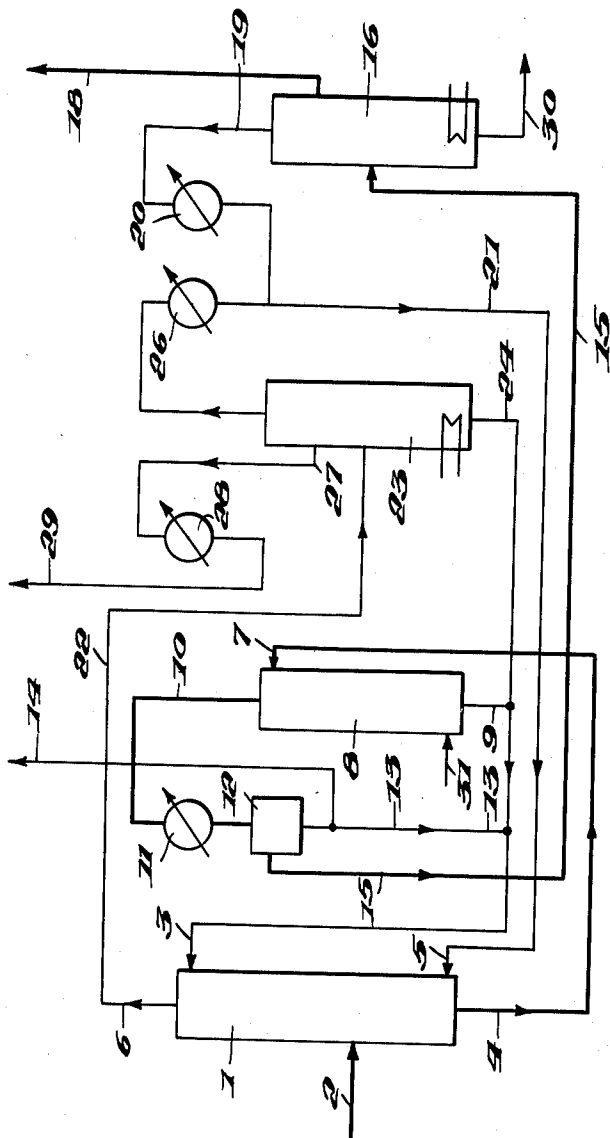


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1

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RECOVERY OF AROMATIC AND OLEFINIC HYDROCARBONS

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The present invention relates to a process for recovering pure aromatics, such as benzene, toluene and xylene, from hydrocarbon mixtures, especially gasolines, which contain a considerable proportion of unsaturated compounds by partially hydrogenating the mixture and then extracting the desired components.

More particularly, the invention comprises a process for recovering pure aromatics from cracked gasolines (benzines), gasolines obtained by pressure gasification processes, gasolines recovered from low temperature carbonizations and generally hydrocarbon mixtures which contain a high content of unsaturated compounds besides aromatics. There are a large number of processes by which pure aromatics can be recovered from hydrocarbon mixtures by extraction. However, in these the hydrocarbon mixtures are not introduced since they are passed through a pretreatment in order to make them suitable for the extraction. The pretreatment depends on the properties and source of the starting materials. When products from reforming of petroleum hydrocarbons are employed, it is sufficient merely to produce the corresponding boiling point cut. But when coke plant benzine, petroleum gasification benzine, cracked gasolines, etc., are employed, a chemical treatment is necessary. In recent times these crude products are catalytically hydrogenated before further treatment. The hydrogenation of the products suitable for recovery of aromatics occurs under such conditions that all of the unsaturated compounds are saturated but none of the aromatics are hydrogenated.

A very important source for recovering aromatics are liquid hydrocarbon mixtures which are obtained as by-products in the pyrolysis of petroleum hydrocarbons in the production of heating gas or lower olefins. By-products of similar composition also result under certain conditions in the pyrolysis of solid fuels, that is, by low temperature carbonization or gasification under pressure. These hydrocarbon mixtures are distinguished from coke plant benzine which has an aromatic content of 97 to 98% by a lower content of aromatics and a larger proportion of non-aromatic unsaturated constituents.

The technical use of such unsaturated hydrocarbon oils, which can contain 50% or more olefins, causes important difficulties. They are essentially unsuited for recycling to the cracking because they consist in part of thermally very stable compounds. Their use in oil burners is just as unsuited since they cause fouling of the burner. Their use as a motor fuel is only possible after a costly catalytic hydrogenation and the catalytic hydrogenation is only considered economically feasible when products of higher value, for example, pure aromatics, can be recovered from the hydrogenated raffinate. However, very much hydrogen is consumed for the hydrogenation due to the high unsaturated hydrocarbon content. Heretofore these disadvantages had to be accepted since economic possibilities for the use of such cracked products were not known.

In known processes it was only possible to extract the aromatics from mixtures which in addition consisted almost solely of saturated non-aromatics. The cracked gasoline which is very interesting for the recovery of

2

aromatics previously could only be subjected to extraction after the unsaturated aliphatic hydrocarbons had been completely hydrogenated.

It is an object of the present invention to provide a process for recovering the aromatics and olefins from these olefin rich hydrocarbon mixtures, wherein the olefins need not be first substantially completely converted into paraffins in an additional step of the process, that is, into products which possess little value. Olefins also present a valuable raw product for a different synthesis when they are in admixture with paraffins.

Aromatic and olefinic hydrocarbons can be recovered according to the invention from hydrocarbon fractions having a high content of unsaturated compounds, especially from cracked gasolines and low temperature carbonization gasolines by first removing the polyunsaturated components in a known way, while to a great extent retaining the olefins, and subsequently extracting the aromatics with a solvent containing a pyrrolidone compound.

The separation of the diolefins and acetylenic compounds which have a strong tendency to form resins, and which are present in small amounts in the crude product mentioned, by a prehydrogenation under mild conditions, a bleaching earth treatment at elevated temperature or through the influence of a polymerization catalyst is known. Use was made of these type processes especially before the complete hydrogenation of the olefinic compounds since in the presence of these resin forming substances the hydrogenation or the necessary preceding vaporization or heating of the crude product caused difficulties.

It has now been found that this pretreatment for separating the polyunsaturated components while retaining a large mono-olefin content, results in a product from which the pure aromatics can be recovered with the help of a pyrrolidone solvent. Pyrrolidone itself or its derivatives, as, for example, N-alkylpyrrolidone, N-oxyalkylpyrrolidone and N-acylpyrrolidone which have already been used to separate the aromatics from the paraffins, surprisingly also are suitable for recovering aromatics from mono-olefin rich fractions, insofar as these fractions are substantially freed of polyunsaturated components. According to the process of the invention it is therefore also possible to separate starting materials which no longer contain easily polymerizable resin forming compounds (polyunsaturates) directly to olefin rich and aromatic fractions.

The pyrrolidones expediently are employed as a mixture with small amounts of water for the extraction according to the invention. A mixture of N-methylpyrrolidone with 15 to 30% water is especially well suited. The selective solvent mixture is added preferably in such amounts that the volume ratio of the aromatics present in the starting mixture to the solvent amounts to 0.2 to 0.005.

The extraction of the aromatics is preferably carried out in a multi-stage counterflow apparatus in which the mixture to be separated is introduced into one of the central stages. The selective solvent is introduced into one end of the counterflow apparatus. The saturated and unsaturated non-aromatics, which flow countercurrent to the selective solvent, leave the extraction apparatus at the same end. The aromatics contained in the starting material are dissolved in the selective solvent and leave the extraction apparatus with this solvent.

Expediently a non-aromatic anti-solvent is introduced at the same end as that where the aromatics and selective solvent leave the extractor, so as to flow through the apparatus countercurrent to the selective solvent. The non-aromatic anti-solvent must be easily separable from the aromatics to be recovered through distillation, and it should only slightly dissolve in the selective solvent.

Preferably, a hydrocarbon fraction boiling below 60° C. is employed as the anti-solvent and the volume ratio of aromatics to anti-solvent should be between 1.2 and 0.5. A part of the recovered aromatics can be introduced in the form of an extract recycle together with the anti-solvent or in place of it.

The selective solvent is separated from the aromatics by distillation and recycled back into the extraction apparatus for reuse. The anti-solvent, when used, is also separated from the non-aromatics in a separating column and recycled into the extraction process. When an anti-solvent is used, the solubility of the aromatic mixture in the solvent in the presence of the anti-solvent should be about 20 to 70%. The extraction can take place at room temperature or also at elevated temperatures as well as under pressure.

With the process according to the invention a cracked gasoline containing less than 50% aromatics, which in addition consists chiefly of unsaturated hydrocarbons, can be processed to aromatics without trouble. The bromine number of such a mixture is about 80 g./100 g. To refine these products by hydrogenation more than 110 normal cubic meters of hydrogen per 1000 kilograms of charge are used up and it is necessary to employ temperatures of 300 to 400° C. at high pressures, that is, reaction conditions are required which make a hydrogenation apparatus that is very costly necessary. The great heat of the reaction and other phenomena also cause considerable technical difficulties.

According to the invention it was found possible to remove the materials which disturb the extraction through a pretreatment requiring only a small amount of hydrogen using a mild, pressureless hydrogenation at temperatures below 100° C. in the presence of a noble metal catalyst, whereby the bromine number is lowered only to a value between 20 and 60 g./100 g. Comparatively small amounts of hydrogen are required for this pretreatment. When the pretreatment leaves a product still containing small amounts of polyunsaturates which cannot be separated from the aromatics by the extraction, the extract can undergo a post-treatment with various agents. Such post-treatment in view of the smaller volume of liquid involved and its more uniform composition is simpler than carrying out a complete hydrogenation of the crude product. Such post-treatment can, for example, be carried out with bleaching earth, sulfuric acid or fused alkalis.

The accompanying drawing is a schematic flow diagram of an illustrative embodiment of an extraction process according to the invention.

As shown in the drawing, the starting mixture was fed to a 30 stage extraction column 1 by means of inlet 2. The solvent was supplied at 3. The solvent left the column 1 at 4 together with the aromatics contained in the starting mixture. A hydrocarbon mixture boiling under 50° C., consisting chiefly of pentane, was introduced as an anti-solvent at 5. The pentane flowed countercurrent to the solvent and carried the non-aromatics with it, with which it left the extraction at 6. The solvent enriched with aromatics coming from 4 was carried by way of 7 into the stripper column 8, in which the dissolved aromatics were separated from the solvent which was recycled by way of 9 and 3 into the extraction column 1. The column 8 was heated if necessary with steam supplied at 31. The vapor of aromatics and water, carried with the aromatics, was separated from the stripper column 8 at 10, condensed in cooler 11 and separated in separator 12 into an aqueous and a hydrocarbon phase. The water was again supplied to the solvent recycle in the necessary amounts by way of 13. Excess water left the system at 14. The separated aromatics were carried over line 15 into the indirectly heated distillation column 16. In the upper part of column 16 pure benzene was recovered which left the system at 18. The solvent separated from the extraction still contained

small amounts of anti-solvent with which the solvent was in contact. This pentane was distilled off in the head of column 16 and carried by way of 19 after condensation in the cooler 20 over the lines 21 and 5 back into the extraction column. A small residue collected in the base of column 16 and was removed at 30. This residue contained constituents boiling higher than benzene. The principal part of the anti-solvent together with the non-aromatics left the extraction column at 6 and flowed by way of line 22 into the indirectly heated distillation column 23. In its bottom end the small amount of solvent, which was taken along with the non-aromatics, was recovered and returned to the solvent recycle by way of 24 and 3. The pentane distilled off at 25 was condensed in cooler 26 and flowed by way of lines 21 and 5 back into the recycle. The non-aromatics contained in the starting mixture were taken out of column 23 at side outlet 27, condensed in cooler 28 and left the system at 29.

The following examples were carried out employing this system.

Example 1

A hydrocarbon mixture, resulting as a by-product from the thermal cracking of petroleum to gaseous olefins, of the following composition served as the starting material for the recovery of benzene:

| | Percent |
|---------------------------------|---------|
| Benzene ----- | 23 |
| Toluene ----- | 22 |
| Xylene ----- | 8 |
| Higher aromatics ----- | 3 |
| Unsaturated non-aromatics ----- | 30 |
| Saturated aromatics ----- | 14 |

The product which has a bromine number of 83 g./100 g. was first catalytically hydrogenated over a palladium catalyst with 2% palladium on alumina with 98% hydrogen at 50 atmospheres and 50° C. in the liquid phase. The amount of cracked hydrocarbon passed over the catalyst amounted to 1 kg. per liter of catalyst per hour. After the hydrogenation the bromine number was reduced to 30 g./100 g. A fraction boiling up to 90° C. containing all the benzene and only traces of toluene was removed from this partially hydrogenated cracked hydrocarbon product. Such fraction was extracted in the system schematically illustrated in the drawing employing four times the amount of solvent consisting of 85% N-methylpyrrolidone (NMP) and 15% water. 30 parts pentane were supplied as the anti-solvent per 100 parts of the fraction introduced. A benzene with a crystallization point of 5.5° C. was recovered in 99.5% yield.

Example 2

The same cracked hydrocarbon mixture that was used in Example 1 was employed for recovery of benzene, toluene and xylene. For this purpose it was first hydrogenated with the aid of a nickel catalyst that contained 15% nickel and had been reduced at 350° C. using 98% hydrogen at 50 atmospheres and 70° C. The amount of cracked hydrocarbon passed over the catalyst amounted to 1 kg. per liter of catalyst per hour. The hydrogenation caused the bromine number to decrease to a value of 41 g./100 g. By fractionation the constituents boiling below 150° C. were separated and the distillate extracted in a similar system as employed in Example 1 with the same solvent. The amount of solvent was 3.5 times the amount of starting material and the amount of pentane employed was half as large as the mixture introduced. The recovered extract contained small amounts of polyunsaturated hydrocarbons. These were removed by treatment with bleaching earth at 200° C. under pressure. A pure benzene with a crystallization point of 5.5° C. in approximately quantitative yield was obtained from the thus treated extract. The recovered toluene and xylene were 99.8 to 99.9% pure and thus very highly pure.

We claim:

1. In an extraction process for preparing a very pure aromatic hydrocarbon fraction from a hydrocarbon mixture containing a large proportion of poly-unsaturated hydrocarbons, the steps comprising in combination subjecting the mixture to selective hydrogenation at a temperature below 100° C. in the presence of a noble metal catalyst and hydrogen under mild hydrogenation conditions to yield a mixture consisting of mono-olefins and aromatics and thereafter extracting the aromatics by contacting the resulting mixture with a selective solvent consisting essentially of a major proportion of N-methyl pyrrolidone and a minor proportion of water, removing said selective solvent with said aromatics dissolved therein and recovering the aromatics to yield an aromatic hydrocarbon fraction which is at least 99.8% pure. 15

2. The process of claim 1 wherein said selective solvent comprises a mixture of N-methyl pyrrolidone and 15 to 30% by weight water.

3. The process of claim 1 wherein an anti-solvent comprising a hydrocarbon fraction boiling below 60° C. is also employed in the extraction process. 20

4. The process of claim 1 wherein the volume ratio of said aromatics to said solvent is 0.2 to 0.05.

5. The process of claim 1 wherein an anti-solvent comprising a hydrocarbon fraction boiling below 60° C. is also employed in the extraction process, the volume ratio of said aromatics to the anti-solvent being 1.2 to 0.5. 25

6. In a process for preparing very pure benzene from hydrocarbon mixtures containing a large proportion of poly-unsaturated hydrocarbons, the steps comprising in combination subjecting the mixture to selective hydro- 30

genation at a temperature of about 50° C. in the presence of a palladium catalyst and hydrogen under mild hydrogenation conditions to yield a mixture consisting of mono-olefins and aromatics, separating the hydrocarbons which boil below 90° C. from the resulting mixture and contacting these hydrocarbons which boil below 90° C. with a selective solvent consisting essentially of N-methyl pyrrolidone and about 15 to 30% water and an anti-solvent consisting essentially of a hydrocarbon fraction boiling below 60° C., removing said selective solvent with benzene dissolved therein and recovering the benzene to yield benzene which is at least 99.8% pure and has a crystallization point of 5.5° C.

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