

Separation of Ethylbenzene from C7⁺-Cut Naphtha

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ABSTRACT: A fractional distillation process for separating ethylbenzene (EB) from a feed mixture C7⁺-cut naphtha, comprising nonaromatics, BTX, EB, styrene, and C8⁺ fraction, was used. Primarily, 29.63 wt % EB in the bottom was obtained. Redistillation of the bottom component produced 63.98 wt % EB in the 2nd cut; finally, this cut was used as a feed to distillation process and 83.21 wt % EB was obtained in distillate, and

this feed was used directly for dehydrogenation process to produce styrene monomer. All of the distilled fractions were analyzed by gas chromatography instrument. © 2006 Wiley Periodicals, Inc. *J Appl Polym Sci* 102: 2795–2798, 2006

Key words: separation technique; ethylbenzene; styrene; C7⁺-cut naphtha

INTRODUCTION

Ethylbenzene (EB), used as a raw material in the production of styrene monomer, is commercially produced from alkylation of benzene with ethylene. The cost and competing demands for necessary benzene and ethylene feed streams have prompted new efforts to recover EB from various C8 aromatic feed streams. Such feed streams, for instance, include C8 aromatic extracts produced by a typical solvent extraction process from a pyrolysis gasoline or from naphtha that has been reformed with a platinum-halogen-containing catalyst. For separating nonaromatics from C7⁺-cut, nowadays liquid–liquid extraction or extractive distillation methods are used.^{1–4} Because of the great difference between atmospheric boiling point of benzene (80.15°C) and toluene (110.7°C) with that of EB (136.15°C), benzene and toluene can be separated from C7⁺-cut by atmospheric distillation.⁵ Heavy aromatics and *o*-xylene at bottom can be separated by towers of fractional distillation⁶ and by azeotropic distillation using water (because *o*-xylene does not form any azeotropic system). *o*-xylene can also be adsorbed by charcoal.⁷ The most important azeotropic agent that can be used for separating EB from *p*- and *m*-xylenes is methyl formate.^{8–10} EB can also be separated from *p*- and/or *m*-xylenes by using extractive distillation method.^{11–14} Adsorption methods comprise selective adsorption of EB on a silicate adsorp-

tion bed.¹⁵ One separation process for EB in different mixtures of other C8 aromatics is using Cs-exchanged zeolite X adsorbent¹⁶ or Sr-or-K and Sr-exchanged X or Y zeolite,^{17,18} or Na-type Y zeolite.¹⁹ The different systems of desorption are also utilized.^{20,21}

In addition, C8 aromatic cuts of hydrogenated pyrolysis naphthas or reformates prepared by fractionation without solvent extraction contain varying amounts of EB (20 wt %). C7⁺-cut can be another source for separation of EB from cut naphtha, for example, C7⁺-cut of P.G.H. plant of Arak (Iran) Petrochemical that contains 26 wt % EB on average. In feeds with quantity of nonaromatics higher than 20 wt %, it is better that at first these hydrocarbons are separated and then other steps are taken. But in C7⁺-cut of P.G.H. unit of Arak Petrochemical, the quantity of nonaromatic hydrocarbons is usually less than 3 wt % and almost 90% of them have boiling points near boiling point of benzene or toluene, and in separation steps of benzene and toluene, they are also separated. Thus the separation of nonaromatics is not necessary in the beginning.

In this work, because of little amount of nonaromatic hydrocarbons in C7⁺-cut naphtha and possibility of separation of benzene and toluene with atmospheric distillation, and also possibility of utilizing EB containing impurity of xylenes and some heavy aromatics as feed in styrene monomer manufacturing, atmospheric distillation procedure was used.

Materials

The C7⁺-cut naphtha (analytical data are given in Table I) was obtained from P.G. H. unit of Arak Petrochemical; *n*-butanol (99%) and acetic acid (extra pure) were also supplied by Arak Petrochemical.

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TABLE I
Gas Chromatography Results and Mass Balances for C7⁺-cut Naphtha and the First Distillation Process

	Feed (<i>V</i> = 1200 mL)		1st cut (<i>V</i> = 108 mL) <i>T</i> = 74–76°C		2nd cut (<i>V</i> = 404 mL) <i>T</i> = 103–107°C		Residue (<i>V</i> = 688 mL)	
	wt %	Mass (g)	wt %	Mass (g)	wt %	Mass (g)	wt %	Mass (g)
Non aromatics	1.29	13.52	4.56	4.28	2.13	7.48	0.25	1.48
Benzene	9.37	97.92	95.31	89.64	1.95	6.88	0.25	1.52
Toluene	36.29	379.28	0.31	0.12	89.69	315.6	10.53	63.08
Ethylbenzene	18.76	169.04	–	–	5.55	19.52	29.63	177.56
<i>p</i> -& <i>m</i> -Xylenes	2.35	24.58	–	–	0.68	2.36	3.72	22.27
<i>o</i> -Xylene	2.04	21.34	–	–	–	–	3.56	21.33
Styrene	2.82	29.51	–	–	–	–	4.2	29.47
Heavier	27.07	282.89	–	–	–	–	47.14	282.48

Apparatus

Gas chromatography using a Varian 3400 gas chromatograph, equipped with a capillary DB column (1.60 × 0.25 mm; film thickness = 1.0 μm) and a flame ionization detector, was used. Two standard Vigreux columns 90 cm high and a standard Vigreux column 75 cm high with glass covers were used.

EXPERIMENTAL

The first distillation process

Separation of benzene and toluene was carried out in a 2-L round-bottom distillation balloon equipped with three Vigreux columns (255 cm high in total). Fractional distillation was carried out at 74–76°C at atmospheric pressure (609 mmHg) to separate 1st cut (Benzene). Temperature range for separating 2nd cut was 103–107°C. Gas chromatography results and mass balances for this experiment are presented in Table I.

The second distillation process

Separation of EB from the bottom of the 1st experiment was carried out at atmospheric pressure using three Vigreux columns (255 cm high in total). Fractional distillation was carried out at 74–110°C at atmospheric pressure (609 mmHg) to separate 1st cut. Temperature

range for separating 2nd cut was 120–131°C. Gas Chromatography results and mass balances for this experiment are presented in Table II.

The third distillation process

Fractional distillation (atmospheric) of 2nd cut of previous experiment (the 2nd cut of the 2nd experiment) for separating toluene, *o*-xylene, and heavy aromatics was carried out. In this experiment, lower half of the column was covered by aluminum foil. At the beginning of receiving the distillate, 10 mL of distillate with boiling point of 103–120°C was received and swept away (Mass balances indicated by this 47.1% of nonaromatics and 47.3% of toluene were eliminated). Fractional distillation was carried out at 127–131°C to separate distillate. Gas chromatography results and mass balances for this experiment are presented in Table III.

For gas chromatography analyses, a split/splitless injector at 220°C and a temperature programming mode with an initial column temperature of 50°C for 10 min increased linearly to 200°C at a rate of 5°C/min, and held at the upper temperature for 10 min were used. The detector was maintained at 260°C and carrier gas was N₂ with pressure of 10 PSI. Area normalization method was used for quantitative analyses of cuts.

TABLE II
Gas Chromatography Results and Mass Balances for the Second Distillation Process

	Feed (<i>V</i> = 688 mL)		1st cut (<i>V</i> = 73 mL) <i>T</i> = 74–110°C		2nd cut (<i>V</i> = 300 mL) <i>T</i> = 120–131°C		Residue (<i>V</i> = 315 mL)	
	wt %	Mass (g)	wt %	Mass (g)	wt %	Mass (g)	wt %	Mass (g)
Non aromatics	0.25	1.48	0.41	0.26	0.98	2.57	–	–
Benzene	0.25	1.52	2.39	1.52	–	–	–	–
Toluene	10.53	63.08	92.04	58.52	1.33	3.47	–	–
Ethylbenzene	29.63	177.56	5.16	3.28	63.98	167.17	2.59	7.1
<i>p</i> -& <i>m</i> -Xylenes	3.72	22.27	–	–	8.02	20.96	0.47	1.3
<i>o</i> -Xylene	3.56	21.33	–	–	1.64	4.29	6.22	17.05
Styrene	4.2	29.47	–	–	2.27	5.93	8.58	23.54
Heavier	47.14	282.48	–	–	21.77	56.88	82.14	225.35

TABLE III
Gas Chromatography Results and Mass Balances for the Third Distillation Process

	Feed ($V = 300$ mL)		Distillate ($V = 213$ mL) $T = 127-131^{\circ}\text{C}$		Residue ($V = 77$ mL)	
	wt %	Mass (g)	wt %	Mass (g)	wt %	Mass (g)
Non aromatics	0.98	2.57	0.73	1.36	–	–
Toluene	1.33	3.47	0.99	1.83	–	–
Ethylbenzene	63.98	167.17	83.21	154.37	11.36	7.62
<i>p</i> - and <i>m</i> -Xylenes	8.02	20.96	10.45	19.39	1.56	1.04
<i>o</i> -Xylene	1.64	4.29	0.65	1.21	4.49	3.00
Styrene	2.27	5.93	2.95	5.48	0.54	0.37
Heavier	21.77	56.88	1.01	1.88	82.05	54.78

RESULTS AND DISCUSSION

The first distillation process

91.5 wt % of primary benzene was obtained in 1st cut and 90.6 wt % of primary EB was obtained in the remainder. 83.2 wt % of primary toluene was obtained in 2nd cut. Redistillation of 1st and 2nd cuts increased benzene and toluene purity up to 99.9 and 91.6%, respectively.

The second distillation process

1. All of the primary benzene was obtained in 1st cut.
2. 92.8% primary toluene was obtained in 1st cut.
3. 94.1% of primary EB remained in 2nd cut.
4. 79.9% of primary *o*-xylene remained in residue.
5. 79.8% of primary heavy aromatics were obtained in residue.

This experiment was complementary to the 1st experiment for separating benzene, toluene, and nonaromatics. If we combine the results of the two experiments, we come to the conclusion that 85.3% of EB of primary feed was obtained in 2nd cut of 2nd experiment. 99.1% of primary toluene, all the primary benzene, and 81% of primary nonaromatics were separated from EB. This experiment also showed some errors in mass balances for nonaromatics, which were not detrimental to the study's main objective (production of styrene from cut containing EB).

The third distillation process

1. 92.3% of primary EB was obtained in distillate.
2. 92.5% of primary *p*- and *m*-xylenes were obtained in distillate.
3. 96.3% of primary heavy aromatics remained in residue.
4. 69.9% of primary *o*-xylene remained in residue.

This experiment was complementary to the 2nd experiment for separating *o*-xylene and heavy aro-

omatics. If results of experiments of 1, 2, and 3 are combined, we will notice that 89.9% of nonaromatics of primary feed were separated from EB.

At last, dehydrogenation of EB from the feed containing 81.21% EB, 2.93 wt % of styrene monomer, and 1 wt % maximum heavy aromatics was carried out at 700°C in the presence of water using alumina (2500 mesh) as catalyst to produce styrene monomer. The yield was 72.4 wt % in 2.0 h. This experiment showed that the feed containing 83.21% of EB (distillate from experiment (c)) can be a good feed for styrene monomer production plants.

By using azeotropic method with acetic acid or *n*-butanol, separation of EB from xylenes was also carried out for the cut containing 83.21 wt % EB to increase the concentration of EB until 89.17%, but the experiments showed that a feed with 83.21 wt % of EB was a good feed for styrene monomer production.

CONCLUSIONS

1. Since wt % of nonaromatics in C7⁺-cut of P.G.H. unit of Arak Petrochemical is usually less than 3 wt %, separating them in the beginning is not necessary and 89.9 wt % of them were separated from EB in separation steps of benzene and toluene.
2. By fractional distillation using Vigreux columns with the height of 255 cm, 91.5% of primary benzene was obtained with purity of 95.31%. By fractional distillation, 83.20 wt % of primary toluene was obtained with purity of 89.69%.
3. By fractional distillation, 79.90 wt % of *o*-xylene and 99.00% of heavy aromatics of primary feed were separated from EB.
4. The EB was selectively converted into styrene monomer from a mixture of hydrocarbons containing 81.21 wt % EB with 72.4 wt % yield.
5. Using azeotropic methods, concentration of EB increased to 89.19%.

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