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METHOD OF SEPARATING HYDROCARBONS

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This invention relates to a method for separating hydrocarbons and particularly to a process for separating aromatic hydrocarbons containing eight carbon atoms per molecule.

An object of this invention is to separate hydrocarbons having closely related boiling points.

Another object of this invention is to separate hydrocarbons present in fractions of aromatic hydrocarbons containing eight carbon atoms per molecule.

Another object of this invention is to separate ethylbenzene from a mixture also containing xylenes, particularly meta- and para-xylenes.

One embodiment of this invention relates to a process for separating hydrocarbons present in a narrow boiling hydrocarbon fraction which comprises commingling said fraction with boron trichloride, fractionally distilling the resultant mixture and separately collecting the different fractions.

Another embodiment of this invention relates to a method of separating ethylbenzene from a fraction comprising essentially ethylbenzene and the xylenes which consists in mixing said fraction with boron trichloride, fractionally distilling the resultant mixture, and separately collecting the different fractions.

A further embodiment of this invention relates to a process for separating ethylbenzene from a fraction comprising essentially ethylbenzene and the xylenes which consists in mixing with said fraction from about 0.2 to about 2 liquid volumes or boron trichloride to form a mixture, fractionally distilling said mixture, and separately collecting the different fractions.

I have found that boron trichloride in admixture with a hydrocarbon fraction boiling near 135° C. and containing principally meta-xylene, para-xylene and ethylbenzene becomes enriched in ethylbenzene in the lower boiling fractions but that the ethylbenzene concentration falls off in the higher boiling fractions and conversely the para-xylene content is relatively lower in the low-boiling fractions and higher in the high-boiling fractions. This observation is employed advantageously in the present process as a method of separating these isomeric alkyl aromatic hydrocarbons which boil too near the same boiling point temperature to permit a separation to be made by a simple fractional distillation; para-xylene, however, can be separated by a distillation procedure.

In applying my separation method to a mixture of C_8 aromatic hydrocarbons comprising ethylbenzene and the xylenes, particularly meta-

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xylene and para-xylene, the procedure consists in mixing one volume of the aromatic hydrocarbon fraction with from about 0.2 to about 2 liquid volumes of boron trichloride and then subjecting the resultant mixture to a fractional distillation. As boron trichloride is a liquid which boils at a temperature of about 13° C. and melts near −107° C., the mixing with the aromatic hydrocarbon fraction is preferably carried out in a closed reactor which may be operated under pressure and may also be cooled by suitable means. From the reactor-mixer, the resultant mixture is then conducted to suitable fractional distillation equipment using either batch-type or continuous-type of fractional distillation.

In a typical batch-type operation, the mixture of aromatic hydrocarbons and boron trichloride is distilled through a suitable fractional distillation column and the distillate is collected in several fractions of gradual increasing boiling point. Each of these separate fractions may then be subjected in turn to another fractional distillation to effect further concentration or enrichment of ethylbenzene and the xylenes in different portions of the distillate.

The distillation treatment may also be carried out in a continuous manner by continuously charging a portion of the boron trichloride-aromatic hydrocarbon fraction to a fractional distilling column which is operated so as to take overhead a relatively lower boiling fraction which is thus separated from higher boiling materials which are withdrawn from the bottom of the fractionator and if desired are conducted to another similar fractional distillation column. Also the overhead distillate from this column in which the ethylbenzene content has been increased relatively to the xylene content may be conducted to another similar fractional distillation column in order to effect further ethylbenzene enrichment of the low boiling fraction thereof.

The use of boron trichloride as an additive to hydrocarbon fractions to achieve isomer separation by extractive distillation may also be extended to other hydrocarbon systems. Thus, for example, it may be employed to effect separation of benzene and cyclohexane which can not be separated by simple distillation methods. Other hydrocarbon fractions containing saturated hydrocarbons and aromatic hydrocarbons or containing unsaturated hydrocarbons such as olefinic hydrocarbons may also be subjected to this separation treatment by utilizing boron trichloride as

an additive and then fractionally distilling the resultant mixture.

The nature of this invention is illustrated further by the following example which should not be construed to limit unduly the generally broad scope of the invention.

A mixture of xylenes and ethylbenzene of known composition was distilled in the presence of boron trichloride. The several fractions taken overhead were freed of boron trichloride by water-washing and analyzed by the ultraviolet method. Most of the added boron trichloride distilled before the hydrocarbon part, but small amounts of boron trichloride continued to come overhead with the hydrocarbon fractions. This could possibly indicate a constant boiling mixture of boron trichloride and hydrocarbon.

A run was carried out using as charging stock a mixture of isomers analyzing para-xylene 35%, meta-xylene 34%, ortho-xylene 0%, and ethylbenzene 31%.

50 ml. of isomer mixture was mixed with 46 ml. of BCl_3 and distilled to give the following data:

Table

Cut No.	B. P. °C.	Wt. Per-cent	Analysis, Per cent [a]			
			p-xylene	m-xylene	o-xylene	ethylbenzene
[b]						
0	Below 120					
1	130–103	17	32	27	0	41
2	130–134	37	34	30	0	36
3	134	29	36	35	0	29
Bottoms		11	38	42	2	18

[a] After water-washing fraction.
[b] Most of BCl_3 added distilled here.

From the above table, it is noted that ethylbenzene was concentrated in fraction 1 while fraction 3 and the distillation bottoms became more enriched in the mixture of para-xylene and meta-xylene. The indicated presence of 2% of ortho-xylene in distillation bottoms may be within the limits of error of the methods employed in analyzing the different fractions obtained in this distillation; the possibility of its arising from a re-arrangement reaction, however, is not ruled out. These hydrocarbon determinations were carried out by means of ultraviolet analysis supplemented by infrared.

The ethylbenzene which is separated from xylenes in this process may be dehydrogenated to styrene in the presence of a dehydrogenation catalyst or it may be used as an intermediate for organic synthesis. The xylenes which are also obtained from this separation treatment may be used as solvents or they may be oxidized to produce benzene dicarboxylic acids, some of which have utility in the manufacture of resins and plastics.

I claim as my invention:

1. A method of separating ethylbenzene from a fraction comprising essentially ethylbenzene and xylenes which comprises mixing said fraction with liquid boron trichloride, fractionally distilling the resultant mixture, and separately collecting the different fractions.

2. A process for separating ethylbenzene from a fraction comprising essentially ethylbenzene and xylenes which comprises mixing with said fraction from about 0.2 to about 2 liquid volumes of boron trichloride to form a mixture, fractionally distilling said mixture, and separately collecting the different fractions of distillation product.

3. A process for separating ethylbenzene from a fraction comprising essentially ethylbenzene, meta-xylene and para-xylene which comprises mixing with said fraction from about 0.2 to about 2 liquid volumes of boron trichloride to form a mixture, fractionally distilling said mixture, separately collecting the different fractions of distillation product, recovering ethylbenzene from the lower boiling fractions of said distillation product, and recovering xylenes from the higher boiling fractions of said distillation product.

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