

Description

The invention relates to a process for the separation of aromatics from feed hydrocarbon mixtures which contain these compounds and non-aromatics and have a boiling range between 40 and 170°C, the feed hydrocarbon mixture being subjected, without prior separation into individual fractions, to an extractive distillation using N-substituted morpholines, the substitutes of which do not have more than seven carbon atoms, as a selective solvent. The invention is here based on the object of obtaining an aromatics concentrate, suitable for use as a blending component for carburettor fuels, from the said feed hydrocarbon mixtures.

The measures initiated in recent years in the interest of protecting the environment have, in the motor vehicle field, had the result that the demand for lead-free carburettor fuels has constantly risen and will also rise yet further in the future. The reason is that poisoning of the catalysts, which are increasingly provided downstream of spark-ignition engines for reducing the output of pollutants, can be avoided by means of these lead-free carburettor fuels.

At the same time, however, the lead-free carburettor fuels must meet the same quality requirements, especially with respect to their knock resistance, as the corresponding leaded carburettor fuels. The required octane numbers must therefore be obtained by the addition of other substances and/or by a different fuel composition. It has already been known for a long time that the knock resistance of a carburettor fuel can be increased by an addition of benzene. Because of the carcinogenic properties of benzene, however, there have been endeavours recently to minimise the benzene content of the fuel as far as possible. This has therefore had the result that a variety of other methods for improving the octane number were developed. Apart from the increased use of alkylate gasolines and polymer gasolines, certain alcohols such as, for example, methanol,

isopropanol and tert.butanol, as well as certain ethers such as, for example, methyl tert.-butyl ether and amyl ether, are also used as octane number improvers. Very often, the required octane number in the carburettor fuel is also adjusted by an addition of aromatics concentrates which, apart from a little benzene, contain above all C₇- to C₉-aromatics.

The production of such aromatics concentrates suitable as blending components for carburettor fuels is therefore gaining increasing importance. At the same time, these aromatics concentrates should not have an unduly high benzene content. This is desired not only because of the carcinogenic properties of benzene, as already mentioned, but above all also because benzene has a lower octane number-improving effect as compared with other aromatics such as, for example, toluene. Suitable starting materials for the production of such aromatics concentrates are especially aromatics-containing hydrocarbon mixtures from petroleum processing, such as, for example, reformates and platformates. On the other hand, feed hydrocarbon mixtures of high benzene content such as, for example, pyrolysis gasoline or crude coke oven benzene, are less suitable for the said purpose for the reasons described above.

Since these suitable feed hydrocarbon mixtures normally have a wide boiling range between 40 and 170°C, the separation of the aromatics concentrates from these feed hydrocarbon mixtures has hitherto been carried out in practice exclusively by liquid-liquid extraction, using solvents conventional for this purpose, such as, for example, polyethylene glycol, sulfolan, N-methylpyrrolidone and others. In order to improve the selectivity, greater or lesser quantities of water are here normally added to the solvent used, and this has a very disadvantageous effect on the energy consumption. Moreover, the liquid-liquid extraction is frequently carried out with the use of a so-called counter-solvent such as, for example, pentane. The use of such additives, however, without doubt represents a considerable complication of

the process since, on the one hand, the pure products obtained in this way always contain certain quantities of these extraneous materials, which must afterwards be removed with increased expenditure on energy and equipment, and, on the other hand, the use of these additives can as such cause additional costs. Moreover, for carrying out the liquid-liquid extraction, expensive extractors such as, for example, so-called mixer/settler extractors or extractors with moving internals, must be used because of the viscosity and temperature conditions applicable.

In addition to high operating costs, liquid-liquid extraction therefore also involves high capital costs. Admittedly, DE-C-1,568,940 has disclosed an extractive distillation process of the type mentioned at the outset. The point of this process, however, is the production of aromatics having the highest possible purity or, alternatively, the production of hydrocarbon mixtures which are intended to be largely free of aromatics. This means that the process according to this citation is intended to be used both in those cases where the highest possible purity of the extract obtained (aromatics) is important and in those cases where the highest possible purity of the raffinate obtained (paraffins) is important. Corresponding to this objective, this process must be operated at a high feed product/solvent weight ratio, which leads to a correspondingly high energy consumption per kg of feed product.

In the achievement of the object underlying the invention, however, it is of very decisive importance that the aromatics concentrates suitable as a blending component for carburettor fuels can be produced in a particularly simple and inexpensive manner. At the high production capacities of such plants, the energy consumption is in fact a very essential factor which decisively influences the applicability of the process on a large industrial scale.

This object is achieved by a process of the type mentioned at the outset, which is characterized, accord-

ing to the invention, in that the extractive distillation for the production of an aromatics concentrate, which is suitable for use as a blending component for carburettor fuels is carried out with N-formylmorpholine as the selective solvent while maintaining a feedstock/solvent ratio of from 1:2 to 1:3, virtually all the low-boiling non-aromatics of a boiling range of up to about 105°C and a predominant part of the higher-boiling non-aromatics of a boiling range of 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 other hydrocarbons in the extract and these are used wholly or partially as a blending component.

As a result of using extractive distillation, the above-described disadvantages of liquid-liquid extraction are avoided in the process according to the invention since, on the one hand, the solvent employed according to the invention is used without any added water and, on the other hand, columns of relatively simple design can be used, as is generally usual in extractive distillation. Since, when carrying out the process according to the invention, a very low feedstock/solvent ratio in the range from 1:2 to 1:3 can also be used, the energy requirement per kg of feedstock is correspondingly low.

The illustration shows a flow diagram of the process according to the invention in a greatly simplified representation. The feed hydrocarbon mixture used for processing is here introduced without any pre-fractionation via line 1 into the middle section of the extractive distillation column 2 provided with internals (trays). The raffinate hydrocarbons then escape over the top from the extractive distillation column 2 and pass via line 4 into column 5, where the raffinate hydrocarbons are separated by distillation from solvent remainders. The latter pass via line 6 into line 3, through which the solvent used is introduced into the upper section of the extractive distillation column 2. The raffinate hydrocarbons freed from solvent are taken

off from the top of column 5 via line 7 and passed to their further use. The extract hydrocarbons are taken off together with the bulk of the solvents via line 8 from the bottom of the extractive distillation column 2 and passed from there into the middle section of the stripping column 9 which, if appropriate, can also be provided with internals (trays). In this column, the extract hydrocarbons consisting mainly of aromatics are stripped out of the solvent, and the recovered solvent accumulating in the bottom of the stripping column 9 is recycled via line 3 to the extractive distillation column 2. The extract hydrocarbons freed from solvent are, by contrast, taken off via lines 10 or 11 from the stripping column 9 and passed to their further use.

The flow diagram shown in the illustration contains only those plant items which are absolutely necessary for explaining the process according to the invention, whereas all subsidiary equipment, which is not directly connected with the invention, was not shown in the flow diagram. This applies in particular to the heat exchangers for heat exchange between the individual process streams, the reboilers for heating the individual columns, the equipment for regeneration or make-up of spent solvent and all the instrumentation.

For carrying out the process according to the invention, the following variants are possible:

1. The operating conditions in the extractive distillation column 2 are adjusted such that the benzene contained in the feed hydrocarbon mixture is largely enriched in the extract and a raffinate low in benzene is obtained. In the stripping column 9, the benzene contained in the extract is then separated by distillation from the other aromatics and taken off as saleable pure benzene with a non-aromatics content of < 1000 ppm as the top product via line 10, whereas the aromatics concentrate, which is used as a blending component and in this case is virtually more or less free of benzene, is removed from the stripping column 9 as a side stream via line 11 or via a side

column provided at this point and not shown in the flow diagram.

2. In this case, the operating conditions of the extractive distillation column 2 are adjusted such that a part of the benzene contained in the feed hydrocarbon mixture passes over the top with the raffinate and the benzene content then still remaining in the aromatics concentrate of the extract does not exceed a desired maximum value which is below 5% by weight. When processing the extract in the stripping column 9, the aromatics concentrate obtained, serving as a blending component, is here taken off exclusively via line 10, whereas the side take-off via line 11 is left inoperative.
3. 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 blending component is not regarded as an interference, the extractive distillation column 2 can, finally, be operated under such conditions that all the benzene passes virtually completely into the extract. In this case, however, as distinct from the process variant 1, no separation of the benzene from the other aromatics takes place in the stripping column 9. This means that in this case the aromatics concentrate in its entirety is taken off from the stripping column 9 via line 10 and the side take-off via line 11 remains inoperative.

The raffinates obtained when carrying out the process according to the invention can be taken to further processing as so-called chemical naphtha. Thus, these raffinates can be used, for example, as a starting material for pyrolysis to ethylene or for isomerisation processes. The aromatics concentrates obtained by the process according to the invention and used as a blending component then have only a low non-aromatics content which amounts to between 0.5 and 5.0% by weight.

The efficiency of the procedure according to the invention is demonstrated by the process examples which

follow. In all three process examples, N-formylmorpholine was used as the selective solvent for the extractive distillation. In each case, the extractive distillation column 2 here had 50 trays. In all three cases, the feed hydrocarbon mixture was fed at a temperature of 70°C to the extractive distillation column 2, and the top temperature of this column was in each case about 100°C.

In process example 1, the feed hydrocarbon mixture used was a so-called reformat from petroleum processing, having an aromatics content of 65% by weight and an octane number (RON) of 92, process variant 2 being applied.

In process example 2, a so-called platformate having an aromatics content of 42% by weight and an octane number (RON) of 83 was used as the starting material, process variant 2 again being applied.

In process example 3, finally, the same reformat as in process example 1 was used once more as the starting material. In this case, however, processing of this starting material was by process variant 1.

The most important experimental results are summarised in the table which follows.

Table:

Process example no.	1	2	3
Line 1: (Feed product)	7 kg/h 25 kg/h 30 kg/h 3 kg/h 35 kg/h 70°C 92	3 kg/h 17 kg/h 20 kg/h 2 kg/h 58 kg/h 70°C 83	7 kg/h 25 kg/h 30 kg/h 3 kg/h 35 kg/h 70°C 92
Line 7: (Raffinate)	6.4 kg/h 34.1 kg/h 80°C	2.8 kg/h 57.0 kg/h 80°C	0.2 kg/h 34.1 kg/h 80°C
Line 10: (Aromatics concentrate)	0.9 kg/h 0.6 kg/h 25.0 kg/h 30.0 kg/h 3.0 kg/h 0.2 bar 84°C 112	1.0 kg/h 0.2 kg/h 17.0 kg/h 20.0 kg/h 2.0 kg/h 0.2 bar 84°C 110	1000 ppm non-aromatics 6.2 kg/h 0.2 bar 32°C
Line 11: (Aromatics concentrate after benzene stripping)			0.9 kg/h 0.6 kg/h 25.0 kg/h 30.0 kg/h 3.0 kg/h 112 90°C
Total energy requirement of the plant:	75,348 kw/h (18,000 kcal/h)	79,534 kw/h (19,000 kcal/h)	77,860 kw/h (18,600 kcal/h)



Patent Claims

1. Process for the separation of aromatics from feed hydrocarbon mixtures which contain these compounds and non-aromatics and have a boiling range between 40 and 170°C, the feed hydrocarbon mixture being subjected, without prior separation into individual fractions, to an extractive distillation using N-substituted morpholines, the substituents of which do not have more than seven carbon atoms, as a selective solvent, characterized in that the extractive distillation for the production of an aromatics concentrate, which is suitable for use as a blending component for carburettor fuels, is carried out with N-formylmorpholine as the selective solvent while maintaining a feedstock:solvent ratio of from 1:2 to 1:3, virtually all the low-boiling non-aromatics of a boiling range of up to about 105°C and a predominant part of the higher-boiling non-aromatics of a boiling range of 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 other hydrocarbons in the extract and these are used wholly or partially as a blending component.
2. Process according to Claim 1, characterized in that the aromatics concentrates produced have non-aromatics contents of 0.5 to 5.0% by weight.
3. Process according to Claims 1 and 2, characterized in that pure benzene with a non-aromatics content of < 1000 ppm is taken off as top product from the stripping column, whereas the hydrocarbons used as a blending component are taken off as a sidestream or via a side column from the middle section of the stripping column.
4. Process according to Claims 1 to 3, characterized in that the operating conditions in the extractive distillation column are adjusted such that a part of the benzene contained in the feed hydrocarbon mixture is distilled off together with the non-aromatics as raffinate over the top of the extractive distillation



column, and that the benzene fraction remaining in the extract does not exceed a desired maximum value which is below 5% by weight.



As printed

Claims

1. Process for the separation of aromatics from feed hydrocarbon mixtures which contain these compounds and non-aromatics and have a boiling range between 40 and 170°C, the feed hydrocarbon mixture being subjected, without prior separation into individual fractions, to an extractive distillation using N-substituted morpholines, the substituents of which do not have more than seven carbon atoms, as a selective solvent, characterized in that the extractive distillation for the production of an aromatics concentrate, which is suitable for use as a blending component for carburettor fuels, is carried out with N-formylmorpholine as the selective solvent while maintaining a feedstock:solvent ratio of from 1:2 to 1:3, virtually all the low-boiling non-aromatics of a boiling range of up to about 105°C and a predominant part of the higher-boiling non-aromatics of a boiling range of 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 other hydrocarbons in the extract and these are used wholly or partially as a blending component.

2. Process according to Claim 1, characterized in that the aromatics concentrates produced have nonaromatics contents of 0.5 to 5.0% by weight.

3. Process according to Claims 1 and 2, characterized in that pure benzene with a non-aromatics content of < 1000 ppm is taken off as top product from the stripping column, whereas the hydrocarbons used as a blending component are taken off as a sidestream or via a side column from the middle section of the stripping column.

4. Process according to Claims 1 to 3, characterized in that the operating conditions in the extractive distillation column are adjusted such that a part of the benzene contained in the feed hydrocarbon mixture is distilled off together with the non-aromatics as raffinate over the top of the extractive distillation column, and that the benzene fraction remaining in the extract does not exceed a desired maximum value which is below 5% by weight.

Revendications

1. Procédé pour isoler des aromatiques de mélanges d'hydrocarbures de départ, qui contiennent ces composés et des non-aromatiques et qui possèdent un intervalle d'ébullition entre 40 et 170°C, dans lequel le mélange d'hydrocarbures de départ est soumis, sans avoir été préalablement fractionné en fractions distinctes, à une distillation extractive en utilisant comme solvant sélectif des morpholines N-substituées dont les constituants ne comprennent pas plus de sept atomes de carbone, caractérisé par le fait que, pour préparer un concentré d'aromatiques approprié pour être utilisé comme additif pour carburants légers, la distillation extractive est exécutée avec de la N-formyl-morpholine comme solvant sélectif, en respectant un rapport de 1:2 à 1:3 entre le produit de départ et le solvant, et dans lequel les non-aromatiques à bas point d'ébullition, possédant un intervalle d'ébullition allant jusqu'à environ 105°C sont extraits pratiquement totalement et les non-aromatiques à point d'ébullition plus élevé, possédant un intervalle d'ébullition entre environ 105 et 160°C, sont soutirés en majeure partie de la colonne de distillation extractive en qualité de raffinat, en tête, après quoi le solvant est séparé des autres hydrocarbures de l'extrait par une opération de distillation, dans une colonne de rectification placée en aval, et ces autres hydrocarbures sont utilisés en totalité ou en partie comme additifs.

2. Procédé selon la revendication 1, caractérisé par le fait que les concentrés d'aromatiques produits possèdent des teneurs en non-aromatiques de 0,5 à 5,0 % en poids.

3. Procédé selon les revendications 1 et 2, caractérisé par le fait que l'on soutire de la colonne de rectification, en tant que produit de tête, du benzène pur possédant une teneur en non-aromatiques inférieure à 1000 ppm, tandis que les hydrocarbures servant d'additifs sont soutirés de la partie centrale de la colonne de rectification en qualité de courant latéral ou par l'intermédiaire d'une colonne latérale.

4. Procédé selon les revendications 1 à 3, caractérisé par le fait que les conditions de travail dans la colonne de distillation extractive sont réglées de manière qu'une partie du benzol contenu dans le mélange d'hydrocarbures de départ soit éliminée par distillation, en tête de la colonne de distillation extractive, conjointement avec les non-aromatiques, en qualité de raffinat, et par le fait que la fraction de benzol qui reste dans l'extrait n'excède pas une valeur maximale désirée, qui est inférieure à 5 % en poids.