

UNITED STATES PATENT OFFICE

2,532,276

PRODUCTION AND RECOVERY OF
PARA-XYLENE

Stanley Francis Birch, Frederick Arnold Fidler,
and John Norman Haresnape, Sunbury-on-
Thames, England, assignors to Anglo-Iranian
Oil Company Limited, London, England, a
British joint-stock corporation

No Drawing. Application April 3, 1947, Serial No.
739,261. In Great Britain April 12, 1946

6 Claims. (Cl. 260-668)

1

The invention relates to the production and recovery of para-xylene, and is more particularly concerned in obtaining an increased yield of para-xylene from hydrocarbon mixtures in which it is contained.

Hitherto para-xylene was obtained by separation in known manner from petroleum and coal tar xylene fractions, normally consisting essentially of ortho-, meta- and para-xylenes and ethyl benzene, the content of para-xylene varying between 10 and 20%.

We have now found that it is possible to isomerise the ortho- and meta-xylenes contained in such xylene fractions to para-xylene under carefully controlled conditions, and thereby to increase the amount of para-xylene recoverable from such fractions.

According to the invention, an aromatic hydrocarbon fraction of coal tar or petroleum origin and boiling in the range of 135°-150° C. is treated in known manner to separate the ethyl benzene and para-xylene from the ortho- and meta-xylenes, which are then passed to a catalytic isomerisation stage in which part of the meta- and ortho-xylenes are converted into para-xylene, and the para-xylene recovered from the isomerisation product.

In a preferred method of carrying out the invention an aromatic hydrocarbon fraction boiling in the range 135-150° C., is fractionated to produce a light fraction boiling up to about 137° C., and containing the bulk of the ethyl benzene present in the aromatic hydrocarbon fraction, and an intermediate fraction of narrow boiling range and containing a high proportion of para-xylene, and a residue consisting essentially of ortho- and meta-xylenes. The intermediate fraction is cooled to a temperature within the range 0°-50° C. in order to remove the bulk of the para-xylene by crystallisation, the mother liquors together with the residue from the fractionation stage being passed to a catalytic isomerisation stage in which part of the ortho- and meta-xylene are converted into para-xylene, and the para-xylene separated from the isomerisation product.

In a modification of the process of the invention a xylene cut, boiling between 135° and 150° C., is isolated and fed to a fractionating column of 50-100 plates, operating with a reflux ratio of at least 10 to 1, to remove overhead a fraction boiling up to 138° C. and containing substantially all the ethyl benzene. The residue is then fed to a similar column operating with the same reflux ratio to produce a concentrate with

2

an approximate boiling range of 138 to 139.5° C., and containing about 40-50% of para-xylene, and a residue containing principally meta- and ortho-xylenes. Although it is generally preferred to conduct the distillation as a continuous process, it will be understood that the separation of these fractions may also be carried out in a suitable batch distillation unit.

The para-xylene concentrate is cooled to a low temperature of the order of 0° C. to crystallise out the para-xylene and the residue, together with the meta- and ortho-xylenes passed to the isomerisation stage. The product from the isomerisation stage is passed to a fractionating column as used for the first fractionation, to produce a para-xylene concentrate and a residue consisting largely of meta- and ortho-xylenes, the para-xylene being added to the previously separated para-xylene and the residue of ortho- and meta-xylenes being returned to the isomerisation stage.

According to a further modification of the process of the invention the aromatic xylene fraction is first fractionated to remove the ethyl benzene, the residue consisting essentially of the isomeric xylenes then being cooled to about -40° C. to -50° C., to remove the bulk of the para-xylene by crystallisation, the mother liquors containing the ortho- and meta-xylenes being passed to a catalytic isomerisation stage in which part of the ortho- and meta-xylenes are converted into para-xylene, and the para-xylene separated from the isomerisation product.

According to a still further modification of the process of the invention the aromatic xylene fraction is first fractionated to provide an overhead fraction rich in ethyl benzene, para-xylene and meta-xylene, an intermediate cut containing a high concentration of meta-xylene, and a residue containing ortho-xylene and higher boiling aromatics. The overhead fraction is cooled to about -40° C. to -45° C. and centrifuged whereby a solid of high concentration of para-xylene is separated and the mother liquors thereafter fractionally distilled in a column of about 100 theoretical plates. In this distillation zone an overhead fraction is obtained containing a high concentration of ethyl benzene, a residue containing a high concentration of meta-xylene and an intermediate cut containing substantial proportions of para-xylene and meta-xylene. This intermediate cut is cooled to about -40° C. to -45° C. and centrifuged, the solid obtained being essentially para-xylene. The mother liquor from this second centrifuging process is blended with

the intermediate cut obtained in the first distillation stage and fed to a catalytic isomerisation stage in which part of the ortho-xylene and meta-xylene is converted into para-xylene and thereafter the para-xylene separated from the isomerisation product.

The method of separating the para-xylene formed in the isomerisation zone is not an essential feature of the present invention and may be effected by any process known in the art. If desired, the para-xylene may be separated by any of the methods described above for the separation of para-xylene in the feedstock, for example, by recycling the isomerisation product to the initial feedstock or to the feedstock to a second or later distillation stage.

The process conditions in the isomerisation stage will depend upon the nature of the catalyst used. It is known to carry out isomerisation reactions in liquid and vapour phase over aluminium halide catalysts supported or unsupported, and also over aluminium halide-hydrocarbon complexes. Using catalysts of this general character usual process conditions include pressures in the range 1-50 atmospheres and temperatures in the range 38° C.-177° C.

A particularly advantageous method of operation of the catalytic isomerisation of the present invention using aluminium halide catalysts is described in the specification of British Patent No. 556,894.

Other catalysts which may be used for carrying out the catalytic isomerisation in accordance with the present invention are those synthetic catalysts which have a powerful catalytic effect on the cracking of high-molecular-weight hydrocarbons, such as the higher boiling cuts from petroleum, or from pure paraffin, from olefine, from naphthene hydrocarbons, or from aromatic hydrocarbons containing side chains of more than one carbon atom, into hydrocarbons of lower molecular weight. Typical examples of such catalysts are silica-alumina, silica - alumina - zirconia, silica-magnesia and silica-zirconia gels. The cracking catalysts of this type are usually operated at temperatures in the range 260° C.-677° C.

The isomerisation product is found to consist essentially of an equilibrium mixture of the three isomeric xylenes having a content of para-xylene of between 20 and 30%, and the equilibrium mixture may be fractionated into a para-xylene concentrate, and a fraction consisting essentially of ortho- and meta-xylenes, the meta- and ortho-xylenes being returned to the isomerisation stage, while para-xylene is crystallised out from the concentrate, and if desired may be further purified by re-crystallisation; the process of the invention has thus the considerable advantage that from a given quantity of xylene cut, it is possible to obtain an improved yield of para-xylene.

The xylene fraction may be derived from coal tar, the so-called 3° xylol cut being a suitable fraction, or from petroleum fractions, such as straight run naphthas, and thermally and catalytically cracked naphthas. Aromatic hydrocarbons are removed from the naphtha fractions by an extractive process, such as solvent extraction, extractive distillation and azeotropic distillation. It may be possible to isolate an aromatic xylene fraction of sufficient purity from certain catalytically cracked naphtha fractions by distillation alone.

Such aromatic hydrocarbon fractions usually contain, in addition to ethyl benzene and the xylenes, small proportions of cyclo-paraffins and

paraffins, and in the case of cracked naphthas, of unsaturated hydrocarbons. The aromatic hydrocarbon content of the fraction should be as high as possible in order to minimise carbon deposition on the catalyst in the isomerisation stage.

The invention is illustrated but in no way limited by the following example.

Example

The feedstock to the process was the whole of the material of a 95% aromatic extract of Iranian benzene boiling above 125° C. The feedstock was fractionally distilled in a 100 plate column at a reflux ratio of 10 to 1 to yield three fractions as follows:

Fraction 1, (49.65 per cent of the whole) was the lowest boiling fraction and had the composition (wt. per cent).

Ethylbenzene	30.49
Para-xylene	28.13
Meta-xylene	38.99
Non-aromatics	2.39

Fraction 2, (16.74 per cent of the whole) had the composition

Para-xylene	4.02
Meta-xylene	94.56
Ortho-xylene	1.42

Fraction 3, the residue (33.61 per cent of the whole) was ortho-xylene and higher aromatics, from which ortho-xylene was recovered by simple fractionation.

Fraction 1 was cooled to -45° C. and centrifuged. The solid so recovered (16.33% of the fraction and 8.12% of the original feed) was 93% para-xylene. The mother liquors (41.53% of the original feed) had the composition (wt. %)

Ethylbenzene	36.96
Para-xylene	16.31
Meta-xylene	43.79
Non-aromatic	3.45

These mother liquors were fractionated in a 100 plate column. From this fractionation were obtained three fractions as follows:

Fraction 4, which was 90% ethylbenzene concentrate containing 91.3% of the ethylbenzene originally present.

Fraction 5, the next boiling fraction (39.72% of the mother liquors and 16.50% of the original feed) of wt. % composition.

Ethylbenzene	7.96
Para-xylene	35.13
Meta-xylene	55.81
Non-aromatics	1.10

Fraction 6, the residue, which was 23.4% of the mother liquors and 9.73% of the original feed, was 92.9% meta-xylene and 7.1% para-xylene.

Fraction 5 was cooled to -40° C. and centrifuged and the separated solid (23.35% of fraction 5 and 3.6% of the original feed) was 96.4% para-xylene and 3.6% meta-xylene. The mother liquors from this second centrifuging (12.65% of the original feed) had the wt.% composition

Ethylbenzene	10.30
Para-xylene	16.46
Meta-xylene	71.92
Non-aromatics	1.32

5

This material was blended with fraction 2 and fraction 6 to yield a product of wt. % composition

Ethylbenzene	3.21
Para-xylene	8.66
Meta-xylene	87.10
Ortho-xylene	0.62
Non-aromatics	0.41

This blend amounted to 39% of the original feed, and formed the feedstock to an isomerisation stage using silica-alumina gel catalyst at 350° C. and a liquid feed rate of 1 volume liquid per volume of catalyst per hour, yielding a product of composition about

Ethylbenzene	4.0
Para-xylene	20.4
Meta-xylene	59.4
Ortho-xylene	16.0
Non-aromatics	0.6

This product was fractionated in the same way as the original feed to yield a para-xylene concentrate of composition close to that of fraction 5, a meta-xylene concentrate of composition close to that of fraction 2 and an ortho-xylene residue. The recovery of para-xylene from the para-xylene concentrate followed the course described above.

We claim:

1. A process for the production of para-xylene from an aromatic hydrocarbon mixture boiling in the range 135° C. to 150° C. and derived from a mineral oil selected from the group coal tar and petroleum, wherein the mixture is fractionally distilled to provide an overhead fraction rich in ethyl benzene, para-xylene and meta-xylene, an intermediate cut rich in meta-xylene and a residue fraction rich in ortho-xylene, the overhead fraction being passed to a low temperature filtration zone wherein para-xylene is separated as a solid, fractionally distilling the residue obtained from said low temperature filtration to obtain a para-xylene enriched fraction containing at least 25% by weight of para-xylene and a meta-xylene enriched fraction containing less than 10% by weight of para-xylene and thereafter subjecting the para-xylene enriched fraction to low temperature filtration for the recovery of para-xylene and subjecting the said meta-

6

xylene enriched fraction together with said intermediate cut rich in meta-xylene to catalytic isomerisation at a temperature within the range of 260° C. to 677° C. to convert at least part of said meta-xylene to para-xylene, and recovering para-xylene from the isomerisation product.

2. A process according to claim 1 in which ethyl benzene is recovered as an overhead fraction from the fractional distillation of said filtration residue.

3. A process according to claim 1 in which the residue obtained from the low temperature filtration of said para-xylene enriched fraction is subjected to catalytic isomerisation with said meta-xylene enriched fraction and said intermediate cut rich in meta-xylene.

4. A process according to claim 1 in which the low temperature filtration is conducted in the range -50° C. to -40° C.

5. A process according to claim 1 in which the catalytic isomerisation is carried out in the presence of an aluminum halide as catalyst.

6. A process according to claim 1, in which the catalytic isomerisation is carried out in the presence, as catalyst, of a silica-containing gel selected from the group consisting of silica-alumina gel, a silica-alumina-zirconia gel, a silica-magnesia gel and a silica-zirconia gel.

STANLEY FRANCIS BIRCH.
FREDERICK ARNOLD FIDLER.
JOHN NORMAN HARESHAPE.

REFERENCES CITED

The following references are of record in the file of this patent:

UNITED STATES PATENTS

Number	Name	Date
1,940,065	Spannagel et al.	Dec. 19, 1933
2,282,231	Mattox	May 5, 1942
2,403,757	Reeves	July 9, 1946
2,435,792	McArdle et al.	Feb. 10, 1948

OTHER REFERENCES

Norris et al., "The Rearrangement of the Xylenes by Aluminum Chloride," Jour. Amer. Chem. Soc., vol. 61, pages 2131-2134 (Aug., 1939), 4 pages.