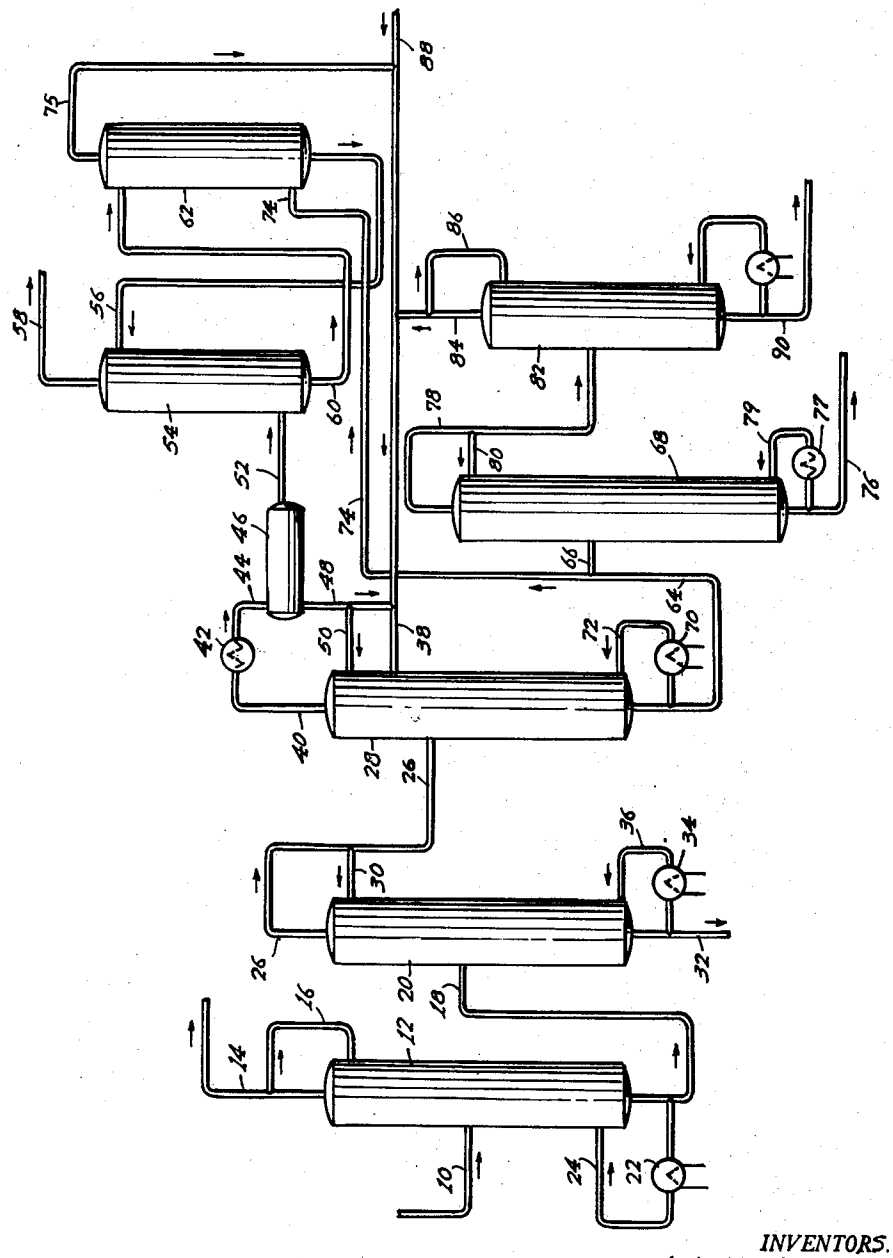
Aug. 19, 1958 E. M. GLAZIER ET AL 2,848,387

SEPARATION OF AROMATIC AND NON-AROMATIC HYDROCARBONS

Filed March 3, 1954



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United States Patent Office 2,848,387 Patented Aug. 19, 1958

2,848,387

SEPARATION OF AROMATIC AND NON-AROMATIC HYDROCARBONS

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Application March 3, 1954, Serial No. 413,856

6 Claims. (Cl. 202—42)

This invention relates to the separation of aromatic hydrocarbons from other hydrocarbons of the same boiling range and more particularly to the separation of aromatic hydrocarbons boiling in the range of the xylenes by azeotropic distillation and extraction procedures.

The increased demand for aromatic hydrocarbons has made it necessary to find sources of these materials other than the by-products from the coking of coal. Processes for the reforming of petroleum hydrocarbons, and particularly for the reforming of heavy naphthas, to improve gasolines produce hydrocarbon streams which are rich in aromatics. Aromatic hydrocarbons of special value in the gasoline boiling ranges are ortho- and para-xylene and ethylbenzene. However, the aromatic hydrocarbons prepared by the reforming of petroleum hydrocarbons are present in complex mixtures with non-aromatic compounds such as naphthenic, paraffinic and olefinic hydrocarbons. Separation of the aromatic compounds in the xylene boiling range from the non-aromatic hydrocarbons present in the reformate by the usual distillation processes is not commercially feasible because of the presence in the reformate of non-aromatic materials having substantially the same volatility as the xylenes.

It has been found that the aromatic and non-aromatic fractions of mixtures of hydrocarbons may be separated by the addition of acetonitrile to the reformate as an azeotrope former. Then, on the azeotropic distillation of the reformate to which the acetonitrile has been added, an azeotrope of acetonitrile and non-aromatic hydrocarbons is distilled overhead. Acetonitrile is a desirable azeotrope former in that it is inert to both the aromatic and non-aromatic fractions of the reformate and may be used in relatively small amounts to give efficient separation of aromatics and non-aromatics. In addition, the boiling point of acetonitrile is sufficiently low to allow substantially complete separation from the aromatic hydrocarbons. However, acetonitrile is a rather expensive agent which must be substantially completely removed from both the aromatic and non-aromatic hydrocarbons if its use as an azeotropic former is to be commercially feasible. The efficient recovery of acetonitrile from the acetonitrile-non-aromatic hydrocarbon azeotrope can not be accomplished by distillation followed by a simple extraction with water since acetonitrile and water form an azeotrope.

This invention resides in a process for the separation of aromatic and non-aromatic hydrocarbons in complex mixtures of hydrocarbons by the azeotropic distillation of a mixture of aromatic and non-aromatic hydrocarbons with acetonitrile to separate a distillate of an azeotrope of acetonitrile and non-aromatic hydrocarbons and bottoms of aromatic hydrocarbons. The azeotropic distillation is followed by extraction of acetonitrile from the overhead product of the azeotropic distillation with water and the subsequent extraction of the water extract with aromatic hydrocarbons to separate acetonitrile from the water.

The single figure of the drawings is a diagrammatic flow sheet of a process for the separation of aromatic and non-aromatic hydrocarbons in the xylene boiling range according to this invention. Apparatus such as valves, pumps, some of the heat exchange equipment and other auxiliary equipment have been omitted from the drawings in order to simplify them.

In a process according to this invention, a complex mixture of aromatic and non-aromatic hydrocarbons is introduced through a line **10** into a distillation tower **12**. The mixture of hydrocarbons passing through line **10** may be prepared by any desired process. A typical source of hydrocarbons is a reformate stream from the catalytic reforming of a heavy naphtha. Tower **12** is operated to distill overhead a fraction boiling at temperatures lower than the lower limit of the boiling range of the hydrocarbon feed to the azeotropic distillation to be described. The distillate from tower **12**, which is suitable for use in gasoline, is delivered through a line **14** to product recovery apparatus, not shown. A portion of the overhead is condensed and returned as reflux to tower **12** through a line **16** in order to obtain the desired fractionation in tower **12**. The bottoms from tower **12**, constituting the higher boiling fraction of the reformate, are withdrawn through line **18** and delivered to a second distillation tower **20**. A portion of the bottoms from tower **12** is heated in a reboiler **22** and returned through line **24** to tower **12** to supply the heat requirements for the operation of tower **12**.

Tower **20** is operated to separate as a bottoms product those hydrocarbons in the reformate boiling at temperatures higher than the upper limit of the boiling range of the feed stock to the azeotropic distillation with acetonitrile. The distillate from tower **20** is withdrawn from the tower **20** through line **26** and delivered as hydrocarbon feed stock to an azeotropic distillation tower **28** which is preferably operated at substantially atmospheric pressure. A portion of the distillate from tower **20** is condensed and returned to the tower as reflux through line **30**. The bottoms fraction from tower **20** is withdrawn through a line **32** and discharged from the system of this invention. A portion of the bottoms product is vaporized in a reboiler **34** and returned through line **36** to tower **20** to satisfy the fractionation requirements of the tower.

Towers **12** and **20** and their operation are described and illustrated as typical apparatus for the preparation of a charge stock of suitable boiling range from a catalytic reformate. The towers **12** and **20** can be of conventional design and operation and may operate at any desired pressure, however, this invention is not restricted to apparatus or processes employing the conventional charge stock preparation described in connection with the operation of towers **12** and **20**. Similarly, the boiling range of the feed stock introduced into tower **28** through line **26** will vary, depending upon the aromatic fractions to be recovered. In the separation of aromatics boiling in the xylene boiling range, it is preferred that the feed stock to tower **28** have a boiling range of approximately 260° F. to 300° F. in order to include substantially all of those aromatic hydrocarbons, and at the same time provide a narrow cut of hydrocarbons that may be efficiently separated and will avoid overloading azeotropic distillation tower **28**.

Acetonitrile for the azeotropic distillation is introduced into tower **28** through line **38** through which acetonitrile recovered from the azeotropic distillation products in the manner hereinafter described is recycled to the tower **28**. An azeotrope of non-aromatic hydrocarbons and acetonitrile boiling at approximately 173° F. and containing about 70 percent by volume acetonitrile is formed in the tower **28** and distilled overhead through line **40**. An

aromatic hydrocarbon fraction having a low concentration of acetonitrile is withdrawn from the bottom of tower **28**. The azeotrope is delivered through line **40** to a condenser **42** in which the azeotrope is condensed, and the resulting liquid is delivered through line **44** to a settling tank **46**. The condensation of the azeotrope results in the formation of an acetonitrile-rich phase and a non-aromatics-rich phase. The acetonitrile-rich phase, containing approximately 8.3 percent non-aromatics and 88.5 percent acetonitrile, settles to the bottom of settling tank **46** from which it is withdrawn through a recycle line **48** and split into two parts, one of which is refluxed to the top of azeotropic distillation tower **28** through line **50** and the other returned to the tower **28** through acetonitrile line **38**.

The non-aromatics-rich phase, containing about 91 percent non-aromatics and 7.7 percent acetonitrile, which collects in the top of the settling tank **46**, is withdrawn from settling tank **46** through a line **52** and delivered to the bottom of a water-extraction tower **54**. The non-aromatic hydrocarbons pass upwardly through the absorption tower **54** in countercurrent contact with water which is introduced into the top of the tower **54** through a line **56**. The water strips the acetonitrile from the non-aromatic hydrocarbons and those hydrocarbons are discharged from the top of water-extraction tower **54** through a line **58** and discharged from the system. Water-extraction tower **54** is operated under sufficient pressure to keep the system in the liquid phase at the desired extraction temperature. A pressure of 50 p. s. i. absolute, for example, is satisfactory. The concentration of acetonitrile in the effluent non-aromatic product from tower **54** can be adjusted to the most economic level by variations in the column heights, quantity of solvent circulated, and the temperature in towers **54** and **62**.

The aqueous extract of acetonitrile is discharged from the bottom of tower **54** through a line **60** and delivered through that line to the top of an aromatics-extraction tower **62**. Acetonitrile and water form an azeotrope which may not be separated by direct distillation. Separation of the water and acetonitrile is accomplished according to this invention by extracting the acetonitrile from the water with an aromatic hydrocarbon fraction preferably obtained from the aromatic hydrocarbon fraction withdrawn from the bottom of tower **28**.

The bottoms from the acetonitrile distillation tower **28** contain approximately 99.5 percent aromatic hydrocarbons and 0.5 percent of acetonitrile. Aromatic hydrocarbons are withdrawn from the azeotropic distillation tower **28** through a line **64** and delivered through a feed line **66** to a distillation tower **68** in which the ortho-xylene is separated from the other aromatics. A portion of the bottoms from the tower **28** is heated in a reboiler **70** and returned to tower **28** through a line **72** to supply the heat for the azeotropic distillation.

A stream of aromatic hydrocarbons is taken from line **64** through a line **74** and delivered to the bottom of the aromatics-extraction tower **62**. The aromatic hydrocarbons pass upwardly through tower **62** countercurrently to the aqueous extract of acetonitrile from tower **54** and scrub the acetonitrile from the water. The solution of acetonitrile in the aromatic hydrocarbons is discharged from the top of tower **62** through a line **75** and returned through that line to acetonitrile feed line **38** to supply a portion of the acetonitrile for the operation of azeotropic distillation tower **28**. The aqueous raffinate is withdrawn from the bottom of aromatics extraction tower **62** and recycled through line **56** for use as solvent in tower **54**.

Usually it will be desirable to separate the different aromatic constituents in the stream withdrawn from the bottom of azeotropic distillation tower **28**. Separation of ortho-xylene from the other xylenes and ethylbenzene is accomplished by precision fractionation in the tower **68** to provide a bottoms stream, 95 percent of which is ortho-xylene, which is withdrawn from tower **68** through line **76**. Tower **68** is provided with a conventional reboiler **77** and return line **79** at the bottom of the tower.

The overhead product from tower **68**, consisting primarily of a mixture of meta- and para-xylenes, ethylbenzene and the small amount of acetonitrile in the feed to tower **68**, is withdrawn through line **78**. A portion of the overhead product is recycled through line **80** as reflux for the tower **68**. Substantially complete separation of the acetonitrile from the meta- and para-xylene can easily be obtained in a distillation tower **82** in which the acetonitrile is separated as an overhead product. Acetonitrile withdrawn overhead from tower **82** is delivered through line **84** to the acetonitrile feed line **38** for azeotropic distillation tower **28**. A portion of the overhead product is condensed and refluxed through line **86** to the tower **82**. Acetonitrile may be added to the system directly at tower **28** or at any convenient point such as line **88**. The bottoms product withdrawn from tower **82** through line **90**, consisting of a mixture of meta- and para-xylene and ethylbenzene, contains approximately 0.1 percent acetonitrile. Further separation of the mixture of isomers of xylene and ethylbenzene to the pure individual compounds may be accomplished by conventional procedures, for example by fractional crystallization.

As a specific example of the process of this invention, reformate from the hydro-reforming of a West Texas heavy naphtha and having a boiling range of 295° F. to 448° F. is charged to the system. A 266° F. to 302° F. cut is separated by distillation from the reformate for feed stock to the azeotropic distillation. The 266° F. to 302° F. cut constitutes approximately 12.5 percent of the reformate and contains about 55 percent by volume aromatics. An azeotrope containing approximately 70 percent acetonitrile and substantially all of the non-aromatic hydrocarbons in the feed to the azeotropic distillation is distilled overhead in the azeotropic distillation. The azeotropic distillation is operated at substantially atmospheric pressure at which pressure the azeotropic distills at approximately 173° F.

The non-aromatic-rich fraction which separates from the acetonitrile when the distillate from the azeotropic distillation is condensed is extracted with water at a temperature of about 130° F. and a pressure of 50 p. s. i. absolute to form a raffinate of non-aromatic hydrocarbons containing approximately 0.8 percent acetonitrile. The acetonitrile remaining in the raffinate is lost from the system with the non-aromatic fraction.

The aqueous extract of acetonitrile which contains about 25 percent acetonitrile is then extracted with a mixture of xylenes and ethylbenzene to produce an aqueous raffinate phase containing about 1.2 percent acetonitrile. The extract phase of acetonitrile in the aromatic hydrocarbons contains approximately 16 percent acetonitrile.

In the system illustrated in the drawings the ortho-xylene discharged from the process as bottoms from tower **68** is substantially completely free of acetonitrile. The mixture of ethylbenzene and meta- and para-xylene discharged from tower **82** contains only approximately 0.1 percent acetonitrile. The aqueous raffinate from tower **62** and the extract of aromatics and acetonitrile from that tower are recycled in the system. Thus the only loss of acetonitrile from the system is in the raffinate from tower **54** containing 0.8 percent acetonitrile and the bottoms from tower **82** containing 0.1 percent acetonitrile.

The process of this invention allows substantially complete separation of aromatic and non-aromatic hydrocarbons boiling in the xylene boiling range. All products discharged from the system are very low in acetonitrile content; hence, the amount of acetonitrile required to replace losses is low. In addition acetonitrile is an efficient azeotrope former which forms an azeotrope of approximately two parts of acetonitrile to one part of

non-aromatic hydrocarbons, thereby allowing the use of a small amount of acetonitrile as compared with other azeotrope formers in the azeotropic distillation.

We claim:

1. In a process for the separation of aromatic hydrocarbons from non-aromatic hydrocarbons in a mixture of aromatic and non-aromatic hydrocarbons by the azeotropic distillation of the mixture of aromatic and non-aromatic hydrocarbons in the presence of acetonitrile to form a volatile azeotrope of non-aromatic hydrocarbons and acetonitrile, and a bottoms product comprising aromatic hydrocarbons, a process for recovering acetonitrile from the non-aromatic hydrocarbons comprising extracting acetonitrile from the non-aromatic hydrocarbons with water to form an extract of water and acetonitrile and a raffinate of substantially acetonitrile-free non-aromatic hydrocarbons, extracting acetonitrile from said extract with aromatic hydrocarbons, recycling the extract of aromatic hydrocarbons and acetonitrile to the azeotropic distillation step, and recycling the raffinate of water from the extraction with aromatic hydrocarbons to the step of extracting acetonitrile from non-aromatic hydrocarbons.

2. A process for the separation of aromatic hydrocarbons from a complex mixture of hydrocarbons containing aromatic and non-aromatic hydrocarbons boiling within the same temperature range comprising distilling the complex mixture in the presence of acetonitrile to distill an azeotrope of non-aromatic hydrocarbons and acetonitrile as an overhead product and withdrawing a stream of aromatic hydrocarbons as a bottoms product, extracting a mixture of non-aromatic hydrocarbons and acetonitrile from the distillate of the azeotropic distillation with water to separate acetonitrile from the non-aromatic hydrocarbons to form an extract of water and acetonitrile, extracting the extract of water and acetonitrile with a portion of the aromatic hydrocarbons removed as a bottoms product from the azeotropic distillation to form an aqueous raffinate and an extract of aromatic hydrocarbons and acetonitrile, recycling the extract of aromatic hydrocarbons and acetonitrile to the azeotropic distillation, recycling the aqueous raffinate to the extraction of the non-aromatic hydrocarbons and acetonitrile, distilling the aromatic hydrocarbons withdrawn as a bottoms product from the azeotropic distillation to separate acetonitrile in an overhead product, and recycling the thus distilled acetonitrile to the azeotropic distillation.

3. A process for the separation of aromatic hydrocarbons consisting principally of xylenes and ethylbenzene from a complex mixture of aromatic and non-aromatic hydrocarbons distilling in the range of approximately 260° F. to 300° F. comprising azeotropically distilling the complex mixture in the presence of acetonitrile to form an overhead distillate product consisting of an azeotrope of acetonitrile and non-aromatic hydrocarbons and an aromatics bottoms product, condensing the azeotropic distillate and settling the condensate to separate an acetonitrile-rich phase and a non-aromatic hydrocarbons-rich phase, recycling the acetonitrile-rich phase to the azeotropic distillation, extracting the non-aromatic hydrocarbons-rich phase with water to form an aqueous extract of acetonitrile, extracting the aqueous extract with aromatic hydrocarbons from the bottoms product of the azeotropic distillation to form an extract of aromatic hydrocarbons and acetonitrile and a raffinate of water, recycling the extract of aromatic hydrocarbons and the acetonitrile to the azeotropic distillation step, recycling the raffinate of water to the extraction of the non-aromatic hydrocarbons-rich phase, distilling the aromatic hydrocarbons from the azeotropic distillation to form a bottoms product of ortho-xylene and a distillate product of meta- and para-xylene, ethylbenzene and acetonitrile, stripping acetonitrile from the distillate product to form a substantially acetonitrile-free bottoms product of meta- and para-xylene and ethylbenzene, and recycling the acetonitrile stripped from the aromatic hydrocarbons to the azeotropic distillation step.

4. A process for the separation of aromatic hydrocarbons from a hydrocarbon fraction containing aromatic hydrocarbons and non-aromatic hydrocarbons which distill in the same temperature range, comprising distilling the hydrocarbon fraction in the presence of acetonitrile to distill an azeotrope of acetonitrile and non-aromatic hydrocarbons as an overhead product and aromatic hydrocarbons substantially free of non-aromatic hydrocarbons as a bottoms product, condensing the azeotrope, separating the condensed azeotrope into an acetonitrile-rich phase and a non-aromatic hydrocarbons-rich phase, recycling the acetonitrile-rich phase to the distillation, extracting acetonitrile from the non-aromatic hydrocarbons-rich phase with water to form a raffinate of non-aromatic hydrocarbons substantially free of acetonitrile and an extract of acetonitrile and water, extracting acetonitrile from the extract of water and acetonitrile with aromatic hydrocarbons to form an extract of acetonitrile and aromatic hydrocarbons and an aqueous raffinate, recycling the aqueous raffinate to the extraction of the non-aromatic hydrocarbons-rich phase, and returning the extract of an acetonitrile and aromatic hydrocarbons to the distillation.

5. A process as set forth in claim 4 in which the ratio of aromatic hydrocarbons to water in the extraction of the aqueous extract of acetonitrile is in the range of about 1.5:1 to 2.5:1.

6. A process for the separation of aromatic hydrocarbons boiling in the xylene range from a mixture distilling in the range of approximately 260° F. to 300° F. of the aromatic hydrocarbons with non-aromatic hydrocarbons, comprising distilling the mixture in the presence of acetonitrile to distill an azeotrope of acetonitrile and non-aromatic hydrocarbons as an overhead product and aromatic hydrocarbons as a bottoms product, condensing the azetrope, separating the condensed azeotrope into an acetonitrile-rich phase and a non-aromatic hydrocarbons-rich phase, recycling the acetonitrile-rich phase to the distillation, extracting acetonitrile from the non-aromatic hydrocarbons-rich phase with water to form a raffinate of non-aromatic hydrocarbons substantially free of acetonitrile and an extract of acetonitrile and water, extracting acetonitrile from the extract of water and acetonitrile with aromatic hydrocarbons to form an extract of acetonitrile and aromatic hydrocarbons and an aqueous raffinate, recycling the aqueous raffinate to the extraction of the non-aromatic hydrocarbons-rich phase, and returning the extract of acetonitrile and aromatic hydrocarbons to the distillation.

References Cited in the file of this patent

UNITED STATES PATENTS

2,305,106	Pratt	Dec. 15, 1942
2,434,322	Latchum et al.	Jan. 13, 1948
2,444,893	Lake	July 6, 1948
2,568,159	Medcalf et al.	Sept. 18, 1951
2,690,417	Shalit et al.	Sept. 28, 1954

FOREIGN PATENTS

593,463	Great Britain	Oct. 17, 1947