light fraction (CI) coming from the lower boiling temperature at 300°C and the fraction 300°C+ with the pour point less than -25°C recovered after distillation of the deparaffined, desulfurized, if appropriate, and dearomatized effluents.

The system for implementing the method comprises:

- a separation unit (DF) in communication with a deparaffining reactor (R1);
- a deparaffining reactor (R1) including at least two catalytic beds for the soft cracking section (S1) and for the olefin hydrogenation section (S2), said deparaffining reactor being supplied by a hydrocarbon fraction with a upper boiling temperature at 300°C (or 300°C+) coming from the separation unit (DF) in two fractions 150°-300°C (or 150-300) and 300°C+ by distillation of a gas oil fraction coming from any crude oil refining method;
- at least a hydrodearomatization reactor (R2) in communication with both the deparaffining reactor (R1) and at least one atmospheric distillation tower (DA1),
- at least one atmospheric distillation tower (DA1).

In a preferred embodiment, the 300°C+ fraction comes from a separation tank (DF) arranged upstream of the deparaffining reactor (R1) separating a gas oil fraction coming

from any crude oil refining method, into two fractions 150°-300°C (or 150-300) and 300°C+.

In a preferred embodiment, the system for implementing the method according to the invention comprises a unit for separation into two or more fractions (DA2) arranged on the outlet pipe for the effluents coming from the deparaffining reactor (R1).

For example, the deparaffined effluent can be distilled in a distillation unit DA2 into two fractions, three fractions or four deparaffined fractions;

- a C1 to C4 hydrocarbon fraction and a hydrocarbon fraction with more than 5 carbon atoms (or C5+),

- or a C1 to C4 hydrocarbon fraction and two hydrocarbon fractions, one distilling C5 at 150°C (or C5-150) fraction) and the other distilling above 150°C (or 150°C+)

- or a C1 to C4 hydrocarbon fraction and three hydrocarbon fractions, one distilling C5 at 150°C (or C5-150), the second distilling from 150 to 300°C (or 150-300) and the third distilling above 300°C (or 300°C+).

In a particular embodiment of the invention, the deparaffining and hydrodearomatization reactors are combined in the same reactor, catalytic beds being distributed into two sections, the deparaffining section (SR1) and the dearomatizing section (SR2), said two sections being separated by a cavity (30) serving to mix the deparaffined effluent with liquid or gaseous liquid compounds intended to adjust the temperature of the effluents entering the dearomatizing section. Said cavity (30) can be empty or filled all or in part with inert materials serving to mix gases and liquids.

Said effluents are chosen preferably amongst hydrogen and/or recycled CI fractions and/or 300°C+ with a pour point less than -25°C recovered after the atmospheric distillation tower (DA1).

A second subject matter of the invention is the fraction 300°C+ obtained according to the method of the invention, with pour point less than -40°C and boiling point higher than 300°C and final boiling temperature less than or equal to 500°C, with fraction interval less than 100°C, sulfur concentration less than 10 ppm and aromatic concentration less than 500 ppm and containing more than 30% by weight of naphthenic compounds and less than 5% by weight of normal paraffins. Mononaphthenic compounds represent more than 20% by weight of the naphthenic compounds.

Preferably, such fraction has a fraction interval less than or equal to 85%, preferably a sulfur concentration less than 5 ppm and an aromatic concentration less than 300 ppm, where said preferences can be achieved independently from one another or in combination.

Of course, a fraction 300°C+ refers to one or a plurality of 300°C+ fractions, with boiling temperature comprised between 300°C and 450°C and with a fraction width less than or equal to 75°C, preferably less than 65°C.

Said 300°C+ fraction or fractions comprise less than 35% by weight of hydrocarbons having a chain longer than 22 carbon atoms and more than 65% by weight of hydrocarbons having a chain length of less than 22 carbon atoms.

In one embodiment, the 300°C+ fraction has an initial boiling point higher than or equal to 330°C.

In one embodiment, the 300°C+ fraction has a percentage of polycyclic naphthenic compounds less than 20%, preferably less than 10%.

A third subject matter of the invention is the use of the 300°C+ fraction or fractions as a solvent in phytosanitary applications, inks and sealant or else as fluid for metalworking. Said applications require low pour points while having qualities of purity and a significant non-VOC character (volatile organic compounds) for domestic uses.

To describe the invention more precisely, figures representing the different forms of implementation of the invention are given to support the present description.

Figure 1 represents a system for implementing the method of the invention, for which two separate reactors (R1) and (R2) are represented respectively for the steps of deparaffining and dearomatizing.

Figure 2 represents a system for implementing the method of the invention for which a single reactor is represented closing two distinct sections (SR1) and (SR2) respectively for the stems of deparaffining and dearomatizing, a cavity (30) separating said two sections.

Figure 3 represents soft cracking and continuous hydroprocessing sections in the deparaffining reactor R1 or SR1 in Figures 1 and 2.

In Figure 1, a load of gas oil (GO) coming from any crude oil refining methods is fed in through the pipe (10) into the separator serving a fractionated distillation DF referenced (1) where said is separated into two fractions, a light fraction (CI) removed from DF through the pipe (12) and a heavy fraction CL removed from DF through the pipe (11).

Said heavy fraction CL is sent to the deparaffining reactor R1 referenced (2) supplied in parallel by hydrogen arriving through pipes (31) then (32). All the deparaffined effluent is sent through the pipe (14) into an atmospheric distillation unit DA2, referenced (5). Two, three or four effluents are distilled depending on the choice of application

envisaged, only the deparaffined fraction CDP removed through the pipe (15) being sent to the dearomatizing step.

For example, the deparaffined effluent can be distilled in a distillation unit DA2 into two fractions, three fractions or four deparaffined fractions;

- a hydrocarbon fraction from C1 to C4 again called “fuel gas”, removed through the pipe (21) and a hydrocarbon fraction of more than 5 carbon atoms (or C5+) removed through the pipe (15) toward the dearomatizing reactor R2 referenced (3),

- or one hydrocarbon fraction from C1 to C4 discharged through the pipe (21) and two hydrocarbon fractions, one distilling C5 at 150°C (or C5-150) discharged through the pipe (22) and the other distilling above 150°C (or 150°C+) discharged through the pipe (15) to the reactor dearomatizing R2 referenced (3),

- or one hydrocarbon fraction from C1 to C4 discharged through the pipe (21) and three hydrocarbon fractions, one distilling C5 at 150°C (or C5-150) discharged through the pipe (22), the second distilling from 150 to 300°C (or 150-300) discharged through the pipe (23) and the third distilling above 300°C (or 300°C+) discharged through the pipe (15) to the reactor dearomatizing R2 referenced (3).

The CDP fraction discharged through the pipe (15) is sent through the pipe (16) into the reactor R2 referenced (3) supplied in parallel by hydrogen coming from the pipe (31) via the pipe (33).

The deparaffined and dearomatized effluent is recovered at the outlet of reactor R2 (3) through the pipe (17) and sent to a distillation unit DA1 referenced (4) to be distilled therein into at least four fractions:

- the fraction(s) 300°C+ recovered through the pipe (18),
- the fraction (150-300) discharged through the pipe (27),
- the fraction (C5-150) discharged through the pipe (26),
- and the fraction C1-C4 or “fuel gas” discharged through the pipe (25).

In a certain embodiment, the light fraction recovered through the pipe (12) at the outlet of the separator DF (1) can be fed in, in all or in part via the pipe (24) into the CDP effluent before the entrance thereof into the reactor R2 (3).

Furthermore, the fractions (C5-150) at the outlet from the distillations DA1 and DA2 can advantageously be mixed, just like the fractions (150-300) with all or part of the light fraction CI in the pipe (12) then at the outlet of the distillation DA1 (4).

In certain preferred embodiments, the heavy fraction CL at the outlet of the separator DF (11) is only partially sent to the reactor R1 (2), a part of said fraction sent through the pipe (20) being mixed with the deparaffined CDP effluent.

Similarly, if the aromatic content is too high in the fraction 300°C+ or the viscosity of the CDP effluent is insufficient, a part of the fraction 300°C+ at the outlet from the distillation DA1 (4) is recycled via the pipe (28) in the pipe (16) leading the CDP effluent into the reactor R2 (3).

Figure 2 is different from Figure 1 in that only one reactor (5) is shown for the deparaffining and the dearomatizing steps comprising two sections, of for deparaffining SR1 referenced (2) and a dearomatizing section SR2 referenced (3), these two sections being separated by a cavity (30). In this Figure, a load of gas oil (GO) coming from any crude oil refining methods is introduced through the pipe (10) into the separator DF referenced (1) where said is separated into two fractions, a light fraction (CI) removed from DF (1) through the pipe (12) and a heavy fraction CL removed from DF (1) through the pipe (11).

Said heavy fraction CL is sent to the section SR1 (2) of the reactor (5) supplied in parallel by hydrogen arriving through pipes (31) then (32) to be deparaffined there. The whole deparaffined fraction is sent to the section SR2 (3), possibly after having been mixed in the cavity (30) separating the two sections, with the additional hydrogen arriving through the pipe (33). Said injection of hydrogen is useful to the dearomatizing reaction but also has the purpose of adjusting the inlet temperature of the load or the deparaffined fraction in the section SR2 (3) by quenching, serving to lower the temperature at the inlet to section SR2 (3).

In a particular embodiment of the invention, it is also possible to inject all or part of the light fraction (CI) via the pipe (24) into the cavity (30) to be dearomatized like the heavy deparaffined fraction (CL). The quantity of hydrogen will consequentially be adjusted as well as the inlet temperature into the section SR2 (3).

Like in Figure 1, the deparaffined and dearomatized effluent is recovered at the outlet of reactor (5) through the pipe (17) and sent to a distillation unit DA1 referenced (4) to be distilled there into at least four fractions:

- the fraction(s) 300°C+ recovered through the pipe (18),
- the fraction (150-300) discharged through the pipe (27),
- the fraction (C5-150) discharged through the pipe (26),
- and the fraction C1-C4 or “fuel gas” discharged through the pipe (25).

Similarly, if the aromatic concentration is too high in the 300°C+ fractions, a part of the 300°C+ fraction at the outlet from the distillation DA1 (4) is recycled via the pipe (28) into the cavity (30) of the reactor (5) to be again dearomatized therein in the section SR2 of said reactor (5).

Figure 3 represents a fraction from the deparaffining reactor (2) from Figure 1 or from the deparaffining section SR1 (2) of the reactor (5). Said fraction presents the distribution of deparaffining (S1) and hydroprocessing (S2) catalyst layers. S1 is chosen amongst soft cracking hydroparaffining catalysts on a silicate base supporting nickel and possibly tungsten like KF1102 marketed by the ALBEMARLE company. S2 is a traditional hydroprocessing catalyst on an alumina base supporting a metal pair chosen amongst the pairs cobalt/molybdenum, nickel/tungsten, cobalt/tungsten and nickel/molybdenum. S2 can be KF647 also sold by ALBEMARLE. In a preferred embodiment of the invention, the first and third layers are filled with the deparaffining catalyst S1 and comprise the largest volumes (31% and 46% by volume). The second and fourth layers are only filled with S2 each occupying a volume of 11.5%. In Figure 3, the heavy fraction (CL) to deparaffin is fed into the reactor (2) of Figure 1 through the pipe (13), hydrogen is injected through the pipe (32) and the deparaffined effluent is recovered through the pipe (14).

The performances of the present invention will be illustrated in the continuation of the present description, but the examples do not aim at limiting the range thereof.

EXAMPLE 1

The present example describes the preparation of a deparaffined and dearomatized fraction according to the invention, with initial boiling temperature higher than 300°C and with pour point less than -30°C.

The operation is as described in Figure 1 using the catalysts described hereinabove for Figure 3, in the deparaffining reactor (2). In the dearomatizing reactor, a nickel catalyst on alumina is used, the quantity of nickel being greater than 10% by weight and the specific surface area being greater than 140mm^2/g.

The temperature of the reaction in the deparaffining reactor was 305°C under a pressure of 30 barg, with a defined Hourly Volume Speed (HVS) corresponding to the ratio of the charge flow rate (m3/h) to the catalyst volume (m3/h) of 1h^{-1} and a hydrogen covering of 250 Nl (NL: Normal Liter) of hydrogen per liter of hydrocarbon charge. In the dearomatizing reactor, the temperature was 245°C under a pressure of 160 barg, a hydrogen cover of 250 Nl of hydrogen per liter of hydrocarbon charge and a HVS of 0.4 h^{-1}. The characteristics of the products from the start to the end of the reaction chain are given in Table 1 below.

TABLE 1

Characteristics	GO before DF	Fraction 300°C+

		Before R1 (2)	After DA2	After R2 and DA1
% weight of Aromatics	17.5	9.8	13.8	127ppm
% weight of n-paraffins	21.5	27.7	6.3	4.5
% weight of isoparaffins	35	38.4	42.7	47.1
% weight of total Naphthenic compounds	25.8	24.1	34.4	48.3
% weight of mononaphthenic compounds	20.8	23.2	-	35.8
% weight of olefin compounds ASTM D2710 (gBr_2/100g sample)	0.52	0.35	0.7	<0.05
% weight of Saturated compounds <C9	<0.09	0	<0.1	<0.1
Viscosity at 40°C (mm^2/s), ASTM D445	4.5	7.7	8.7	8.7
Sulfur (ppm) ASTM D5453	2	2.4	3.9	<1
Nitrogen (ppm) by chemiluminescence	<0.5	<0.5	<0.5	<0.5
Distillation fraction (°C) ASTM D86	236-365	296.8-369.3	327.9-371.4	314-367.3
Pour point (°C) ASTM D5950 with reference to D97 (3-points)	- 4	+ 12	- 40	- 40

Aniline point (°C) ASTM D-611	-	-	-	98.7

It should thus be noted that through the method of the invention, hydrocarbon fluids are obtained, devoid of aromatics and of all types of pollutants, usable as solvents, with distillation fraction higher than 300°C and the pour point of same being equal to - 40°C. It should be noted that the quantity of naphthenic compounds is very much greater than 40% by weight in said hydrocarbon, the quantity of mononaphthenic compounds being less than 20% by weight. Said pollutants, correspond in particular to olefins, sulfur compounds and nitrogen compounds.

EXAMPLE 2

The present example compares the characteristics of products obtained in example 1, referenced X, with the characteristics of products obtained from hydroparaffining mainly isomerizing gas oil or hydrocracked and hydrodearomatized gas oil fractions. Said products coming from the prior art are referenced respectively T1 and T2.

The compared characteristics are given in Table 2 below.

TABLE 2

Characteristics	X	T1	T2
ppm by weight of aromatics	127	264	70
% weight of n-paraffins	4.5	0.1	16
% weight of isoparaffins	47.1	74.2	59.9
% weight of total Naphthenic compounds	48.3	24.8	24.1
% weight of mononaphthenic compounds	35.8	18.9	22.4

Sulfur (ppm) by the UV method	<1	<1	<1
Viscosity at 40°C (mm^2/s), ASTM D445	8.7	10.3	6.1
Distillation fraction (°C), ASTM D86	314-367	334-378	305-347
Pour point (°C), ASTM D5950 with reference to D97 (3-points)	-40	-35	0
Aniline point (°C), ASTM D611	98.7	108	101

It should be noted that the deparaffining serves to decrease the pour point of the fraction with boiling point higher than 300°C, to -40°C. It should be noted that comparatively between the fractions X and T1, the concentration of mononaphthenic compounds is very different, for X, same being greater than 20% and even greater than 30% by weight while same remains very much less than 20% by weight for T1. The reduction of the aniline point for the fraction X indicates an improvement in solvent power.

MENETELMÄ KORKEAMMAN KUIN 300 °C:N KIEHUMISLÄMPÖTILAN JA MATALAMMAN TAI YHTÄ SUUREN KUIN -40 °C:N JÄHMETTYMISPISTEEN OMAAVIEN HIILIVETYLIUOTTIMIEN SAAMISEKSI

PATENTTIVAATIMUKSET

1. Menetelmä hiilivetyliuottimien tuottamiseksi, joiden rikkipitoisuus on pienempi kuin 10 ppm, aromaattisten hiilivetyjen pitoisuus on pienempi kuin 500 ppm, kiehumisen alkupiste on korkeampi tai yhtä suuri kuin 300 °C ja lopullinen kiehumispiste on matalampi tai yhtä suuri kuin 500 °C määritettynä ASTM D86 -standardin mukaisesti enintään 100 °C:n fraktiovälille, ja jähmettymispiste on matalampi kuin -25 °C ASTM D5950 -standardin mukaisesti, menetelmän käsittäessä seuraavat vaiheet:

– vahanpoiston (2) hiilivetyfraktiosta, jonka kiehumisen alkupiste on korkeampi kuin 300 °C, joka on peräisin kaasuöljyfraktion tislaamisesta (DF) kahdeksi fraktioksi, yhdeksi kevytfraktioksi (CI), jonka lopullinen kiehumispiste on matalampi kuin 300 °C, ja ainakin yhdeksi raskasfraktioksi (CL), jonka kiehumisen alkupiste on korkeampi tai yhtä suuri kuin 300 °C,

jossa kaasuöljyfraktio valitaan ilmakehän paineessa tislatuista kaasuöljyistä, tyhjiötislatuista kaasuöljyistä, vetykrakatuista kaasuöljyistä, katalyyttisesti krakatuista kaasuöljyistä, lämpökrakatuista kaasuöljyistä, koksauskaasuöljyistä, deasfaltoiduista kaasuöljyistä, kaasuöljyistä, joiden rikkipitoisuus on suurempi kuin 15 ppm, joista poistetaan rikki vetykäsittelyllä ja/tai vetykrakkauksella, ja koko vahapoistetun effluentin (14) tai sen osan talteen ottamisen, vahanpoistovaiheen käsittäessä ainakin kaksi mietokrakkausosiota (S1), jotka vaihtelevat olefiinihydrogenaatio-osioiden (S2) kanssa, mietokrakkausosioiden käsittäessä silikaliittipohjaista katalyyttiä, joka valitaan silikaateista, joissa piidioksidi/alumiinioksidi-suhde on suurempi kuin 200, joka käsittää 0 - 10 painoprosenttia ainakin yhtä ryhmän VIII metallia ja mahdollisesti 0 - 10 painoprosenttia ryhmän VI metallia; näiden silikaliittien kyetessä tukemaan yksistään nikkeliä tai nikkeli/volframiyhdistelmää, olefiinihydrogenaatio-osiot käsittävät katalyyttiä, joka on alumiinioksidi, joka tukee metalliyhdistelmää, joka valitaan kobolttti/molybdeeni-, nikkeli/volframi-, kobolttti/volframi- ja nikkeli/molybdeeniyhdistelmien joukosta,

jossa vahanpoistovaihe suoritetaan vetypaineessa lämpötilassa, joka vaihtelee välillä 150 °C - 450 °C, ja paineessa, joka vaihtelee välillä 10 to 400 bar,

– koko vahapoistetun effluentin tai sen osan hydrodearomatisaation (3) nikkeliä alumiinioksidilla käsittävän katalyytin läsnä ollessa paineessa, joka vaihtelee välillä 60 - 200 bar, ja lämpötilassa, joka vaihtelee välillä 80 °C - 250 °C, ja jossa mainitusta vahapoistetusta effluentista on aiemmin mahdollisesti poistettu rikki etukäteen, jos sen rikkipitoisuus on suurempi kuin 15 ppm, ja osittaisen

vahanpoiston tapauksessa vahapoistettu effluentti viedään ennen hydrodearomatisaatiovaihetta lisäerotusvaiheeseen (DA2), jossa vahapoistettu effluentti erotetaan ainakin kahdeksi effluentiksi, yhdeksi C1-C4-hiilivetyfraktioksi (21) ja ainakin yhdeksi vahapoistetuksi fraktioksi (15), jonka ainakin yksi osa tislautuu yli 300 °C:ssa ja jonka jähmettymispiste on matalampi tai yhtä suuri kuin -40 °C,

– vahapoistetun fraktion talteen ottamisen, jolle on mahdollisesti tehty rikinpoisto ja dearomatisaatio,

– mainitun vahapoistetun ja dearomatisoidun fraktion tislaamisen (DA1) sen erottamiseksi kahdeksi vahapoistetuksi fraktioksi, kolmeksi vahapoistetuksi fraktioksi tai neljäksi vahapoistetuksi fraktioksi;

– yhdeksi C1-C4-hiilivetyfraktioksi (21) ja yhdeksi hiilivetyfraktioksi, joissa hiilivedyissä on enemmän kuin viisi hiiliatomia (15);

– tai yhdeksi C1-C4-hiilivetyfraktioksi (21) ja kahdeksi hiilivetyfraktioksi, joista yksi C5 tislautuu 150 °C:ssa (22) ja toinen tislautuu yli 150 °C:ssa (15),

– tai yhdeksi C1-C4-hiilivetyfraktioksi (21) ja kolmeksi hiilivetyfraktioksi, joista ensimmäinen C5 tislautuu 150 °C:ssa (22), toinen tislautuu 150 °C:ssa - 300 °C:ssa ja kolmas tislautuu yli 300 °C:ssa (15),

– ja lopuksi ainakin yhden fraktion talteen ottamisen, joka tislautuu lämpötilassa, joka on ainakin 300 °C (300 °C+), jonka jähmettymispiste on matalampi kuin -40 °C, joka on käyttökelpoinen liuottimena, tämän fraktion tislausvälin ollessa matalampi kuin 100 °C.

2. Patenttivaatimuksen 1 mukainen menetelmä, **tunnettu** siitä, että vahanpoistovaihe suoritetaan vetypaineessa lämpötilassa, joka vaihtelee välillä 280 °C - 380 °C, ja paineessa, joka vaihtelee välillä 20 - 200 bar.

3. Jonkin edellä olevan patenttivaatimuksen mukainen menetelmä, **tunnettu** siitä, että vahapoistetusta effluentista peräisin oleva vahapoistettu fraktio, jolla on tislauksen korkein kiehumisen alkupiste, viedään hydrodearomatisaatiovaiheeseen, jälkimmäisen käsittäessä yhden tai useamman hydrodearomatisaatio-osion.

4. Jonkin edellä olevan patenttivaatimuksen mukainen menetelmä, **tunnettu** siitä, että fraktio 300 °C+, jonka jähmettymispiste on matalampi kuin -40 °C, joka otetaan talteen ilmakehän paineessa suoritetun tislauksen viimeisen vaiheen jälkeen, otetaan talteen kokonaisuudessaan tai osittain

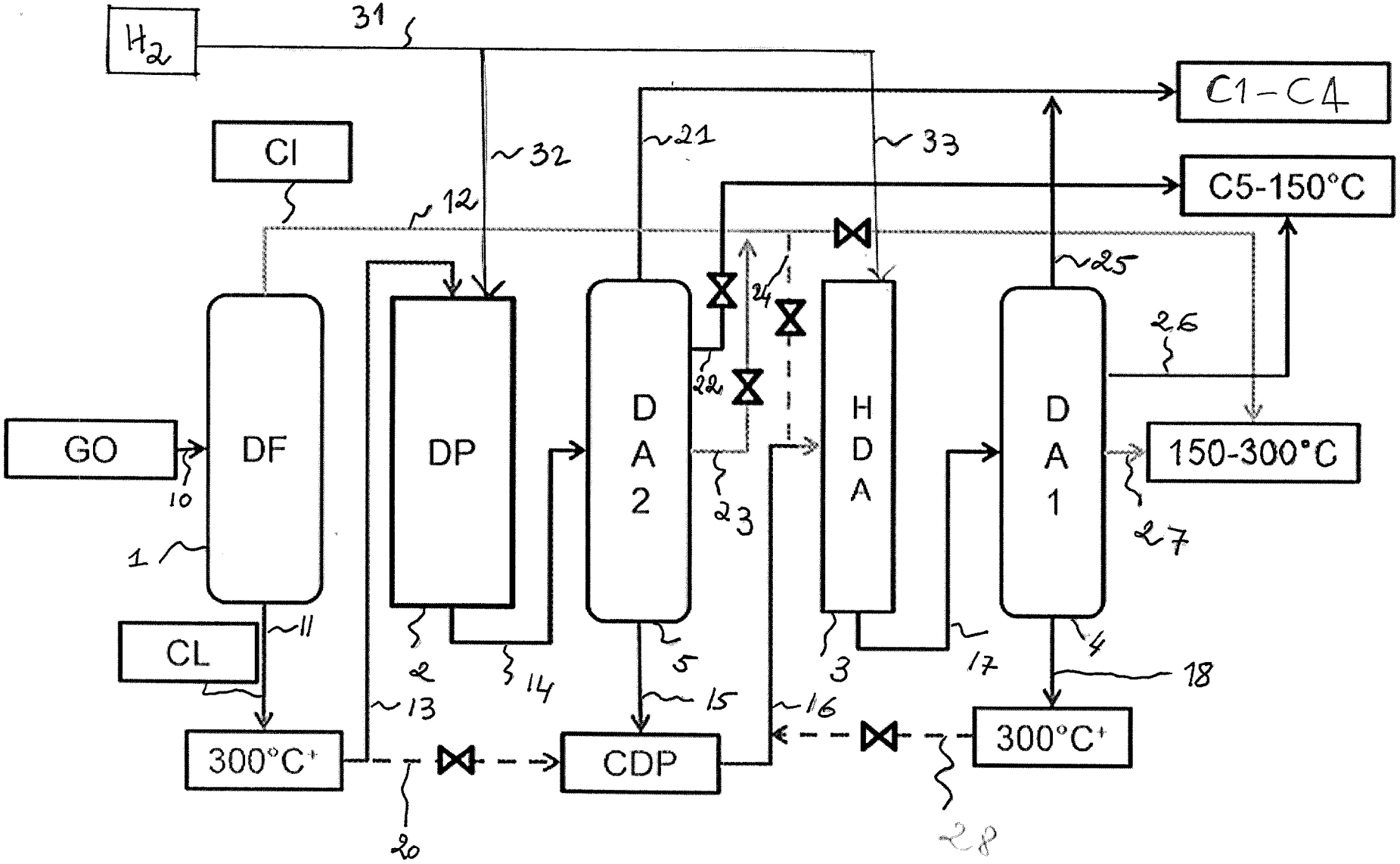
kierrättämällä (28) ainakin osa vahapoistetusta fraktiosta, joka viedään hydrodearomisaatiovaiheeseen.

5. Jonkin patenttivaatimuksen 1 - 4 mukainen menetelmä, **tunnettu** siitä, että hydrodearomatisaatio- ja vahanpoistovaiheet suoritetaan samassa reaktorissa, jossa katalyyttikerrokset on erotettu ontelolla (30), joka sallii vahapoistetun effluentin sekoittumisen nestemäisten tai kaasumaisten yhdisteiden kanssa, vedyn kanssa tai ilmakehän paineessa käytetyn tislauskolonnin (DA1) jälkeen talteen otettujen CI- (24) ja/tai 300 °C+ -fraktioiden, joiden jähmettymispiste on matalampi kuin -40 °C, kierrätyksen (28) kanssa.

6. Fraktio (300 °C+), jonka jähmettymispiste on matalampi kuin -25 °C, kiehumisen alkupiste on korkeampi kuin 300 °C ja lopullinen kiehumispiste on matalampi tai yhtä suuri kuin 500 °C, jonka fraktioväli on matalampi kuin 100 °C, jonka rikkipitoisuus on pienempi kuin 10 ppm ja aromaattisten hiilivetyjen pitoisuus on pienempi kuin 500 ppm, joka on saatu jonkin patenttivaatimuksen 1 - 5 mukaisella menetelmällä, **tunnettu** siitä, että se sisältää yli 30 painoprosenttia naftaleeniyhdisteitä ja alle 5 painoprosenttia normaaleja paraffiineja, ja että mononaftaleeniyhdisteet edustavat yli 20 painoprosenttia naftaleeniyhdisteistä.

7. Patenttivaatimuksen 6 mukaisen fraktion käyttö liuottimena sovelluksissa, jotka liittyvät kasvinsuojelutuotteisiin, musteisiin ja tiivistekitteihin, tai myös metallintyöstönesteenä.

Figure 1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31
C1-C4
CI
32
21
33
C5-150°C
12
25
24
26
22
GO
DF
DP
D A 2
H D A
D A 1
150-300°C
10
1
23
27
CL
11
2
14
5
3
17
4
18
13
15
16
300°C+
CDP
300°C+
20
28

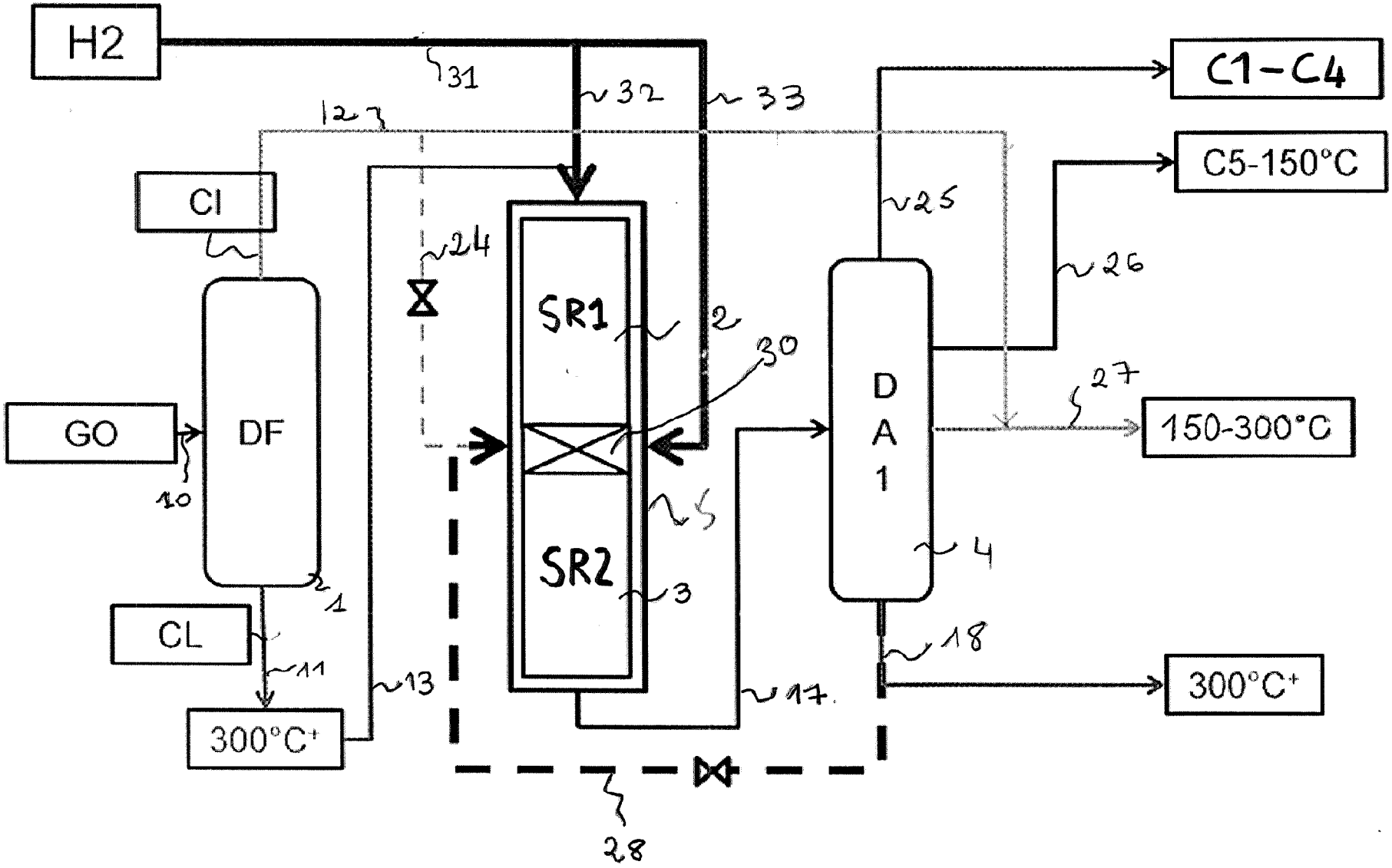
H2
31
32
33
127
CI
24
SR1
2
30
25
C1-C4
C5-150°C
26
27
150-300°C
GO
DF
10
1
SR2
3
5
DA
1
4
CL
11
13
18
300°C+
17
300°C+
28

Figure 2

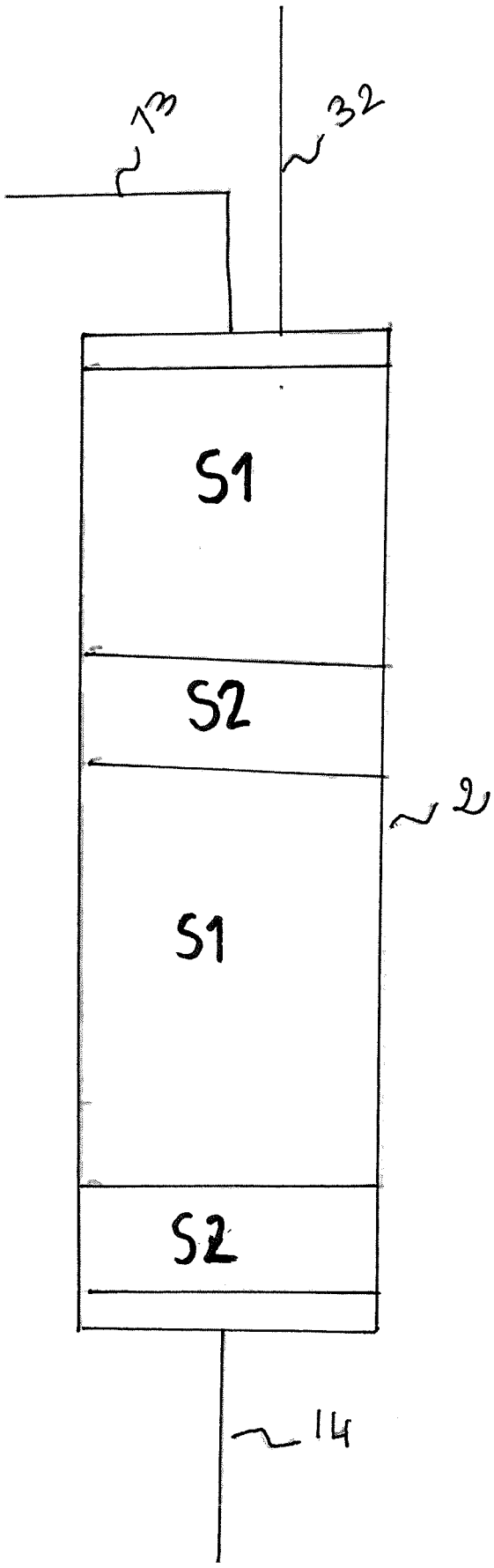

Figure 3