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(54) **Title**: PROCESS FOR PURIFYING A LIQUID HYDROCARBON FUEL

(57) **Abrégé/Abstract**:

Process for purifying a liquid hydrocarbon fuel comprising 5 % by weight or less of high molecular weight contaminants, wherein the fuel is contacted with a hydrophobic non-porous or nano-filtration membrane and the purified product stream is recovered as the permeate.

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(54) Title: PROCESS FOR PURIFYING A LIQUID HYDROCARBON FUEL

(57) Abstract: Process for purifying a liquid hydrocarbon fuel comprising 5 % by weight or less of high molecular weight contaminants, wherein the fuel is contacted with a hydrophobic non-porous or nano-filtration membrane and the purified product stream is recovered as the permeate.

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PROCESS FOR PURIFYING A LIQUID HYDROCARBON FUEL

The present invention relates to a process for purifying a liquid hydrocarbon fuel by removing high molecular weight contaminants.

Liquid hydrocarbon fuels, in particular gasoline may contain high molecular weight contaminants, such as polymerised or oligomerised (higher) olefins, polyaromatic hydrocarbons, and sulphur compounds.

Polymerised or oligomerised olefins and polyaromatic hydrocarbons may be the intrinsic result of the gasoline production process. Catalytically cracked gasoline contains substantial amounts of olefins, which may oligomerise during the fractionation process after the actual cracking process. Also in the final gasoline product, olefins may polymerise in an oxidation reaction which can be catalysed by copper.

In transportation fuels, such as gasoline, these high-molecular contaminants give rise to deposits in for example the combustion chamber and the injection valves. These deposits negatively affect vehicle performance and emissions.

The high molecular weight contaminants are typically present in relatively small amounts up to 5% by weight based on total weight of the liquid fuel. However, often amounts as low as 3% by weight or less or even 1% by weight or less already lead to the above-mentioned problems.

In general, several separation techniques are known in the art for separating contaminants from the actual product based on the difference in molecular weight. One such known and applied technology is distillation, wherein a separation takes place on the basis of differences in boiling points between the various components, which differences are related to the differences in volatility between the various components. However, the fact that high molecular weight contaminants are present in such small amounts makes that a distillative treatment is a relatively expensive way of purifying the product. Namely, in such distillative treatment the actual product forming the bulk of the stream to be treated would have to be evaporated, recovered as the gaseous top fraction and subsequently condensed for further use, whereas the high molecular weight contaminants would have to be recovered as the liquid bottom fraction. Beside the energy-intensive nature of this treatment, a lot of equipment would also be required to carry out the distillative treatment. Moreover, the high temperatures normally applied in distillation increase the danger of (thermal) decomposition of the hydrocarbon product. This could lead to product loss and fouling of the equipment. It will be appreciated that these factors render the distillative treatment unattractive from an economic perspective.

The present invention aims to provide a method for effectively and cost-efficiently removing the high molecular weight contaminants.

These and other objectives were realised by using a membrane separation treatment to remove the high molecular weight contaminants from the liquid hydrocarbon fuel.

Accordingly, the present invention relates to a process for purifying a liquid hydrocarbon fuel comprising 5% by weight or less of high molecular weight contaminants, wherein the fuel is contacted with a hydrophobic non-porous or nano-filtration membrane and the purified product stream is recovered as the permeate.

The advantage of using a membrane separation is that, as opposed to distillation, there is no need to change the phase of the hydrocarbon fuel to be treated. This saves on energy, and costs less hardware. As opposed to absorption the membrane separation does not require a desorption step nor does it result in a voluminous reject consisting of the laden sorbent, which is also a possible consequence of absorption. As opposed to membrane separation over a porous membrane, the presently proposed membrane separation has the advantage that no blocking of membrane pores can occur, as the transmission of the permeate takes place via the solution-diffusion mechanism (see hereinafter).

The separation in accordance with the process of the present invention aims to split the product into two fractions: a permeate and a retentate. The permeate has been upgraded in the sense that its contamination level has been lowered. Consequently, the risk of deposit forming when used in a combustion engine is minimised.

The stage cut -defined as the weight percentage of the original fuel that passes through the membrane and is recovered as permeate- can vary within broad limits: 30 to 99% by weight, preferably 50 to 95% by weight.

The liquid hydrocarbon fuel to be treated contains 5% by weight or less of high molecular weight contaminants based on total weight of the fuel. However, the present method is particularly suitable when the liquid hydrocarbon fuel to be treated contains 3% by weight or less, more suitably 1% by weight of high molecular weight contaminants. Even at high molecular weight contaminant levels of 0.1% by weight or less the method of the present invention is highly effective.

The liquid hydrocarbon fuel to be treated is preferably a transportation fuel, such as gasoline, kerosene or diesel. Kerosene, for example, might be treated in order to improve the cold flow properties. The process according to the present invention is suitable to remove contaminants from kerosene that have a molecular weight above 300, more suitably above 400. More preferably, the fuel to be treated is gasoline. High-molecular contaminants in gasoline that cause deposits typically have a molecular weight in the range of from 200 to 900. It will be appreciated that, if contaminants having a molecular weight above 900 are present in a gasoline fuel, these will simultaneously be removed by the process according to the present invention.

An additional advantage of the present invention is that it offers the opportunity to upgrade both large and small parcels of transportation fuel. A typical example of small parcel treatment would be the installation of a small membrane unit at a fuel depot or at the retail end, i.e. just before delivery of the fuel to the end user.

In the process of the present invention at least 50% by weight of all contaminants in this molecular weight range are removed, suitably at least 60% by weight and more suitably at least 80% by weight is removed.

The membrane used is hydrophobic and may be either a non-porous or a nano-filtration membrane. The membrane should be hydrophobic, since the stream to be treated is a hydrocarbon fuel which should be capable of passing through the membrane. The membrane suitably has a thickness of 0.5 to 30 µm, more suitably of 1 to 10 µm. The membrane is typically supported on at least one substrate layer to provide the necessary mechanical strength. Such membranes are often referred to as composite membranes or thin film composites. Generally, a composite membrane may be composed of a non-porous or nano-filtration membrane supported on a micro-filtration or ultra-filtration membrane or on another porous material. This substrate may in return be supported on a further porous support to provide the required mechanical strength. The non-porous or nano-filtration membrane may also be used without a substrate, but it will be understood that in such a case the thickness of the membrane should be sufficient to withstand the pressures applied. A thickness greater than 10 µm may then be required. This is not preferred from a process economics viewpoint, as such thick membrane will significantly limit the throughput of the membrane, thereby decreasing the amount of purified product which can be recovered per unit of time and membrane area.

Hydrophobic nano-filtration membranes are known in the art and (potential) applications described are, for instance, the treatment of waste streams, separating dissolved lubricating oils from organic solvents, separating organic catalyst complexes from organic solvents or separating low molecular weight oligomers dissolved in organic solvents in paint wastes.

In general nano-filtration membranes which are useful for the purpose of the present invention should have a cut-off value in terms of molecular weight of 200-2000 Dalton. In the art of membrane separation processes, cut-off values of membranes are usually expressed in Dalton and are based on a determination by gel permeation chromatography (GPC) using polystyrene calibration standards. Suitable hydrophobic nano-filtration composite membranes and their preparation are, for instance, disclosed in US-A-5,205,934 and US-A-5,265,734. These composite membranes comprise an underlying porous substrate membrane, such as a micro-filtration or ultra-filtration membrane, which substrate may have been treated with a pore protector prior to coating it with a silicone layer which subsequently is cross-linked. Examples of suitable substrate materials are polyacrylonitrile, polyvinylidene fluoride, polyether imide and polyamide imide. The pore protector may be a hydroxy-terminated polysiloxane. The final silicone coating and the pore-protecting silicone layer typically have a thickness of 50-500 nm. Another example of suitable hydrophobic nano-filtration composite membranes is disclosed in US-A-5,151,182 and comprises a cross-linked layer having a thickness of less than 1 μm, which layer includes a polysulfone type polymer and/or a polyphenylene oxide type polymer as well as at least one chloro- or bromomethylated polyphenylene oxide type polymer supported on a solvent stable porous membrane substrate. Cross-linking is effected by using an amine as cross-linking agent. The substrate suitably is insolubilised polyacrylonitrile.

The coated substrate membrane may be supported on a porous support to increase the mechanical strength. Examples of suitable support materials include polyethylene, polypropylene, nylon, vinyl chloride polymers, aromatic polyimides, polystyrene, polysulfon, polyesters such as polyethylene terephthalate, glass fibers, and inorganic supports based on alumina and/or silica. The composite membrane may have any desired shape, e.g. cylindrical or planar.

In case a non-porous membrane is used, transmission of the permeate takes place via the solution-diffusion mechanism: the hydrocarbons to be permeated dissolve in the membrane matrix and diffuse through the thin selective membrane layer, after which they desorb at the permeate side. The main driving force for permeation is hydrostatic pressure.

An advantage of using hydrophobic non-porous membranes as compared to the use of nano-filtration membranes is that there is no plugging effect, i.e. there is no possibility of the membrane becoming blocked by larger molecules plugged in the pores. This could happen in porous membranes, as a result of which it is more difficult to regenerate the flux. Therefore, it is preferred for the purpose of the present invention to use a non-porous membrane. However, it is emphasised that nano-filtration membranes could also be used in the process of the present invention.

Non-porous membranes as such are known in the art and in principle any hydrophobic non-porous membrane capable of retaining 50% by weight or more of high molecular weight contaminants in a hydrocarbon fuel and through which hydrocarbon fuels as specified above can be transmitted via the solution-diffusion mechanism, can be used. Typically such membranes are cross-linked to provide the necessary network for avoiding dissolution of the membrane once being in contact with a liquid hydrocarbon product. Cross-linked non-porous membranes are well known in the art. In general, cross-linking can be effected by in several ways, for instance by reaction with cross-linking agents, and can optionally be enhanced by irradiation.

One example of suitable, presently available cross-linked non-porous membranes are cross-linked silicone rubber-based membranes, of which the polysiloxane membranes are a particularly useful group of membranes. Typically, the polysiloxanes contain the repeating unit -Si-O-, wherein the silicon atoms bear hydrogen or a hydrocarbon group. Preferably the repeating units are of the formula (I)

$$-[\mathrm{Si}(R)(R')-O-]_n- \qquad \text{(I)}$$

In the above formula, R and R' may be the same or different and represent hydrogen or a hydrocarbon group selected from the group consisting of alkyl, aralkyl, cycloalkyl, aryl, and alkaryl. Preferably, at least one of the groups R and R' is an alkyl group, and most preferably both groups are methyl groups. Very suitable polysiloxanes for the purpose of the present invention are (-OH or $-NH_2$ terminated) polydimethylsiloxanes. The cross-linking is then effected through the reactive terminal -OH or $-NH_2$ group of the polysiloxane. Preferred polysiloxane membranes are cross-linked elastomeric polysiloxane membranes. Also other rubbery non-porous membranes could be used. In general, rubbery membranes can be defined as membranes having a non-porous top layer of one polymer or a combination of polymers, of which at least one polymer has a glass transition temperature well below the operating temperature, i.e. the temperature at which the actual separation takes place. Yet another group of potentially suitable non-porous membranes are the so called superglassy polymers. An example of such a material is polytrimethylsilylpropyne.

One example of suitable cross-linked elastomeric polysiloxane membranes are extensively described in US-A-5,102,551. Thus, suitable membranes are composed of a polysiloxane polymer such as described supra having a molecular weight of 550 to 150,000, preferably 550 to 4200 (prior to cross-linking), which is cross-linked with, as cross-linking agent, (i) a polyisocyanate, or (ii) a poly(carbonyl chloride) or (iii) $R_{4-a}Si(A)_a$ wherein A is -OH, $-NH_2$, -OR, or -OOCR, a is 2, 3, or 4, and R is hydrogen, alkyl, aryl, cycloalkyl, alkaryl, or aralkyl. Further details regarding suitable polysiloxane membranes can be found in US-A-5,102,551.

For the purpose of the present invention the preferred non-porous membrane is a cross-linked polydimethylsiloxane membrane.

As indicated herein before the non-porous membrane may be used as such, but may also be supported on a substrate layer of another material. Such substrate layer could be a microporous substrate as described supra in relation to nano-filtration membranes, i.e. it could for instance be a substrate made of polyacrylonitrile, polyvinylidene fluoride, polyether imide or polyamide imide.

The non-porous membrane should retain at least 50% by weight but more preferably at least 80% by weight of high molecular contaminants. It will be appreciated that the molecular weight of the contaminants is different for different fuels to be treated. For gasoline treatment, membranes retaining at least 50% by weight of compounds having a molecular weight of 200 or more can suitably be used. The fraction of high molecular compounds that will be retained by the membrane will depend on the degree of cross-linking of the membrane, the stage cut, the temperature and the interaction between the fluids to be separated and the membrane. At higher temperatures the retention of higher molecular weight components will deteriorate. Furthermore, since a non-porous membrane does not have a sharp cut-off value, compounds having a lower molecular weight will pass more easily through the non-porous membrane than compounds having a higher molecular weight.

It is preferred that the liquid hydrocarbon fuel is contacted with the hydrophobic non-porous or nano-filtration membrane at a trans-membrane pressure in the range of from 2 to 80 bar, more preferably 10 to 50 bar, a flux of between 200 and 5000 kg/m^2 membrane per day (kg/m^2d), more preferably 250 to 2500 kg/m^2d, and a temperature in the range of from 10 to 80 °C, more preferably 10 to 40 °C.

The invention is further illustrated by the following examples without limiting the scope of the invention to these specific embodiments.

Example 1

The experiment was performed using a hydrophobic membrane consisting of a non-porous cross-linked polydimethylsiloxane (PDMS) layer having a thickness of 2 µm supported on an ultra-filtration polyetherimide (PEI) membrane. The membrane was mounted in a flow cell having an inlet for the feed, an outlet for the permeate an outlet for the retentate. The effective membrane area was 100 cm^2.

Finished gasoline without additives was fed from a storage vessel into the flow cell using a feed pump and was circulated over the membrane. The permeate was recovered as product while the retentate was recycled to the storage vessel.

Temperature and pressure during the test were 21 °C and 10 bar, respectively. The runtime of the test amounted 700 minutes, after which 66% by weight of the gasoline supplied was recovered as permeate (i.e. a stage cut of 66%). The average flux was 2200 kg/m^2d.

The feed and the permeate at 66% recovery were analysed by gas chromatography (ASTM D6293-98). As an indication of the amount of high molecular weight contaminants, the amount of unwashed gums (ASTM D381-94) was determined in both the feed and the permeate. The results are indicated in Table 1.

Table 1 Feed and permeate analysis

Components	Gasoline feed	Permeate
naphthenes (%wt)	4.01	4.16
iso-paraffins (%wt)	32.28	32.15
n-paraffins (%wt)	9.38	9.03
cyclic olefins (%wt)	1.57	1.77
iso-olefins (%wt)	8.53	9.02
n-olefins (%wt)	4.09	4.14
aromatics (%wt)	35.69	35.72
unwashed gums (mg/100 ml)	15	2

From Table 1 it can be seen that the content of high molecular contaminants in the permeate fraction is significantly reduced compared to the gasoline feed before the membrane separation. Furthermore, Table 1 shows that all typical gasoline components are passing the membrane non-selectively.

The unwashed gums were analysed by GC-MS. The unwashed gums appeared to be mainly C13-C30 hydrocarbons.

Example 2

Another experiment was performed using a hydrophobic membrane consisting of a non-porous cross-linked poly-dimethylsiloxane (PDMS) layer having a thickness of 10 µm supported on an ultra-filtration PolyAcrylo-Nitrile (PAN) membrane. The membrane was mounted in a flow cell as described in Example 1. The effective membrane area was 100 cm^2.

A finished gasoline without additives feed was fed into the flow cell as described in Example 1.

Temperature and pressure during the test were 21 °C and 10 bar, respectively. The average flux was 500 kg/m^2d.

The concentrations of unwashed gums (ASTM D381-94) and copper, and the colour (ASTM D1500-98) were determined in both the feed and the permeate at 66% recovery. The results are shown in Table 2.

Table 2 Feed and permeate analysis

Components	Gasoline feed	Permeate
Unwashed gums (mg/100 ml)	24	8
Copper (ppb)	22	4
Colour	2.5	1

From Table 2 it can be seen that both the concentration of high molecular contaminants (unwashed

CLAIMS

1. Process for purifying a liquid hydrocarbon fuel comprising 5% by weight or less of high molecular weight contaminants, wherein the fuel is contacted with a hydrophobic non-porous or nano-filtration membrane and the purified product stream is recovered as the permeate.
2. Process as claimed in claim 1, which is a process for purifying a gasoline fuel comprising contaminants having a molecular weight in the range of from 200 to 900.
3. Process as claimed in claim 1 or 2, wherein a hydrophobic non-porous membrane is used.
4. Process as claimed in claim 3, wherein the hydrophobic non-porous membrane is a cross-linked polysiloxane membrane.
5. Process as claimed in claim 4, wherein the cross-linked polysiloxane membrane is a cross-linked polydimethylsiloxane membrane.
6. Process as claimed in any one of the preceding claims, wherein the liquid hydrocarbon fuel is contacted with the membrane at a trans-membrane pressure in the range of from 2 to 80 bar, a flux of between 200 and 5000 kg/m^2 membrane per day and a temperature in the range of from 10 to 80 °C.

gums) and copper in the permeate fraction are significantly reduced compared to that in the gasoline feed before the membrane separation.

The reduction of the copper concentration in a liquid hydrocarbon fuel by the process according to the invention has the advantage that less copper-catalysed polymerisation reactions will occur.