

Improving Energy Efficiency by Using Liquid Benzene in Production of Ethylbenzene from Ethylene and Benzene

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Abstract

The production process of ethyl benzene through the alkylation reaction between ethylene and benzene is a crucial stage in the petrochemical industry, especially as the main raw material in the synthesis of styrene. The development and optimization of this process are important to increase reaction efficiency, reduce production costs, and minimize environmental impacts. This study aims to optimize the operating parameters of the alkylation reactor in order to obtain high ethylene conversion and maximum selectivity to ethyl benzene. The methods used include kinetic reaction modeling, process simulation, and sensitivity analysis to variables such as temperature, pressure, and mole ratio of ethylene to benzene. The simulation results show that the optimum conditions are achieved at a temperature of 650 °F, a pressure of 300 psig, and a mole ratio of 10:1, with ethylene conversion reaching 97.3% and ethyl benzene selectivity of 99.6%. In conclusion, this optimization approach has succeeded in increasing the efficiency of the ethyl benzene production process and can be applied on an industrial scale to improve profitability and operational sustainability.

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1. Introduction

The production of ethylbenzene via the alkylation of benzene with ethylene remains a key process in the petrochemical industry due to its essential role as a precursor in styrene synthesis. Although technological advancements such as the use of solid acid catalysts and simulation tools like Aspen plus have improved process performance, several limitations persist, including incomplete ethylene conversion, low selectivity under certain conditions, and high sensitivity to operating parameters. Recent research has explored alternative catalytic systems, such as acid modified zeolite-Y catalysts, which have demonstrated high activity and selectivity in liquid phase alkylation reaction [1]. In addition,

biobased production methods have emerged as sustainable alternatives; for example, a three-enzyme cascade was developed to convert L-phenylalanine into ethylbenzene with 82% conversion, showcasing the potential of enzyme engineering for green chemical manufacturing [2]. Another innovative approach involves coupling ethane dehydrogenation with benzene alkylation to enhance ethylbenzene yield through tandem catalysis [3]. Despite these advances, a significant research gap remains in the integration of kinetic modeling, process simulation, and sensitivity analysis to determine optimal operating conditions for industrial-scale applications. This study addresses these limitations by developing an optimized process model using Aspen HYSYS, incorporating a modified liquid-phase alkylation route that operates at lower temperatures and eliminates the need for high-temperature

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furnaces. This approach not only reduces capital and operational costs but also improves energy efficiency, offering a novel and economically viable solution for industrial ethylbenzene production [4].

2. Methods

This chapter discusses the methods used in the study of ethylbenzene (EB) production, including a review of the reaction mechanism of benzene alkylation with ethylene and the industrial production process design and simulation approaches. The explanation starts from the details of the reaction pathway and the development of catalytic technologies, both vapor and liquid phase, to the design of reactor systems, separation, and purification strategies to achieve high efficiency and selectivity. In addition, a comparison between old and new generation process technologies is also highlighted to understand the advantages and limitations of each approach in the context of modernizing the petrochemical industry.

2.1 Benzene Alkylation Processes for Ethylbenzene Production

Ethylbenzene production is a key industrial process, primarily driven by the alkylation of benzene with ethylene, and optimized through a series of catalytic and reaction pathway enhancements. The gas-phase alkylation of benzene with ethylene involves a complex reaction network, where both alkylation and dealkylation processes can take place. While ethylbenzene is the primary product, the reaction also yields minor quantities of to produce ethylbenzene diethylbenzene, along with trace levels of toluene, methyl-ethylbenzene, and xylene [5]. Gas-phase alkylation is characterized by a complex network of series and parallel reactions. During the alkylation of benzene, it can react with ethylene to produce

ethylbenzene as well as by-products such as toluene and xylene [6].

Ethylbenzene is primarily synthesized through the alkylation of benzene, with ethylene being the most commonly used alkylating agent (Scheme 1 (1)). During the reaction, ethylbenzene can further react with additional ethylene to produce polyethylbenzenes (EBs), such as diethylbenzenes (DEBs) and triethylbenzenes (TEBs) (Scheme 1 (2)). To enhance ethylbenzene production, these polyethylbenzenes undergo transalkylation with benzene (Scheme 1 (3)), which boosts the ethylbenzene yield by approximately 10%. Initially, the process used aluminum chloride (AlCl_3) as a catalyst for benzene alkylation, but later developments introduced solid acid catalysts like solid phosphoric acid and zeolites [7].

2.2 EB Process Design and Simulation of Ethylbenzene Production

The design and operation of industrial ethylbenzene (EB) production facilities involve a carefully structured process to ensure high efficiency, product purity, and long-term reliability. The industrial production of ethylbenzene (EB) involves three primary stages: first, benzene is alkylated with ethylene in multiple plug flow reactor (PFR) beds to form EB. Next, the mixture undergoes separation in two continuous distillation columns (CDCs) to isolate benzene, EB, diethylbenzene (DEB), polyethylbenzene (PEB), and inert components. Finally, DEB is converted back into EB through transalkylation in a single PFR bed. This study assumes a plant capacity of 368,000 tons of EB per year, reflecting typical output levels of modern EB facilities in the Asia-Pacific region. The plant is designed to operate 8,000 hours annually over a 20-year lifespan. While the minimum required EB purity is 99.95 wt%, the design targets a slightly higher purity of 99.97 wt% to ensure compliance under potential operational disturbances. The process uses fresh benzene and polymer-grade ethylene as its raw materials. Ethane and methane are inerts in the EB process, thus necessitating a purge stream in downstream separation to prevent their accumulation [8]. The first-generation ethylbenzene (EB) production process, introduced by American Hoechst in 1980, combined vapor-phase alkylation and transalkylation in a single reactor by recycling polyethylbenzene to the beginning of the process—similar to traditional aluminum chloride-based methods. In contrast, the more advanced third-generation technology separates transalkylation into a distinct, lower-pressure reaction step. This newer approach significantly improved product yield, purity, and reduced

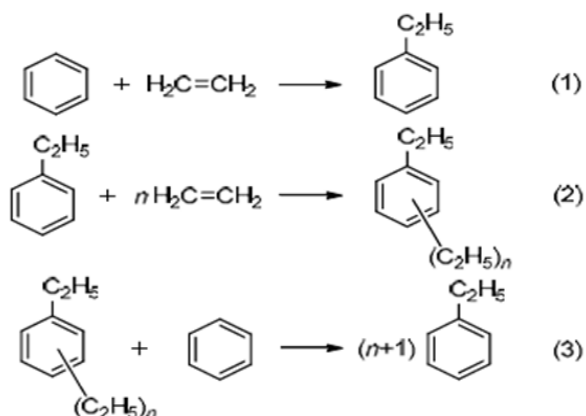


Figure 1. Scheme of alkylation reaction of benzene.

capital costs, making it a popular choice in the 1990s for upgrading older vapor-phase plants. The vapor-phase zeolite process, in particular, proved well-suited for handling dilute ethylene streams, such as those from fluid catalytic cracking (FCC) units in refineries. Before the commercialization of liquid-phase zeolite technologies in the 1990s, vapor-phase zeolite processes dominated new plant construction due to their advantage of avoiding the aqueous waste streams associated with aluminum chloride systems. Since 1980, Mobil–Badger has licensed 31 units using this technology, which continues to be used in plants processing dilute ethylene. Next, there is renewable technology, namely the liquid phase. While there are some distinctions between the two available liquid-phase ethylbenzene production technologies, the most recent versions of both offer reduced capital investment and improved product quality compared to earlier methods that used polymer-grade ethylene. Vapor phase technology, typically licensed by Mobil/Badger, remains the standard for applications involving dilute ethylene [9]. Alkylation of benzene with ethylene is widely applied to produce ethylbenzene that is an important raw material for the production of styrene. MCM-22 has been proven to have superior catalytic performance for the liquid alkylation of benzene with ethylene, which exhibits higher selectivity of ethylbenzene (EB) especially at lower molar ratio of benzene/ethylene than Beta zeolite. MCM-22 belongs to the layered MWW family and contains two independent pore systems. One is intralayer two-dimensional sinusoidal channels consisted of 10-ring (10 MR). The other is interlayer 12 MR supercages with 10 MR windows. Also, some hemi-supercages (pockets) distribute on the surface. The coexisting pore systems of MCM-22 provide shape selectivity for excellent catalytic performance in alkylation, catalytic cracking, isomerization, disproportionation [10].

3. Result and Discussion

3.1 Basic Process Flowsheet and Simulation

Although technology developers typically provide recommended design parameters, constructing a process model for ethylbenzene synthesis along with its simulation remains a highly effective method for adapting the process to specific plant conditions and for improving both resource and energy efficiency [11]. In this study, a simplified process flowsheet for ethylbenzene production was developed and simulated using Aspen HYSYS. The model incorporates essential unit operations, including feed compressors and pumps, heat exchangers, a fixed-bed reactor, and a distillation column for product purification. This

simulation framework facilitates performance evaluation under various operating conditions and serves as a foundation for identifying potential process improvements and cost reductions. Moreover, it offers valuable insights to support process optimization and informed decision making in industrial applications. As highlighted by Marchant [13], a primary objective of process optimization is to enhance the topological design and improve the utilization of sensitive components such as raw material feeds in order to maximize overall plant profitability.

In the modified process design, the reaction is conducted in the liquid phase, where the most widely used reaction is the vapor phase. This change in reaction phase offers a distinct operational advantage. Liquid phase alkylation occurs at a significantly lower temperature compared to vapor phase reactions, thereby eliminating the need for a high temperature furnace. The absence of a furnace not only simplifies the overall process flow but also leads to substantial reductions in both capital investment and operating costs. Equipment associated with high temperature operation, such as specialized materials for furnace construction and energy intensive heating systems can be avoided, making the liquid-phase approach more economical and potentially safer under typical industrial conditions.

The simulated ethylbenzene (EB) production unit operates as an industrial facility, supplying the necessary ethylbenzene for the adjacent styrene monomer unit. In this commercial operation, the alkylation reactors are engineered to achieve complete conversion of ethylene. The synthesis of EB can be represented by the following alkylation reaction [12]:



3.2 Modified Process Flowsheet and Simulation

Despite inherent differences between the two existing liquid-phase technologies, their most recent advancements have led to reductions in capital expenditure and improvements in product quality when compared to earlier processes that relied on polymer-grade ethylene. For dilute ethylene applications, vapor-phase technology is most commonly licensed by Mobil/Badger. In contrast, liquid-phase processes utilize large-pore zeolites, such as MCM-type materials, to overcome diffusional limitations inherent to liquid-phase mechanisms. Given the extended catalyst cycle times, both technology licensors typically recommend off-site catalyst regeneration. This approach reduces the amount of on-site equipment required, ultimately lowering overall investment costs [9].

To further optimize the alkylation process for ethylbenzene production, a process modification was introduced, as illustrated in Figure 2. Initially, pure ethylene at 30 °C and 1 atm is compressed to 500 psig and subsequently heated to 412 °F before entering the reactor. Simultaneously, pure liquid benzene at the same temperature and pressure is pressurized using a pump and combined with recycled benzene under identical conditions. This benzene mixture is also heated to 412 °F and then fed into the reactor. The reactor effluent consists of a liquid-phase mixture containing unreacted ethylene, unreacted benzene, and the desired product, ethylbenzene. This stream is directed to a distillation column for separation. The overhead product, which is rich in unreacted benzene, is recycled back into the system, while the bottom product ethylbenzene with a purity of 99.9% is collected as the final output.

3.3 Comparison of Results Before and After Modification

As noted by previous researcher [14], vapor-phase alkylation requires high temperatures to keep benzene in the vapor state, which also promotes the formation of by-products such as xylenes. In contrast, liquid-phase alkylation operates at lower temperatures, improving energy efficiency and reducing by-product formation. The modification applied in the process design lies in the reaction phase, where the alkylation of benzene is carried out in the liquid phase. This approach differs from previous references, which utilized the vapor phase. The use of the liquid phase offers significant advantages, one of which is the elimination of the need for a heating unit (furnace) due to the relatively lower reaction temperature required. Consequently, the absence of a furnace can reduce both capital and operating costs, making the process more economical and efficient.

Table 1. Comparison between before and after modification.

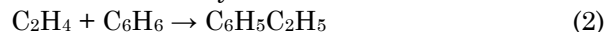
Gas/Liquid Phase EB Synthesis		
Process Conditions	Gas Phase Example 9	Liquid Phase Example 10
Pressure, psig (kPa)	300 (2170)	500 (3550)
Temperature, °F. (°C.)	650 (343)	412 (211)
C2= WHSV	4.0	0.3
C2= conversion, wt. pct.	97.3	99.6
Selectivity, pct.		
Xylene/EB	<0.0005	0.000
DEB/EB	0.087	0.066
C9+/EB	0.099	0.070

The catalytic performance of alumina-bound MCM-22 extrudates was evaluated in the high-pressure liquid-phase ethylation of benzene. Experiments were conducted at a pressure of 500 psig and within a temperature range of 400–500 °F, using a benzene-to-ethylene molar ratio of 10:1. The findings demonstrate that operating under liquid-phase conditions effectively suppresses the formation of polyethylated by-products, thereby improving selectivity toward monoethylbenzene. This trend is substantiated by the comparative data presented in Table 1.

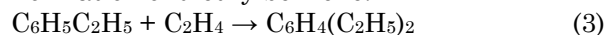
3.4 Thermodynamics Review

The reactions involved in the ethylbenzene formation process include the following alkylation reactions:

Formation of ethylbenzene:



Formation of diethylbenzene:



Thermodynamic review aims to determine the nature of the reaction and the direction of the reaction. Calculations can be done using the standard heat of formation (ΔH_f°) at a pressure of 1 atm and a temperature of 298 K of the reactants and products with the equation:

$$\Delta H_{r\ 298} = \Delta H_{f\ product}^\circ - \Delta H_{f\ reactant}^\circ \quad (4)$$

The thermodynamic analysis of the reaction (Equation 2) results in $\Delta H_{298} = -105.42$ kJ/gmol. Since the resulting ΔH is negative, the reaction is classified as an exothermic reaction. The reversible or irreversible nature of the reaction can be determined from the value of the equilibrium constant.

The reactants used as the basis for thermodynamic analysis are those involved in the ethylbenzene formation reaction in Equation (2). However, as noted by researcher [15], actual industrial alkylation processes occur under non-ideal conditions, which differ significantly from

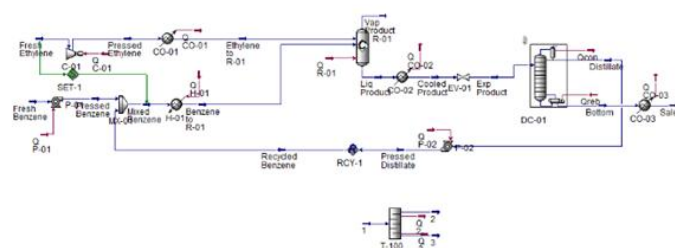


Figure 2. Simulation of the modified process reaction (liquid).

those assumed in ideal gas models. Therefore, to obtain more accurate thermodynamic parameters under realistic operating conditions, it is necessary to employ quantum chemical methods in evaluating these reactions.

3.5 Results

Ethylbenzene is conventionally produced via the vapor-phase benzene alkylation method, as illustrated in Figure 3, operating at 300 psig and 650 °F with a benzene-to-ethylene molar ratio of 10:1, resulting in an ethylene conversion of 97.3%. A more efficient alternative is the liquid-phase method, which operates at 500 psig and 412 °F, achieving a higher ethylene conversion of 99.6% and reduced energy consumption, as it requires only a heater rather than a furnace.

In the liquid-phase process, ethylene and benzene are pressurized, heated, and fed into the reactor. The liquid product is then separated in a distillation column, recycling unreacted benzene and yielding 99.9% pure ethylbenzene. Compared to the vapor phase, the liquid phase process is more energy efficient, cost effective, and delivers better conversion.

4. Conclusion

The study demonstrated that optimizing the liquid phase alkylation of ethylene and benzene, the advantage of this modification is that it eliminates the need for a furnace because the reaction temperature used is not as high as the reaction temperature of the example because it does not require a furnace, the operating and investment costs will be much cheaper and offer substantial improvements in energy efficiency and reactant conversion compared to traditional vapor phase techniques. Operating at 650 °F and 300 psig pressure without the need for a furnace, the process achieves high ethylene conversion (97.3%) and ethylbenzene selectivity (99.6%), while significantly reducing capital and operating expenses. The simplified process design contributes to greater industrial sustainability

through reduced energy demand. The integration of kinetic modeling, Aspen HYSYS simulations, and sensitivity analysis provides a robust framework for developing a cost-effective and environmentally friendly ethylbenzene production system. Future investigations should aim to validate these findings at a pilot scale and explore advanced catalytic materials to further improve the selectivity and durability of the process [16].

CRedit Author Statement

Authors contributions: C. P. Azrie led the conceptualization, oversaw the overall research process, contributed to the writing and revision of the final manuscript, and developed the simulation modeling concept. D. Carmelita performed the thermal calculations, drafted the initial manuscript, and conducted the hysis simulation modeling. F. A. Kusuma was responsible for the development of the methodology, data visualization, and simulation validation. N. P. Azzahra reviewed the comparison between before and after modification, revised the final draft, and made improvements to the physical simulation modeling. All authors have read and agreed to the published version of the manuscript.

References

- [1] Zhang, Y., Liu, H., Wang, Y. (2019). Process simulation and optimization of ethylbenzene production via Aspen Plus. *Chemical Engineering Research and Design*, 147, 1-9. DOI: 10.1016/j.cherd.2019.04.012
- [2] Qin, Z., Zhou, Y., Li, Z., Hohne, M., Bornscheuer, U.T., Wu, S. (2024). Production of biobased ethylbenzene by cascade biocatalysis with an engineered photodecarboxylase. *Angewandte Chemie International Edition*, 63 (e202314566). DOI: 10.1002/anie.202314566
- [3] Sharma, R., Bhan, A. (2020). Selective alkylation of benzene with ethylene over modified zeolite catalysts: A kinetic and mechanistic study. *Journal of Catalysis*, 389, 1-10. DOI: 10.1016/j.jcat.2020.05.002
- [4] Nakamura, K., Tanizaki, S., Tsubokawa, K., Tsuji, E., Suganuma, S., Katada, N. (2024). Ethylation of benzene with ethane over MFI zeolite-supported Pb catalyst. *Catalysis Letters*, 155 (17). DOI: 10.1007/s10562-024-04862-0
- [5] Yan, Q., Wang, D., Zhang, K., Wang, J., Cao, Y., Liu, W., Duan, X. (2025). Insights from thermodynamics analysis of gas-phase benzene alkylation with ethylene. *Chemical Engineering Science*, 121794. DOI: 10.1016/j.ces.2025.121794

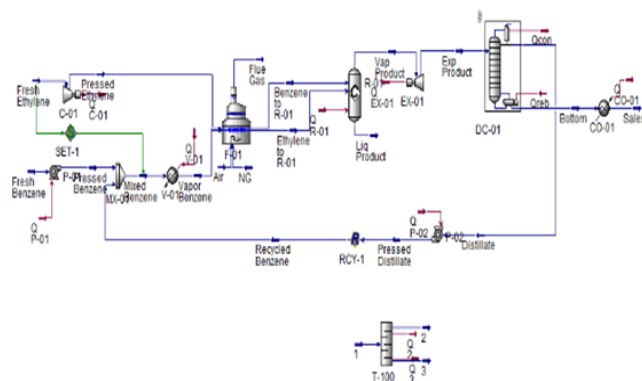


Figure 3. Simulation of the unmodified process reaction (vapor).

- [6] Cao, Y., Taghvaie Nakhjiri, A., Sarkar, S. (2023). Modelling and simulation of waste tire pyrolysis process for recovery of energy and production of valueable chemicals (BTEx). *Scientific Reports*, 13 (1), 6090. DOI: 10.1038/s41598-023-33336-3
- [7] Yang, W., Wang, Z., Sun, H., Zhang, B. (2016). Advances in development and industrial applications of ethylbenzene processes. *Chinese Journal of Catalysis*, 37(1), 16-26. DOI: 10.1016/S1872-2067(15)60965-2
- [8] Ng, Q.H., Sharma, S. S., Rangaiah, G. P. (2017). Design and analysis of an ethyl benzene production process using conventional distillation columns and dividing-wall column for multiple objectives. *Chemical Engineering Research and Design*, 118, 142-157. DOI: 10.1016/j.cherd.2016.10.046
- [9] Welch, V.A., Fallon, K.J., Gelbke, H.P., (2012). Ethylbenzene In Ullmann's Encyclopedia of Industrial Chemistry (Vol. 13). Wiley-VCH Verlag GmbH & Co. KGaA. DOI: 10.1002/14356007.a10 035.pub2
- [10] Wang, Y., Gao, Y., Xie, S., Liu, S., Chen, F., Xin, W., Xu, L. (2018). Adjustment of the Al siting in MCM-22 zeolite and its effect on alkylation performance of ethylene with benzene. *Catalysis Today*, 316, 71-77. DOI: 10.1016/j.cattod.2018.02.040
- [11] Khlebnikova, E., Dolganova, I., Ivashkina, E., Koshkin, S. (2016). Modeling of benzene with ethylene alkylation. *MATEC Web of Conferences*, 6, 01001. DOI: 10.1051/mateconf/20164901001.
- [12] Ebrahim, A.N., Sharak, A.Z., Mousavi, S.A., Aghazadeh, F., Soltani, A. (2011). Modification and optimization of benzene alkylation process for production of ethylbenzene. *Chemical Engineering and Processing: Process Intensification*, 50, 31-36. DOI: 10.1016/j.cep.2010.10.011.
- [13] Marchant, D.C. (2015). Optimization: A perspective on improving an ethylbenzene production design (Undergraduate honors thesis, University of Mississippi). eGrove. https://egrove.olemiss.edu/hon_thesis/265
- [14] Le, Q.N. (1994). Production of ethylbenzene (U.S. Patent No. 5,334,795). United States Patent and Trademark Office. <https://patents.google.com/patent/US5334795A>.
- [15] Chudinova, A.A., Buchatskaya, N.I., Ivashkina, E.N., Salischeva, A.A., Gavrikov, A.A., Nurmakanova, A.E., Khlebnikova, E.S. (2016). Increasing the efficiency of liquid phase alkylation of benzene with propylene using the method of mathematical modelling. *Procedia Engineering*, 152, 25-33. DOI: 10.1016/j.proeng.2016.07.613
- [16] Ivashkina, E., Khlebnikova, E., Dolganov, I., Khroyan, L.A. (2021). Mathematical modelling of liquid-phase alkylation of benzene with ethylene considering the process unsteadiness. *Industrial & Engineering Chemistry Research*. 59, 32, 14537-14543. DOI: 10.1021/acs.iecr.0c02660.