

Description

The invention relates to a process for producing an aromatics concentrate, suitable for use as a blending component for carburettor fuels, from feed hydrocarbon mixtures which have a boiling range between 40 and 170°C and contain a plurality of aromatics in addition to non-aromatics, the feed hydrocarbon mixture being subjected to an extractive distillation using N-substituted morpholines, the substituents of which have at most seven carbon atoms, as the selective solvent, and virtually all the low-boiling non-aromatics having a boiling range up to about 105°C and the predominant part of the higher-boiling non-aromatics having a boiling range between about 105 and 160°C being distilled off as the raffinate over the top of the extractive distillation column, whereas the main quantity of the aromatics and the remaining non-aromatics are taken off as the extract together with the solvent used from the bottom of the extractive distillation column, whereupon the solvent is separated by distillation in a down-stream stripping column from the remaining hydrocarbons of the extract and these are used wholly or partially as a blending component.

A process of the generic type is described in German Offenlegungsschrift 3,612,384 which is not part of the state of the art. In this case, it is provided that the feed hydrocarbon mixture is introduced without prior separation into the extractive distillation column. Particularly suitable feed hydrocarbon mixtures here are reformates and platformates from petroleum processing, having a not unduly high benzene content. However, mixtures of such reformates and platformates with pyrolysis gasolines can also be used.

Admittedly, the final boiling points of these feed products are normally about 170°C. In practice, however, it has been found that this final boiling point is not maintained in many cases since, in the upstream

production processes, condensation products and polymerisation products are formed which have a boiling point higher than 170°C and correspondingly contaminate the reformates and platformates. Since these higher-boiling
5 condensation products and polymerisation products are present in the reformates and platformates in concentrations of up to about 30 % by weight, they can cause interference in carrying out the process described in German Offenlegungsschrift 3,612,384.

10 In fact, it has been found in practice that these condensation products and polymerisation products are concentrated in the selective solvent, since they can be separated from the latter by distillation only incompletely or virtually not at all. With a progressing operating
15 period, this leads to ever increasing contamination of the circulated solvent, so that the selectivity of the latter is continuously reduced and the separation effect in the extractive distillation column is correspondingly diminished.

20 Attempts to separate these condensation products and polymerisation products from the solvent by distillation has not - as already mentioned - led to a satisfactory result, even when expending a great outlay on the distillation. In fact, it has been found that the boiling
25 range of some of these condensation products and polymerisation products corresponds to that of the solvent, so that a separation by distillation is impossible in practice. Hitherto, it has therefore been possible to solve this problem only in such a way that, after a
30 certain operating period, a complete exchange of the contaminated solvent was carried out. It is obvious that this procedure is extremely expensive and hence uneconomical. Moreover, the destruction of the contaminated solvent incurs additional costs, since this can no longer
35 be put to any other use or utilisation.

It is therefore the object of the invention to improve the process according to the parent patent in

such a way that the difficulties described above are avoided.

According to the invention, this object is achieved when, in the processing of feed hydrocarbon mixtures which contain constituents boiling above 170°C, the feed hydrocarbon mixture is subjected to a preliminary distillation in which constituents boiling up to 169°C (under standard conditions) are separated off by distillation and are fed to the extractive distillation, whereas the distillation residue is added to the aromatics concentrate used as a blending component.

The process according to the invention thus provides a preliminary distillation of the feed hydrocarbon mixture in such a way that the top product obtained contains only those constituents which do not lead to any permanent contamination of the solvent in the subsequent extractive distillation. By contrast, higher-boiling constituents, which it would be very difficult or impossible to separate from the solvent, remain in the distillation residue (bottom product) of the preliminary distillation, which residue is, according to the invention, added to the aromatics concentrate used as a blending component. The starting point here was the realisation that the composition of the reformates and platformates normally used as the feed product is as a rule such that non-aromatic compounds are still present in the fraction boiling above 170°C only in very small quantities or not at all. Thus, for example, a typical reformate from petroleum processing has a content of about 3 % by weight of higher-boiling constituents having a boiling point >170°C which, in the process according to the invention, remains in the distillation residue and is added to the aromatics concentrate used as a blending component. The composition of this higher-boiling fraction is here as follows:

Compound:	Boiling point °C	% by weight
	m-Cymene	175
5	Hemellitol	176.1
	p-Cymene	177.1
	N-Butylbenzene	183
	Indane	177.8
	1,2-Diethylbenzene	183.4
10	Durene	196.8
	i-Durene	198
	Tetralin	207.6
	Trimethylethylbenzene	213
	Naphthalene	218
15	Methyltetralin	229
	β -Methylnaphthalene	241
	α -Methylnaphthalene	245
	Diphenyl	255
	Dimethylnaphthalene	268
20	Total:	<u>100.0</u>

The percentage figures above here do not relate to the total quantity of the reformat, but only to the composition of the fraction boiling above 170°C.

When carrying out the process according to the invention, the preliminary distillation can be carried out at a relatively small outlay on investment costs and operating costs (small number of trays and low reflux ratio), since a sharp quantitative separation is not required in this case. Thus, for example, the operating conditions in the preliminary distillation can even be set in such a way that a part of the o-xylene (boiling point 144°C) also remains in the distillation residue from the preliminary distillation, because even in this boiling range there are normally only such small quantities of non-aromatics present in the feed hydrocarbon mixture that these do not manifest themselves by interference when added to the aromatics concentrate used as a blending component. Moreover, it must be taken into

account here that the non-aromatics fraction in the distillation residue from the preliminary distillation is anyway reduced by the fact that azeotropes between aromatics and non-aromatics go predominantly into the top product from the preliminary distillation and are thus subjected to the subsequent extractive distillation process. Thus, for example, n-nonane forms an azeotrope with o-xylene.

A particularly economical embodiment of the process according to the invention results when the preliminary distillation is carried out under an elevated pressure. In this case, the pressure can always be adjusted in such a way that the preliminary distillation can be operated at a temperature higher than that of the extractive distillation, so that the top product vapours arising in the preliminary distillation can be utilised for column heating in the extractive distillation, and the condensate thus arising is passed into the extractive distillation. In this case, the preliminary distillation is operated under a pressure of up to 15 bar.

The figure shows the flow diagram of an embodiment of the process according to the invention, in a greatly simplified illustration. Here, the feed hydrocarbon mixture going to be processed is first introduced via line 1 into column 2, in which the preliminary distillation, according to the invention, of the feed hydrocarbon mixture is carried out. The top product obtained there is passed via line 3 into the middle part of the extractive distillation column 4 provided with internals and/or packing. The hydrocarbons of the raffinate thus escape over the top from the extractive distillation column and pass via line 5 into column 6, in which the hydrocarbons of the raffinate are separated from the solvent residues by distillation. The latter pass via line 7 into line 8, through which the solvent used is introduced into the upper part of the extractive distillation column 4. The raffinate hydrocarbons freed of solvent are taken off via line 9 over the top of column 6 and passed to their further use. The extract hydrocarbons are taken off

together with the main quantity of the solvent via line 10 from the bottom of the extractive distillation column 4 and introduced from there into the middle part of the stripping column 11 which is likewise provided with internals and/or packing. In this column, the extract hydrocarbons mainly consisting of aromatics are stripped out of the solvent, the recovered solvent which is concentrated in the bottom of the stripping column 11 being recycled via line 8 to the extractive distillation column 4. By contrast, the extract hydrocarbons freed of solvent are taken off from the stripping column 11 via line 12 or 13 and passed to their further use.

In the present case, it is assumed that the operating conditions in the extractive distillation column 2 are adjusted such that the benzene contained in the feed hydrocarbon mixture is largely concentrated in the extract and a raffinate low in benzene is obtained. The benzene present in the extract is then separated from the other aromatics by distillation in the stripping column 11 and taken off as saleable pure benzene having a non-aromatics content of < 1000 ppm as the top product via line 12, whereas an aromatics concentrate, which in this case is more or less free of benzene in practice, is removed from the stripping column II via line 13 or via a side column which is provided at this point and not shown in the flow diagram. According to the invention, the distillation residue from the preliminary distillation is then added to this aromatics concentrate. This residue is taken off via line 14 from the bottom of column 2 and admixed to the product stream flowing in line 13, so that the end product stream used as a blending component can be taken off via line 13.

There are also the following possibilities for carrying out the process:

- a) In this case, the operating conditions in the extractive distillation column 4 are adjusted such that a part of the benzene contained in the feed hydrocarbon mixture also passes into the raffinate and the remaining benzene content in the aromatics concentrate

of the extract is then only such that it does not exceed a desired maximum value which is normally below 5 % by weight. In this case, the aromatics concentrate obtained when processing the extract in the stripping column 11 and used as a blending component is taken off exclusively via line 12, while the side take-off via line 13 is not in operation.

- b) If, on the one hand, the benzene content in the feed hydrocarbon mixture is relatively low and, on the other hand, an enrichment of this benzene content in the aromatics concentrate used as a blending component is not regarded as interference, it is possible, finally, to operate the extractive column 2 under operating conditions such that all the benzene passes virtually completely into the extract. As distinct from the process variant described first, however, no separation of the benzene from the other aromatics takes place in this case in the stripping column 11. This means that, in this case, the aromatics concentrate as a whole is taken off via line 12 from the stripping column 11 and the side take-off via line 13 here again is not in operation.

It is obvious that, in these two cases, the distillation residue from the preliminary distillation is added to the aromatics concentrate taken off via line 12, in contradistinction to the illustration in the flow diagram.

The flow diagram shown in the figure contains only the plant components absolutely necessary for explaining the process according to the invention, whereas all subsidiary equipment, which is not directly connected with the invention, has not been shown in the flow diagram. This applies in particular to the heat exchangers for heat exchange between the individual process streams, the circulating reboilers for heating the individual columns, the devices for regenerating or making up the spent solvent, and all the instrumentation equipment.

5 The effectiveness of the procedure according to the invention is demonstrated by the process example which follows. This relates here to the embodiment of the process according to the invention, on which the flow diagram shown in the figure is based. The most important numerical values are summarised in the table which follows. The feed product used was a reformat from petroleum processing, having a benzene content of 4.3 % by weight.

Table:

Composition	Line 1 Feed product for prelim. distil- lation	Line 3 Top product from prelim. distil- lation	Line 9 Raffinate	Line 12 Pure benzene	Line 13 Aromat- ics concen- trate	Line 14 Bottom product from prelim. distil- lation	Line 15 End product (blend- ing comp- onent)
	Kg	Kg	Kg	Kg	Kg	Kg	Kg
C ₄ -C ₇ -Non-aromatics	221.9	221.9	221.9	1000 ppm			
C ₈ Non-aromatics	54.9	54.7	52.3		2.4	0.2	2.6
C ₉ Non-aromatics	17.5	6.1	3.1		3.0	11.4	14.4
C ₁₀ Non-aromatics	2.9	0.2			0.2	2.7	2.9
Benzene	43.0	43.0	1.6	35.8	5.6	-	5.6
Toluene	198.6	197.8	0.1		197.7	0.8	198.5
C ₈ Aromatics	240.1	65.2			65.2	174.9	240.1
C ₉ Aromatics	191.1	7.1			7.1	184.0	191.1
C ₁₀ Aromatics	30.0					30.0	30.0
	1000.0	596.0	279.0	35.8	281.2	404.0	685.2
	=====	=====	=====	=====	=====	=====	=====
	%	%	%	%	%	%	%
Total aromatics	70.3	52.5	0.6		98.0	96.5	97.1
Total benzene				99.9			0.8
Total non-aromatics	29.7	47.5	99.4	1000 ppm	2	3.5	2.1
RON	93				112		

Claims

1. Process for producing an aromatics concentrate, suitable for use as a blending component for carburettor fuels, from feed hydrocarbon mixtures which have a boiling range between 40 and 170°C and contain a plurality of aromatics in addition to non-aromatics, the feed hydrocarbon mixture being subjected to an extractive distillation using N-substituted morpholines, the substituents of which have at most seven carbon atoms, as the selective solvent, and virtually all the low-boiling non-aromatics having a boiling range up to about 105°C and the predominant part of the higher-boiling non-aromatics having a boiling range between about 105 and 160°C being taken off as raffinate over the top of the extractive distillation column, whereupon the solvent is separated by distillation in a downstream stripping column from the remaining hydrocarbons of the extract and these are used wholly or partially as a blending component, characterized in that, in the processing of feed hydrocarbon mixtures which contain constituents boiling above 170°C, the feed hydrocarbon mixture is subjected to a preliminary distillation in which constituents boiling up to 169°C (under standard conditions) are separated off by distillation and are fed to the extractive distillation, whereas the residue from the preliminary distillation is added to the aromatics concentrate used as a blending component.
2. Process according to Claim 1, characterized in that the preliminary distillation is carried out under an elevated pressure, the pressure always being adjusted in such a way that the preliminary distillation can be operated at a temperature higher than that of the extractive distillation, so that the top product vapours arising in the preliminary distillation can be utilised with complete condensation for column heating in the extractive distillation, and the condensate thus arising is passed into the extractive distillation.

3. Process according to Claims 1 and 2, characterized in that the preliminary distillation is carried out under a pressure of up to 15 bar.



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2. Process according to Claim 1, characterized in that the preliminary distillation is carried out under an elevated pressure, the pressure always being adjusted in such a way that the preliminary distillation can be operated at a temperature higher than that of the extractive distillation, so that the top product vapours arising in the preliminary distillation can be utilised with complete condensation for column heating in the extractive distillation, and the condensate thus arising is passed into the extractive distillation.

3. Process according to Claims 1 and 2, characterized in that the preliminary distillation is carried out under a pressure of up to 15 bar.

Revendications

1. Procédé pour fabriquer un concentré de composés aromatiques utilisable comme constituant de mélange pour des carburants légers à partir de mélanges d'hydrocarbures qui présentent un point d'ébullition compris entre 40 et 170°C et qui contiennent, à côté de composés non-aromatiques, plusieurs composés aromatiques, tandis que le mélange d'hydrocarbures mis en oeuvre est soumis à une distillation extractive faisant appel, à titre de solvant sélectif, à des morpholines N-substituées, dont les substituants ne présentent pas plus de sept atomes de carbone, et que pratiquement la totalité des composés non-aromatiques d'un bas point d'ébullition, allant jusqu'à environ 105°C, et que la majeure partie des composés non-aromatiques, dont le point d'ébullition plus élevé est compris entre 105 et 160°C environ, sont soutirés, comme produits de raffinage, à la tête de la colonne de distillation extractive, à la suite de quoi le solvant est séparé, par distillation dans une colonne de séparation installée en aval, des autres hydrocarbures restant dans l'extract et que ces derniers sont mis en oeuvre en tout ou partie à titre de constituant de mélange pour carburants légers, caractérisé par le fait dans le cadre du traitement de mélanges d'hydrocarbures de mise en oeuvre qui contiennent des fractions passant au-dessus de 170°C, le mélange d'hydrocarbures de mise en oeuvre est soumis à une distillation préalable au cours de laquelle on sépare par distillation (dans des conditions normales) les fractions dont le point d'ébullition va jusqu'à 169°C et les affecte à la distillation extractive, tandis que le résidu de la distillation est rajouté au concentré de composés aromatiques servant de constituant de mélange pour carburants légers.

2. Procédé selon la revendication 1, caractérisé par le fait que la distillation préalable est conduite sous une pression accrue, la pression étant chaque fois ajustée de manière telle que la distillation préalable puisse être conduite à une température plus élevée que la distillation extractive, de sorte que les vapeurs des produits de tête recueillies dans la distillation préalable peuvent être utilisées, moyennant condensation complète, pour chauffer la colonne dans la distillation extractive et que le condensat ainsi recueilli est introduit dans la distillation extractive.

3. Procédé suivant les revendications 1 et 2, caractérisé par le fait que l'on travaille, dans la distillation préalable, sous une pression pouvant aller jusqu'à 15 bars.