

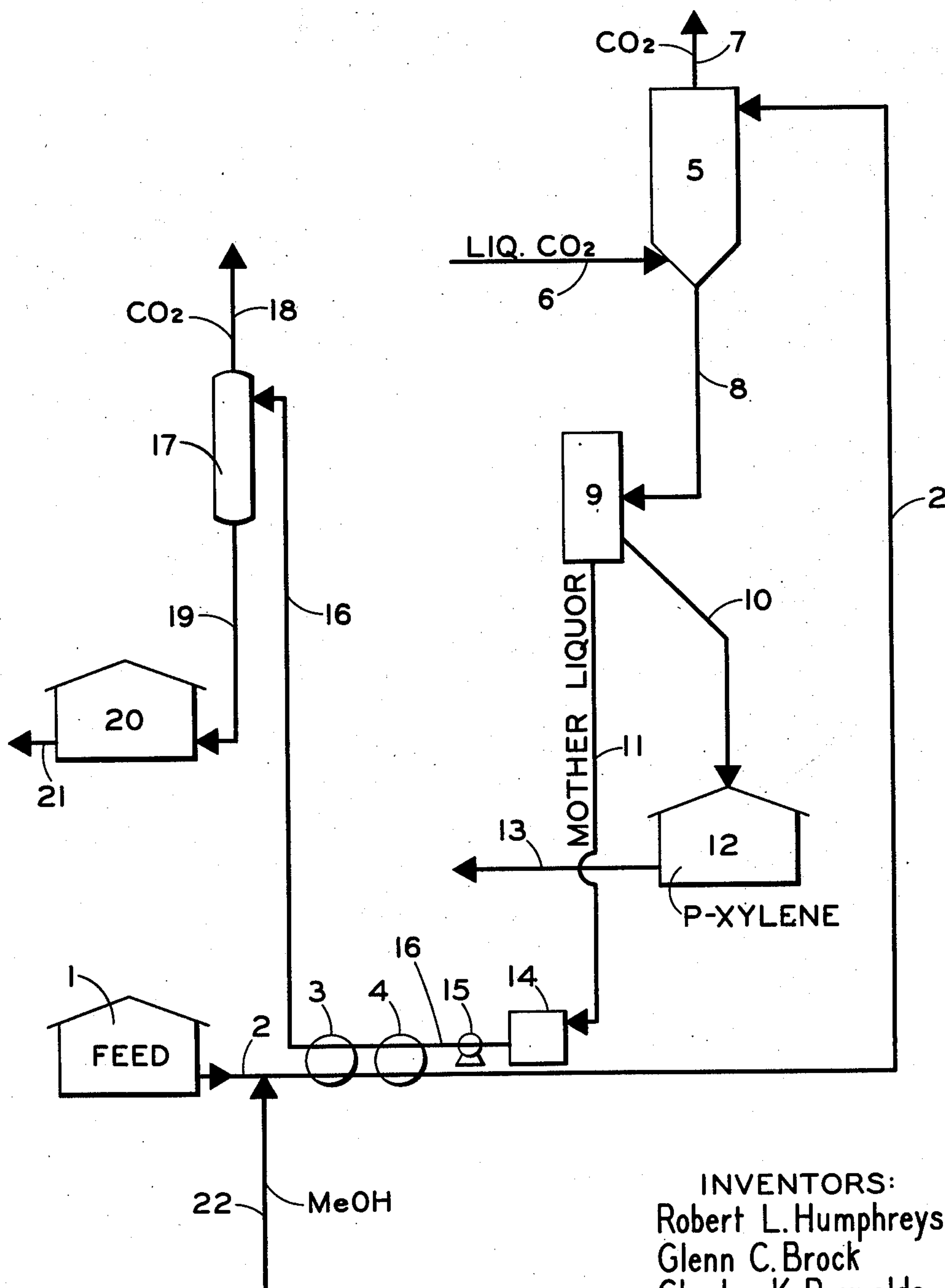
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XYLENE SEPARATION

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## XYLENE SEPARATION

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This invention relates to the separation of paraxylene from hydrocarbon mixtures, consisting predominantly of xylene isomers, by fractional crystallization.

Large quantities of hydrocarbon mixtures consisting predominantly of xylene isomers are produced commercially. Narrow distillation cuts having high contents of the xylene isomers have been separated from coke oven distillates and catalytically reformed naphtha. The desirability of separating the individual xylene isomers from these xylene-rich mixtures has long been evident to industrial chemists. Numerous processes have been proposed to make such separations; these processes are based on differences in both the chemical and physical properties of the xylene isomers. Among the processes which have been proposed is fractional crystallization, usually effected by cooling a xylene mixture in the presence of a substantial quantity of an added diluent or solvent. While the methods which have been proposed are operative, they involve processing difficulties which so effect the economics of the separation that none of them has been adapted to large scale commercial production of individual xylene isomers.

The co-pending application of Arnold, Serial No. 770,587, now U. S. Patent 2,541,682, describes a crystallization process which avoids the employment of diluents and solvents and, consequently, the necessity and expense of recovery systems which the use of these materials involves. The process described in this application consists in the main of a cooling and crystallization step followed by centrifugal filtration. Recently, commercial scale production of paraxylene by modification of the method described in the Arnold application was initiated. The commercial unit developed difficulties which had not been indicated by either laboratory or pilot scale work.

The nature of the commercial process and of the difficulties encountered in its practice will be better understood by reference to the appended drawing, which is a diagrammatic illustration of the apparatus and process flow employed in the commercial unit.

The process feed may be any hydrocarbon mixture consisting predominantly of xylene isomers and having a paraxylene content greater than that necessary to form a eutectic mixture with the metaxylene contained in the feed. Coke oven distillates having xylene contents of 75% and higher are suitable feeds. Xylene-rich fractions separated from catalytically reformed naphtha are also suitable feeds. In the petroleum industry straight run naphthenic distillates boiling in the range about 180 to 340° F. are contacted with

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a silica molybdena catalyst at temperatures around 1000° F. in the presence of hydrogen to increase the aromatic content of the distillate. The product of such a process may be fractionally distilled to separate a fraction boiling in the range about 275 to 300° F. and having a C<sub>8</sub> aromatic content of 50 to 60%. The aromatics contained in this fraction may be concentrated by solvent extraction, for example, or the entire fraction may be subjected to a second pass hydroforming treatment to produce a product yielding a 275 to 295° F. fraction having a C<sub>8</sub> aromatic content in the range of 85 to 90%. Xylene-rich fractions obtained in this manner commonly contain 10 to 15% ethylbenzene, 8 to 12% orthoxylene, 40 to 50% metaxylene, 15 to 20% paraxylene, and 10 to 15% of paraffinic and naphthenic hydrocarbons boiling in the boiling range of xylenes. Stocks of this description are very suitable feeds to the fractional crystallization process.

In recent commercial production of paraxylene a feed containing about 17% paraxylene, 47% metaxylene, 11% orthoxylene, 12% paraffins, and 12% ethylbenzene is passed from feed tank 1 through line 2 into crystallizer 5. The feed en route from the feed tank to the crystallizer passes through heat exchangers 3 and 4 where it is brought into indirect heat exchange with cold mother liquor. During the passage of the feed through heat exchangers 3 and 4, it is cooled from atmospheric temperature to a temperature in the range -20 to -50° F. Although the arrangement is not shown in the drawing, the lines to heat exchangers 3 and 4 are so arranged that either heat exchanger may be by-passed. In addition to the hydrocarbon components of the feed, there may be present minor amounts of water usually not exceeding about 0.05% by weight which is the maximum amount of water capable of being dissolved in the hydrocarbon mixture at atmospheric temperatures. The actual water content of the feed is commonly in the range 0.015 to 0.017% by weight. During the passage of the feed through the heat exchangers, this water of solubility is solidified and accumulates on the heat exchange surfaces as a frost. Periodically, each heat exchanger is by-passed to permit removal of this frost from the heat exchange surfaces. In crystallizer 5 the precooled feed, usually at a temperature of about -40° F., is contacted with a liquid refrigerant such as liquefied ethane, ethylene, methane, or carbon dioxide. Carbon dioxide is the preferred refrigerant and it is introduced into the crystallizer through line 6. Carbon dioxide gas is withdrawn from the crystallizer through line 7. Carbon dioxide is introduced into crystallizer 5 in amount sufficient to cool the feed to temperatures in the range



—75 to —120° F., and preferably in the range about —90 to —110° F. This cooling causes crystallization of paraxylene and the production of a crystal slurry in crystallizer 5. This slurry is withdrawn from crystallizer 5, through line 8, and introduced into centrifuge 9 where the crystals and mother liquor are separated. Centrifuge 9 includes a cage or bowl having perforate walls. The perforate wall is overlaid with a metal screen which in turn is overlaid with a fabric such as canvas. The slurry is in direct contact with the interior fabric surface of the centrifuge bowl. As the bowl is spun, the mother liquor passes successively through the fabric, the screen, and the perforate bowl wall, while the crystals are retained on the surface of the fabric. The crystals are continuously scraped from the interior of the centrifuge bowl and passed through line 10 into tank 12, where they are melted, forming a liquid of very high paraxylene content which is removed from tank 12 through line 13. The mother liquor separated in centrifuge 9 leaves the centrifuge through line 11, passes into tank 14 from which it is pumped by pump 15 through line 16 and the heat exchangers 3 and 4, and flows into flash drum 17 where carbon dioxide gas is flashed from the mother liquor and removed from drum 17 through line 18. The mother liquor freed of carbon dioxide is withdrawn from drum 17 through line 19 and is passed into mother liquor storage tank 20, from which it is withdrawn for use or further processing through line 21.

In conducting commercial scale separations of paraxylene from mixed xylene feeds in the manner above described with reference to the drawing, frequent interruptions of the operation were necessary because of plugging of the fabric lining of the centrifuge bowl or cage and stoppages in line 11 which conducts the mother liquor from the centrifuge to the flash drum. Considerable inconvenience was experienced due to frequent malfunctioning of automatic liquid level control devices in mother liquor tank 14. From present knowledge it appears that all of these difficulties must be charged to the formation of microcrystals in the feed stream during the cooling and crystallization step of the process. Microcrystalline solids formed during the cooling step appear to cause the plugging of the filter screen and fabric of the centrifuge cage. When the filter screen became plugged by the accumulation of microsolids in the apertures of the fabric and screen, the operation was stopped and the fabric and screen were either warmed or washed with a warm hydrocarbon liquid, suitably a portion of the feed. This warming or washing cleared the apertures in the fabric and screen and the operation could be recommenced and continued. The plugging of mother liquor line 11 appears to have resulted from the passage of microcrystalline solids through the apertures of the fabric and screen of the centrifuge cage. These small solid particles appeared to agglomerate in lines 8 and 11 and to adhere to the interior walls of the line, gradually building up to deposits of such size as to cause a stoppage in the line. The difficulty of operating automatic liquid level control devices in mother liquor tank 14 also appears to be attributable to the agglomeration of microcrystalline particles in the mother liquor stream to produce solid particles of such size as to produce malfunctioning of the liquid level control apparatus. Interruption of the separation process directly attributable to the aforementioned difficulties were of such frequency

and duration that they seriously affected the operating factor of the unit.

It has been found that all of the aforementioned difficulties of operation may be substantially completely eliminated by introducing a minor amount of a low molecular weight alcohol, ketone or aldehyde into the xylene feed stream. These low molecular weight materials do not usually contain more than three to four carbon atoms. The low molecular weight alcohol, ketone or aldehyde may be introduced at the point indicated in the drawing by the junction of line 22 with line 2, or, if desired, it may be introduced into the slurry flowing from crystallizer 5 to centrifuge 9 through line 8. Very small amounts of the low boiling alcohol have been found effective to eliminate the aforementioned operating difficulties. Amounts less than 1% by volume based on the feed volume of the feed are entirely adequate for this purpose. Generally, the amount of low boiling alcohol, ketone or aldehyde introduced lies in the range 0.01 to 0.5% by volume, and preferably in the range about 0.05 to 0.25% by volume. Larger amounts of a low boiling alcohol, ketone or aldehyde, for example, 5% by volume, are operative but produce no incremental beneficial effects and present problems of product purification and alcohol recovery. When the amount of alcohol, ketone or aldehyde used is in the range 0.01 to 0.5 volume per cent based on the feed volume, no treatment of the paraxylene product to recover the alcohol, ketone or aldehyde is necessary, and the amount of alcohol, ketone or aldehyde adhering to the paraxylene crystals is extremely small. Neither is it necessary to treat the mother liquor for alcohol, ketone or aldehyde removal when the mother liquor is put to the usual uses, for example, as a component of a solvent or of motor fuel, or when it is subjected to further processing as for metaxylene recovery. In the event that it is desired to remove the alcohol, ketone or aldehyde from the mother liquor for any reason, such removal is readily effected by recourse to a simple water wash of the mother liquor.

During a 72 hour test period in which a crystallization unit conforming essentially to the one illustrated in the drawing was operated with liquid carbon dioxide as the refrigerant and without the addition of any alcohol, ketone or aldehyde, the average feed rate to the unit was 735 gallons per hour. During this test period the fabric and screen of the filter cage were washed three times to clear the apertures of these materials and mother liquor line 11 on two occasions became plugged to such a degree that the operation had to be interrupted and the line cleared.

During a second 72 hour test period, the plant was operated treating the same feed stream under identical conditions with the exception that methanol was introduced into the feed through line 22 at the rate of 2 gallons of methanol per 1000 gallons of feed. During this run a substantially higher average feed rate of 973 gallons per hour was maintained. During this second test period no washing of the fabric and screen of the centrifuge cage was required and no stoppage of the mother liquor line occurred. Subsequently, the unit was continuously run for a period of 25 days, during which time no interruption of the processing was required either to wash the fabric and screen of the filter cage or to clear the mother liquor line. During operation of the crystallization unit with the introduction of



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methanol into the feed, it was found that the paraxylene crystals gathered in the centrifuge were larger than those recovered during operation without methanol and that the mother liquor was drained from the filter cake in the centrifuge more rapidly and more completely when methanol was employed. It was found that the paraxylene content of the product recovered from paraxylene tank 12 averaged from 84 to 85% paraxylene during operation without the addition of alcohol, and that the product recovered when alcohol was employed in the process had an average paraxylene content in the range 88 to 89%. The incremental purity is presumed to result from the fact that the paraxylene crystals formed in operation with methanol are larger and that the mother liquor holdup in the filter cake comprised of these larger crystals is lower. The results obtained with methanol in the commercial scale tests are consistent with the results which such scale tests indicate can be obtained with other low molecular weight alcohols, low molecular weight ketones and low molecular weight aldehydes.

When an alcohol is employed in the process for the purpose set forth methanol is preferred, but other low boiling alcohols are operative, especially ethanol, propanol, ethylene glycol, and glycerine are suitable. When a ketone is employed it is preferred to use either acetone or methyl ethyl ketone, although other low molecular weight ketones are operative. When an aldehyde is employed it is preferred to employ acetaldehyde or propionaldehyde.

From the foregoing it will be evident that significant improvements in processing rates and product purity are obtained in commercial scale separation by fractional crystallization of paraxylene from hydrocarbon mixtures consisting predominantly of xylenes, by the inclusion of minor amounts of a low molecular weight alcohol, ketone or aldehyde, or mixtures thereof, to the feed to the separation unit.

We claim:

1. In a process for the separation of paraxylene from hydrocarbon mixtures consisting predominantly of xylene isomers comprising the steps of cooling the mixture to crystallize paraxylene and filtering the cooled mixture to separate paraxylene crystals from the mother liquor, the improvement which comprises introducing a small amount in the range 0.01 to 5% by volume of a material selected from the group consisting of alcohols containing 1 to 4 carbon atoms, ketones containing 3 to 4 carbon atoms and aldehydes containing 1 to 4 carbon atoms into the hydrocarbon mixture prior to the separation of the paraxylene crystals from the mother liquor.

2. The method as defined in claim 1, wherein the material is an alcohol containing 1 to 4 carbon atoms and the amount added is in the range 0.01 to 1% by volume based on the hydrocarbon mixture.

3. The method as defined in claim 2, wherein the alcohol is methanol and the amount added is in the range 0.01 to 1% by volume based on the hydrocarbon mixture.

4. The method as defined in claim 2, wherein the alcohol is ethanol and the amount added is in the range 0.01 to 1% by volume based on the hydrocarbon mixture.

5. The method as defined in claim 2, wherein the alcohol is ethylene glycol and the amount added is in the range 0.01 to 1% by volume based on the hydrocarbon mixture.

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6. The method as defined in claim 1, wherein the material is a ketone containing 3 to 4 carbon atoms and the amount added is in the range 0.01 to 1% by volume based on the hydrocarbon mixture.

7. The method as defined in claim 1, wherein the material is an aldehyde containing 1 to 4 carbon atoms and the amount added is in the range 0.01 to 1% by volume based on the hydrocarbon mixture.

8. In a process for the separation of paraxylene from hydrocarbon mixtures consisting predominantly of xylene isomers comprising the steps of cooling the mixture to crystallize paraxylene and filtering the cooled mixture to separate paraxylene crystals from the mother liquor, the improvement which comprises introducing a small amount in the range 0.01 to 0.5% by volume of an alcohol containing 1 to 4 carbon atoms into the hydrocarbon mixture prior to the cooling step.

9. In a process for the separation of paraxylene from hydrocarbon mixtures consisting predominantly of xylene isomers comprising the steps of cooling the mixture to crystallize paraxylene and filtering the cooled mixture to separate paraxylene crystals from the mother liquor, the improvement which comprises introducing a small amount in the range 0.05 to 0.25% by volume of an alcohol containing 1 to 4 carbon atoms into the hydrocarbon mixture prior to the separation of the paraxylene crystals from the mother liquor.

10. In a process for the separation of paraxylene from a xylene-rich distillation fraction separated from catalytically reformed naphtha comprising the steps of cooling the fraction to crystallize paraxylene and filtering the cooled fraction to separate paraxylene crystals from the mother liquor, the improvement which comprises introducing a small amount in the range 0.01 to 1% by volume of an alcohol containing 1 to 4 carbon atoms into the distillation fraction prior to the separation of the paraxylene crystals from the mother liquor.

11. In a process for the separation of paraxylene from hydrocarbon mixtures consisting predominantly of xylene isomers comprising cooling the mixture by contacting it with a cold metallic heat exchange surface to crystallize paraxylene, the improvement which comprises introducing a small amount in the range from 0.01 to 5% by volume of a material selected from the group consisting of alcohols containing 1 to 4 carbon atoms, ketones containing 3 to 4 carbon atoms and aldehydes containing 1 to 4 carbon atoms into the hydrocarbon mixture prior to contacting the mixture with the cold metallic surface.

12. The method as defined in claim 11, wherein the selected material is methanol.

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