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configured so that large exchange areas are present both between the two liquid phases and between the liquid phases and the vapour phase, and

d) the necessary mass transfer conditions in the extractive distillation column are ensured by using any sort of packed column and excludes the use of plate columns, and

e) the optimum separating performance is achieved by selecting the solvent feed temperature.

AUSTRALIA

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**ORIGINAL
COMPLETE SPECIFICATION
STANDARD PATENT**

Application Number:

Lodged:

Invention Title: PROCESS FOR SEPARATING HYDROCARBON MIXTURES BY
EXTRACTIVE DISTILLATION

The following statement is a full description of this invention, including the
best method of performing it known to :-US

Process for separating hydrocarbon mixtures by extractive distillation.

5 The invention relates to a process for separating hydrocarbon mixtures by extractive distillation with selective solvents or solvent mixtures, in which the feedstock is introduced in the central part of the extractive distillation column and the solvent or solvent mixture used is introduced into the upper part, and the
10 lower boiling hydrocarbons of the feedstock in the solvent-hydrocarbon mixture are drawn from the extractive distillation column over the head, while the higher boiling hydrocarbons of the feedstock together with the greater part of the solvent are obtained as the bottom
15 product of the extractive distillation, and the bottom product is transferred from the extractive distillation column into a downstream stripping column in which the hydrocarbons and the solvent are separated from one another by distillation.

20 Extractive distillations of the type mentioned above are now used successfully in a whole series of industrial processes, for example for obtaining pure aromatic compounds or butadiene from feedstocks containing these compounds and for separating butanes and
25 butenes. The N-substituted morpholines, especially N-formylmorpholine, as well as N-methylpyrrolidone and dimethylformamide, have proved to be particularly successful solvents. However, in all extractive distillation processes the process conditions and the solvent
30 have hitherto been selected so that only one vapour phase and one liquid phase occurred in the extractive distillation column. Those skilled in the art always started from the idea that the occurrence of systems with miscibility gaps, in which two liquid phases are formed
35 in the extractive distillation column, must be avoided. These ideas were chiefly based on the fact that under the

existing conditions which have so far been normal .
 extractive distillation the presence of a second
 hydrocarbon-rich liquid phase substantially impairs the
 separation result or in some cases even makes the sepa-
 5 ration impossible. The reasons for the poor separation
 can be found on the one hand in the unfavourable mass
 transfer conditions, as it is usually much more difficult
 to establish thermodynamic equilibrium between two liquid
 phases than between a vapour phase and a liquid phase.
 10 On the other hand the thermodynamic conditions for
 separation are impaired by the appearance of miscibility
 gaps, for example because of a relatively small change in
 vapour pressures or the formation of heteroazeotropes.

For the reasons mentioned, solvents which are in
 15 fact characterized by a high selectivity, i.e. a great
 influence on the relative volatility, towards the hydro-
 carbons to be separated but which form two liquid phases
 with them under the technically relevant concentration
 and/or temperature conditions have not so far been used
 20 for extractive distillation. Tetramethylsulphone, known
 under the trivial name of sulfolan, which has only
 achieved any industrial significance in liquid-liquid
 extraction, can be cited as an example of this.

The object of the invention is to provide an
 25 extractive distillation process for separating hydro-
 carbon mixtures which is characterized by great economic
 improvements in areas of application known per se and
 which makes possible a greater selection of solvents.

The process of the type referred to at the outset
 30 which solves this problem is characterized in accordance
 with the invention by the application of features a to
 c) of the main claim.

Rejecting the previous notions of those skilled
 in the art, the invention starts from the knowledge that
 35 solvents which are characterized by a high selectivity
 for the particular separating task, but which also form

miscibility gaps with the hydrocarbons in the liquid phase under the concentration and temperature conditions used in practice, can be used perfectly well in extractive distillation provided that very specific conditions are maintained in the extractive distillation.

The process according to the invention therefore, in particular, permits the use of those solvents which are characterized by a higher selectivity for the particular separating task than the solvents used previously but which have not been used because of the tendency to form miscibility gaps.

However, the process according to the invention also permits the use of those solvents the use of which is already known in extractive distillation for certain separation tasks. In this case it is then possible to work with substantially lower operating temperatures in the extractive distillation than was previously normal. That is to say, it has been found for many solvents that the tendency to form miscibility gaps only occurs at relatively low temperatures. If, in spite of this, it is now possible in accordance with the invention to work in this temperature range, then this signifies a not inconsiderable energy saving. In addition to this the selectivity of the solvent for the given separation task increases with falling operating temperature.

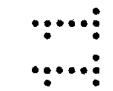
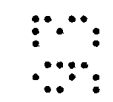
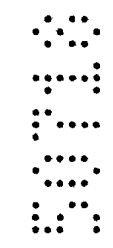
When carrying out the process according to the invention the process conditions in the extractive distillation must however be selected so that two liquid phases occur over a considerable part of the total height of the extractive distillation column. Preferably, between 10 and 20% of the column height should lie in the region of two phase formation and only in the remaining lower part of the column should just one homogeneous liquid phase be present.

In addition to this the mass transfer conditions in the extractive distillation column must be configured

5 that large exchange areas are present both between the
 two liquid phases and between the liquid phases and the
 vapour phase. This can be brought about, for example, by
 providing internal fittings or column packings in the
 extractive distillation column which ensure the formation
 of very thin liquid layers. On an industrial scale
 column packings which are specifically arranged for this
 purpose, e.g. so-called structured packings such as, for
 example, so-called Mellapack packings, or expanded metal
 10 internal fittings are provided. ~~It is also possible to~~
 fulfill the required mass transfer conditions by using
 column trays designed specifically for the purpose.
 These column trays ensure a good distribution of the
 liquid phases between one another with at the same time
 15 a high exchange area with the vapour phase. However,
 when these types of column trays are used a certain
 pressure drop must be accepted in the extractive distil-
 lation column. Finally, there is also the possibility of
 providing for the necessary mass transfer by mechanical
 20 dispersion of the liquid phases and the vapour, e.g.
~~through the use of stirrers.~~

As the hydraulic conditions in the extractive
 distillation column, such as layer thickness and mixing
 of the two liquid phases, play a decisive role when
 25 carrying out the process according to the invention, it
 is advisable that the throughput quantity of feedstock
 and solvent does not exceed a value of 200 m³ per m²
 column cross-section and hour. The maximum throughput
 quantity is particularly dependent on the type of column
 30 internal fittings and the viscosity of the solvent. With
 the separation process and use of structured column
 packings described here the maximum throughput quantity
 is approximately 50 m³ per m² column cross-section and
 hour.

35 The solvent used in accordance with the invention
 is characterized by a very high selectivity and a



relatively low solvent power, so the lower solvent power results in a greater volatility, even for the components of the feedstock to be withdrawn from the bottom of the extractive distillation column. In practice the bottom temperature in the extractive distillation column can therefore be set significantly lower than when using solvents with higher solvent powers. This results in a lower heat consumption for the extractive distillation, which also makes it possible to use a lower grade of steam for heating the column system, e.g. low pressure steam instead of medium pressure steam.

The conventional apparatus and plant in general use for extractive distillation can be used for carrying out the process according to the invention. The process procedure for the mode of operation according to the invention is shown in simplified form in the flow diagram shown in the drawing. The hydrocarbon mixture to be separated is introduced in a liquid state through line 1 into the central part of the extractive distillation column 2 which is provided with the internal fittings needed to produce the necessary mass transfer conditions as described in greater detail above. The solvent is introduced through line 3 into the extractive distillation column 2 at the top and flows down over the internal fittings in this column during which it picks up the less volatile hydrocarbons. The more volatile hydrocarbons escape through line 4 at the top of the column and can be condensed in condensation equipment not shown in the flow diagram. The liquid bottom product consists of the solvent and the hydrocarbons dissolved therein, and is withdrawn from the extractive distillation column 2 through line 5 and passes into the stripping column 6 in which the hydrocarbons are separated from the solvent by distillation. The solvent is removed from the column bottom through line 7 and, after appropriate cooling which is generally achieved in an economical inter-

From the heat system within the plant, gases pass through line 3 back into the extractive distillation column 2, while the hydrocarbon vapours escape from the stripping column 6 over the head and are transferred for further processing through line 8. Impurities can build up in the solvent in the course of time, so the branch line 9, through which, with valve 10 in the appropriate position, a part quantity of the solvent can pass to the regenerating device 11, is provided in the region of line 7. The regenerated solvent is then returned through line 12 back into the circuit (line 7), while the impurities removed are withdrawn from the regenerating device through line 13. Finally, line 14 serves for supplying fresh solvent. Naturally, the plant is provided with the necessary auxiliary equipment for carrying out the process according to the invention such as, for example, measuring and control equipment and heat exchangers. However, as this auxiliary equipment is not directly necessary for describing the process sequence it has not been shown in the drawing.

The process according to the invention can be used for various separating tasks. For example, the process can be used for obtaining pure aromatic compounds from hydrocarbons containing aromatic compounds. Sulphones or their mixtures, N-substituted morpholines or their mixtures and, preferably, a mixture of N-formylmorpholine and tetramethylsulphone (sulfolan) can be used here as the solvent. The use of N-substituted morpholines or their mixtures for the separating task mentioned is in fact already known. However, the process according to the invention differs from the previously conventional mode of operation through the use of a lower solvent feed temperature, lying between 50 and 70°C, in the extractive distillation. In this case the solvent feed temperature is approximately 10 to 30°C lower than with the known mode of operation with a homogeneous

liquid phase. A further area of application of the process according to the invention is the separation of diolefins, olefins and paraffins from hydrocarbon mixtures which contain these compounds and boil in the range between -12 and +50°C at normal pressure, using sulphones or their mixtures as the solvent. Finally, the process according to the invention can also be used for the separation of olefins and paraffins from hydrocarbon mixtures which contain these compounds and boil in the range between -12 and +50°C at normal pressure, in which N-substituted morpholines or their mixtures can again be used as the solvent. The use of these solvents for this separating task is in fact also already known, but the process according to the invention again differs from the previously normal mode of operation by the use of a lower solvent feed temperature, lying between 40 and 70°C, in the extractive distillation. Here again the solvent feed temperature is approximately 10 to 30°C lower than with the known mode of operation with a homogeneous liquid phase.

The internal reflux in the extractive distillation column is increased in each case due to the lower solvent feed temperature. In this way the same separation efficiency as before is achieved at a lower solvent:feedstock ratio, while at the same time the formation of two liquid phases in the extractive distillation column is achieved.

The effectiveness of the process according to the invention is substantiated by the two comparison trials described below:

The first trial (Table 1) relates to the separation of butanes and butenes by extractive distillation, in which a C₄ cut from pyrolysis gasoline, which had previously passed through a butadiene extraction and etherification with methanol to give methyl tertiarybutyl ether with the removal of 2-methylpropene, was used as

7. In part 1 of this trial, a solvent was used which comprised 50% N-formylmorpholine (NFM) and 50% morpholine as a solubilizer. In part 2, in contrast pure N-formylmorpholine (NFM) was used as the solvent.

5 The second comparison trial Table 2 relates to obtaining pure aromatic compounds by extractive distillation from a mixture of pyrolysis gasoline and catalytic reformat. N-formylmorpholine (NFM) was used as the solvent in part 1 of the trial, and tetramethylene-sulphone (sulfolan) in parts 2 and 3. In part 3 the operation was carried out with a lower solvent:feedstock ratio than in part 2. This leads to a lower heat consumption, but at the same time the purity of the benzene obtained drops somewhat lower.

15 Both comparison trials were carried out in an extractive distillation plant of the type described above in connection with the drawing. In parts 2 and 3 of the trials, in which two liquid phases are formed in the extractive distillation, structured packings made of expanded metal were placed in the extractive distillation column. At the same time the height of the extractive distillation column was reduced by about 30 % for parts 2 and 3. In both comparison trials the trial conditions were kept constant over 72 hours. The important trial conditions and separation results are summarized below in Tables 1 and 2.

Separation of butanes and isobutane by
extractive distillation

Solvent		50% NFM	50% NFM
		solubilizer	
Solvent feedstock	kg kg	17	17
5	ED column throughput	kg h	
	- concentration solvent free)	wt. %	
	- head of ED column	wt. %	
	iso-butane	wt. %	23.72
10	n-butane	wt. %	73.32
	1-butene	wt. %	2.94
	trans-2-butene	wt. %	0.02
	cis-2-butene	wt. %	0.0005
	- feedstock	wt. %	
15	iso-butane	wt. %	6.84
	n-butane	wt. %	22.44
	1-butene	wt. %	43.04
	trans-2-butene	wt. %	11.97
	cis-2-butene	wt. %	15.71
20	- bottom of ED column	wt. %	
	iso-butane	wt. %	-
	n-butane	wt. %	1.85
	1-butene	wt. %	59.27
	trans-2-butene	wt. %	22.06
25	cis-2-butene	wt. %	16.82
	Operating temperature		
	ED column bottom	°C	154
	Operating pressure	bar	5.9

	Height of homogeneous liquid phase in the ED column	%	100	22
<hr/>				
	Heat consumption rel. to feedstock	kcal/kg	1199	563
5				
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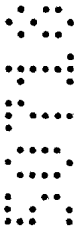


Table 2: Generation of pure benzene by extractive distillation

Solvent		NFM	sulfolan	sulfolan	
Solvent/feedstock	kg/kg	2.5	2.5	2.2	
5	ED column throughput concentration (solvent free)	kg/h			
	- head of ED column				
	non-aromatics	wt.%	97.20	97.12	97.20
10	methylcyclohexane	wt.%	0.54	0.62	0.54
	benzene	wt.%	2.26	2.26	2.26
	- feedstock				
	non-aromatics	wt.%	46.1	46.1	46.1
	methylcyclohexane	wt.%	0.3	0.3	0.3
15	benzene	wt.%	53.6	53.6	53.6
	- bottom of ED column				
	non-aromatics	ppm	-	-	-
	methylcyclohexane	ppm	795	94	788
	benzene	wt.%	99.92	99.99	99.92
20	Operating temp.				
	ED column bottom	°C	156	158	151
	Operating pressure	bar	2.3	2.3	2.3
	Height of homogeneous liquid phase in the				
25	ED column	%	100	80	60
	Heat consumption rel. to feedstock	kcal/kg	152	133	118

These trial results show that a significant reduction in heat consumption relative to the feedstock is achieved when using the process according to the invention, the energy consumption being almost halved in comparison trial 1. Added to this is also the reduction in plant costs arising from the reduction in height of the extractive distillation column. The desired objective of improved economy of the extractive distillation is therefore achieved.



THE CLAIMS DEFINING THE INVENTION ARE AS FOLLOWS:

1. Process for separating hydrocarbon mixtures by extractive distillation with selective solvents or solvent mixtures, in which the feedstock is introduced in the central part of the extractive distillation column and the solvent or solvent mixture used is introduced into the upper part, and the lower boiling hydrocarbons of the feedstock in the solvent-hydrocarbon mixture are drawn from the extractive distillation column over the head, while the higher boiling hydrocarbons of the feedstock together with the greater part of the solvent are obtained as the bottom product of the extractive distillation, and the bottom product is transferred from the extractive distillation column into a downstream stripping column in which the hydrocarbons and the solvent are separated from one another by distillation, characterized in that

a) solvents are used which are characterized by a high selectivity with respect to the particular separating task and which also form miscibility gaps with the hydrocarbons in the feedstock under the concentration and temperature conditions used,

b) the process conditions in the extractive distillation are selected so that two liquid phases occur over a considerable part of the total height of the extractive distillation column, and

c) the mass transfer conditions in the extractive distillation column are configured so that large exchange areas are present both between the two liquid phases and between the liquid phases and the vapour phase, and

d) the necessary mass transfer conditions in the extractive distillation column are ensured by using any sort of packed column and excludes the use of plate columns, and

e) the optimum separating performance is achieved by selecting the solvent feed temperature.

2. The process according to claim 1, characterized in that the packed column has a random packing.



3. The process according to claim 1, characterized in that the packed column has a structured packing.

4. A process according to any one of claims 1 to 3, characterized in that the operating conditions are adjusted so that between 10 and 90% of the column height of the extractive distillation column lies in the region of the formation of two liquid phases and only in the remaining lower part of the extractive distillation column is one homogeneous liquid phase present.

5. A process according to any one of claims 1 to 4, characterized in that the necessary mass transfer conditions in the extractive distillation column are ensured by placing column packings or internal fittings in the column which either guarantee the formation of very thin liquid layers or in some other way provide for good mixing and distribution of the individual phases.

6. A process according to any one of claims 1 to 5 characterized in that the throughput quantity of feedstock and solvent in the extractive distillation column does not exceed the value of 200 m³, per m² column cross-section and hour.

7. A process according to claim 6 characterized in that the throughput quantity of feedstock and solvent in the extractive distillation column does not exceed the value of 50 m³, per m² column cross-section and hour.

8. The use of the process according to claims 1 to 7 for obtaining pure aromatic compounds from hydrocarbon mixtures containing aromatic compounds, characterized in that sulphones or their mixtures are used as the solvent.



9 The use of the process according to any one of claims 1 to 7 for obtaining pure aromatic compounds from hydrocarbon mixtures containing aromatic compounds using N-substituted morpholines or their mixtures as the solvent, characterized in that the extractive distillation is carried out at a solvent feed temperature between 50 and 70°C.

10. Application of the process according to claims 1 to 7 for obtaining pure aromatic compounds from hydrocarbon mixtures containing aromatic compounds, characterized in that a mixture of N-formylmorpholine and tetramethylenesulphone (sulfolan) is used as the solvent.

11. The use of the process according to any one of claims 1 to 7 for separating diolefins, olefins and paraffins from hydrocarbon mixtures which contain these compounds and boil in the range between -12 and +50°C, characterized in that sulphones or their mixtures are used as the solvent.

12. The use of the process according to any one of claims 1 to 7 for separating olefins and paraffins from hydrocarbon mixtures which contain these compounds and boil in the range between -12 and +50°C using N-substituted morpholines or their mixtures as the solvent, characterized in that the extractive distillation is carried out at a solvent feed temperature between 40 and 70°C.

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ABSTRACT

Process for separating hydrocarbon mixtures by extractive distillation.

In this process solvents are used which are
5 characterized by a high selectivity with respect to the
particular separating task and which also form
miscibility gaps with the hydrocarbons in the feedstock
under the concentration and temperature conditions used.
The mass transfer conditions in the extractive distilla-
10 tion column are configured so that large exchange areas
are present both between the two liquid phases and
between the liquid phases and the vapour phase.

