PRODUCTION OF ETHYLBENZENE FROM BENZENE AND ETHYLENE BY LIQUID-PHASE ALKYLATION USING ZEOLITE CATALYSTS

Aspen Model Documentation

Index

Process Summary

This Aspen Plus simulation models the production of ethylbenzene (EB) by liquid-phase benzene alkylation. It is intended to resemble Lummus Crest/Unocal/UOP liquid-phase alkylation process that uses a zeolite catalyst in both their alkylation and the transalkylation reactors, commercialized in 1989. In the Aspen model, the plant (base case) is designed to produce 1,150 million lb/yr (522,000 t/yr) of EB from benzene and ethylene. This capacity is sufficient to supply feedstock for the production of 1,000 to 1,075 million lb/yr (454,000 to 488,000 t/yr) of styrene. The process consists of the alkylation and EB recovery sections. Results from the Aspen simulation shows that the purity of EB obtained is approximately 99.9%. Vent gas (722 lb/hr) from a scrubber reflux drum and residue (1,866 lb/hr) from the bottom of the polyethylbenzene column are used as fuel. Wastewater (43 lb/hr) containing trace light paraffins, ethylene, benzene, and EB from the scrubber reflux drum is sent to wastewater treatment.

About This Process

Most commercial ethylbenzene (EB) is produced from benzene and ethylene by vapor-phase or liquid-phase alkylation. These reactions can be classified by catalyst type: zeolite-based or Lewis acid catalysts. These two types of catalysts have different reaction mechanisms and also result in different by-products. The alkylation by-products, mainly diethylbenzene, can be converted to EB by transalkylation. In 1989, Lummus Crest/Unocal/UOP commercialized a new liquid-phase alkylation process that uses a zeolite catalyst in both the alkylation and the transalkylation reactors. Mobil/Badger introduced a third-generation vapor-phase alkylation process, with a secondary reactor added and only one alkylation reactor required. Some of these processes allow the use of dilute ethylene feedstock, although with modifications. The first commercial installation of a vapor-phase alkylation process using dilute ethylene feedstock from fluidized catalytic cracking came on stream at Shell's Stanlow plant in 1991. Other noncommercial processes for EB production include the use of Catalyst Distillation Technologies' (CDTECH's) catalytic distillation process, benzene alkylation with ethanol, and 4-vinylcyclohexene (VCH) dehydrogenation. Table 1 provides a summary of the commercial processes for producing EB and their licensor.

TABLE 1. COMMERCIAL PROCESSES FOR PRODUCING EB

Process Type / Technology	Licensor / Developer
Alkylation of benzene with ethylene:	
Vapor-phase, zeolite-based	Mobil/Badger
Liquid-phase, zeolite-based	Lummus Crest/Unocal/UOP
Liquid-phase, $AlCl_3$-based	Monsanto/Lummus Crest
Liquid-phase, $AlCl_3$-based	Union Carbide/Badger
Liquid-phase, $AlCl_3$-based	Petroflex
Liquid-phase, BF_3-based (Alkar^{TM})	UOP
Separation from C_8 aromatics:	
Distillation (superfractionation)	Badger
Extraction and purification	Eurotecnica
Liquid-phase adsorption	UOP

This Aspen simulation model the liquid-phase benzene alkylation using a zeolite catalyst, which is a relatively new process, developed by Lummus Crest/Unocal/UOP. The liquid-phase alkylation process uses a zeolite catalyst that Union Oil of California (Unocal) developed for hydrocracking, later modifying it for EB production (330770, 330773, 517045, 517088, 517090). Lummus Crest/Unocal/UOP commercialized the process in 1989. Only one alkylation reactor is required because the catalyst needs to be regenerated only once a year, during normal plant shutdown. In addition, xylenes formation is minimized, which results in simpler purification steps and allows the use of smaller equipment to remove by-products. The low operating temperature also reduces energy costs and allows the use of carbon steel rather than stainless steel as the material of construction. The Unocal catalyst is environmentally inert, which avoids the disposal problems associated with the process using $AlCl_3$ catalyst.

Alkylation is conducted at 175-315^{0}C (350-600^{0}F) and about 500 psig with liquid benzene feed. The total liquid hourly space velocity (LHSV) is in the range of 4 to 100 (equivalent to a WHSV of about 5-135), and the overall benzene/ethylene mol ratio is 3-10. Benzene is alkylated in the presence of an alkylation catalyst by introducing a mixture of fresh and recycle benzene into a reactor having at least two catalyst beds. All the benzene feed is introduced into the first bed, whereas fresh ethylene is fed into each bed and is essentially completely converted in each bed. The reactor is adiabatic; the temperature rise in each bed is controlled so that it does not exceed 56^{0}C (100^{0}F), and the outlet temperature is kept about the same for each bed by introducing ethylene and cooling the effluent between beds. However, the complexity of the reactor beds is not depicted in the Aspen model. In the reactor, the overall A/E ratio is reduced, while the A/E ratios for each stage are maintained high enough to limit the temperature rise in order to improve selectivity and lengthen catalyst life.

A separate reactor transalkylates by-products, mainly diethylbenzene, to EB. The transalkylation reactor, which also uses a zeolite catalyst, operates at 230-340^{0}C (450-650^{0}F) and 250-700 psig, and uses a WHSV of 2-10 and a phenyl/ethyl group mol ratio of 4-10. Because transalkylation reactions evolve insignificant heat and are limited by chemical equilibrium, the transalkylation reactor is operated isothermally.

In an optional diphenylalkane converter, the PEB column bottoms can be converted to benzene, EB, PEB, and high boiling compounds (517088). The diphenylethane converter is loaded with zeolite catalyst and operated at 232^0 to 371^{0}C (450^0 to 700^{0}F) with residence times of 10 to 60 minutes. Alternatively, the effluent from the alkylation reactor can be mixed with the recycled PEB and introduced directly into the transalkylation reactor to reduce the benzene recycle rate. The feed ethylene concentration can be as low as 30%, with the reactor modified to provide additional residence time to accommodate the accumulation of inerts.

In addition to acidic zeolite/alumina and Y-zeolite/alumina, other zeolite-based catalysts such as dealuminized mordenite (517085), alumina/magnesium silicate (517084), and zeolite beta/alumina (517075) are also cited. However, yields with these catalysts are lower.

A moving bed reactor with at least one stage of catalyst bed has been proposed (517033). The bed is moved countercurrently with respect to the olefin and benzene feed, and the catalyst is continuously withdrawn from the bottom of each stage into a holding tank. Periodically, the catalyst is regenerated in a kiln under a controlled oxygen atmosphere. After regeneration, the catalyst is transferred to a holding tank for continuous or periodic feed to the top of each stage.

In a catalytic distillation process, the catalyst bed also functions as a distillation unit (517070). This technology was originally developed to produce tert-amyl-methyl ether (TAME), ethyl-tert-butyl ether (ETBE), or methyl-tert-butyl ether (MTBE) using an acidic ion-exchange resin. For EB production, ethylene is fed below the Y-zeolite catalyst bed, and excess benzene is added through the reflux. EB is recovered from the bottoms.

Process Definition

The Aspen Plus model is developed to simulate the steady-state production of EB by liquid-phase benzene alkylation using zeolite catalyst. The design is intended to resemble the new liquid-phase EB process offered by Lummus Crest, which uses a zeolite catalyst developed by Unocal. In the liquid-phase process the alkylation reactor operates at higher pressure but lower temperature than the vapor-phase alkylation process. Figure 1 in the Aspen Plus model file shows the process flow diagram, which consists of the benzene alkylation and EB recovery sections.

In the Aspen model, ethane and 1,2-diphenylethane are used to represent the light paraffins and heavies respectively. The alkylation by-products also include xylenes and PEB. Compound o-xylene is used to represent the xylenes. Since PEB is essentially diethylbenzene, 1,4-diethylbenzene is used to represent PEB. The distillation columns are assumed to have tray efficiencies of about 0.65. Thus, the number of trays used in the Aspen simulation is approximately 0.65x the number of trays shown in the PEP Report. Aspen Plus Radfrac models are used to represent the distillation columns. Due to insufficient kinetics information, Aspen Plus RSTOIC reactor models are used to represent R-101 and 2. The reactor is considered to have 2 valid phases; vapor and liquid phases.

The aromatic stream (which primarily consists of benzene and some EB) from the EB recovery section is preheated in effluent exchangers E-103A and B by exchanging heat with the combined effluent of the alkylation and the transalkylation reactors. Subsequently, the aromatic stream is further heated in feed preheater E-104 to 263°C (505°F). Most of the aromatic stream is combined with ethylene to feed alkylation reactor R-101. A small fraction of the aromatic stream, together with the recycled PEB from the EB recovery section, is diverted to feed transalkylation reactor R-102.

The alkylation reactor consists of four stages. All of the benzene required for alkylation is charged into the first stage while fresh ethylene is introduced into all the four stage. Each stage is packed with zeolite catalyst. In the Aspen model however, both the benzene and ethylene feeds are mixed and fed into the alkylation reactor. Under about 500 psig operating pressure, benzene and heavier aromatics remain in the liquid form. With a total benzene/ethylene feed molar ratio of 7.2 and a total WHSV of 5.9 (equivalent to a WHSV of 0.27 based on ethylene), the conversion based on ethylene is nearly 100%, and selectivities to EB and PEB are 92.0 mol% and 3.3 mol%, respectively. After being separated, PEB is fed to the transalkylation reactor to produce more EB. Other by-products include light paraffins, heavies, and xylenes in the EB product. Because the alkylation is exothermic, an adiabatic temperature rise occurs across the catalytic bed; the rise is limited to less than 56°C (100°F) by coordinating the ethylene feed rate to each stage. The effluents from the first two stages are cooled to generate medium-pressure (150 psi) steam in alkylation intercoolers. The effluents are further quenched by mixing with

the fresh ethylene introduced to the next stage of the reactor. The interstage cooling or cooling by mixing with fresh ethylene introduced at various stages is not included in the Aspen simulation. The reactors operate in cycles of 1 year, and the catalyst is regenerated during plant shutdown.

In separate transalkylation reactor R-102, EB is also produced by transalkylation. After reaction with benzene, PEB reaches equilibrium. The reaction is carried out almost isothermally at 250°C (482°F) and 510 psig in the presence of a zeolite catalyst similar to the one used for alkylation.

The liquid effluents from the alkylation and transalkylation reactors are combined and cooled to 198°C in effluent exchangers E-103A and B by exchanging heat with the aromatic feed stream from the EB recovery section. The combined effluent is then flashed at 135 psig in flash drum V-201 to vaporize some of the benzene. The resulting vapor stream, together with the vapor effluent from the alkylation reactor, is sent to the bottom of vent gas scrubber C-201 to strip off the light paraffins and to supply heat to the scrubber. In the meantime, fresh benzene is fed to C-201 to remove entrained water, which is sent for wastewater treatment. The noncondensable light paraffins from the C-201 overhead are purged and credited as fuel.

From the bottom of C-201, the dry aromatic stream is combined with the liquid phase from the flash drum to feed benzene fractionator C-202. The aromatic stream, consisting mainly of benzene, is recovered from the overhead of C-202 and is recycled to the alkylation section. The bottoms from C-202 are fed to column C-203 to recover EB overhead. After being cooled to 66°C (150°F) in air cooler E-206, EB is sent to rundown tanks. The bottoms from C-203 are fed to column C-204, which is operated under vacuum, where PEB is recovered overhead. The recovered PEB stream is recycled to the transalkylation reactor. Residue from the bottom of C-204 is sent to storage and is credited as fuel. In columns C-202 through C-204, hot oil is used in the reboilers and low-pressure steam is generated in the condensers.

Process Conditions

Table 2 provides the list of important blocks, design bases and assumptions for the process.

TABLE 2. ETHYLBENZENE FROM BENZENE AND ETHYLENE BY LIQUID-PHASE ALKYLATION
USING ZEOLITE CATALYST, DESIGN BASES AND ASSUMPTIONS
Capacity 1,150 million lb/yr (522,000 t/yr)
EB at 0.90 stream factor

References	517088, 517045, 330770, 330773	
	Alkylation Reactor	Transalkylation Reactor
Reactor	Fixed bed, four stages with interstage cooling	One fixed bed
Catalyst	Y-zeolite (90%) and alumina hydrogel (10%)	Y-zeolite (90%) and alumina hydrogel (10%)
Catalyst life (years)	2	2
Reactor temperature (^{0}C)	245-270	250
Reactor pressure (psig)	500	510
WHSV	5.9 lb of total feed/lb of catalyst/hr	6.0 lb of total feed/lb of catalyst/hr
	0.27 lb of ethylene/lb of catalyst/hr	--
Feed ratio (mol/mol)	7.2 (benzene/ethylene)	13 (benzene/PEB)
	6.8 (phenyl/ethyl group)	5.8 (phenyl/ethyl group)
Conversion (%)	~99.5 on ethylene	92.9 on PEB
	13.4 on benzene	
Selectivity (mol%)		
To EB	91.6	~100[a]
To PEB	3.3	--
Overall selectivity (mol%)		
To EB	98.2	
Plant yields (mol%)		
On ethylene	98.2	
On benzene	98.4	
Net consumption/production (lb/lb of EB)		
Ethylene	0.26913	
Benzene	0.74844	
Vent gas	0.00496	
Residue	0.01281	
Column internals		
C-201, Vent Gas Scrubber	Valve trays	
Design Spec	No design spec	
C-202 Benzene Fractionator	Valve trays	
Design Spec	Mass recovery of EB in the bottom stream = 93.534 %	
C-203 EB Column	Valve trays	
Design Specs	Mass recovery of EB in the distillate = 98.4 %	
	Mass recovery of PEB in the bottom stream = 99.9 %	
C-204 PEB Column	Valve trays	
Design Specs	Mass recovery of PEB in the distillate = 98.8 %	
	Mass recovery of Heavies in the bottom stream = 99.4 %	
Components		
Lites	By-products/constituent of raw material	
Ethylene	Raw material	39,285 lb/hr
Benzene	Raw material	109,054 lb/hr
EB	Product	145,710 lb/hr
Xylene	By-product	
P-EB	By-product/Intermediate product	
H2O	Constituent of raw material	
Heavies	By-product	

[a] In the transalkylation reactor, selectivity is defined as: (mol of EB produced)/(mol of PEB converted + mol of benzene converted) x 100.

Physical Property Methods and Data

The physical property method used in the Aspen Plus simulation is RK-SOAVE. The RK-SOAVE property method uses the:

- Redlich-Kwong-Soave (RKS) cubic equation of state for all thermodynamic properties except liquid molar volume.
- API method for liquid molar volume of pseudocomponents and the Rackett model for real components.

This property method is comparable to the PENG-ROB property method. It is recommended for gas processing, refinery, and petrochemical applications, appropriate for our model. The RK-SOAVE property method has built-in binary parameters, RKSKIJ, that are used automatically in ASPEN PLUS for VLE and LLE calculations. The available built-in binary parameters can be reviewed using the property parameters binary interaction RKSKIJ-1 form. Data Regression System (DRS) can also be used to determine the binary parameters from experimental phase equilibrium data (usually binary VLE data).

Chemistry/Kinetics

Reactors

This Aspen simulation models the liquid-phase benzene alkylation using a zeolite catalyst, which is a relatively new process, developed by Lummus Crest/Unocal/UOP. The main reaction and the major side reactions are similar to those in vapor-phase alkylation, except that the aromatic reactant and the products are in the liquid form:

$$C_6H_6(l) + n\,C_2H_4(l) \rightarrow C_6H_5(CH_2CH_3)_n(l)$$
$$\Delta H_R^o = -25.82 \text{ kcal/gmol}$$
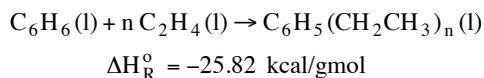
where n = 2 to 6 and the ΔH^o_R is the average heat of reaction per mole of ethylene. Diethylbenzene is the dominant PEB, and the distribution shifts toward diethylbenzene as the aromatic/ethylene (A/E) ratio increases. Other side reactions produce light paraffins, xylenes, cumene, polycyclic compounds, and compounds with boiling points between those of EB and diethylbenzene.

The alkylation by-products, mainly diethylbenzene, can be converted to EB by transalkylation. Transalkylation conducted in the presence of hydrogen can prolong catalyst life (517132, 517089). The major reaction in the transalkylation reactor is (higher PEB also transalkylates to one EB and a PEB with one less ethyl group):

$$C_6H_6(l) + C_6H_4(CH_2CH_3)_2(l) \rightarrow 2C_6H_5CH_2CH_3(l)$$
$$\Delta H_R^o = -1.3 \text{ kcal/gmol}$$
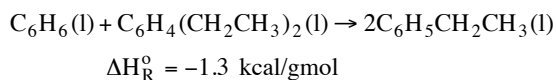
The reactions (with their conversions) used to model the RSTOIC reactor R-101 and 2 in the Aspen model are summarized below:

R-101:
  Ethylene + Benzene $\rightarrow$ EB   (Fractional conversion = 91.56% Ethylene)
  2 Ethylene + Benzene $\rightarrow$ PEB   (Fractional conversion = 6.55% Ethylene)
  Ethylene + Benzene $\rightarrow$ Xylene   (Fractional conversion = 0.02% Ethylene)
  2 Ethylene + 2 Benzene $\rightarrow$ Lites + Heavies   (Fractional conversion = 1.4% Ethylene)
R-102:
  PEB + Benzene $\rightarrow$ 2 EB   (Fractional conversion = 92.9% PEB)

References

--　　　Wang, S.-H., "Styrene, Supplement C," Process Economics Program Report No. 33C (March 1993)

517088　Sardina, G.D., et al. (to Lummus Crest), "Manufacture of Alkylbenzenes," PCt Int. Appl. 89/10910 (Nov 16, 1989)

517045　Inwood, T.V., et al. (to Union Oil of California), "Liquid-Phase Alkylation and Transalkylation Process," US 4,459,426 (July 10, 1984)

330770　Wight, C.G. (to Union Oil of California), "Manufacture of Ethylbenzene," US 4,169,111 (Sept. 25, 1979)

330773　Ward, J.W., et al. (to Union Oil of California), "Alkylation of Aromatic Hydrocarbons," US 4,185,040 (Jan. 22, 1980)

517132　Idemitsu Kosan, "Preparation of Monoalkylbenzene Used to Manufacture e.g., Ethylbenzene," Japan Kokai 1-135728 (May 29, 1989)

517089　Suciu, G. D., et al. (to Lummus Crest), "Improved Process for the Transalkylation of Polyalkylbenzenes," PCt Int. Appl. 89/12613 (Dec. 28, 1989)

517090　West, M., et al. (to Union Oil of California), "Alkylation Catalyst and Processes for Its Use," PCt Int. Appl. 90/14160 (Nov. 29, 1990)

517070　Smith, L.A., Jr. (to Chemical Research and Licensing), "Alkylation of Organic Aromatic Compounds," US 4,849,569 (July 18, 1989)

517084　Berna Tejero, J.L., et al. (to Petroquimica Espanola), "Alkylation of Aromatic Hydrocarbons in a Fixed Bed Catalytic Process," European 306,181 (June 7, 1989)

517075　Innes, R.A., et al. "Liquid Phase Alkylation or Transalkylation Process Using Zeolite Beta," US 4,891,458 (Jan. 2, 1990)

517085　Juguin, B., et al. (to Institut Francis du Petrole), "Synthesis of Alkylbenzene(s)," European 366,515 (May 2, 1990)

517033　Johnson, R.C., et al. (to Lummus Crest), "Alkylation of Benzene in a Moving Bed," US 4,973,780 (Nov. 27, 1990)

Report by: Noni Lim
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