Nov. 23, 1954 J. H. ARNOLD 2,695,323

PRODUCTION OF PARA XYLENE

Original Filed April 26, 1947 4 Sheets-Sheet 1

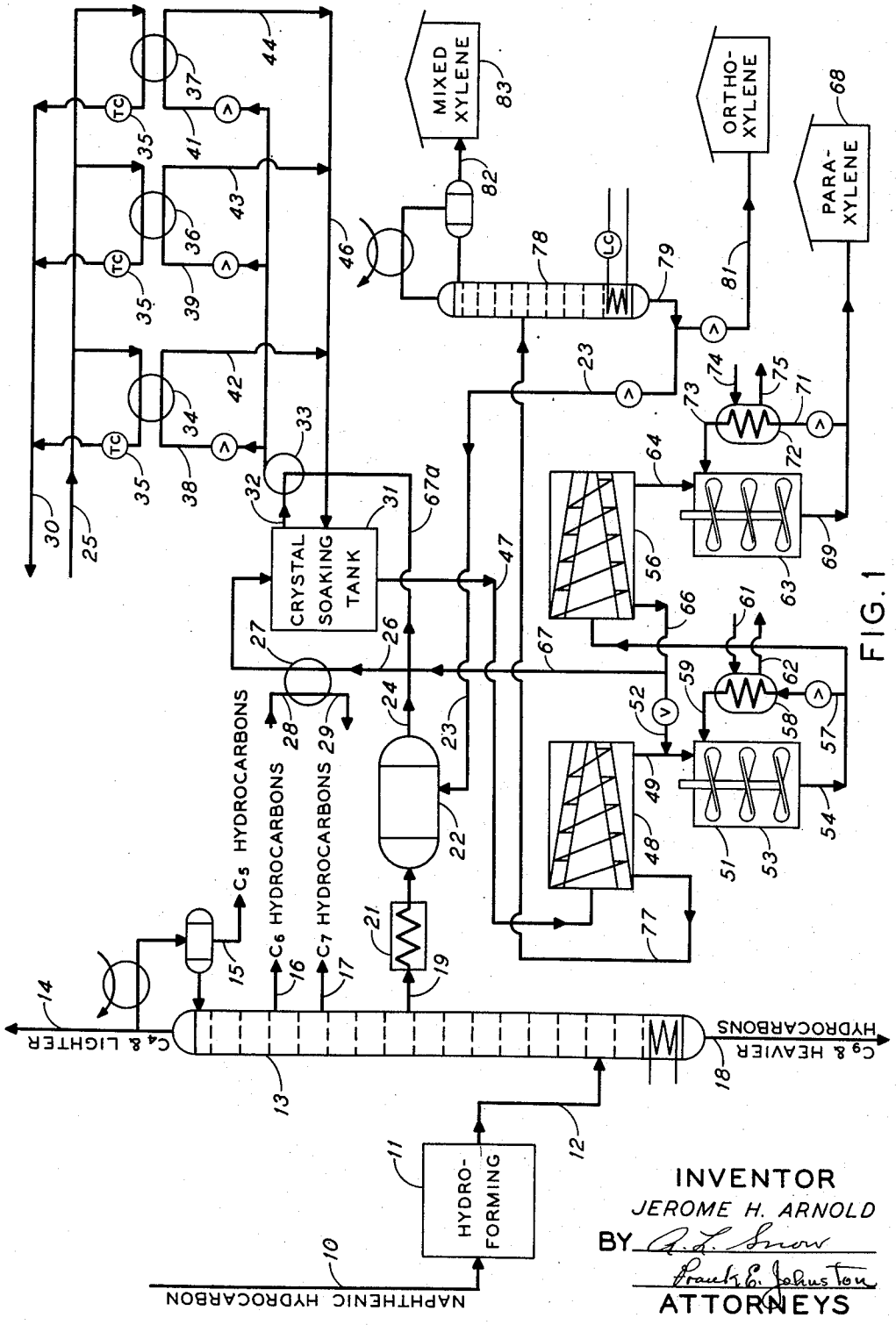



FIG. 1

INVENTOR
JEROME H. ARNOLD
BY A. L. Snow
Frank E. Johnston
ATTORNEYS

Nov. 23, 1954 J. H. ARNOLD 2,695,323

PRODUCTION OF PARA XYLENE

Original Filed April 26, 1947 4 Sheets-Sheet 2

FIG. 2

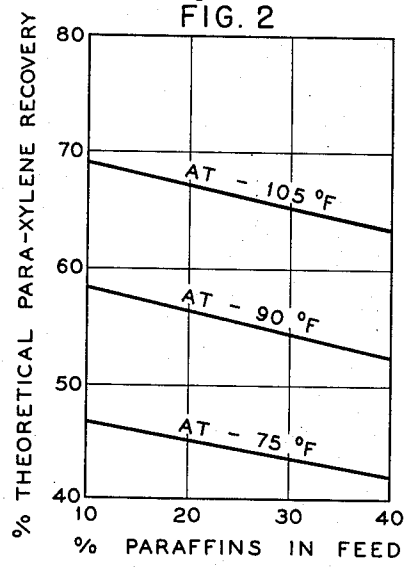



FIG. 3

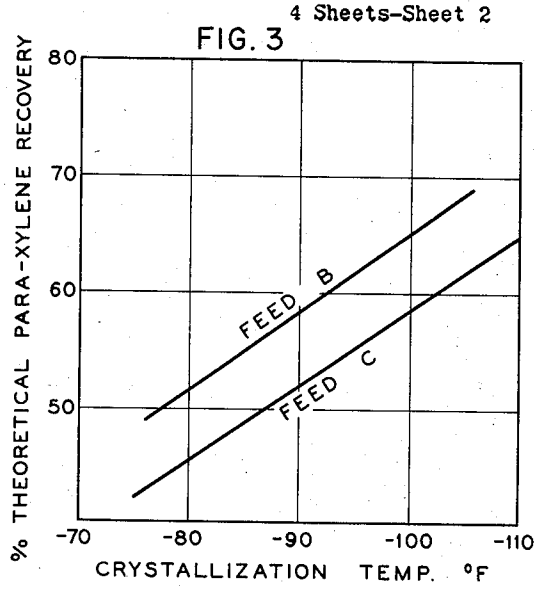



FIG. 4

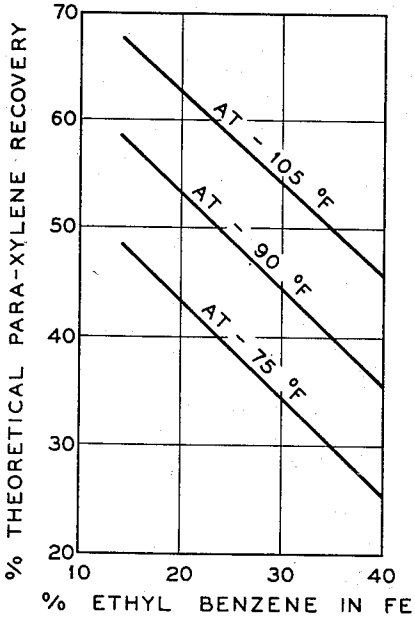
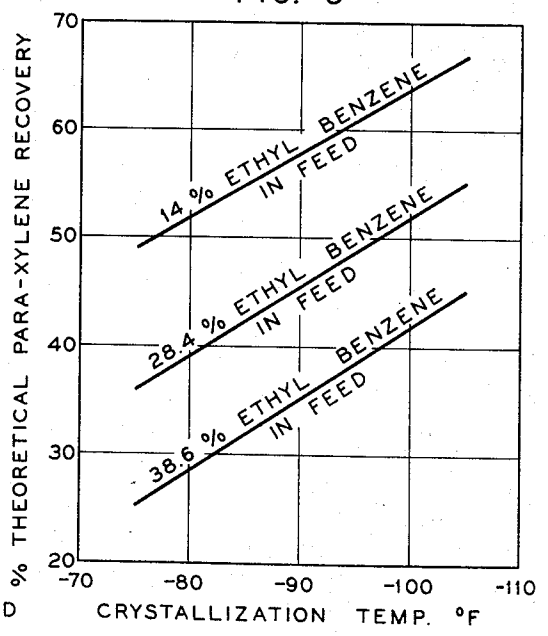



FIG. 5




INVENTOR
JEROME H. ARNOLD
BY O. L. Snow
Frank E. Johnston
ATTORNEYS

Nov. 23, 1954 J. H. ARNOLD 2,695,323

PRODUCTION OF PARA XYLENE

Original Filed April 26, 1947 4 Sheets-Sheet 3

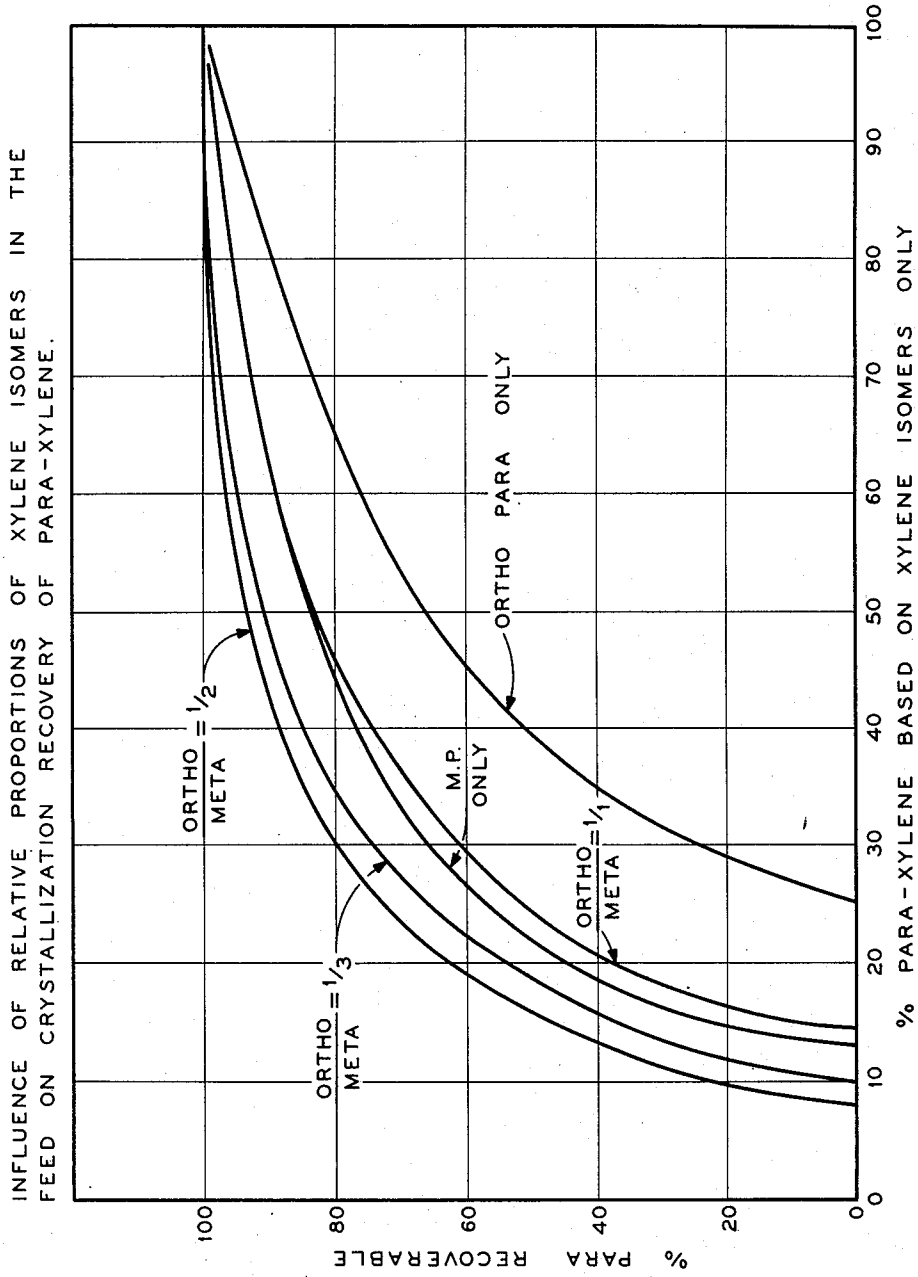



FIG. 6

INVENTOR
JEROME H. ARNOLD
BY R. L. Snow
Frank E. Johnston
ATTORNEYS

Nov. 23, 1954 J. H. ARNOLD 2,695,323

PRODUCTION OF PARA XYLENE

Original Filed April 26, 1947 4 Sheets-Sheet 4

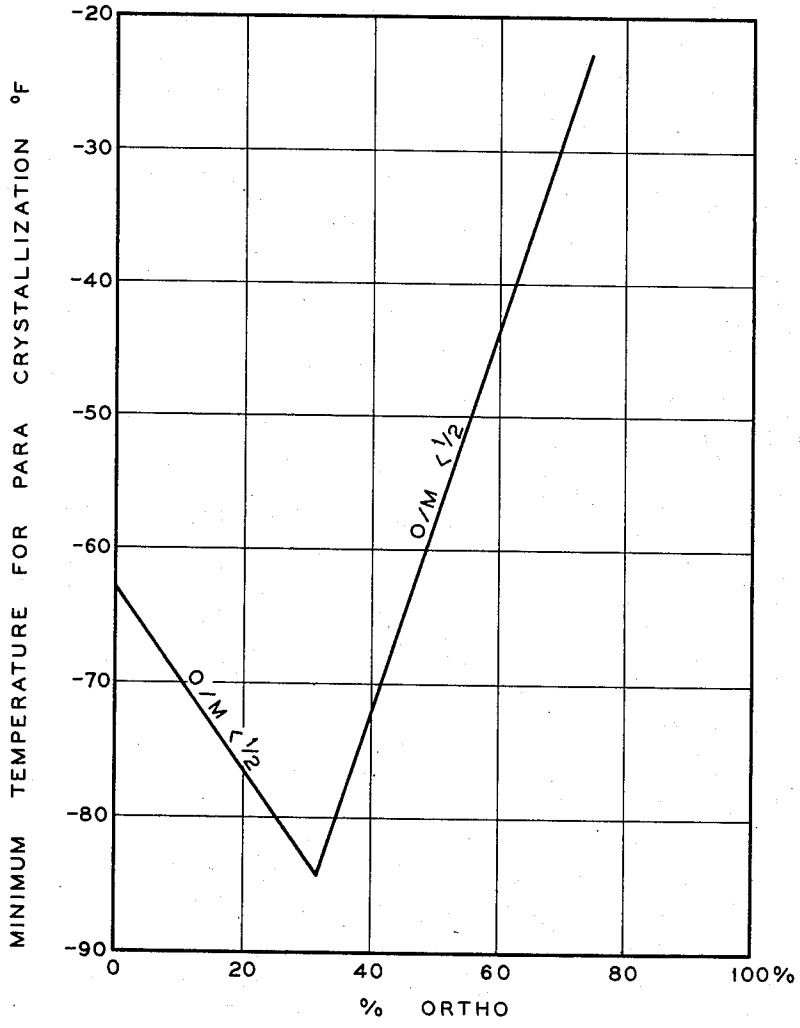



FIG. 7

INVENTOR
JEROME H. ARNOLD
BY A. L. Snow
Frank E. Johnston
ATTORNEYS

United States Patent Office

2,695,323

Patented Nov. 23, 1954



2,695,323

# PRODUCTION OF PARA XYLENE

Jerome Howard Arnold, Albany, Calif., assignor to California Research Corporation, San Francisco, Calif., a corporation of Delaware

Original application August 26, 1947, Serial No. 770,587. Divided and this application January 16, 1951, Serial No. 206,278

3 Claims. (Cl. 260—674)

This invention relates to the recovery of para xylene from a xylene rich fraction consisting essentially of a complex mixture of xylenes with aromatic and non-aromatic hydrocarbons boiling in the same range as the para xylene. More particularly, the invention involves the production of para xylene from a mixture of non-aromatic petroleum hydrocarbons.

This application is a division of application Serial No. 770,587, filed August 26, 1947, now United States Patent No. 2,541,682.

A complex hydrocarbon fraction with which the present invention is concerned primarily and from which para xylene may be recovered, typically contains only a minor proportion of para xylene. The proportion of para xylene in such mixtures seldom is more than 30% by volume and usually is less than about 21% by volume of the hydrocarbon fraction but should be more than about 10% of the xylenes present in the mixture. The major portion of the mixture comprises aromatic hydrocarbons boiling within 11° F. of the para xylene and including from at least about 5% up to as much as 20% or more of ethyl benzene based on the entire hydrocarbon fraction. The ethyl benzene content may be from 50 to 100% by volume of the para xylene content. Of these aromatic hydrocarbons at least about 50% by volume of the xylenes in the fraction is meta xylene, with minor amounts of ortho xylene not exceeding about 20% by volume. Additionally, the xylene fraction usually contains at least about 5% and up to 20% or more (based on the entire hydrocarbon fraction) of unsulfonatable hydrocarbons of unknown constitution, generally identified as paraffinic, which may boil as much as 50° F. below the para xylene and not more than about 20° F. above the para isomer. These paraffinc hydrocarbons may be present in amounts of from 25 to 100% by volume based on the para xylene content and include acyclic saturated hydrocarbons which either boil within the range or form constant boiling mixtures with the xylenes. Examples of such paraffinic hydrocarbons are various isomeric octanes and nonanes. The presence of cyclic paraffins, i. e., naphthenes boiling from 50° F. below to 20° F. above para xylene is not precluded.

An analysis of a xylene fraction typifying the above discussed composition is:

| Hydrocarbon: | Per cent by volume |
|---|---|
| Ortho xylene | 12 |
| Meta xylene | 48 |
| Para xylene | 18 |
| Ethyl benzene | 9 |
| Paraffins and/or naphthenes | 13 |

Characteristic boiling ranges of xylene fractions with which this invention deals are from 230° F. to about 300° F., more desirably boiling within the range of from 270 to about 300° F. and preferably within the range of from 270 to about 290° F.

The foregoing specific example has the following boiling range characteristics in an ASTM–D–86 distillation:

| Initial: | Temperature, ° F. |
|---|---|
| 5 | 272 |
| 10 | 274 |
| 20 | 275 |
| 30 | 275 |
| 40 | 275 |
| 50 | 276 |
| 60 | 276 |
| 70 | 276 |



| Initial: | Temperature, ° F. |
|---|---|
| 80 | 276 |
| 90 | 278 |
| 95 | 279 |
| End point | 314 |

The recovery of para xylene from such complex mixtures is not simple, since the presence of not only the isomeric xylenes but also paraffins and aromatics isomeric to the xylenes, particularly of ethyl benzene, complicate and obscure the purification problem. Methods for recovering para xylene from its isomers have been proposed and prior proposals are of two general types, each of which has significant disadvantages and high cost factors. One type of proposal has involved extensive chemical alteration of one or more of the hydrocarbon components in the xylene system to afford elimination and separation of the components. Such methods involve relatively expensive chemical conversions with attendant loss and normally require reconversion of the resulting chemical derivatives back to the desired hydrocarbon with additional loss at this stage as well as an overall useless consumption of chemical treating agent. Alternatively, physical methods heretofore proposed have recognized the complicating and obscure effects of aromatic and non-aromatic hydrocarbons in the xylene fraction and have attempted to solve this problem by removal thereof.

Spannagel Patent No. 1,940,065 allegedly recovers para xylene by crystallization but first purifies the xylene fraction by distilling off "any aliphatic hydrocarbons, ethyl benzene and the like, boiling below para and meta xylene," to avoid the complicating effects of these impurities. In this patent ortho xylene also is removed and an intermediate meta, para xylene cut boiling from 136–140° C., and evidently free of complicating hydrocarbon impurities, is utilized in the crystallization step. Thus, in prior processes it appears that there has been an attempt to avoid unpredictable, obscuring and complicating effects of ethyl benzene by removal thereof as well as elimination of aliphatic hydrocarbon impurities. These purification treatments require extensive, elaborate and costly equipment particularly in the elimination of ethyl benzene by distillation.

Reference also has been made to the use of technically pure xylene of commerce for the separation of ortho, meta and para xylenes. As distinguished from crude xylenes the "pure" xylenes of commerce contain no more than 3% and usually less than 1% of paraffins boiling within the range of from 279 to 285° F. Likewise, the ethyl benzene content of "pure" xylenes of commerce sometimes called "technically pure" is less than 15%.

Contrary to the apparent beliefs of those skilled in the art, it has been discovered that para xylene can be recovered in relatively good purity by crystallization from ortho and metal xylenes in the presence of from 5 to 20% or more by volume of ethyl benzenes as well as in the additional presence of from 5 to 20% or more paraffins boiling within the range of from 230 to 300° F.

The unpredictability of this discovery can be better appreciated when it is noted that these hydrocarbons not only alter the crystallization temperature of para xylene by solvent action but that para xylene forms binary, ternary and quaternary crystals with various of the components and that the various components likewise form such complex crystals and eutectic mixtures with each other. The complexity and unpredictability of the system is illustrated by the following list of crystal types in the four-component system—ethyl benzene, ortho, meta, para xylene:

Para, ortho, xylene binary
Para, meta, xylene binary
Ortho, meta, xylene binary
Ortho, meta, para xylene ternary
Para xylene, ethyl benzene binary
Para xylene, ortho xylene, ethyl benzene ternary
Para xylene, metal xylene, ethyl benzene ternary
Ortho xylene, meta xylene, ethyl benzene ternary
Ortho xylene, ethyl benzene binary
Meta xylene, ethyl benzene binary
Para xylene, ortho xylene, meta xylene, ethyl benzene quaternary

The foregoing list of course is an oversimplification, since it ignores the obscuring effects of the multi-component paraffinc portion of the xylene fraction.

According to the present invention, in brief, para xylene is separated from the above-described xylene-rich hydrocarbon mixtures by chilling to a temperature of from —75° F. to —120° F., preferably from —80° F. to —110° F. and more desirably to a temperature below —80° F. and just above that represented by one of the following equations:

(1) When the ortho xylene content is less than about one-half the percentage of the meta xylene:

$$T_2 = -62° F. - 0.3X - 1.4Y - 0.65Z$$

where $T_2$ equals minimum temperature in ° F., X equals per cent paraffins in feed, Y equals per cent ethyl benzene in feed and Z equals per cent ortho xylene in feed.

(2) When the ortho xylene content is greater than one-half the percentage of meta xylene:

$$T_2 = -84.5° F. - 0.3X - 1.4Y + 1.3\ (Z-33)$$

where $T_2$ equals minimum temperature in ° F., X equals per cent paraffins in feed, Y equals per cent ethyl benzene in feed and Z equals per cent of meta xylene in the feed.

(3) When the ortho xylene content equals one-half the percentage of meta xylene:

$$T_2 = -84.5° F. - 0.3X - 1.4Y$$

where $T_2$ equals minimum temperature in ° F., X equals per cent paraffins in feed and Y equals per cent ethyl benzene in feed.

In practicing the invention in its preferred embodiment, para xylene is produced and recovered from non-aromatic petroleum hydrocarbons. A suitable xylene fraction is obtained by aromatization, preferably by the so-called hydroforming process in which a naphthenic petroleum fraction is aromatized and xylenes are produced. This type of process is well-known in the petroleum industry. However, because the chemistry involved and the mixtures obtained are extremely complex, careful coordination of feed stocks and hydroforming conditions is necessary to obtain best results and to yield a preferred xylene fraction for recovery of para xylene in accordance with this invention.

The present invention is particularly adapted to the treatment of an equilibrium xylene mixture from hydroformed non-aromatic petroleum fractions. The term "equilibrium xylene mixture" is here utilized to designate a xylene fraction containing ortho, meta and para xylenes in the equilibrium proportions resulting from hydroforming or other suitable aromatization process, that is, in which the relative proportions are about o:m:p::2:6:2. The additional ethyl benzene and paraffins hereinbefore described are also present. Although, the invention is particularly adapted to the treatment of this specific type of mixture, it will be understood that the invention is also applicable to other xylene fractions of the compositions hereinbefore described. To avoid prolixity, the remainder of this description will be made with reference to xylene fractions derived from hydroforming operations.

In order to produce para xylene from non-aromatic petroleum hydrocarbons, proper selection of feed stocks and aromatizing conditions is important and essential to the most successful practice of the invention.

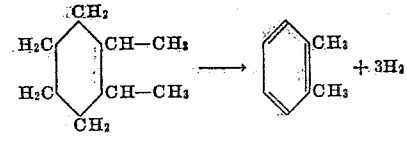
## FEED STOCKS

Naphthenic hydrocarbon mixtures from naphthene-type petroleum crude oils comprise one preferred type of feed stock. Such mixtures are normally termed "straight run distillates" in the petroleum industry, although other aromatizable hydrocarbons or distillates may be substituted therefor. The hydrocarbons present in this preferred feed stock are believed to consist largely of cyclo-aliphatic hydrocarbons with six carbon atoms in the cyclo-aliphatic ring and with aliphatic side chains attached to the ring. Some five and seven carbon atom cyclo-aliphatic rings may be present. Both the number of side chains and the length of each chain attached to the foregoing rings vary among the many compounds normally present in a petroleum hydrocarbon mixture. In general, these variables are a function of the average molecular weight or, more particularly, the boiling range and distillation curve of the petroleum fraction. A naphthenic hydrocarbon mixture consisting essentially of hydrocarbons having from six to twelve carbon atoms in the molecule and preferably composed at least predominantly of hydrocarbons containing from seven to eight carbon atoms at present is regarded as a more desirable feed stock. The fraction selected desirably should boil within the range of from about 180° F. to about 420° F. and preferably from about 180° F. to about 320° F. In some instances an even more narrow cut boiling from 230° F. to 275° F. is preferred. Open chain paraffinic hydrocarbon fractions of these boiling ranges are not precluded.

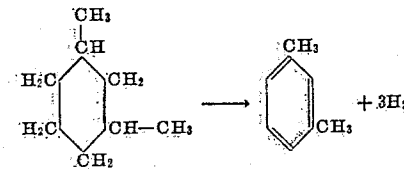


## AROMATIZATION

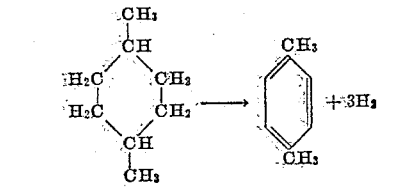
As previously set forth, an initial step in the exemplary process comprises aromatization of the particular petroleum feed stock selected. Where a naphthenic hydrocarbon mixture is utilized, the conversion of hydrocarbons to aromatics is believed to occur by dehydrogenation of the six carbon atom rings from cycloaliphatic to aromatic while leaving alkyl groups attached to the residual nucleus. For example:



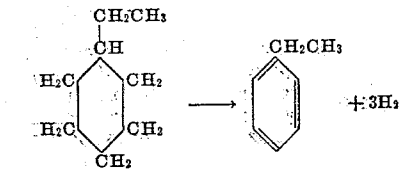

Ortho dimethyl cyclohexane




Meta dimethyl cyclohexane



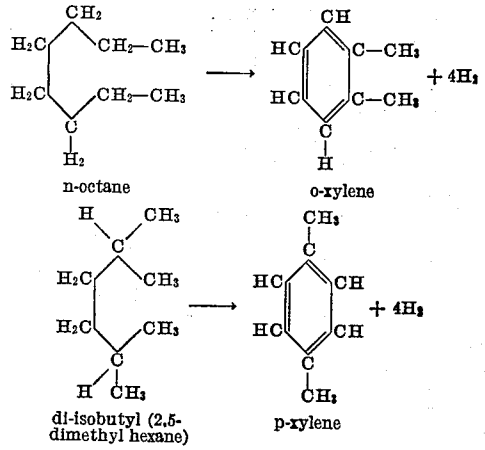

Para dimethyl cyclohexane




Ethyl cyclohexane

Isomerization of any $C_7$ alicyclic rings present and dehydrogenation to aromatic compounds also is believed to occur. Likewise, $C_5$ alicyclic rings containing side chains are converted to aromatics by isomerization and dehydrogenation. These various reactions represent an over-simplification of the aromatization reactions which may actually occur, since de-alkylation and shortening of side chains as by cracking undoubtedly take place. In any event, the aromatization reaction product comprises a highly complex mixture of aromatics and also contains non-aromatic hydrocarbons, such as saturated or unsaturated paraffins and naphthenes. The overall complexity of the mixture and the relative proportion of the above-mentioned non-aromatic components depend upon the effectiveness of the particular aromatization process as well as upon the specific hydrocarbon feed stock selected. It is for this reason that a highly naphthenic hydrocarbon feed stock boiling within the ranges previously disclosed are preferred, since the reaction products therefrom are better adapted to subsequent processing steps involved in the production of isomeric xylenes. However, it is possible, but less desirable, to obtain operative aromatic fractions from open chain paraffinic hydrocarbons by known

reactions, such as dehydrogenation and cyclization illustrated by the following reactions:




Processes for effecting such aromatization reactions and catalysts therefor are known in the petroleum art. Likewise, aliphatic olefins are convertible to aromatics by known cyclization and dehydrogenation reactions similar to the foregoing. These various known processes may be utilized within the broader aspects of this invention and are embraced within the term "aromatization" as used in the present specification.

The preferred aromatization process known as "hydroforming" is characterized by aromatization in the presence of controlled amounts of hydrogen and a vanadium oxide or molybdenum oxide catalyst. As an example of the preferred process, a hydrocarbon feed, such as a naphthenic petroleum distillate, boiling within the range of 180° F. to 320° F., and obtained, for instance, by fractional distillation of a crude petroleum (from Kettleman Hills Oil Field in California) is passed at from about 900° F. to about 1200° F., desirably about 1000° F., over a vanadium oxide-alumina or molybdenum oxide-alumina catalyst. Space rate desirably is from 0.1 to about 2.0 volumes of liquid hydrocarbon feed per volume of catalyst per hour, and it is preferred to maintain a partial pressure of hydrogen in the reaction zone of from about 30 to about 300 pounds per square inch. The reaction product from such a hydroforming operation will contain not only the desired xylenes and additional aromatic hydrocarbon but also aliphatic hydrocarbons boiling over a wide range, including $C_4$ and like materials. Initially, therefore, it is necessary to recover a xylene fraction from this reaction mixture.

In the drawing, Fig. 1 is a schematic flow sheet of a typical process and suitable apparatus for practicing the process of this invention.

Figs. 2 and 3 illustrate graphically the effect of paraffins upon crystallization temperature and recovery of para xylene.

Figs. 4 and 5 illustrate the effect of ethyl benzene on crystallization temperature and recovery of para xylene; and

Fig. 6 reveals the influence of relative proportions of the xylene isomers on crystallization recovery of para xylene.

Fig. 7 shows the effect of ortho xylene concentration on optimum crystallization temperatures and at different ratios of ortho to meta xylenes.

Referring to Fig. 1 of the drawing, a naphthenic hydrocarbon feed is introduced by way of line **10** to a hydroforming unit **11** and non-aromatic petroleum hydrocarbons such as the naphthenic petroleum distillate boiling within the range of 180–320° F., as previously described, is converted to a complex aromatic hydrocarbon fraction. Desirably the particular hydroforming operation is that previously described and exemplified as a preferred process. The hydrocarbon effluent flows by way of line **12** to a fractionating column **13** where separation is effected. As here shown, the fractionation is effected in a single column although a multiplicity of fractionating units may be utilized. $C_4$ and lighter hydrocarbons are taken as overhead through line **14** while $C_5$, $C_6$ and $C_7$ hydrocarbon fractions are removed separately as side streams by way of lines **15**, **16** and **17** respectively. $C_9$ and heavier hydrocarbons are discharged as bottoms by way of line **18**.



The xylene-rich hydrocarbon mixture from which para xylene is to be recovered is withdrawn from fractionating column **13** by way of line **19** and flows through cooler **21** to surge tank **22**.

The xylene-rich hydrocarbon fraction containing paraffins and ethyl benzene, as hereinbefore described, flows from surge tank **22** to and through the para xylene recovery system. Although not essential to operability of the process, it will be found highly desirable in various instances to adjust the ratio of ortho to meta xylene in this xylene feed stock in order to enhance recovery of the para isomer. The ortho xylene content of a fraction prepared by hydroforming is less than the preferred ratio, and as here shown ortho xylene is added to the hydrocarbon mixture in surge tank **22** by line **23**, and the ortho to meta xylene ratio is thereby adjusted to approximately 1:2. The blended hydrocarbon mixture so formed then flows by way of lines **24** and **26** through heat exchanger **27** where the temperature of the mixture is initially lowered, most desirably by indirect heat exchange with mother liquor from the crystallization operation. This mother liquor flows through inlet and outlet conduits **28** and **29**, but for purposes of simplicity connections with the mother liquor lines are not shown.

It has been found that recovery of para xylene can be enhanced and superior results obtained by avoiding shock cooling of the entire xylene stream or conversely by maintaining the stock at crystallizing temperature for a substantial length of time to allow growth of crystals and insure dissipation of any adverse effects of localized shock cooling. Best results have been obtained with at least ten minutes and more desirably with twenty minutes or more residence time at crystallizing temperatures. As here shown the xylene stream flows into a suitable heat insulated soaking or crystal growing tank **31** where it is reduced to crystallizing temperature by mixing with previously cooled xylene stock. The xylene stock is retained at crystallizing temperature until the desired crystal form is obtained, that is, until shock crystals are largely removed by remelting and recrystallization or by equilibrium exchange with larger crystals which will be retained and recovered satisfactorily in subsequent filtering operations. Generally, a residence time of about twenty minutes is preferred.

Extremely rapid cooling of the incoming xylene stream adversely effects para xylene recovery, tends to lower the purity of product, and produces undesirably fine crystals which can be separated from the mother liquor only with great difficulty, if at all. Thus, a cooling rate in the order of 50° F. a minute in a batch process produces such adverse effects, whereas a cooling rate through the crystallization temperature range in the order of 1 to 10° F. a minute gives a good yield of filterable crystals of relatively high purity. More desirably, a cooling rate below about 5° F. a minute through the crystallization temperature range may be utilized.

Crystallizing temperature is maintained in soaking tank **31** by circulation of a xylene side stream through chillers by way of line **32**. Thus, circulation pump **33** forces the xylene through temperature-controlled chillers **34**, **36** and **37** connected in parallel, as shown, by valve-controlled inlet lines **38**, **39** and **41**. Desirably, circulation pump **33** is designed and controlled to force the xylene mixture through the chiller tubes at a sufficient velocity and under adequate pressure to cause turbulent flow. The term "turbulent flow" here is used in the commonly accepted hydraulic sense. Such turbulent flow is adapted to prevent or minimize localized shock cooling of the xylenes at the surface of the heat exchange tubes in coolers **34**, **36** and **37**. Additionally, crystal growth and adherence on the walls of such heat exchange tubes is reduced to a minimum by the use of high velocities, especially those exceeding the minimum for turbulent flow. For example, supercooling may be effected in the heat exchange tubes and the supercooled liquid returned to the crystallization tank before crystal formation is completed. After reduction to a crystallization temperature at least as low as that to be maintained in soaking tank **31**, the xylene mixture is passed through chiller discharge lines **42**, **43**, **44** and return header **46** to the crystal soaking or growing tank. The chilled xylene mixture is dispersed with the crystal slurry in tank **31** and an equilibrium temperature condition is reached therewith.

Any suitable refrigerant is supplied to the chillers by way of inlet header **25** and outlet **30**. Liquefied ethylene,

ethane or methane are examples of suitable refrigerants. As here indicated, temperature controls 35 are provided in the refrigerant discharge line of each of the chillers to regulate the flow of refrigerant therethrough. Desirably, these controls are responsive to the temperature of the xylene mixture in discharge lines 42, 43 and 44 respectively.

Upon completion of the crystal growing operation in tank 31, the slurry of para xylene crystals in the remaining liquid hydrocarbon mixture is conveyed by suitable means, as indicated by line 47, to a crystal separation and recovery unit. As illustrated herein, crystal separation and purification are effected by a combination of centrifugal filters and an agitated tank washer. Initially the crystals in slurry from tank 31 are separated in a centrifugal filter 48 at a temperature of from about —75° F. to about —120° F., more desirably —80° F. to —110° F., and preferably from —80° F. to "$T_2$" as previously defined, and conveyed as indicated by line 49 to crystal washer 51. Any suitable washing fluid may be utilized, such as isopentane, alcohol or the like, but as here shown a para xylene saturated hydrocarbon mixture is introduced by way of valve controlled line 52 with the slurry and the mixture intimately contacted by agitators 53. The resultant slurry flows through outlet line 54 to a second centrifugal filter 56. In order to maintain and control the temperature in washer 51, a portion of the washing liquid in stream 54 is bypassed through valve-controlled line 57, heater 58 and return line 59 to washing tank 51. Steam or other fluid heating agent is supplied to heater 58 as indicated by inlet and outlet lines 61 and 62.

The crystal slurry from washer 51 is separated in the second stage centrifugal filter 56, and the purified crystals removed and transferred to melting tank 63 as indicated by line 64. The filtrate from this second stage separation is discharged by way of line 66. This filtrate comprises a xylene fraction saturated with respect to para xylene at filtration temperature. A portion thereof flows by way of valve-controlled line 52 to be utilized as the washing liquid in tank 51. The remainder of the filtrate from unit 56 passes by way of recycle line 67 through heat exchanger 27, and preferably is blended with the xylene feed stock, before it is introduced into soaking tank 31.

In some instances it will be found desirable to minimize crystal formation in chillers 34, 36 and 37 by recirculating the filtrate of recycle line 67 through the heat exchanger tubes 38, 39 and 41 together with, or in lieu of, xylenes from crystal forming tank 31. A by-pass line 67*a* from recycle line 67 to pump 33 is provided for this purpose.

Purified crystals of paraxylene in tank 63 are melted and passed to storage 68 by way of line 69. A portion of the melted stock is by-passed through valve-controlled line 71, heater 72 and return line 73, the heated xylene serving to melt crystals fed to the system. Heat is supplied by hot water or any other suitable fluid introduced through line 74 and discharged through line 75.

The two-stage filtration and crystallization system preferably is operated with first-stage filter 48 maintained at a lower temperature than second-stage filter 56. A portion of the crystals discharged from washer 51 is allowed to melt so that the filtrate from unit 56 is para xylene of the desired purity, thereby furnishing a wash liquid rich in para xylene by way of valve-controlled line 52 for removing entrained less-pure mother liquor from the crystals in washer 51. Temperature in such a washing operation may be from about +20° F. to +35° F. although lower temperatures may be used, depending upon purity and yields desired.

Mother liquor from first stage filter 48 is discharged by way of outlet conduit 77, and in the embodiment here illustrated passes to fractionating column 78 wherein an ortho xylene fraction is separated by distillation.

In this distillation a relatively high purity ortho xylene fraction (for example, 95% or higher) can be obtained by superfractionation, which is a preferred type of operation for the present invention. The ortho xylene is removed from the distillation as a bottoms fraction by way of discharge line 79. A portion of the ortho xylene desirably is recycled by way of valve-controlled line 23 to feed surge tank 22 in an amount sufficient to adjust the ortho xylene content of the feed as previously disclosed herein. The remainder of the ortho xylene flows to storage by way of valve-controlled line 81. Overhead from superfractionator 78 passes by way of line 82 to storage 83. This overhead fraction consists of a mixture of xylenes, primarily meta xylene with minor amounts of ortho and para xylenes as well as with paraffins and ethyl benzene contained in the original feed stock.

With respect to the separation of an ortho xylene fraction by distillation and superfractionation, it should be noted that it will be necessary to maintain the non-aromatic hydrocarbon content of the xylene fraction supplied to superfractionator 78 below about 15% by weight. When necessary this initial purification may be effected in any suitable manner as, for example, by an initial extractive distillation of the xylene, or by liquid phase selective solvent extraction or the like. The superfractionation itself requires a highly efficient fractionating column. One equivalent to 35 theoretical plates is necessary for practical operation, more desirably about 45 and preferably about 60 theoretical plates are utilized. Reflux ratios on distillate of from about 7:1 to about 12:1 have been found satisfactory. Very close temperature regulation is important, and the distillation is so sensitive that control by temperature responsive device has been found to give inefficient though operable separation. A preferred method of superfractionation is to operate the fractionating unit continuously at a given constant feed rate while (1) removing overhead distillate and bottoms at a constant ratio corresponding to the feed rate and in a relative proportion such that the desired purity of the ortho xylene may be maintained, and (2) maintaining a constant volume of liquid and still bottoms by controlling the rate of heat input thereto. Maintenance of the constant volume of bottoms may be effected, for example, by a constant level control which increases the amount of steam admitted to the still heating unit when the level of the still bottoms begins to rise, and decreases steam input when the volume of bottoms begins to drop below the predetermined level. With the benefit of the foregoing instructions, those skilled in the art can effect superfractionation of a mother liquor boiling within the range of, for example 275–295° F. and having a non-aromatic hydrocarbon content of less than about 15% by weight.

To further illustrate the invention and guide those skilled in the art in the practice thereof, data showing effective recovery of para-xylene in the presence of different amounts of paraffins and at different temperatures are presented graphically in Fig. 2. The feeds B and C referred to in Fig. 3 had the following composition:

| | Feed B, percent | Feed C, percent |
|---|---|---|
| Paraffins | 10.2 | 38.6 |
| Ethyl benzene | 11.8 | 8.4 |
| Ortho xylene | 4.5 | 4.3 |
| Meta xylene | 53.5 | 35.4 |
| Para xylene | 20.0 | 13.3 |

Figs. 2 and 3 illustrate that the presence of paraffins tend to decrease para xylene recovery at any given temperature, but that this decrease in recovery is avoidable by further reducing crystallization temperature within the limits and in the manner herein disclosed; that is, by lowering the temperature 0.3° F. for each per cent of paraffins present.

Figs. 4 and 5 establish the effects of the presence of ethyl benzene and show that it tends to decrease p-xylene recovery at any given temperature to a greater extent than do the paraffins. Likewise, the data illustrate that this decrease in recovery is avoidable by reducing crystallization temperature within the limits and in the manner herein disclosed, that is, by lowering crystallization temperature as previously disclosed about 1.4° F. for each percentage of ethyl benzene present in the feed.

Figs. 6 and 7 show the effects of ortho xylene to meta xylene ratio on para xylene recovery and on optimum crystallization temperature. The data of these two figures are based on compositions containing para xylene in excess of the xylene eutectics. Thus, when the ortho-meta xylene ratio is less than one-half, crystallization temperature should be decreased about 0.65° F. for each per cent of ortho xylene present. When the ratio of ortho to meta xylene is greater than one-half, the optimum crystallization temperature for any given feed con-

taining para xylene in excess of the eutectic proportion should be increased about 1.3° F. for each per cent of ortho xylene present in excess of 33, based on the xylenes. Again, when the ortho to meta xylene ratio is the optimum 1:2, then the most desirable crystallization temperature is −84.5° F. decreased by the correction factors previously disclosed for paraffin and ethyl benzene contents only.

An exemplary process was carried out and data obtained in a simplified apparatus consisting of a fritted glass filter surrounded by a cooling bath to maintain the filtration at specified temperatures. Crystals were filtered from the mother liquor by applying vacuum, and the crystal cake of para xylene was air-dried for a measured time interval. Crystals were weighed and purity determined by the freezing point method. To regulate the sweating of the crystal cake and eliminate ice formation on the filter, the air used for drying was first chilled with an alcohol solid $CO_2$ bath. In these runs the percentage of paraffins was varied by adding the unsulfonatable residue (that is, the paraffinic hydrocarbons) of a xylene fraction formed by hydroforming a petroleum hydrocarbon fraction as previously described herein. By utilizing this particular mixture of paraffins, representative results were obtained without the necessity of identifying the exact composition and proportions of the different paraffinic components. Tables I and II give the results of representative runs made in the foregoing manner, Table I showing the effect of paraffins:

TABLE I

*Effect of paraffins on the recovery of para xylene*

| | Feed B | Feed C |
|---|---|---|
| Percent ethyl benzene | 11.8 | 8.4 |
| Percent o-xylene | 4.5 | 4.3 |
| Percent m-xylene | 53.5 | 35.4 |
| Percent p-xylene | 20.0 | 13.3 |
| Percent paraffins (Kattwinkle) | 10.2 | 38.6 |

Conditions:
(1) Charge: 50 g. feed
(2) Vacuum: Flowmeter with #30 orifice, 20 cm. Hg
(3) Drying air cooled in alcohol $CO_2$ bath
(4) Cake air dried 2 minutes

| Charge | Percent paraffins | Crystallizing temperature, °F. | Cooling time, minutes | Time at cryst. temp., minutes | Percent p-xylene in crystals | Percent recovery p-xylene |
|---|---|---|---|---|---|---|
| 50 g. "B" | 10.2 | −75 | 20 | 5 | 80.0 | 45.9 |
| | | −75 | 28 | 20 | 80.5 | 48.8 |
| | | −100 | 35 | 10 | 68 | 66.2 |
| | | −106 | 30 | 30 | 72 | 69.5 |
| 50 g. "C" | 38.6 | −90 | 25 | 20 | 74.7 | 53.0 |
| | | −106 | 60 | 40 | 74.3 | 63.7 |
| | | −110 | 25 | 10 | 77 | 67.6 |

In Table II are shown data on the effects of successively increased percentages of ethyl benzene obtained by addition of ethyl benzene to the original charge stock.

TABLE II

*Effect of ethyl benzene on recovery of para xylene*

| Charge stock: | Percent |
|---|---|
| ethyl benzene | 14.0 |
| o-xylene | 6.1 |
| m-xylene | 49.3 |
| p-xylene | 19.1 |
| paraffins | 11.5 |

Conditions:
(1) Charge: 50 cc. toluene plant topping still overhead
(2) Vacuum: Flowmeter with #30 orifice, 20 cm. Hg
(3) Drying air cooled in alcohol $CO_2$ bath
(4) Cake air dried 2 minutes

| Percent ethyl benzene | Crystallizing temperature, ° F. | Cooling time | Time at at cryst. temp. | Percent p-xylene in crystals | Percent p-xylene recovered |
|---|---|---|---|---|---|
| 14.0 | −75 | 35 | 10 | 76.0 | 46.8 |
| 28.4 | −75 | 30 | 30 | 74.3 | 38.3 |
| 38.6 | −75 | 23 | 30 | 68.5 | 27.6 |
| 14.0 | −90 | 20 | 20 | 74.7 | 58.5 |
| 14.0 | −90 | 20 | 30 | 76.8 | 58.8 |
| 21.8 | −90 | 16 | 5 | 76.0 | 50.2 |
| 38.6 | −90 | 22 | 5 | 70.4 | 37.4 |
| 38.6 | −90 | 20 | 10 | 72.0 | 36.8 |
| 14.0 | −102 | 35 | 5 | 74.0 | 66.7 |
| 28.4 | −105 | 25 | 10 | 71.0 | 56.0 |
| 38.6 | −105 | 25 | 5 | 69.2 | 47.0 |

A second series of exemplary runs was made with centrifugal separation of para xylene crystals. The filtration was effected in equipment consisting of a perforated basket centrifuge lined with muslin. An agitated chilling vessel was provided for cooling the feed stock by internal refrigeration by direct addition of Dry Ice. In addition to the mixing effected by evaporated $CO_2$, mechanical agitation was utilized to aid in controlling the temperature of the charge stock and in reducing agglomeration of the solid $CO_2$.

The para xylene crystal slurry was fed by gravity into the centrifugal filter, and a pump was provided for recirculation of the cooled mother liquor from the filter back to the agitating vessel. The centrifugal pump, agitator and pipe lines were suitably insulated to maintain low temperatures. Means for measuring temperatures in the agitator and of the inlet and outlet of the centrifuge were provided. In operation, the whole system was gradually cooled to the desired crystallization temperature by addition of solid $CO_2$ to the agitator and continuous recirculation of the xylene mother liquor through the agitator and centrifugal filter. Purification of the crystals in situ was effected in two stages; first, extraction of impurities by circulation of the mother liquor through the filter cake for a substantial period after crystallization temperature is reached; and secondly, by drawing off the mother liquor and allowing the filter cake to rise in temperature sufficiently to "sweat" out hydrocarbon impurities while continuing operation of the centrifuge to remove liquefied impurities so released. Data from these runs are given in Table III:

TABLE III

| Charge stock: | Percent |
|---|---|
| ethyl benzene | 14.0 |
| o-xylene | 6.1 |
| m-xylene | 49.3 |
| p-xylene | 19.1 |
| paraffins | 11.5 |

| Crystallizing temp., ° F. | Final centrifuge period, minutes | R. P. M. of centrifuge | Purity of p-xylene, percent | Recovery of p-xylene charged, percent |
|---|---|---|---|---|
| −70 | 10 | | 93 | 9.7 |
| −80 | 10 | | 87.2 | 30.7 |
| −75 | 10 | | 85.5 | 48.0 |
| −90 | 15 | | 83.5 | 58.4 |
| −84 | 15 | | 88.2 | 56.8 |
| −87 | 20 | | 86.3 | 58.7 |
| −91 | 12 | | 87.0 | [a] 30.5 |
| −95 | 82 | | 92.0 | [a] 42.2 |
| −90 | 70 | | 95.7 | 57.5 |
| −90 | 58 | | 88 | 58 |
| −90 | 93 | | 96 | [b] 50.6 |
| −90 | 69 | [c] 1,450 | 98 | 58 |
| −80 | 50 | [c] 1,450 | 90 | [b] |
| −100 | [d] 68 | [c] 1,450 | 95 | 59 |

[a] Equipment was cork insulated for this and ensuing runs. Low recovery due to increased speed of centrifuge.
[b] Some mechanical loss of product from centrifuge.
[c] Centrifuge modified to permit measurement of R. P. M. For this run the speed of the final centrifuge period was increased to 2,600 R. P. M.
[d] This period was reduced by increasing the air flow through the centrifuge.

It is readily apparent from the foregoing description that various modifications of the process can be made within the spirit of the present invention and the scope of the appended claims. For the sake of simplicity and clarity, apparatus has not been shown in detail in the

drawing but is illustrated only as to major unit operations in the process. Many detailed pumps, valves, condensers, heat exchangers, temperature controls and the like have been omitted, since any suitable form of apparatus incorporating these features can be supplied in obvious manner by those skilled in the art.

I claim:

1. In a process of recovering para xylene from mixtures of ortho, meta and para xylenes by chilling a xylene fraction to a temperature of from about —75° F. to —120° F., the steps of feeding said xylene fraction to a crystal forming zone comprising a relatively large body of liquid xylenes containing para xylene crystals suspended therein, continuously circulating a portion of the xylene liquid from said crystal forming zone through a chiller and there cooling it by indirect heat exchange to a temperature below that of the crystal-forming zone, returning chilled xylenes to said crystallizing zone whereby crystal forming temperatures are maintained, and reducing crystal deposition in said chiller by maintaining turbulent flow through said chiller.

2. In a process of recovering para xylene from a xylene fraction by chilling said xylene fraction to a temperature of from about —75° F. to about —120° F., the steps of feeding said xylene fraction to a crystal-forming zone comprising a relatively large body of liquid xylenes containing para xylene crystals suspended therein, continuously circulating a portion of the xylene liquid from said crystal forming zone through a chiller, supercooling said xylene liquid in said chiller by indirect heat exchange, reducing crystal deposition in said chiller by passing xylene liquid through it in turbulent flow and returning said super-cooled liquid to said crystal-forming zone prior to completion of crystal formation.

3. A process for separating para xylene from hydrocarbon mixtures consisting predominantly of xylene isomers which comprises maintaining a relatively large body of the hydrocarbon mixture containing a part of its para xylene in crystal form at a temperature in the range about —75° to —120° F. in a crystallizing zone, continuously circulating a portion of the mixture from the crystallizing zone in turbulent flow through a chilling zone and there cooling it by indirect heat exchange to a temperature lower than that of the crystallizing zone but not substantially below —120° F., and returning said circulated portion to the crystallizing zone, withdrawing hydrocarbon mixture containing para xylene crystals from the crystallizing zone and separating para xylene crystals by filtration, and introducing fresh hydrocarbon mixture into the crystallizing zone.

**References Cited** in the file of this patent

UNITED STATES PATENTS

| Number | Name | Date |
|---|---|---|
| 1,940,065 | Spannagel | Dec. 19, 1933 |
| 2,383,174 | Wier | Aug. 21, 1945 |
| 2,398,526 | Greenburg | Apr. 16, 1946 |
| 2,400,883 | Keeling et al. | May 28, 1946 |
| 2,435,792 | McArdke et al. | Feb. 10, 1948 |
| 2,541,682 | Arnold | Feb. 13, 1951 |