

PROCESS FOR THE SEPARATION OF A LIQUID MIXTURE

The invention relates to a process for the separation of a liquid mixture of two components A and B by contacting the mixture with an extracting agent in which component B is soluble and component A is substantially insoluble, subsequently separating
5 component A from the extracting agent which contains the dissolved component B and finally separating component B from the extracting agent.

This is a well-known process, particularly for the separation of a mixture of two liquids, and is usually called extraction.
10 Component A is called the raffinate and component B is called the extract. However, mixtures of a liquid and a solid material may also be separated in this way. The extracting agent is sometimes referred to as solvent, in particular when a single solid and a single liquid component are involved. Naturally, the mixture may
15 comprise more than two materials, but according to the present process it is divided into two components.

This process has a drawback in the problems generally posed by the working-up of a certain amount of extracting agent which extracting agent may be recirculated time and again for re-use
20 after component B has been separated therefrom; but it is this very separation that takes so much energy, for instance in the form of heat, which has to be supplied to a distillation unit.

It is the object of the invention to reduce the cost of this separation. This is achieved according to the invention by the use
25 of a membrane along which are passed on one side the flow of the mixture of components A and B and on the other side the flow of the extracting agent containing the dissolved component B, with the membrane selectively allowing the passage of the extracting agent. In this way the extracting agent is separated at least
30 partly from component B.

The invention therefore provides a process for the separation of a liquid mixture of two components A and B by contacting the mixture with an extracting agent in which component B is soluble

and component A is substantially insoluble, subsequently separating component A from the extracting agent which contains the dissolved component B and finally separating component B from the extracting agent, characterized in that a stream of the mixture is passed
5 along one side of a membrane along both sides of which a flow can be maintained, while a previously formed stream of the extracting agent containing the dissolved component B is passed along the other side of the membrane, with the membrane being substantially permeable to the extracting agent, but non-permeable to component
10 A, after which the mixture of components A and B which has taken up the extracting agent at least partly is passed to a separator in which component A is separated from the extracting agent containing the dissolved component B, thus forming the stream that is passed along the other side of the membrane.

15 In itself the use of membranes is known - for instance in dialysis processes - but in the known membrane processes some component or impurity or other migrates through the membrane, whereas in the present invention it is the solvent that migrates through the membrane. In the case of a membrane along both sides
20 of which a flow can be maintained, a liquid to be purified may be present on one side and a sweep liquid on the other side. In addition, the known membrane processes have been put to use almost exclusively in inorganic chemistry, for instance in the desalination of seawater or in kidney dialysis, but the invention is
25 particularly - though not exclusively - suitable for use in organic processes, in particular for the extraction processes used in the petroleum industry for separating hydrocarbon mixtures.

The invention therefore relates in particular to a process for the extraction of a hydrocarbon mixture by contacting it with
30 an extracting agent according to the invention generally described hereinbefore.

Examples of such hydrocarbon extractions are given in Table A hereinafter.

TABLE A

Name of process	Mixture	Component A	Component B	Extracting agent
1. deasphaltenizing	vacuum residue	asphaltenes	deasphaltenized oil	propane, butane
2. furfural ex- traction	(deasphaltenized) residual oil, spindle oil, heavy cycle oil	furfural raffinate	furfural extract (lub oil)	furfural
3. phenol ex- traction	(deasphaltenized) residual oil, spindle oil, heavy cycle oil	phenol raffinate	phenol extract	phenol
4. SO ₂ extrac- tion	(deasphaltenized) residual oil, spindle oil, heavy cycle oil	SO ₂ raffi- nate	SO ₂ extract	liquid SO ₂
5. NMP ¹⁾ extrac- tion	(deasphaltenized) residual, spindle oil, heavy cycle oil	NMP ¹⁾ raffinate	NMP ¹⁾ extract	NMP ¹⁾
6. edeleanu extraction	(unrefined) kerosine fraction	(refined) kerosine	KEREX* (aromatics)	liquid SO ₂
7. edeleanu extraction	(unrefined) gasoline fraction	SO ₂ raffi- nate	superbenzex (aromatics)	liquid SO ₂

* registered Trade Mark

TABLE A

Name of process	Mixture	Component		Extracting agent
		A	B	
8. sulfolane ²⁾ extraction	platformate	sulfolane ²⁾ raffinate	aromatic extract	sulfolane ²⁾
9. glycol extraction	platformate	glycol raffinate	aromatic extract	diethylene glycol ³⁾
10. NMP ¹⁾ extraction	platformate	NMP ¹⁾ raffinate	Aromatic extract	NMP ¹⁾
11. dewaxing	waxy lubricating oil	paraffinic wax	dewaxed oil	methyl ethyl ketone, propane
12. urea dewaxing	heavy gas oil, fuel oil	n-paraffin wax/urea adduct	dewaxed oil	dichloromethane

1) N-methylpyrrolidone

2) tetrahydrothiophene 1,1-dioxide

3) alternatively, triethylene glycol or tetraethylene glycol may be used

Processes 11 and 12 of Table A relate to liquid-solid separations, the other processes are liquid-liquid extractions. Asphaltenes (process 1) may at times be very tough, yet from a physical point of view they form a liquid.

5 The measure taken according to the invention has the advantage that the extracting agent, which used to be separated from component B in a cumbersome and costly manner (for instance through distillation, crystallization or stripping) and subsequently reintroduced into the mixture to be separated, is now transferred
10 in a simple way from component B which has already been separated to the mixture that has yet to be treated. Separation and reintroduction can be carried out at the same temperature and pressure, which means an important saving in energy cost.

 Depending on the conditions used a larger or a smaller
15 portion of the total quantity of extracting agent will be transferred through the membrane. Therefore, there will be certain cases in which one more final separation will be carried out, but this separation will always be carried out on a smaller scale and therefore be less expensive than a process which is not preceded
20 by the removal of extracting agent through a membrane.

 If the separator in which component A is separated from the stream of extracting agent and component B is not quite perfect, viz. if, upon leaving the separator, component A is still mixed with a (small) quantity of extracting agent, then a final separation
25 of extracting agent and component A should still be carried out. In the processes used up till now that separation was usually carried out by distillation, crystallization or stripping, but also in these processes a membrane along both sides of which a flow can be maintained may be used, if desired, and thus the extracting agent may be transferred at least partly to the mixture
30 to be separated. In this case the membrane to be used should be substantially impermeable to component B. However, in view of the relatively small quantities of extracting agent which in actual practice are generally yielded by component A, the saving achieved will be less here.

The membrane is substantially permeable to the extracting agent and impermeable to component A. In a certain embodiment of the invention the membrane is also substantially permeable to component B, which is advantageous when the concentration of component B is higher in the mixture of components A and B than in the stream containing the extracting agent. In that case the existing concentration gradient allows component B to diffuse from one side of the membrane to the other, which is just what is aimed at, viz. separation of components A and B. But if the concentration of component B in the stream containing the extracting agent is higher and the membrane is permeable to component B, care should be taken that this concentration is reduced, for instance by the addition of extracting agent. The latter in other words means a higher "solvent ratio".

It is known that in membrane processes such as those according to the invention concentration polarization may arise. As a consequence, in the present process, where the extracting agent diffuses from the "other side" to the "one side" of the membrane, a layer almost exclusively consisting of component B may form along the "other side" of the membrane and, similarly, a layer almost exclusively consisting of extracting agent may form along the "one side" of the membrane. Naturally, this local reversal of the concentration gradient has a restraining influence on the diffusion of the extracting agent. In order to prevent such concentration polarization, the streams are preferably pumped rapidly along both sides of the membrane and - in order not to use too large a membrane surface - the streams are recirculated. Thus, as homogeneous a mixture as possible will constantly be present both on one side and on the other side of the membrane. Pumping rates will preferably be so high that a molecule which can diffuse through the membrane will pass along the membrane some 10 to 30 times before diffusing through it.

Firstly this means that preferably part of the mixture of components A and B which has taken up the extracting agent at least partly, is reintroduced into the stream of the mixture of

components A and B (upstream of the membrane) and is thus passed along the "one side" of the membrane again. An additional advantage is that the mixture of components A and B is prediluted prior to being passed along the membrane. Particularly in the case of highly viscous liquids, such as residual oils, this is an advantage since this improves their pumpability and/or offers the opportunity of lowering the temperature.

Secondly, this means that preferably part of the stream of the extracting agent containing the dissolved component B, which is passed along the "other side" of the membrane is reintroduced into the stream of the extracting agent containing the dissolved component B, and is thus passed along the "other side" of the membrane again.

Although in a number of cases a single membrane will be sufficient, there are many cases in which - in view of the imperfections of the commercially available units - the use of more than one membrane will be preferred, either for achieving a higher capacity (parallel arrangement), or deeper extraction (series arrangement). In the latter embodiment a number of membranes are arranged in series, the stream of components A and B which has been passed along the "one side" of any of the membranes subsequently being passed along the "one side" of the following membrane - if present - and, similarly, the stream of the extracting agent containing the dissolved component B, which has been passed along the "other side" of any of the membranes subsequently being passed along the "other side" of the preceding membrane - if present. Obviously, if no following or preceding membrane is available, the stream is further treated as described hereinbefore on the subject of a single membrane. In other words, then the stream of components A and B is supplied to the separator and the other stream, now consisting almost entirely of pure component B, may optionally be subjected to a final purification treatment (e.g. stripping).

When more than one membrane is used, the number of membranes will be dependent on the type of process, the supply rates per

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unit time and the size of the membranes, but preferably the number will be 2 to 20, in particular 4 to 10.

The membrane material may be chosen from the materials known for the purpose, such as polyethylene, polypropylene, cellulose acetate, butyl rubber, methyl rubber, silicon rubber, polystyrene, polytetrafluoro-ethylene and other polymeric materials. The material should be insoluble both in components A and B and in the extracting agent, and it should also be totally or practically impermeable to component A and, on the other hand, permeable to the extracting agent. Fouling of the membrane by solid or viscous elements of the mixture of components A and B need not be feared, because it has been ascertained that the membrane remains clean in actual practice. It is assumed that the membrane is continuously rinsed by diffusing extracting agent.

The configuration in which the membrane material is used may be one of the membrane units along both sides of which a flow can be maintained which in themselves are known, such as the flat sheet or the tubular membrane unit. However, such configurations are not very economical of space and therefore do not achieve a high packing density (m^2 membrane/ m^3 apparatus).

Preference is given to the use of the spirally wound membrane which has been described in the Applicant's Netherlands Patent Application No. 8200880 of even date. The latter membrane combines the advantages - such as pressure resistance, low initial expense and high packing density - of the well-known spirally wound membranes along one side of which a flow can be maintained with the possibility of maintaining a flow on both sides.

The invention will now be illustrated in more detail with the aid of the figures. Figure 1 represents a general flow diagram of the process according to the invention and Figures 2 and 3 are elaborations thereof representing flow diagrams of a solvent dewaxing unit and a deasphaltenizing unit, respectively.

Figure 1 very schematically indicates the way in which a mixture to be separated (A + B) is fed to a membrane unit (M), where extracting agent (E) joins the stream of the mixture to be

separated. The resulting stream is then fed to a separator (S), where component A is separated off. The remainder, viz. component B and the extracting agent, is recirculated to the membrane unit (M) in order to transfer the extracting agent to a fresh supply of mixture to be separated. If the membrane is permeable to component B and if the concentration of component B is higher in mixture (A + B) than in mixture (E + B), there will also be migration of component B along the membrane in the direction opposite to that of the extracting agent (dashed line B¹).

10 Disregarding many details Figure 2 shows a flow diagram of a unit for dewaxing with the aid of a solvent, which, according to the invention, includes a membrane unit. The feed, for instance a waxy furfural raffinate, is supplied through line 1 to a membrane unit 2, where solvent (extracting agent) 3 joins the feed. As
15 solvent a mixture of aromatics (benzene, toluene, etc.) and methyl ethyl ketone may be used. Through conduits 4 and 5 the feed and the solvent are transferred further via a heat exchanger 6 and a cooler 7, to a vacuum rotary drum filter 8. In cooler 7 the feed and the solvent are cooled down to a temperature of about - 20°C
20 in order to allow the paraffins present therein to crystallize. The paraffin crystals are washed on the drum of drum filter 8 using a thin stream of solvent 9 and subsequently scraped off and, together with a small quantity of solvent still present, carried off through conduit 10 to a wax-processing unit 11, where what is
25 called "slack wax" 12 is separated from the solvent, which, through conduit 13, is fed to a recirculation line 14. The filtrate from the vacuum rotary drum filter 8, which consists of dewaxed oil and solvent, is passed through a conduit 15 via heat exchanger 6 and fed to membrane unit 2. Both in heat exchanger 6
30 and in membrane unit 2 the feedstock is pre-cooled to some extent by its indirect contact with the cold filtrate. After a considerable part of the solvent has diffused through the membrane (stream 3), the dewaxed oil, together with the remainder of the solvent, is fed through conduit 16 to a unit 17 for the processing of
35 dewaxed oil. In reality unit 17 will generally comprise two

flashing columns - one operated at low pressure and temperature and one at higher pressure and temperature - followed by a steam stripper, in conjunction with distillation columns for the removal of water from the solvent and a number of pumps, burners and
5 reflux pipes, which together have been drawn as unit 17. The required heat is supplied by a heat exchanger 18. Here dewaxed oil 19 is in the end separated from the solvent which, through conduits 20 and 14 and via a cooler 21, is reintroduced into the system, that is to say, the feedstock present in line 5.

10 Figure 3 is a drawing of a flow diagram of a deasphaltenizing unit. For the sake of simplicity, most of the ancillary equipment known in itself and not essential to the invention has been left out of this diagram as well.

Through a conduit 31 the feedstock, usually a vacuum residue,
15 is fed to a mixing vessel 32, where the feed is prediluted with a stream of feed already diluted with extracting agent leaving a conduit 33. Mixing vessel 32 also acts as a buffer vessel so as to eliminate changes in the supply. From mixing vessel 32 there is a continuous discharge, through conduit 34, of a stream part of
20 which is fed, through a conduit 101 to a membrane unit 100 and the remaining part through conduits 106 and 201 to a membrane unit 200. In these membrane units a certain amount of extracting agent, represented as streams 102 and 202, respectively, diffuses from a stream of deasphaltenized oil and solvent, supplied via conduits
25 103 and 203, respectively, through the membrane into the stream of the prediluted feed which has been supplied through conduits 101 and 201, respectively and is discharged through conduits 104 and 204, respectively. Conduit 104 is connected with conduit 33 which leads to the mixing vessel and conduit 204 recirculates part of
30 the diluted feed to membrane unit 200 through a conduit 205 and conduit 201, while the rest of the diluted feed is fed to a next membrane unit through a conduit 206. The stream of deasphaltenized oil with extracting agent, which has released part of the extracting agent in membrane units 100 and 200, respectively, is dis-
35 charged through conduits 107 and 207, respectively. Part of it is

recirculated to the original membrane unit through conduits 108 and 103 and 208 and 203, respectively, while the remainder is discharged through conduits 109 and 209, respectively. Conduit 209 is connected with the preceding membrane unit by conduit 103, while conduit 109 is connected with a stripper unit 35, in which the last residues of extracting agent 36 are removed from the stream of deasphaltenized oil 37 with the aid of steam.

The number of membrane units may vary, but in the embodiment described here the number is 7. For convenience units 300, 400 and 500 have been left out of the figure: only units 600 and 700 have been included therein. Corresponding numbers indicate corresponding parts: for instance conduit 601 corresponds with conduits 201 and 101. The part of the stream of feed with extracting agent which is discharged through conduit 706 is fed to what is called a rotating-disc-contactor 38, where this stream is split up into an asphaltenes fraction which is discharged through a conduit 39 and a fraction of deasphaltenized oil with extracting agent which is run through a conduit 40 into conduit 703, with the object of removing the solvent in membrane unit 700 (and subsequently in units 600, 500, etc.). The asphaltenes fraction is freed from remaining extracting agent, if any, in a stripper 41, so that in the end a quantity of asphaltenes can be discharged through conduit 42, and a quantity of extracting agent through conduit 43. Both the streams of conduits 43 and 36 are recirculated through a conduit 44 to the rotating-disc-contactor 38 so as to enable all the extracting agent to be mixed with the feed.

The generation of steam and the subsequent separation of steam and extracting agent (e.g. propane) in stripping unit 35 will require a certain amount of energy which will be greater in proportion as the fraction of extracting agent in the deasphaltenized oil is larger. According to the invention this fraction is small, since as much extracting agent as possible is transferred to the fresh feed via membrane units 100, 200 and so on. When a special membrane material, such as polypropylene, is used, there will in addition be a considerable part of deasphaltenized oil

that is transferred direct from streams 101, 201, etc. into streams 107, 207, etc. via membranes 100, 200, etc., which results in additional savings on the overall cost.

Although the transfer of extracting agent drawn in this figure is a countercurrent one, this transfer may naturally also take place co-currently.

Example

For further elucidation of the process according to the invention the results will now be given of an experiment in a dewaxing unit as described and drawn in Figure 2. Using a polypropylene-polyethylene copolymer membrane of 1 μ m in thickness, in the spiralled configuration described hereinbefore, almost 74% of the solvent (50 %v methyl ethyl ketone, 50 %v toluene) present in stream 15 is transferred from there to stream 4. Table B gives a summary of the effect this has on the processing of the dewaxed oil. All the quantities given are expressed in tons per day (tpd).

TABLE B

Membrane	Composition	Stream number				
		15	3	16	19	20
without	dewaxed oil (tpd)	299	---	299	299	---
	solvent (tpd)	1714	---	1714	---	1714
with	dewaxed oil (tpd)	299	---	299	299	---
	solvent (tpd)	1714	1264	450	---	450

It is clear that according to the invention stream 16 contains much less solvent than it does in the embodiment in which no membrane is used and that, consequently, less solvent need be flashed and stripped in processing unit 17. Therefore, less heat

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is required for the removal of the solvent from the dewaxed oil
(8708 MJ/h instead of 21855 MJ/h).



C L A I M S

1. A process for the separation of a liquid mixture of two components A and B by contacting the mixture with an extracting agent in which component B is soluble and component A is substantially insoluble, subsequently separating component A from the extracting agent which contains the dissolved component B and finally separating component B from the extracting agent, in which process a stream of the mixture is passed along one side of a membrane along both sides of which a flow can be maintained, while a previously formed stream of the extracting agent containing the dissolved component B is passed along the other side of the membrane, with the membrane being substantially permeable to the extracting agent, but non-permeable to component A, after which the mixture of components A and B which has taken up the extracting agent at least partly is passed to a separator in which component A is separated from the extracting agent containing the dissolved component B, thus forming the stream that is passed along the other side of the membrane.
2. A process as claimed in claim 1, in which the membrane is also substantially permeable to component B and that the concentration of component B is higher in the mixture of components A and B than in the stream containing the extracting agent.
3. A process as claimed in claim 1 or 2, in which part of the mixture of components A and B which has taken up the extracting agent at least partly, is reintroduced into the stream of the mixture of components A and B and thus passed along the "one side" of the membrane again.
4. A process as claimed in any one of the preceding claims, in which part of the stream of the extracting agent containing the dissolved component B which is passed along the "other side" of the membrane, is reintroduced into the stream of the extracting agent containing the dissolved component B, and is thus passed along the "other side" of the membrane again.

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5. A process as claimed in any one of the preceding claims, in which a number of membranes is arranged in series, in which process, continually, the stream of components A and B which has been passed along the "one side" of any of the membranes is subsequently passed along the "one side" of the following membrane and in which, similarly, the stream of the extracting agent containing the dissolved component B which has been passed along the "other side" of any of the membranes is subsequently passed along the "other side" of the preceding membrane.
- 10 6. A process for the separation of a liquid mixture as claimed in claim 1, substantially as hereinbefore described with reference to the Example and the Figures.
- 15 7. A component A or B, separated from a mixture of components A and B using a process as claimed in any one of the preceding claims.

