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AROMATIC SEPARATION PROCESS

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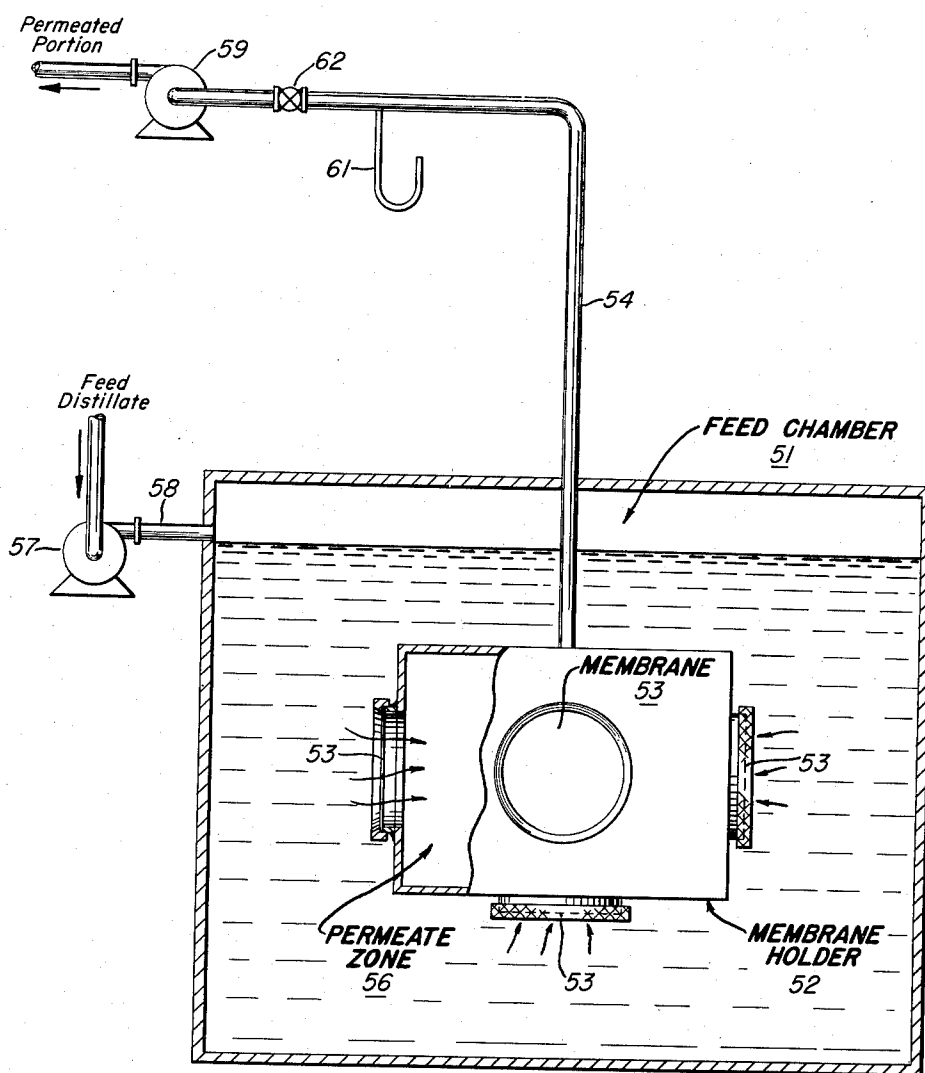


Fig. 2

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2,970,106

AROMATIC SEPARATION PROCESS

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This invention relates to the separation of aromatic hydrocarbons from mixtures thereof with other hydrocarbons, and particularly concerns the separation of aromatics from hydrocarbon distillates.

An object of the present invention is to provide a process for separating aromatic hydrocarbons from hydrocarbon distillates containing a mixture of aromatic and non-aromatic hydrocarbons. Another object is to provide a process for increasing the concentration of aromatic hydrocarbons in a hydrocarbon distillate. A further object is to provide a process for recovering substantially pure aromatic hydrocarbons from hydrocarbon distillates. A still further object is to provide a method for segregating naphtha fractions into fractions of higher and lower octane number. These and other objects of the invention will be apparent from the detailed description thereof.

The present invention utilizes the discovery that when a hydrocarbon distillate is charged to a permeation step and permeated and nonpermeated portions are recovered, the permeated portion is not only enriched in aromatics but also has a markedly different composition with respect to other component hydrocarbons. Because of the change in composition, the permeated portion can be distilled into a high boiling fraction even richer in aromatics and a low boiling fraction poorer in aromatics than the total permeated portion. The non-permeated fraction can similarly be distilled to produce a high boiling fraction rich in aromatics and a low boiling fraction poor in aromatics. Unless the permeation step precedes the distillation step, it is not possible to obtain this effect of highly concentrating the aromatic hydrocarbon.

In accordance with the present invention a hydrocarbon distillate charge which has a definite boiling range and contains aromatic and other hydrocarbons is subjected to a permeation step. In this step the charge distillate is contacted with one side of a plastic permeation membrane which preferentially permeates aromatic hydrocarbons. A portion of the charge mixture is permeated through the membrane and from the opposite side of the membrane is recovered the permeated portion having a higher concentration of aromatic hydrocarbons than is present in the charge distillate. The non-permeated portion of the charge has a lower concentration of aromatics than is present in the charge distillate. The permeated portion is then distilled to separate a lower boiling fraction from a higher boiling fraction. The higher boiling has a higher concentration of aromatics than was present in the permeated portion passed to the distillation step, and the lower boiling fraction from the distillation step has a lower concentration of aromatics than was present in the permeated portion passed to the distillation step. The non-permeated portion may similarly be subjected to a distillation step to separate a lower boiling fraction from a higher boiling fraction. The higher boiling fraction will likewise have a higher concentration of aromatics and the lower boiling fraction will have a lower concentration of aromatics than the concentration of aro-

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5 matics in the non-permeated portion passed to the distillation step. When the charge distillate to the process is a naphtha such as a reformed naphtha or a catalytically cracked naphtha, the present invention provides a technique for segregating the naphtha into various high octane and low octane fractions. The high boiling fraction of the permeated portion of the naphtha charge will be very rich in aromatics and will have a very high octane number. The low boiling fraction of the permeated portion of the charge naphtha may be recycled to the permeation step. The high boiling fraction of the non-permeated portion of the naphtha charge may likewise be recycled to the permeation step, and the low boiling fraction of the non-permeated portion of the naphtha will be very low in aromatics and is discarded from the process. Various naphtha fractions, e.g. a toluene-xylene fraction, may be charged to the process of this invention to produce select high octane and low octane fractions. A narrow boiling naphtha distillate, such as is rich in aromatic hydrocarbons having a specific number of carbon atoms per molecule, e.g. a toluene fraction or a xylene fraction, may be processed by this invention to produce the substantially pure aromatic hydrocarbon.

Rather than carry out the distillation of the permeated portion in a separate vessel, the permeation process may be operated so as to perform a distillation function. In this aspect of the invention the charge distillate is introduced in the liquid phase into the charge zone of the permeation vessel. A portion of the charge distillate is permeated through the membrane into the permeate zone (the latter is separated from the charge zone by the permeation membrane) and as the permeating distillate passes into the permeate zone, conditions of temperature and pressure are maintained therein such as to cause the permeated portion of the distillate to remain partly in the liquid state and partly in the vapor state. The higher boiling liquid portion of the permeated distillate will have a higher concentration of aromatics than is present in the vaporous portion of the permeated distillate, and it would also be higher than the concentration of aromatics in the distillate charged to the permeation step.

Figure 1 illustrates an embodiment of the present invention for segregating a naphtha fraction into component fractions of high and low octane numbers. This schematic diagram depicts a method for recovering a substantial yield of 108.6 F-1 clear octane (extrapolated) naphtha.

In this embodiment 100 volumes of naphtha (100 volumes is chosen here since percentages are easily determinable therefrom, but this may represent typical flows of 10,000–20,000 bbls./day) is passed by way of line 11 to a naphtha hydroforming operation indicated herein by block 12. This naphtha charged to the hydroforming operation will generally have an octane number of 40–60 F-1 clear and will usually boil over the range of about 180° to 400° F. Any of the naphtha hydroforming processes may be used. Processes which employ a supported platinum catalyst such as platinum on alumina are preferred since they produce the maximum yields of highest octane naphtha of the various commercial naphtha hydroforming processes. In the hydroforming process the naphtha is contacted with the catalyst in the presence of hydrogen at a temperature in the range of about 850° to 1000° F., a pressure in the range of about 50 to 800 p.s.i.g., advantageously about 200–400 p.s.i.g. Hydrogen is employed in the amount of about 1,000 to 10,000 cu. ft./bbl. of naphtha charge. Space velocities of from 0.1 to 5 WHSV may be used. In the embodiment shown herein the Ultraforming process, which is a relatively low pressure regenerative catalyst process, is used to produce a stabilized C₅ to 400° F. hydroformate having a 99.9 F-1 clear octane number.

The hydroformate is produced in 81% yield based upon naphtha charge and has an aromatics content of 69%.

The C₅—400 hydroformate consisting of 81 volumes is passed by way of line 13 into fractionator 14 wherein it is split into two fractions. A lower boiling fraction containing benzene and lower boiling hydrocarbons is taken overhead by way of line 16. The higher boiling fraction which contains toluene and higher boiling hydrocarbons is removed from the bottom of fractionator 14 by way of line 17. A cut point of 190° F. or thereabouts may be used in fractionator 14. The overhead fraction removed by way of line 16 may boil over the range of about 70 to 190° F. It comprises 19.4 volumes and contains only 6% aromatics. Because of its low octane number it is not a suitable stock for blending to make high octane gasoline. The bottoms from fractionator 14 is passed by way of line 17 into fractionator 18 wherein it is split into an overhead toluene-xylene fraction and a bottoms fraction containing C₉ and higher aromatics. Fractionator 18 may be operated at a cut point of 280° F. or thereabouts. The overhead fraction is removed by way of line 19. It boils over the range of about 190–280° F. and constitutes 21.1 volumes. Its aromatic content is 72%. Because its aromatic content can be increased and its octane number improved in a practical fashion, it is employed as the charge stock to the permeation-distillation process of this invention. The bottoms from fractionator 18 is removed by way of line 21. It boils over the range of about 280–400° F. and consists of 40.5 volumes. This fraction has an aromatics content of 98% and has a very high octane number making it exceedingly suitable for blending to produce very high octane gasolines.

In its fundamental form a permeation vessel consists of an enclosed vessel separated into two chambers or zones by the permeation membrane. The charge mixture to be processed is introduced into one chamber wherein it contacts one side of the permeation membrane. The permeation membrane is a thin plastic film through which aromatic hydrocarbons permeate at a more rapid rate than do the other hydrocarbons contained in the distillate charged to the permeation vessel. Examples of permeation membranes are films of cellulose esters, cellulose ethers, blends of cellulose esters and cellulose ethers and other cellulose derivatives. The cellulose derivatives may be modified by reacting the free hydroxyl groups contained therein with an organic reagent such as aldehydes, aldehyde-alcohol mixtures, organic diisocyanates, organic monoisocyanates, organic phosphorous halides, or by a sequence of modifications such as modification with an aldehyde followed by modification with an organic diisocyanate. Various modified cellulose ester and/or ether derivatives are set out in Martin et al. S.N. 687,284. Films of copolymers of vinyl chloride and vinylidene chloride may be used. Synthetic rubber-type membranes may also be employed. Because the aromatic hydrocarbon is more soluble in the permeation membrane than are the aliphatic and cycloaliphatic hydrocarbons, the aromatic hydrocarbons permeate through the membrane at a greater rate and thus the permeated portion of the charge mixture has a higher concentration of aromatics than does the charge mixture or the non-permeated portion of the charge mixture. Best results can be obtained by using a permeation membrane which has the highest selectivity for permeating aromatics in preference to other hydrocarbons at the highest possible rates, but the particular membrane used is not of critical importance so long as it performs the function of permeating aromatics in preference to other hydrocarbons. The permeation membrane employed should be as thin as possible and yet provide the required strength to withstand differential pressure across the permeation membrane which may be from 1 to 500 p.s.i.g. The membrane is a film usually less than 10 mils in thickness and suitably may be from 0.1 to 2 mils in thickness.

Permeation is a non-equilibrium process, i.e. the concentration of the hydrocarbons in contact with the charge side of the permeation membrane must be higher than the concentration of the hydrocarbons in contact with the permeate side of the membrane, or otherwise permeation will not occur. Non-equilibrium conditions are usually provided for by rapidly withdrawing the permeated portion from contact with the permeate side of the membrane. As to the physical conditions employed during permeation, the hydrocarbon distillate introduced into the charge or feed zone may be in the liquid state, and the permeated portion may be removed from the opposite side of the membrane in the vapor or liquid state, preferably in the vapor state; or the hydrocarbon distillate introduced into the feed zone may be in the vapor state and the permeated portion removed from the opposite side of the membrane also in the vapor state. Temperatures as high as the permeation membrane is capable of withstanding without rupturing due to thermal instability in the presence of the mixtures undergoing separation are generally employed, since the rate of permeation increases substantially as the temperature of permeation is increased. The permeation membrane is usually supported by a porous backing material to assist it in withstanding the pressure differential between the feed and the permeate zones.

The toluene-xylene fraction of hydroformate is passed by way of line 19, together with certain streams which are recycled and which will be discussed in detail later, into the charge zone 21 of permeation vessel 22. This stream is introduced at a temperature of about 250° F. and under sufficient pressure to maintain it in the liquid state. A modified cellulose acetate-butyrate membrane, denoted here as 23, of 0.5 mil thickness is used. The charge hydrocarbon distillate remains in charge zone 21 until approximately half of it has permeated through the membrane into permeate zone 24 which is maintained at a pressure of 25 mm. Hg abs. The first increment of the permeated distillate will have the greatest enrichment of aromatics, and subsequent increments of permeated distillate will have somewhat lower aromatic concentrations. The particular percentage of the charge distillate which is permeated through the membrane can be varied between about 5% or even less up to about 75% or even more, depending upon the concentration of the aromatics in the charge distillate and the concentration of aromatics desired in the permeated portion. In this embodiment the 50% of the charge distillate which is permeated through the membrane exists in permeate zone 24 in the vapor state and is rapidly withdrawn therefrom to maintain non-equilibrium conditions in the permeation vessel 22.

The permeated portion comprises 21.1 volumes and has an aromatics concentration of 87.5%. It is compressed and liquefied and passed by way of line 26 into fractionator 27. The permeated distillate charge to fractionator 27 is split therein into an overhead low boiling fraction and a bottoms high boiling fraction. The aromatics are present in a higher concentration in the bottoms fraction than in the overhead fraction. In carrying out this splitting operation, the greater the percentage of the charge to the fractionator which is taken overhead, the higher will be the concentration of aromatics in the bottoms fraction. As the percentage of the bottoms fraction is increased and the percentage of the overhead fraction is decreased the concentration of the aromatics in the bottoms fraction will gradually diminish but will at all times be higher than the concentration of aromatics in the permeated distillate sent to the fractionator. Therefore the splitting operating carried out in fractionator 27 may be adjusted to produce a bottoms fraction consisting of from 5 to 95% of the permeated distillate charged to the fractionator, the particular percentage of bottoms depending upon the concentration of aromatics desired in the bottoms fraction and the concentration of aromatics in the permeated distillate charged to the fractionator. In this embodiment 7.4 volumes of the permeated distillate are

taken overhead from fractionator 27. This overhead fraction contains 72% aromatics, and it is passed by way of line 28 into line 19 by which it is recycled as part of the charge to permeation vessel 22. The bottoms fraction, which comprises 13.7 volumes, contains somewhat more than 96% aromatics. It is removed from fractionator 27 and passed by way of line 29 to line 21. This bottoms fraction is thereafter blended with the 280–400° F. fraction of the hydroformate to produce 54.2 volumes of hydroformate containing 98% aromatics and having an octane number of 108.6 F–1 clear. By use of the present invention it is possible to produce higher yields of a given octane number hydroformate than by hydroforming the naphtha at a severity sufficient to produce the designated octane number. To illustrate, naphtha can be hydroformed under high severity conditions and then fractionated to recover a higher boiling portion having this same octane number of 108.6 F–1 clear, but the yield based upon naphtha charged to the hydroformer is only 51.2 volume percent whereas by use of the present invention the yield is 54.2 volume percent based upon naphtha charged to the hydroformer. The present invention also segregates portions of the hydroformate having low aromatic contents which may be further processed to increase their octane number and then blended into the 108.6 F–1 clear naphtha.

Referring to permeation vessel 22, the non-permeated portion of the hydroformate is withdrawn therefrom and passed by way of valved line 31 into the charge zone 32 of a second permeation stage depicted here as permeation vessel 33. This stream comprises 21.1 volumes and contains 53% aromatics. The permeation conditions employed in this second permeation stage are the same as those described for the first permeation stage carried out in permeation vessel 22, except that approximately two-thirds of the charge to permeation vessel 33 is permeated rather than 50% as in permeation vessel 22. The portion of the charge mixture which permeates through the membrane 34 into permeate zone 36 is removed rapidly therefrom, liquified, and passed by way of line 37 into line 19 by which it is recycled as a portion of the charge to the first permeation stage depicted here as permeation vessel 22. This permeated portion which is recycled consists of 13.7 volumes and has an aromatics content of 72%. The non-permeated portion withdrawn from permeation vessel 33 consists of 7.4 volumes and has an aromatics content of 17.7%. It is passed by way of line 38 to line 16 wherein it is blended with the C₅–190° F. fraction of reformate. Blending of these streams produces 26.8 volumes of hydroformate having an aromatics content of 9.2%. This low octane blend can be hydroformed to improve its octane number, or portions of the blend can be isomerized or otherwise processed to improve the octane number. While approximately two-thirds of the charge to the second permeation stage was permeated, the amount which is permeated can be varied between about 5% or less up to 75% or even more, depending upon the degree of enrichment in aromatics concentration desired in the permeated portion.

In place of the second permeation stage, the non-permeated portion of the hydroformate from the first permeation stage can be subjected to distillation to separate it into lower and higher boiling fractions. The higher boiling fraction will have a higher concentration of aromatics than the charge to the distillation step, and the lower boiling fraction will have a lower concentration of aromatics than the charge to the distillation step. In this embodiment the non-permeated portion of hydroformate from permeation vessel 22 may be passed by way of valved line 39 into distillation tower 41. The splitting operation may be adjusted to produce a bottoms stream containing about 72% aromatics and an overhead stream containing a lower concentration of aromatics than is present in the charge stream in line 39. The bottoms stream may be passed by way of line 42 to line 19 by which it is returned

to permeation vessel 22. The overhead stream is removed by way of line 43 and may be blended with the C₅–190° F. fraction of hydroformate. If desired, the distillation tower 41 may be operated so as to remove from 5% or less up to 95% or more overhead. The greater the percentage of the charge which is removed overhead, the higher will be the concentration of aromatics in the bottoms fraction. The operation and functioning of distillation tower 41 is thus similar to distillation tower 27.

Distillation towers 27 and 41 need not be highly efficient fractionating units as a general rule. Because of this, a distillation effect can be obtained by operating permeation vessel 22 under conditions of temperature and pressure so that a portion of the permeate exists in the liquid state and a portion exists in the vapor state. Each of the portions are separately and rapidly withdrawn from permeate zone 24 to prevent the permeation process from reaching equilibrium on opposite sides of the membrane. At a given permeation operating temperature, the pressure in permeate zone 24 may be increased to cause increasing amounts of permeated distillate to exist in the liquid state in permeate zone 24. By suitable adjustment of the pressure the permeate can be split into a vapor portion comprising between 5 and 95% of the permeate and a liquid portion and thus achieve an effect similar to the use of a distillation tower. If desired, permeation vessel 33 of this embodiment may be operated in this manner to obtain a fractionating effect upon the permeate. It is obvious that a number of permeation stages followed by one or more distillation stages, or a number of consecutive permeation and distillation steps can be arranged in practicing this invention.

While the illustrated embodiment of the invention employs a specific fraction of hydroformate as the charge distillate to the invention, it is obvious that the total hydroformate or different fractions thereof may be so processed. Similarly, other naphtha such as catalytic naphtha or fractions thereof, virgin naphtha, thermally cracked naphtha, etc. may be processed to segregate high octane fractions from low octane fractions or to recover substantially pure aromatic fractions. Hydrocarbon distillates boiling above the naphtha boiling range may also be processed to produce fractions having increased concentrations of aromatics. Thus fuel oil fractions such as kerosene, gas oils, catalytic cycle oils and the like may be employed as the hydrocarbon distillate charge to this invention to segregate such distillates into fractions of higher and lower aromatics content. Such stocks are thereby improved for use as fuel oils or as cracking stocks and at the same time high aromatics fractions useful for other purposes are recovered. Hydrocarbon distillates boiling up to about 600–700° F. may be employed in this invention. Besides petroleum distillates, hydrocarbon distillates obtained from the refining of coal tar, shale oil, hydrogenation of coal or coke, etc. may be processed to recover the aromatics therefrom.

Illustrative of the invention are certain experiments which were carried out. A hydroformed naphtha was fractionated to recover a 200–400° F. fraction containing about 80% aromatics. This fraction was segregated by a combination of permeation and distillation into a fraction containing 95% aromatics (70 volume percent yield) and a fraction containing 51% aromatics (30 volume percent yield). This latter fraction was then charged to a permeation vessel and approximately one-half of it was permeated and had an aromatics content of 77% by volume. The non-permeated portion (also called the permeant) had an aromatics content of 28% by volume. The permeate and the permeant fractions were then distilled on a 35 tray Oldershaw column at 10:1 reflux ratio.

Attached Figure 2 represents in schematic form the permeation apparatus employed in the experiments. It consisted of a box-like feed chamber 51 for the charge distillate introduced therein: a smaller size membrane holder 52 of box-like shape having five open faces across

which the permeation membranes 53 are sealed, the sixth face having sealed thereto a line 54 for removing the portion of the distillate which permeates through the membranes into the interior (permeate zone 56) of the membrane holder. The entire membrane holder was positioned within feed chamber 51. Pump 57 passed the charge mixture (which had been heated to the desired permeation operating temperature) through line 58 into feed chamber 51 until the liquid level of the charge mixture was substantially above membrane holder 52. The permeated portion was continuously withdrawn from permeate zone 56 through line 54 by means of vacuum pump 59. Manometer 61 and pressure regulating valve 62 were used to measure and regulate the pressure in permeate zone 56. The total surface area provided by the membranes was approximately 22 sq. in. In the permeation experiments the distillate charged to the feed chamber was maintained at a temperature of about 250° F. while employing pressure sufficient to maintain distillate in the liquid state in the feed chamber. The permeate zone was maintained at about 25 mm. Hg abs.

The permeation membrane used in the experiments was a modified cellulose acetate-butyrate membrane. It was prepared by dissolving 30 gm. of cellulose-butyrate (AB-504-40), which had 1.00 free hydroxyl groups per anhydroglucose molecule, 0.50 acetyl group and 1.5 butyryl groups per anhydroglucose molecule, in 320 ml. dioxane and heating to about 135° F. Three ml. of concentrated HCl diluted to 10 ml. with dioxane was added followed by the addition of 19.5 gm. of 2-ethylhexaldehyde dissolved in 50 ml. of dioxane. The reaction mixture was then heated at 135° F. for one hour. Thereafter it was diluted with 300 ml. of ethanol, and then a 60-40 ethanol-water mixture was added to cause the cellulosic polymer to precipitate from the solution in the form of a gel. Excess liquid was removed from the gel and the latter was then air dried. 2.66 gm. of the air dried material was dissolved in 40 ml. of dry dioxane. Three drops of N-methylmorpholine and 0.055 gm. of 2,4-tolylene diisocyanate were added and the mixture was heated at 150° F. for 0.5 hour. Films of 0.5 mil thickness were cast from this solution onto steel panels and cured under heat lamps for about one hour. Thereafter the aldehyde-diisocyanate modified cellulose ester films were removed and used.

Distillation of the permeated and non-permeated portions of hydroformate revealed various fractions thereof to have the compositions shown in Table 1 and Table 2.

TABLE 1
Distillation of permeated hydroformate

Overhead Temp., ° F.	Overhead Fractions		Bottoms Fractions	
	Vol. Percent Overhead	Percent Aromatics in Overhead	Vol. Percent Bottoms	Percent Aromatics in Bottoms
Charge.....	0	-----	100	77.2
226-230.....	19.6	31.4	80.4	88.3
233-235.....	39.5	56.6	60.5	90.7
239-250.....	59.5	65.3	40.5	94.6
286.....	74.5	70.6	25.5	96.4

TABLE 2
Distillation of non-permeated portion of hydroformate

Overhead Temp., ° F.	Overhead Fractions		Bottoms Fractions	
	Vol. Percent Overhead	Percent Aromatics in Overhead	Vol. Percent Bottoms	Percent Aromatics in Bottoms
Charge.....	0	-----	100	2.80
153-210.....	20.4	5.2	79.6	33.7
210-244.....	40.9	12.8	59.1	38.3
244-277.....	61.3	11.7	38.7	53.5
277-286.....	76.6	19.7	23.4	54.6

The above tables show the bottom fractions to contain ever increasing concentrations of aromatics as larger amounts are taken overhead.

A heavy fraction of catalytic naphtha having an ASTM boiling range of 212-340° F. 90% FBP and an octane number of 93.8 F-1 clear was employed as a charge distillate to a combination of permeation and distillation steps. A permeation operating temperature of 340° F. and a permeate pressure of 200 mm. Hg abs. were used. The permeation membranes were 0.3 mil thickness cellulose acetate-butyrate modified by reaction with formaldehyde and then tolylene diisocyanate. The same general procedure was employed in making these films as discussed previously except that the cellulose acetate-butyrate was AB-381-0.5 which contained 1.0 acetyl group, 1.67 butyryl groups, and 0.33 free hydroxyl group per anhydroglucose unit. Both 5 and 15% portions of the heavy catalytic naphtha were permeated and thereafter distilled in a 15 tray Oldershaw column at a 10:1 reflux ratio. Octane numbers (F-1 clear) of the catalytic naphtha charged to the permeation vessel, the permeated portions, and the distilled permeated portions were determined and are reported in Table 3 which follows.

TABLE 3
Permeation and distillation of catalytic naphtha

Material	Percent of Naphtha Permeated	Permeate Distilled	Octane Number F-1 Clear
Cat. Naphtha.....	-----	-----	93.8
Permeate.....	5	None.....	97.9
		60% Overhead.....	95.3
		40% Bottoms.....	101.6
Permeant (85%).....	15	None.....	97.6
		60% Overhead.....	95.1
		40% Bottoms.....	101.1
			92.6

Illustrating the ability of the present invention to produce substantially pure aromatics from a mixture thereof with other hydrocarbons is the following experiment. A naphtha fraction boiling over the range of 208-232° F. which contained 47.6 volume percent toluene, 3-4% olefins and about 50% saturated hydrocarbons was used as the charge distillate. An aldehyde-diisocyanate modified cellulose acetate-butyrate membrane of the type previously discussed was employed as the permeation membrane. The permeation temperature was 340° F. Charge distillate in the feed chamber was maintained in the liquid state. The permeate pressure was maintained at 400 mm. Hg abs. until about 32% of the charge distillate had permeated and it was then increased to 700 mm. Hg abs. As the hydrocarbons permeated through the membrane they were collected in six individual fractions. The cumulative volume of permeate and the cumulative concentration of toluene in the permeated fractions was determined, as was also the concentration of toluene in the permeant fractions corresponding to the permeate fractions. This information is presented in Table 4 which follows.

TABLE 4
Permeation of toluene cut

Fraction Nos. Collected	Permeate Fractions		Permeant Fractions	
	Vol. Percent Permeated	Vol. Percent Toluene	Vol. Percent Permeant	Vol. Percent Toluene
Charge.....	0	-----	100	47.6
1.....	9.9	63	90.1	45.9
2.....	18.6	65.3	81.4	43.6
3.....	25.2	65.3	74.8	41.7
4.....	31.6	65.2	68.4	39.5
5.....	39.5	64.0	60.5	37.0
6.....	46.9	62.5	53.1	34.5

The permeate fractions collected were then combined (46.9 volume percent of the charge distillate to the permeation vessel) and distilled in a 20 plate Oldershaw column at a 5:1 reflux ratio. 10% cuts were taken overhead, the cuts combined with the preceding cuts, and the concentration of toluene measured. The concentration of toluene in the remaining bottoms fraction after each cut was taken overhead, was also determined. These results are shown in Table 5 which follows.

TABLE 5

Distillation of 47% permeated toluene cut

Overhead Temp., ° F.	Overhead Fractions		Bottoms Fractions	
	Vol. Percent Overhead	Percent Toluene in Overhead	Vol. Percent Bottoms	Percent Toluene in Bottoms
Charge	0	—	100	62.5
201-208	10	7.5	90	69.0
208-210	20	9.5	80	76.2
210-214	30	12.3	70	84.5
214-225	40	17.3	60	93.3
225-228	50	29.3	50	96.4
228-230	60	39.2	40	98.4
230-232	70	47.1	30	99.5
232	80	53.6	20	100

It is apparent from the above that essentially pure toluene, or whatever degree of purity is desired, can be recovered from a mixture thereof with close boiling non-aromatic hydrocarbons.

Thus having described the invention what is claimed is:

1. A process which comprises contacting a distillate charge aromatics-containing hydrocarbon mixture having a definite boiling range with one side of a plastic permeation membrane which preferentially permeates aromatics and non-aromatics separable therefrom by distillation, permeating a portion of the charge mixture through said membrane, said permeated portion comprising aromatics and reduced concentration of closely boiling non-aromatics, separately recovering permeated and non-permeated portions having higher and lower concentrations of aromatics respectively than the charge mixture, and distilling the permeated portion to separate a lower boiling fraction from a higher boiling fraction which higher boiling fraction has a higher concentration of aromatics than the permeated portion which is passed to the distillation step and a higher concentration of aromatics than could be obtained by only distilling the distillate charge.

2. The process of claim 1 wherein the non-permeated portion is distilled to separate a lower boiling fraction from a higher boiling fraction, the latter fraction having a higher concentration of aromatics than the non-permeated portion passed to the distillation step.

3. The process of claim 1 wherein the charge mixture boils within the naphtha boiling range.

4. The process of claim 1 wherein the charge mixture is reformed naphtha.

5. The process of claim 1 wherein the charge mixture is catalytically cracked naphtha.

6. The process of claim 1 wherein the charge mixture is a narrow boiling distillate rich in aromatic hydrocarbons having a specific number of carbon atoms per molecule.

7. A process which comprises splitting a reformed naphtha into a benzene and lower boiling fraction, an intermediate toluene-xylene fraction, and a higher boiling fraction containing C_9 and higher boiling aromatics, charging the intermediate toluene-xylene fraction in the liquid state to the first of a series of permeation vessels comprised of charge and permeate zones that are separated from each other by permeation membranes which preferentially permeate aromatics, permeating a portion of the charge mixture through the permeation membrane

into the permeate zone from which it is rapidly removed in the vapor state, said permeated portion having a higher concentration of aromatics than is present in the charge to the first permeation vessel and lower concentration of

8. In a permeation process wherein a hydrocarbon distillate containing both aromatic and non-aromatic components is separated by permeation through a plastic permeation membrane which preferentially permeates aromatics and non-aromatics separable therefrom by distillation, the permeated portion comprising aromatics and reduced concentration of closely boiling non-aromatics, the improved operating technique which comprises maintaining a temperature and pressure on the permeated hydrocarbons downstream of the membrane for effecting vaporization of all non-aromatic hydrocarbon permeate and liquefaction of substantially pure aromatics and thus effecting separation of said substantially pure aromatics by combined permeation and distillation.

9. A process for treating hydroformed naphtha, which process comprises distilling said hydroformed naphtha to obtain a high boiling stream consisting almost entirely of aromatics and a distillate stream containing a mixture of aromatics with other hydrocarbons, permeating a portion of the distillate stream through a non-porous plastic membrane to obtain a first permeate which is higher in aromatics content and lower in closely boiling non-aromatics content than the original distillate stream, withdrawing a non-permeated portion, distilling the first permeate to obtain a bottoms fraction consisting essentially of aromatic hydrocarbons and an overhead fraction which contains a lower percentage of aromatics than the first permeate and combining said bottoms fraction with said high boiling stream.

10. The method of claim 9 which includes the step of passing the non-permeated portion from which first permeate was separated through a second permeation zone and therein obtaining a second permeate and combining said second permeate with said distillate stream.

11. The method of claim 9 which includes combining said overhead fraction with said distillate stream.

12. The method of claim 9 which includes the steps of combining the overhead fraction with the distillate stream and also combining with said distillate stream a second permeate obtained by permeation of the non-permeated portion separated from first permeate.

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