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PRODUCTION OF PARAXYLENE

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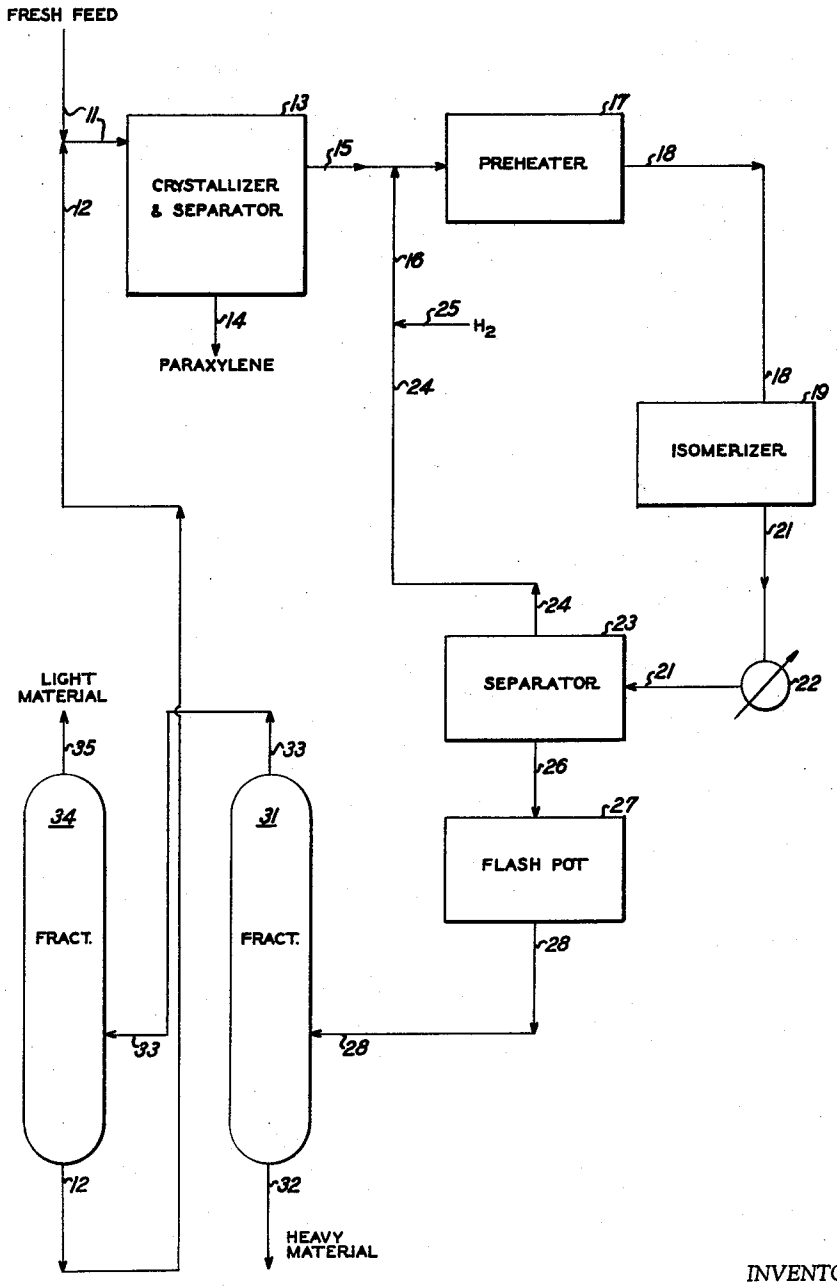

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PRODUCTION OF PARAXYLENE

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This invention is concerned with the preparation of isomeric aromatic hydrocarbons; more particularly, it is concerned with the preparation and separation of C–8 aromatic hydrocarbons. In a particular embodiment, the invention is concerned with the production of paraxylene by the conjoint use of crystallization and isomerization techniques.

In a particular embodiment the present invention is concerned with treatment of the effluent of a C–8 isomerizer in order to separate the isomerizate from light and heavy ends.

Paraxylene is a chemical of growing commercial importance, being utilized, for example, as a precursor for terephthalic acid, one of the constituents of polyester fibers and resins. In the past, paraxylene has been separated by crystallization from various C–8 aromatic hydrocarbon refinery streams. More recently, paraxylene has been obtained by such crystallization technique followed by isomerization of the crystallizer effluent to enrich the paraxylene content thereof. Such process is illustrated by "Petroleum Refiner," August 1958, page 208.

In one embodiment the present invention embraces in sequential operation for the production of paraxylene, the steps of separating by crystallization paraxylene from a mixture consisting predominantly of aromatic hydrocarbons, said mixture containing paraxylene and at least one other xylene isomer, subjecting the residuum of said aromatic hydrocarbon mixture to isomerization conditions to produce a mixture of paraxylene-enriched isomerizate, a lighter than C–8 fraction and a heavier than C–8 fraction, introducing said mixture into a first fractionation zone, removing heavier than C–8 fraction from the bottom of a first fractionation zone, removing said lighter than C–8 fraction and said isomerizate as overhead from said first fractionation zone, introducing said lighter than C–8 fraction and said isomerizate into a second fractionation zone, removing said lighter than C–8 fraction as overhead from said second fractionation zone and said isomerizate from the bottom of said second fractionation zone, admixing said isomerizate and fresh aromatic hydrocarbon feed to form a mixture consisting of predominantly aromatic hydrocarbons and repeating the sequential operation.

In a further embodiment the present invention embraces in a sequential operation for the production of paraxylene, the steps of separating by crystallization paraxylene from a mixture consisting predominantly of aromatic hydrocarbons, said mixture containing paraxylene and at least one other xylene isomer, subjecting the residuum of said aromatic hydrocarbon mixture to isomerization conditions to produce a second mixture of a paraxylene-enriched isomerizate, a lighter than C–8 fraction and a heavier than C–8 fraction, partially flashing said second mixture and introducing said partially flashed mixture into a first fractionation zone, removing the heavier than C–8 fraction from the bottom of said

first fractionation zone, removing said lighter than C–8 fraction and said isomerizate as overhead from said first fractionation zone, introducing said lighter than C–8 fraction and said isomerizate into a second fractionation zone, removing said lighter than C–8 fraction as overhead from said second fractionation zone and said isomerizate from the bottom of said second fractionation zone, admixing said isomerizate and fresh aromatic hydrocarbon feed to form a mixture consisting predominantly of aromatic hydrocarbons, and repeating the sequential operation.

The present invention is illustrated by the attached drawing in which a C–8 aromatic hydrocarbon stream such as is obtained from a refinery stream is introduced through line 11 together with a recycle isomerizate (hereinafter described) from line 12 into crystallization zone 13. Crystalline paraxylene is removed from said zone 13 via line 14 by means such as centrifugation. The residuum of the aromatic hydrocarbon stream together with hydrogen from line 16 is fed via line 15 to the preheater 17 and thence via line 18 to isomerizer 19. The crude isomerizate effluent flows via line 21 through heat exchanger 22 to a liquid-gas separator 23. The hydrogen gas is recycled via line 24 with make-up hydrogen being introduced via line 25. The crude isomerizate effluent, containing a lighter than C–8 fraction, a paraxylene enriched isomerizate and a heavier than C–8 fraction, flows via line 26 to flash pot 27 where a portion of the crude isomerization effluent is flashed, and the liquid-vapor is transported via line 28 to a first fractionation zone 31. The heavy ends of said crude isomerization effluent are removed from first fractionation zone 31 as bottoms via line 32. An overhead vapor stream containing the isomeric C–8's and the lighter than C–8's is removed from first fractionation zone 31 via line 33 and fed to second fractionation zone 34. The lighter than C–8's are removed as overhead from second fractionation zone 34 via line 35. The recycle isomerizate is removed from fractionation zone 34 via line 12 and combined with fresh feed.

The procedure of the present invention enables more economic operation than heretofore known in the art.

For example, in previous methods of operation, the effluent from the isomerizer was partially vaporized as above described and introduced into a first fractionation zone from which the heavy ends and isomerizate were removed as bottoms and the light aromatics as overhead. This necessitated the vaporization of the bottoms from the first fractionation zone for introduction into a second fractionation zone from which the recycled isomerizate was removed as overhead and the heavy ends as bottoms. Thus, the present invention provides a distinct advantage in that, utilizing the present invention, greatly reduced vaporization heat requirements result as compared to prior processes, and economic advantage obviously accrues.

The invention is illustrated by but not necessarily restricted to the following examples in which parts by weight are percent by weight apply unless otherwise indicated.

Example 1

About 100 parts of fresh feed having a composition of about 23% ethylbenzene, 17% paraxylene, 37%

metaxylene, 23% othoxylene and the rest hydrocarbon impurities are combined with about 500 parts recycle isomerizate having a composition of about 17% ethylbenzene, 17% paraxylene, 38% metaxylene, 26% orthoxylene and the rest lower and higher boiling impurities. The resulting mixture is fed to a crystallization and separation zone wherein paraxylene crystals are formed by cooling to about —70° C. and are separated by centrifugation. Approximately 50–60 parts of paraxylene crystals are removed.

The mother liquor is combined with hydrogen (about 450 parts) preheated and flowed through isomerization zone at about 460° C. and 190 p.s.i.g. whereby the paraxylene depleted mixture is isomerized and there is obtained a crude isomerizer effluent containing a paraxylene enriched isomerizate, a heavier than C–8 fraction and a lighter than C–8 fraction. The crude isomerizer effluent together with the excess hydrogen is passed through a liquid gas separator wherein hydrogen is disengaged and recycled. The crude isomerizer effluent comprising about 15% ethylbenzene, 16% paraxylene, 35% metaxylene, 24% orthoxylene, 7% lighter than C–8's and 3% heavier than C–8's is partially flashed at a temperature of about 40° C. and 170 p.s.i.g. and the vapor-liquid mixture is fed into the first fractionation zone where there are removed as bottoms at 203° C. and 31 p.s.i.g. approximately 10–15 parts of a heavier than C–8 fraction. The lighter than C–8 fraction and the paraxylene enriched isomerizate are removed from the first fractionation zone as overhead at 175° C. and 25 p.s.i.g. and fed to a second fractionation zone wherein approximately 35–45 parts of a lighter than C–8 fraction are removed at 118° C. and 16 p.s.i.g. as overhead, and approximately 500 parts of the paraxylene enriched isomerizate are obtained as bottoms at 171° C. and 20 p.s.i.g. and recycled for combination with the fresh feed.

Utilizing this sequence, there is a total heat duty in the first and second fractionation zone of about 360 parts of steam per 100 parts of crude isomerizer effluent fed.

Example 2

The procedure of Example 1 is repeated except that the 35–45 parts of lighter than C–8 fraction is removed as overhead into the first fractionation zone and from the bottom of said fractionation zone there is removed the heavier than C–8 fraction and the paraxylene enriched isomerizate which are fed to the second fractionation zone. In the second fractionation zone the approximately 10–15 parts of heavier than C–8 fraction are removed as bottoms and approximately 500 parts paraxylene enriched isomerizate removed as overhead for recycle and combination with the fresh feed.

Utilizing this method of operation heat duty in the first and second fractionation zone is about 550 parts steam per 100 parts crude isomerizer effluent fed.

A comparison of heat duty in Example 1 and Example 2 illustrates the benefit of the present invention. It is to be noted that the heat duty requirement of Example 2 is more than 150% of the heat duty requirement of the present invention. It will be obvious to those skilled in the art that utilizing the present invention enables more economical and thus advantageous operation than previously known methods.

The fresh xylene feed has a composition generally in the range:

	Percent
Ethylbenzene	0–30
Orthoxylene	15–35
Paraxylene	12–25
Metaxylene	25–50
Other hydrocarbons	trace–2

The crystallization is generally carried out in the range +5 to —74° C., and any suitable heat exchange means may be used such as internal or direct contact with a refrigerant such as ethylene, or indirect contact with the refrigerant. If desired, scraper means may be provided for removing or loosening crystals or solids from heat exchange surfaces. One or more stages of cooling and separating may be used.

The solids separator may be any convenient means, such as a filter, centrifuge, or centrifugal basket.

The isomerization is generally carried out at 425° C. to 500° C., at a pressure of 150–255 p.s.i.g., preferably using 0 to 10 volumes of hydrogen per volume of hydrocarbon vapor.

The isomerizate effluent after separation of the hydrogen has a composition generally in the range:

	Percent
Ethylbenzene	0–30
Orthoxylene	15–25
Paraxylene	16–19
Metaxylene	25–50
Heavier than C–8	2–5
Lighter than C–8	2–10

The refined isomerizate has a composition generally in the range:

	Percent
Ethylbenzene	0–30
Orthoxylene	15–25
Paraxylene	16–20
Metaxylene	25–50

Other hydrocarbons up to 1.5.

The fractionators are operated at temperatures and pressures effective to accomplish the desired separation as above described. Generally, the first fractionator overhead is in the range 60–180° C. and 2 p.s.i.a. to 40 p.s.i.g., and the bottoms are 150–210° C. and 12 to 50 p.s.i.g. The second fractionator overhead is usually about 45–145° C. and 2 p.s.i.g. to 25 p.s.i.g., and the bottoms 110–180° C. and 7 p.s.i.a. to 30 p.s.i.g.

What is claimed is:

1. In a process for the production of paraxylene wherein the paraxylene is crystallized and separated from a mixture containing predominantly C_8 aromatic hydrocarbons; and wherein the residual liquid is isomerized to form an isomerizate enriched in paraxylene, the improvement of: initially fractionating said isomerizate in a first fractionation zone to remove materials heavier than C_8 aromatic hydrocarbons as a bottoms fraction; subsequently introducing the distillate from said first fractionation zone; as a vapor to a second fractionation zone; fractionating said distillate in said fractionating zone to remove materials lighter than C_8 aromatic hydrocarbons as a distillate and recycling the bottoms product from said second fractionation zone containing a purified C_8 aromatic hydrocarbon to said crystallization step.

2. The process of claim 1 wherein the first fractionation zone is maintained at an overhead temperature of from 60 to 180° C. and pressure of 2 p.s.i.a. to 40 p.s.i.g., at a bottoms temperature of 150 to 210° C. and pressure of 12 to 50 p.s.i.g.; and said second fractionation zone at an overhead temperature of about 45 to 145° C. and pressure of 2 p.s.i.g. to 25 p.s.i.g., and a bottoms temperature of 110 to 180° C., and pressure from 7 p.s.i.a. to 30 p.s.i.g.

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