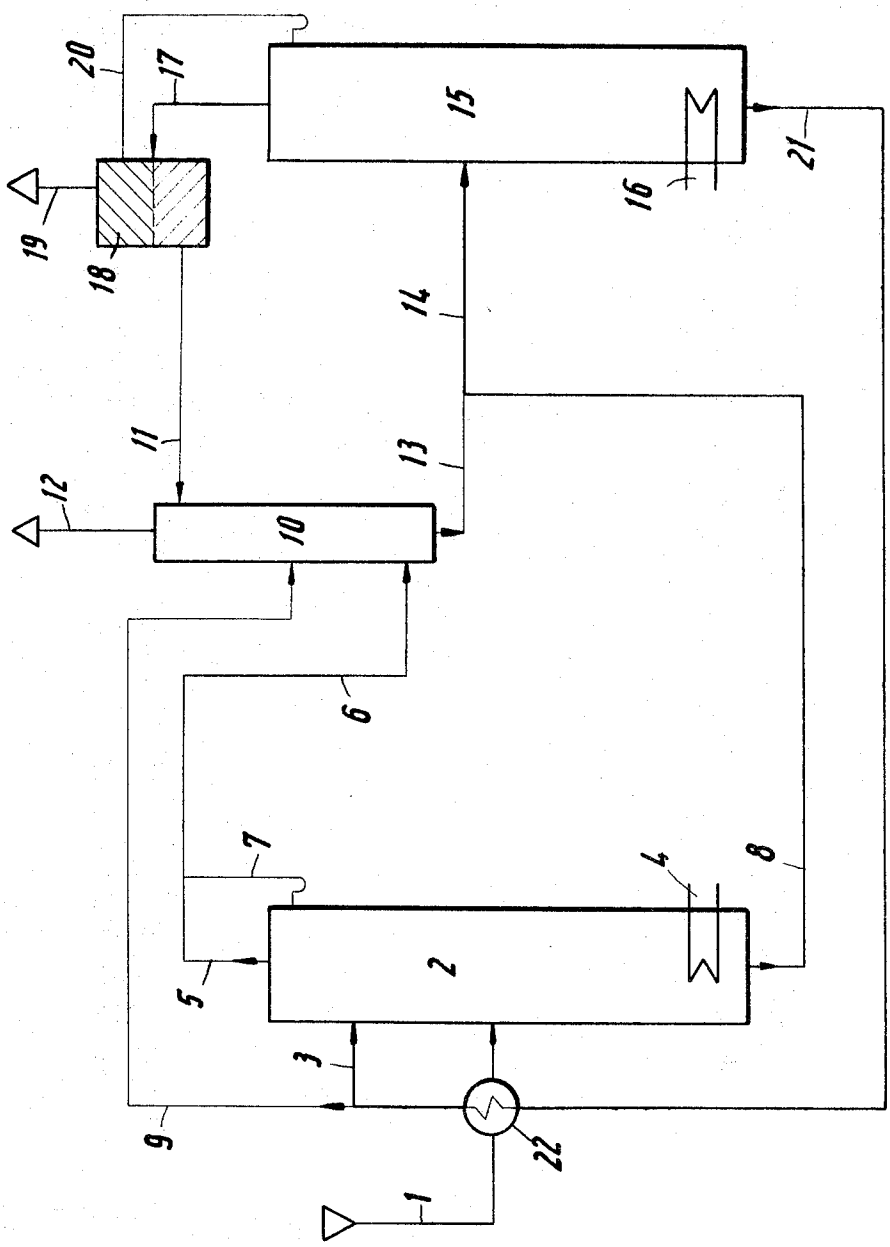
July 6, 1971 E. MÜLLER ET AL 3,591,490

PROCESS OF SEPARATING PURE AROMATIC HYDROCARBONS FROM HYDROCARBON MIXTURES

Filed Nov. 14, 1969



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United States Patent Office 3,591,490 Patented July 6, 1971

3,591,490

PROCESS OF SEPARATING PURE AROMATIC HYDROCARBONS FROM HYDROCARBON MIXTURES

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Filed Nov. 14, 1969, Ser. No. 876,885
Claims priority, application Germany, Nov. 14, 1968, P 18 08 758.6
Int. Cl. B01d 3/40; C10g 21/28
U.S. Cl. 208—313 8 Claims

ABSTRACT OF THE DISCLOSURE

In the recovery of aromatic hydrocarbons from mixtures containing same by extractive distillation utilizing a selective solvent, a purer product in a greater yield can be achieved by passing a portion of the main solvent stream used in the distillation column directly to a countercurrent extraction unit for contact with the raffinate from the distillation column passing in countercurrent flow with water to produce a product mixture from which, after subsequent stripping in a stripping column, aromatic hydrocarbons can be recovered which would have otherwise been lost.

Aromatic hydrocarbons, such as benzene and its lower alkyl substituted derivatives having up to ten carbon atoms in the molecule, have been employed as pure materials in numerous chemical processes. These aromatic compounds are found together with non-aromatic compounds in various hydrocarbon mixtures such as cracked naphtha, hydrofining products, or the like, and in this state form azeotropic mixtures therewith from which the aromatic hydrocarbons cannot be distilled off as pure products.

It is known to recover pure aromatic hydrocarbons from such mixtures by extraction, such as extractive distillation. Extractive distillation has been employed generally when it is desired to recover only a single aromatic compound or aromatic components having the same number of carbon atoms in the molecule. In carrying out such an extractive distillation, a selective solvent is used which has a boiling point that is preferably 50–100° C. above the boiling point of the aromatic compound or fraction to be recovered.

Such hydrocarbon mixtures from which the pure aromatic hydrocarbons can be recovered by extractive distillation often contain, in addition to the main component, small proportions of undesirable higher boiling aromatic materials which have a boiling point within or above the boiling range of the solvent used. In the usual extractive procedures heretofore employed, such aromatic admixtures could not be removed from the system and gradually build up and enrich the solvent, and after a period of time will reduce the selective activity thereof.

The presence of these higher boiling aromatic materials in the mixture may be due to various reasons. For example, in the recovery of pure benzene as a by-product from cracked gasoline produced by thermal cracking in the production of ethylene from light naphtha, the gasoline is initially treated with hydrogen at a relatively low temperature to hydrogenate a major portion of the diolefins present therein to monoolefins while preserving the monoolefins as such. The benzene cut is thereafter distilled from that product and is treated once more with hydrogen at a higher temperature to remove substantially all the sulfur compounds present therein. The olefins will at the same time be hydrogenated to form saturated compounds. This hydrogenation involves a secondary reaction in which the benzene will be alkylated by the olefins. The resulting reaction product will be found to contain alkylbenzenes boiling in the range of 150–250° C. in relatively minor amounts and, in most cases, below 1%.

As a further example, when it is desired to recover pure xylene from a platformate product, the platformate is subjected to a first distillation step to remove an overhead product containing all components having a lower boiling point than xylene. This product is subjected to a second distillation step and a xylene fraction is recovered as a top product. In practice, both steps may be combined in a single distillation operation carried out in a main column and an auxiliary column which will result in a reduction of the prime and operating costs. Partcularly in this case, however, the distillative separation is not highly efficient in that the xylene cut will be found to contain small amounts of C_9 and C_{10} aromatic compounds. This material will remain in the solvent phase when the extract produced by the extractive distillation is processed in the usual manner.

In accordance with the present invention, a process has now been found in which the higher boiling aromatic compounds present in the feedstock employed in an extractive distillation operation can be removed from the system in a relatively simple manner. This process comprises taking a portion of the solvent stream normally fed into the distillation column and passing it directly into approximately the middle stage of a countercurrent extractor into which is fed the condensed overhead product from the distillation column. The overhead product produced by extractive distillation column consists mainly of non-aromatic hydrocarbons and is passed into one end stage of the countercurrent extractor while water is passed into the opposite end stage thereof. This overhead product will be referred to hereinafter in the usual manner as a raffinate. In the countercurrent extractor, the raffinate dissolves the high boiling aromatic compound out of the solvent, and the added water insures that the raffinate flowing out of the extractor is free of solvent. In this way, even solvent vapors which have left the extractive distillation column at the top and have entered the raffinate in uncondensed form are recovered from the latter. From that end stage where the raffinate enters, a mixture of solvent and water is withdrawn and may be separated into its two components either in a separate column or in the solvent stripping column of the extractive distillation column. In the event the latter procedure is followed, the separation will be combined with the processing of the feedstock.

The present invention accordingly provides a process of separating pure aromatic hydrocarbons from mixtures containing such aromatic compounds together with non-aromatic hydrocarbons by an extractive distillation procedure utilizing a selective solvent. The process according to the invention is characterized in that a partial stream of the solvent is fed directly into the middle stage of an extraction unit while water is fed to one end stage, and the non-aromatic compounds which have been separated from the aromatic compounds and are present in the

overhead product or raffinate of the extractive distillation column of the system are fed to the opposite end stage of said extraction unit, whereby aromatic admixtures are separated which have a higher boiling point than the aromatic compound to be recovered and which remain in the solvent when the aromatic compound to be recovered is separated, and/or residual solvent is removed from the overhead product of the extractive distillation.

The selective solvents employed are preferably N-methyl-pyrrolidone or dimethylformamide.

The accompanying drawing is a flow diagram representing a plant for carrying out the process in accordance with the teachings of the invention.

The plant basically consists essentially of the extractive distillation column **2**, a stripping column **15** for processing the product mixture, the countercurrent extractor **10** and the phase separator **18**.

In operating the system in accordance with the present invention, the hydrocarbon mixture to be separated is heated by an indirect heat exchange in the heat exchanger **22** with hot solvent which has been obtained from the processing of the product mixture. The hydrocarbon mixture is then fed through line **1** to the extractive distillation column **2** on a medium level while the hot solvent is fed through line **3** at the top of the column **2**. The overhead product from the extractive distillation column is the raffinate and consists predominantly of non-aromatic compounds and is withdrawn from the column **2** through line **5** and condensed. Part of the condensate is fed through line **6** into an end stage of the countercurrent extractor **10** while the remainder is returned as a reflux through line **7** to the top of the column **2**. An extract or product mixture consisting of a mixture of solvent and aromatic hydrocarbons is withdrawn from the sump of the extractive distillation column **2** and is passed through lines **8** and **14** into the stripping column **15** at a medium level. The distillation residue from the stripping column **15** consists of the recovered solvent, which is recycled for re-use in the distillation column through conduits **21** and **3** and the heat exchanger **22**.

A partial stream of the hot recycled solvent is withdrawn from line **21** and is passed through line **9** and fed directly into an intermediate stage of a multiple stage countercurrent extractor unit **10**. While the raffinate from column **2** is fed to one end stage of the extractor **10** through line **6**, water is supplied to the opposite end stage of the extractor through line **11**. A mixture of water and solvent is recovered from the raffinate phase and removed through line **13** from the countercurrent extractor **10** and is fed through line **14** to the stripping column **15** and processed therein.

A mixture of the hydrocarbons recovered from the product mixture or extract and of water is withdrawn from the top of the stripping column through line **17** and is fed to the phase separator **18**, in which water settles as a heavy phase. Water is returned to the countercurrent extractor through line **11** and thereafter may be circulated from the extractor **10** through the stripping column **15**, the phase separator **18**, and then back to the countercurrent extractor **10**. The pure aromatic compounds are recovered from the stripping column **15** and are separated in the phase separator **18** as a light phase. Part of that light phase is returned as a reflux through conduit **20** to the top of the stripping column **15**. The balance of the pure aromatic compounds is recovered from the phase separator **18** through conduit **19**.

An enriching of higher alkyl aromatic compounds which have a boiling point close to or above the boiling point of the solvent should be avoided. These compounds are dissolved in the raffinate which has been formed by the extractive distillation and with said raffinate are withdrawn through line **12** from the countercurrent extractor **10**.

EXAMPLE 1

In the following example, reference will be made to the flow diagram as illustrating the apparatus used. A reformate was distilled to recover a xylene cut having a boiling range of 135–160° C. and which had the following composition:

	Percent
Toluene	1
C_8 aromatic compounds	80.4
C_9 aromatic compounds	5.9
C_{10} aromatic compounds	0.1
Non-aromatic compounds	12.6

The xylene cut was fed through line **1** to the thirtieth plate of an extractive distillation column **2** having sixty actual plates at a rate of 500 kilograms per hour and at a temperature of 140° C. A selective solvent stream consisting of a mixture of 96% N-methylpyrrolidone, hereinafter referred to as NMP, and 4% C_{10} aromatic compounds was fed to the extractive distillation column **2** through line **3** at a temperature of 100° C. and at a rate of 1230 kilograms per hour. A portion of the solvent stream is taken off before the stream passes through line **3** and used at a later point in the system, as described more fully hereinafter. Heat was supplied at a rate of 130,000 kilocalories per hour in the evaporator **4** of the extractive distillation column **2**. A mixture of the solvent and aromatic hydrocarbons forming the extract or product mixture was withdrawn from the sump of the extractive distillation column **2** through line **8** and passed to the stripping column **15** at a rate of 1696 kilograms per hour.

The resulting vapors formed as the overhead product were withdrawn from the top of the extractive distillation column **2** through line **5** and condensed. The resulting condensate constitutes the raffinate and was found to have the following composition:

	Percent
Toluene	5.1
C_8 aromatic compounds	25.8
Non-aromatic compounds	65.4
NMP (solvent)	1.7

93 kilograms per hour of the formed condensate or raffinate was fed through line **6** to the bottom end stage of a countercurrent extractor unit **10**, which is a mixer-separator column having twelve stages. The remainder of the raffinate was recycled back as a reflux to the distillation column **2** through line **7**. The portion of the solvent stream withdrawn therefrom prior to its passage through line **3** into the column **2**, as hereinbefore indicated, was fed through line **9** directly into one of the intermediate stages of the countercurrent extractor **10** at a rate of 12 kilograms per hour. Water was fed through line **11** to the top end stage of the extractor unit **10** at a rate of 15 kilograms per hour and in countercurrent flow with the raffinate from the distillation column **2**. The purpose of the water is to dissolve out the solvent from the raffinate to permit its recovery and re-use. The small amount of C_{10} aromatic compounds originally present in the solvent stream will be removed during this washing and will be carried off from the top stage of the extractor unit **10**.

A hydrocarbon mixture found to have the following composition:

	Percent
Toluene	5.1
C_8 aromatic compounds	26.1
C_{10} aromatic compounds	0.5
Non-aromatic compounds	68.1

was withdrawn from the extractor **10** through line **12** at a rate of 92 kilograms per hour.

The solvent-water mixture consisting of

48% NMP (solvent)
52% water

was withdrawn from the bottom end stage of the extractor **10** through line **13** at a rate of 28.6 kilograms per hour and was combined with the product mixture or extract collected from the sump of the distillation column **2** through line **8**. The combined mixture was fed through line **14** to the fifteenth plate of the stripping column **15** having 40 actual plates and operating under a pressure of 0.2 kilogram per square centimeter, absolute pressure, and heat at a rate of 100,000 kilocalories per hour supplied to the evaporator **16** of column **15**. The vapors formed at the top of the stripping column **15** were withdrawn through line **17**, condensed and fed into the phase separator **18** wherein an aqueous phase was separated and fed into the extractor **10** through line **11**.

The upper phase formed in the phase separator consists of a hydrocarbon mixture having the following composition:

	Percent
Toluene	0.1
C_8 aromatic compounds	92.6
C_9 aromatic compounds	7.3

Part of the upper phase mixture is withdrawn as pure aromatic compounds from the unit at a rate of 408 kilograms per hour through line **19** and collected. The balance of the separated hydrocarbon mixture was fed through line **20** as a reflux to the stripping column **15**.

A solvent mixture of 96% NMP (solvent) and 4% C_{10} aromatic compounds was removed from the sump of the stripping column **15** through line **21** at a rate of 1250 kilograms per hour. The main part of the solvent mixture was fed back to the extractive distillation column **2** while the remaining portion of the stream amounting to about 1% was fed directly into the extractor **10**.

EXAMPLE 2

A cracked gasoline produced by thermal cracking in the production of ethylene was initially subjected to a hydrogenation whereby substantially only the diolefins were hydrogenated. The resulting hydrogenated product was distilled to recover a benzene cut having a boiling range of 70–82° C. and containing about 80% benzene. This benzene cut was subjected to a second hydrogenation to effect a removal of the sulfur compounds therefrom and to transform all olefins into saturated compounds. Higher alkyl aromatic compounds and partly hydrogenated, condensed ring materials having boiling points between 150° and 250° C. were also formed during this hydrogenation and were present in an amount of 0.2% of the benzene cut. These compounds will be referred to hereinafter as alkylaromatic compounds.

The hydrogenated benzene cut was found to have the following composition:

	Percent
Benzene	80.0
Non-aromatic compounds	19.8
Alkylaromatic compounds	0.2

The formed benzene cut was fed through line **1** to the thirtieth plate of the extractive distillation column **2** having sixty actual plates at a rate of 1,000 kilograms per hour and at a temperature of 80° C. A selective solvent consisting of 92.6% dimethylformamide, hereinafter referred to as DMF, and 7.4% alkylaromatic compounds was fed through line **3** to that extractive distillation column **2** at a temperature of 90° C. and at a rate of 2672 kilograms per hour. Heat at a rate of 300,000 kilocalories per hour was supplied in the evaporator **4** of the extractive distillation column **2**. The raffinate was drawn off from the column **2** through line **6** at a rate of 238 kilograms per hour while the balance of the condensed vapor was fed through line **7** as a reflux to the extractive distillation column **2**. The resulting extract or mixture of solvent and aromatic hydrocarbons was drawn off the sump of the distillation column **2** at a rate of 3432 kilograms per hour through line **8** and fed to the stripping column **15**.

A part of the selective solvent stream was divided from line **3**, and was fed through line **9** at a rate of 27 kilograms per hour, directly to one of the medium stages of the extractor unit **10** of the same construction as the one used in Example 1. The overhead product withdrawn through line **6** from the distillation column **2** was fed to the bottom end stage of the extractor unit **10**. Water at a rate of 35 kilograms per hour was fed to the top end stage of the extractor **10** through line **11**. The alkylaromatic compounds present in an amount of 7.4% in the divided solvent stream supplied through line **9** to the column **2** were dissolved out of the solvent stream in extractor **10** and withdrawn from the top stage of the extractor.

A hydrocarbon mixture having the following composition

	Percent
Benzene	16.7
Alkylaromatic compounds	0.8
Non-aromatic compounds	82.5

was withdrawn from the extractor **10** through line **12** at a rate of 92 kilograms per hour.

A solvent/water mixture consisting of

42% DMF (solvent)
58% water

was withdrawn from the bottom stage of the countercurrent extractor through line **13** at a rate of 60 kilograms per hour and combined with the product mixture or extract drawn from the sump of the extractive distillation column **2** through line **8**. The combined mixture was carried through line **14** into the stripping column **15** at the fifteenth plate thereof. The stripping column **15** being of the same design as that used in Example 1 was operated under a pressure of 0.4 kilogram per square centimeter, absolute pressure, with heat being supplied in the evaporator **16** of column **15** at a rate of 200,000 kilocalories per hour.

The vapors present at the top of the stripping column **15** were withdrawn through line **17**, condensed and then fed into the phase separator **18** wherein an aqueous phase was separated which was fed back into the extractor **10** through line **11**. A portion of the top phase product consisting of pure benzene was withdrawn from the plant through line **19** at a rate of 760 kilograms per hour and collected. The balance of the pure benzene product was fed as a reflux back to the stripping column **15** through line **20**. A mixture of 82.6% DMF (solvent) and 7.4% alkylaromatic compounds was withdrawn from the sump of the stripping column **15** through line **21** at a rate of 2700 kilograms per hour with the main portion thereof being returned to the extractive distillation column **2** through line **3**, with the balance amounting to about 1% being fed directly to the extractor **10** through line **9**.

We claim:

1. In a process of separating pure aromatic hydrocarbons from mixtures containing aromatic hydrocarbons and non-aromatic hydrocarbons by an extractive distillation with a selective solvent, the improvement comprising dividing out a minor portion of the solvent from the main solvent stream normally mixed with the feedstock mixture to a distillation zone, passing said divided out minor portion of said solvent directly into substantially the middle area of an extraction zone, passing water to one end of said extraction zone, collecting an overhead raffinate containing non-aromatic hydrocarbons and solvent from the distillation zone and passing same to the other end of said extraction zone for passage in countercurrent flow therethrough with said water whereby said washing will separate the aromatic hydrocarbon-free solvent from said raffinate.

2. A process according to claim **1**, characterized in that the aromatic hydrocarbon to be recovered consists of benzene.

3. A process according to claim 1, characterized in that the aromatic hydrocarbons to be recovered consist of a mixture of xylenes and ethylbenzene.

4. A process according to claim 1, characterized in that N-methylpyrrolidone is used as a selective solvent.

5. A process according to claim 2, characterized in that dimethylformamide is used as a selective solvent.

6. A process according to claim 1, wherein said hydrocarbon mixture is a xylene cut having a boiling range of 135–160° C.

7. A process according to claim 1, wherein said hydrocarbon mixture is a benzene cut having a boiling range of 70–82° C.

8. A process according to claim 1, wherein one product material from the extraction zone is a water-solvent material free from aromatic hydrocarbons and which is passed to a stripping column in admixture with the product material from the distillation column.

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HERBERT LEVINE, Primary Examiner

U.S. Cl. X.R.

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