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REVIEW ARTICLE

Review of contemporary ethylbenzene production technologies

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Abstract

Objectives. Ethylbenzene is an important intermediate for styrene production. Most of the ethylbenzene synthesized worldwide is used to produce styrene, with smaller amounts used as a solvent or for the production of other chemicals. This article reviews contemporary technologies for the production of ethylbenzene.

Results. The liquid-phase method of ethylbenzene production using zeolite-containing catalysts for alkylation and transalkylation exhibits the highest efficiency and simplicity. In comparison with liquid-phase alkylation catalysts, e.g., aluminum chloride, zeolite-containing catalysts demonstrate high activity, selectivity, stability, and resistance to impurities. In addition, they are non-corrosive, environmentally friendly, regenerable, and have a prolonged cycle length between regenerations. More than half of the ethylbenzene synthesized globally is produced by the Badger EBMax process using a catalyst based on zeolite of the MWW family (MCM-22). This technology enables a low benzene to ethylene ratio (from 2.5 to 4), which reduces the benzene circulation rate, increases efficiency, and reduces the column throughput for benzene extraction. The main part of contemporary research in the field of benzene alkylation with ethylene into ethylbenzene is associated with the creation and use of zeolite-containing catalysts, which are solid porous systems containing an active component and a binder. The active component is USY, beta, mordenite, ZSM-5, ZSM-11, ZSM-12, ZSM-23, ZSM-35, ZSM-48, MCM-22, and MCM-49 zeolites. Among the preferred alkylation catalysts are Beta zeolite or zeolite of the MCM-22 family. The binder is Al_2O_3 , SiO_2 , or amorphous aluminosilicate. Current research also focuses on methods for creating zeolite materials with an increased mesoporous surface area by treating the initial zeolite precursor using various technologies, including combinations of acid treatment and surfactant treatment followed by alkaline solution treatment. Contemporary developments in the field of domestic alkylation and transalkylation catalysts for ethylbenzene production are presented.

Conclusions. The production of ethylbenzene and the further development of technologies for obtaining catalysts for its synthesis are highly promising and important directions in Russia. The technology of liquid-phase alkylation in the presence of contemporary highly active zeolite-containing catalysts offers significant advantages.

Keywords

ethylbenzene, styrene, alkylation, transalkylation, zeolites, zeolite catalysts

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ОБЗОРНАЯ СТАТЬЯ

Обзор современных технологий производства этилбензола

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Аннотация

Цели. Этилбензол (ЭБ) — важный промежуточный продукт для получения стирола. Для производства стирола используется большая часть производимого в мире ЭБ. Меньшее его количество употребляется в качестве растворителя или для производства других химических веществ. Цель данной работы — провести обзор современных технологий производства ЭБ.

Результаты. Показано, что жидкофазный процесс получения ЭБ с использованием цеолитсодержащих катализаторов для алкилирования и трансалкилирования является наиболее перспективным подходом к производству ЭБ вследствие максимальной простоты и эффективности. Используемые цеолитсодержащие катализаторы по сравнению с жидкофазными катализаторами алкилирования, например, хлористым алюминием, отличаются высокой активностью, селективностью, стабильностью, устойчивостью к примесям; кроме того, они некоррозионноактивны, экологичны, регенерируемые, характеризуются высоким межрегенерационным пробегом. Более половины производимого ЭБ в мире получают по технологии EBMax с использованием катализатора на основе цеолита семейства MWW (MCM-22). Технология позволяет использовать низкое соотношение бензола к этилену (от 2.5 до 4), что снижает скорость циркуляции бензола, повышает эффективность и снижает пропускную способность колонны для извлечения бензола. Основная часть современных исследований в области технологии алкилирования бензола этиленом в ЭБ связана с созданием и использованием цеолитсодержащих катализаторов, представляющих собой твердые пористые системы, содержащие активный компонент и связующее вещество. Активным компонентом служат цеолиты USY, Beta, морденит, ZSM-5, ZSM-11, ZSM-12, ZSM-23, ZSM-35, ZSM-48, MCM-22, MCM-49. Предпочтительные катализаторы алкилирования включают цеолит Beta или цеолит семейства MCM-22. Связующими веществами являются оксид алюминия Al_2O_3 , диоксид кремния SiO_2 или аморфный алюмосиликат. Современные исследования также посвящены способам создания цеолитных материалов, имеющих увеличенную площадь мезопористой поверхности, путем различных обработок исходного цеолитного предшественника, включающих комбинации кислотной обработки, обработки поверхностью-активными веществами с последующей обработкой щелочным раствором. Приведены современные разработки в области создания новых российских катализаторов алкилирования и трансалкилирования для получения ЭБ.

Выводы. Производство ЭБ и дальнейшее развитие технологии получения катализаторов для его производства имеют важное значение в России и большой потенциал. Преимуществом обладает технология жидкофазного алкилирования в присутствии современных высокоактивных цеолитсодержащих катализаторов.

Ключевые слова

этилбензол, стирол, алкилирование, трансалкилирование, цеолиты, цеолитные катализаторы

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INTRODUCTION

Among numerous petrochemical processes, the synthesis of ethylbenzene (EB) occupies one of the leading places, since EB is an important intermediate for the production of styrene. In 2023, the total global production capacity of this chemical product amounted to 48 mln t/year¹, continuing to grow rapidly at the level of 4–5% per year².

The list of companies engaged in the production of polystyrene through EB includes *Chevron Phillips Chemical* (USA), *LyondellBasell* (Netherlands), *Honeywell* (USA), *Ineos* (United Kingdom), *Dow Chemical* (USA), *DuPont* (USA), *Shell* (United Kingdom), *TotalEnergies* (France), *Versalis* (Italy), and others. In Russia, EB production is carried out by *Sibur-Khimprom*, *Gazprom Neftekhim Salavat*, *Nizhnekamskneftekhim*, and *Angarsk Polymer Plant*; however, the total capacity of EB production in Russia reaches only about 860000 t/year (1.7% of the global level) [1].

Altogether, there are 70 EB production plants in the world, of which 17 operate on aluminum chloride, a homogeneous catalyst, 28 use the gas-phase technology with heterogeneous zeolite-containing catalysts, and 25 apply a more contemporary liquid-phase technology [2]. In Russia, some enterprises continue to apply the alkylation of benzene with ethylene according to the Monsanto–Lummus method using homogeneous Friedel–Crafts catalysts based on aluminum chloride, including the *Angarsk Polymer Plant* (entered into operation in 1977 with the plant capacity of 55000 t/year) and *Nizhnekamskneftekhim* (entered into operation in 1977 with a capacity of 345000 t/year, designed by Voronezh Branch of the Scientific Research Institute for Synthetic Rubber (NIISK))³.

In addition to the main alkylation reaction, a number of side reactions occur on aluminum chloride to produce polyalkylbenzenes (di-, tri-, and tetraethylbenzenes). They are used to obtain the target product by combining the alkylation reaction with the transalkylation reaction. The transalkylation reaction is reversible. Thus, after isolation from the alkylate product, polyalkylbenzenes are recycled to yield EB. However, the use of aluminum chloride presents numerous technological, environmental, and economic problems associated with

the high corrosive activity of aluminum chloride and its toxicity, difficulties associated with its storage, use, and disposal. Additional challenges are an insufficiently high selectivity of the process (as a rule, the selectivity of the alkylation stage is up to 70%) [3, 4] and a large amount of wastewater, including acidic wastewater, resulting in high costs for its purification.

A solution to the above technological problems of the aluminum chloride-based liquid-phase alkylation technology is the transfer of alkylation and transalkylation stages to heterogeneous zeolite-containing catalysts. Their use simplifies the EB synthesis and reduces the costs involved in raw material preparation, washing the reaction mass, and neutralizing acidic wastewater. Moreover, it significantly reduces equipment corrosion. At the moment, the use of zeolite-containing catalysts for alkylation and transalkylation is the most promising approach to the production of EB^{4,5}. Zeolite-containing catalysts are stable, resistant to impurities, highly active, selective, environmentally friendly, regenerable materials with an extended cycle length. Their advantages also involve the absence of waste and the possibility of using carbon structural steel.

The installations based on a homogeneous catalyst employ the liquid-phase alkylation technology, which facilitates their transfer to a liquid-phase technology based on zeolite-containing catalysts. With such a transfer, part of the rectification equipment can be released, which can be used in another similar process for the rectification of flows [5].

The transition to zeolite technologies for the synthesis of EB has already been implemented both at Russian (*Gazprom Neftekhim Salavat* in 2003 and *Sibur-Khimprom* in 2010 [5]) and foreign enterprises. Over 20 years, significant experience in working with zeolite-containing catalysts has been accumulated.

Several years ago, a process for obtaining EB by gas-phase alkylation of benzene with ethylene over an EBEMAX-1 zeolite-containing catalyst (*Clariant*, Switzerland) was introduced at the *Gazprom Neftekhim Salavat* enterprise in Russia [6]. The process ensures the selectivity of EB formation in the 87.4–91.0% range. However, the technology requires elevated process temperatures (370–420°C), which results in an increased energy consumption, an increased yield of propyl and butylbenzenes (impurities), a lower

¹ <https://www.statista.com/statistics/1063696/global-ethylbenzene-production-capacity/>. Accessed June 28, 2023.

² ICB Americans Chemical Profile. 2007. URL: www.icis.com. Accessed May 16, 2024.

³ Russian Petrochemical Forum. Gas. Oil. Technologies. The 26th International Exhibition. May 22–25, 2018. Ufa.

⁴ Ethylbenzene. Suppliers handbook. Aboutcompanies.ru. URL: <http://b2bpoisk.ru/продукция/этилбензол>. Accessed May 05, 2024. (In Russ.).

⁵ Zamalieva R.R. Friedel–Crafts reaction. Great Russian Encyclopedia. URL: <https://bigenc.ru/c/reaktsiia-fridelia-kraftsa-b039a3>. Accessed May 05, 2024. (In Russ.).

yield of EB, and a shorter service life of the catalyst as compared to that in the liquid-phase process.

In January 2022, the first industrial batch of the Russian KT-GA-1 catalyst based on a zeolite of the Mobil-type Five (MFI) family (Zeolite Socony Mobil-5, ZSM-5⁶) was released for the process of gas-phase alkylation of benzene with ethylene into EB. On July 19, 2022, pilot tests of the catalyst were launched, continuing up to the present day. During the first year of operation, it became obvious that the Russian catalyst was not inferior to its imported counterpart in terms of all aspects. Thus, when using two catalysts—foreign-made EBEMAX-1 and Russian KT-GA-1—the concentration of EB in the EB rectified product comprised 99.76% and 99.85%, respectively. The selectivity of EB formation on the KT-GA-1 catalyst was 86.9–90.4% [6].

A highly selective liquid-phase process for producing EB using the EBMax technology (more than 99%)⁷ under a license from *Badger Licensing* (USA) has been implemented in Russia by *Sibur-Khimprom* (capacity 230000 t/year). The technology employs ExxonMobil zeolite catalysts containing zeolites of the MWW (Mobil twenty-two)⁸ family (MCM-22, Mobil Composition of Matter No. 22). *ExxonMobil* (USA) maintains its position as one of the leading suppliers of catalysts for EB production in the world. Since 2001, almost two-thirds of all new and revamped EB capacities have been licensed by *Badger Licensing* and use *ExxonMobil* catalysts. *ExxonMobil* catalysts used in the *Badger EBMax* and *Badger Vapor Phase*⁹ processes account for more than 56% of the global EB production, exceeding 20 mln metric t/year.

Since 2023, *Nizhnekamskneftekhim* has been upgrading its benzene alkylation unit with a transition to a zeolite-containing catalyst and increasing the EB capacity to 350000 t/year using the *Lummus/UOP EBOne* technology. In 2021, *Nizhnekamskneftekhim* signed an agreement with *Lummus* (USA) to license technologies for the production of EB (EBOne) and styrene monomer (CLASSIC SM). Efforts were implemented to reduce byproduct formation by altering reaction conditions.

However, only the advent of liquid-phase and mixed technologies operating at temperatures below 270°C made it possible to synthesize high-purity EB through zeolite-catalyzed processes. EB-350/SM-400 units will be launched simultaneously with a new EP-600-1 unit (scheduled for early 2026).^{10,11,12}

In this article, we set out to review and compare contemporary technologies for the production of EB, mainly liquid-phase technologies using zeolite-containing catalysts.

1. EB PRODUCTION TECHNOLOGIES

The details of applying zeolite-containing catalysts for EB synthesis involve the implementation of alkylation and transalkylation reactions in separate reactors. Zeolite-containing catalysts have been used in EB production processes since the 1980s in the gas-phase process and, since the 1990s, in the liquid-phase process. Zeolite-containing catalysts were developed by *UOP* (USA) and *ExxonMobil* (USA). *Mobil-Badger* (USA) introduced the first gas-phase process for benzene alkylation with ethylene using a catalyst based on a medium-porosity zeolite of the ZSM-5 type. However, due to the specific structure of this zeolite and the need to overcome diffusion limitations, the alkylation temperature exceeded 400°C.

The structure of this catalyst is characterized by perpendicularly intersecting channels with five-membered rings at the base. Zeolite ZSM-5 demonstrated pronounced activity and resistance to deactivation with coke in gas-phase processes. However, along with the development of liquid-phase technologies, its use in alkylation decreased due to insufficient activity and a tendency to rapid deactivation. However, this catalyst continues to be applied in gas-phase units, in particular, at the transalkylation stage.

At present, EBEMAX-11 and EBUF-1 catalysts manufacturing by *Clariant* are used in gas-phase alkylation, while EBEMAX-2 and EBUF-2 catalysts are used for transalkylation. The patent [7] proposed a method for producing a zeolite-containing catalyst for

⁶ ZSM-5 is a zeolite type according to the atlas of zeolites: Ch. Baerlocher *et al.* *Atlas of Zeolite Framework Types*. Elsevier, 2007. It is a synthetic zeolite belonging to the pentasil family.

⁷ Presentation of EQUATE Petrochemical Company. <https://www.slideserve.com/laith-nunez/eb-plant-equate-petrochemical-company>. Accessed January 10, 2025.

⁸ MWW is a thin-layered (or lamellar) zeolite with a honeycomb-like structure.

⁹ <https://www.exxonmobilchemical.com/en/catalysts-and-technology-licensing/benzene-alkylation/ethylbenzene-alkylation>. Accessed January 09, 2025.

¹⁰ <https://smart-lab.ru/blog/859787.php>. Accessed May 17, 2023. (In Russ.).

¹¹ <https://www.sibur.com/ru/press-center/news-and-press/sibur-postroit-dva-novykh-proizvodstva-v-nizhnekamske-/>. Accessed July 02, 2025. (In Russ.).

¹² <https://www.ogi.com/refining-processing/refining/article/14202241/nknk-lets-contract-to-expand-existing-tatarstan-olefins-complex>. Accessed May 17, 2023.

the alkylation of benzene with ethylene in a gas-phase process based on zeolite ZSM-5 without a binder.

It should be noted that the high temperature of gas-phase alkylation promotes oligomerization, cracking, isomerization, and hydrogen transfer reactions, thus affecting the purity of the final EB. In addition, narrow- and medium-porosity zeolites in the gas-phase process for producing EB are characterized by accelerated deactivation due to coke formation as a result of deposition of large molecules on the active sites of the zeolite. These molecules slowly diffuse from the porous structure of the zeolite.

Other disadvantages of the gas-phase process are related to low selectivity and low EB yield. Despite the efforts made to reduce the formation of byproducts in the gas-phase process by optimizing the reaction conditions, it was only the development of liquid-phase processes operating at temperatures below 270°C that made it possible to efficiently produce high-purity EB (99.9 wt %, with a toluene content of 450 ppmw, cumene of 100 ppmw, diethylbenzene (DEB) of 5 ppmw, xylenes of 10 ppmw). Having been developed in the 1990s, these processes are offered today by leading licensors of EB technologies (*Badger EBMax*, *Lummus EBOne*, and *Versalis*). In order to overcome diffusion limitations in the liquid-phase process, zeolite catalysts containing wide-pore zeolites of the common Faujasite (FAU) and BEA [4] structural types, or the more expensive MWW are used.

Such zeolites possess 3D structures with a branched system of cavities and channels, which improves catalytic activity and reaction selectivity. Lewis and Brønsted acid sites are present on the surface and in the pores of zeolites. These sites play a key role in alkylation catalysis and determine the efficiency of catalysis in the target reactions. Therefore, particular attention is paid to the number, accessibility, and strength of acid sites.

The MCM-22 zeolite of the MWW structural type is characterized by a large pore volume, high acidity, good hydrothermal stability, and molecular sieve properties that ensure high selectivity in alkylation and transalkylation processes [8]. It exhibits a higher selectivity than Beta zeolite, thus reducing the formation of polyalkylbenzenes and heavy products.

In comparison with the gas-phase process, the advantages of the liquid-phase process of benzene alkylation with ethylene involve:

- reduced energy costs due to lower process temperatures;
- increased EB yield and selectivity of its formation;
- reduced byproduct yield;
- increased catalyst service life and long cycle length between regenerations.

In the liquid-phase alkylation of benzene with ethylene using zeolite-containing catalysts, along with EB, the following byproducts are formed: polyethylbenzenes (PEB), in particular DEB and triethylbenzene (TEB), xylenes, and cumene. At the transalkylation stage, DEB and TEB are almost completely converted into EB, with only trace amounts of DEB remaining in the product, which are regulated. The content of xylenes and cumene inseparable during rectification in the product is also regulated.

The selectivity for EB in the liquid-phase process in the presence of zeolite-containing catalysts (in particular, Beta zeolite in the H-form) is at least 80% [4]. Moreover, the additional stage of liquid-phase transalkylation makes it possible to convert the remaining 20% of PEB into EB.

In Russia, zeolite-containing catalysts and technologies for the processes of benzene alkylation with ethylene and benzene transalkylation with DEB were initially developed by specialists of the Grozny Oil Research Institute. Today, active work is underway at the Institute of Petrochemical Synthesis of the Russian Academy of Sciences and the Scientific and Technical center of *Gazprom Neftekhim Salavat* [9]. In addition, *Zeolitika* (Moscow) is creating new technologies for the production of synthetic zeolites. The Boreskov Institute of Catalysis of the Siberian Branch of the Russian Academy of Sciences (Novosibirsk) actively conducts research in the field of chemical catalysis and catalytic processes.

The main part of contemporary research in the field of benzene alkylation technology with ethylene into EB is associated with the creation and use of zeolite-containing catalysts, which are solid porous systems containing an active component and a binder. The active components are Ultrastable Y (USY) zeolites, Beta, mordenite, ZSM-5, ZSM-11, ZSM-12, ZSM-23, ZSM-35, ZSM-48, MCM-22, and MCM-49. The preferred alkylation catalysts include Beta zeolite or a zeolite of the MCM-22 family. The binder is Al_2O_3 , SiO_2 , or amorphous aluminosilicate. After mixing the active component and the binder, granules are formed from the resulting mass, which are then dried and calcined. In some cases, the catalyst is then modified. Typically, the zeolite content in the catalysts ranges from 60 to 80 wt % [10, 11].

The works [12, 13] considered methods for creating zeolite materials with an increased mesoporous surface area compared to the precursor composition. The catalyst precursor composition has a high degree of crystallinity. The technology may involve treating this composition with a surfactant under conditions effective for creating or increasing mesoporosity

in the catalyst precursor composition. Large pore molecular sieves such as Beta zeolite, Zeolite Y, USY, ultrahydrophobic Y (UHP-Y), dealuminated Y (Deal Y), mordenite, ZSM-3, ZSM-4, ZSM-14, ZSM-18, ZSM-20, and mixtures thereof can be used as catalyst precursors.

Another class of molecular sieve materials that may be present in the catalyst precursor composition as an auxiliary component is the group of mesoporous crystalline materials, e.g., MCM-41 and MCM-48 materials. The study [12] reported methods for treating a zeolite material to increase its mesoporous surface area using a combination of acid treatment and surfactant treatment followed by treatment with an alkaline solution.

The surfactant used may be of a cationic nature, e.g., comprising one or more alkyl trimethyl ammonium salts and/or one or more dialkyl dimethyl ammonium salts, or of a non-ionic nature. The examples of suitable commercially available non-ionic surfactants include, e.g., Pluronic™ surfactants (e.g., Pluronic™ P123) manufactured by *BASF Societas Europaea* (Germany).

The acids used to treat the starting zeolite may be any organic or inorganic (mineral) acids. The amount of acid used in the treatment mixture may range from ~3 to ~6 mEq/g of the starting zeolite material, selected such that the pH of the treatment mixture ranged within 3–4. The mixture is then stirred for about 2 h. In addition, the treatment mixture may be heated to a temperature of from ~40 to ~80°C.

After treating the zeolite with the acid and surfactant, a portion of the resulting surfactant-treated zeolite material is recovered from the treatment mixture and washed with deionized water one or several times. Following recovery, the zeolite material is contacted with a base. Suitable bases include NaOH, NH₄OH, KOH, Na₂CO₃, TMAOH, and mixtures thereof. In some implementation variations, the base used may be in the form of an aqueous solution having a concentration in the range of 0.2–15 wt %. The amount of the base used in relation to the initial amount of the starting zeolite material ranges from 0.1 to 20 mmol per gram of the starting zeolite material. The treatment of the surfactant-treated zeolite material with a base can be carried out under elevated temperature conditions, including temperatures from ~50 to ~150°C for 16–18 h.

After treatment with a base, the resulting mesoporous zeolite material is isolated by filtration, washed, and dried. The treated zeolite is then molded with a commercially available alumina binder with a zeolite/binder weight ratio of 65/35. The mixture is extruded into 1/20-inch quadrilobes. The extrudates are dried in a stream of nitrogen at a temperature of 482°C followed by calcination at a temperature of 538°C in air.

It has been found that the treatment of zeolites leads to the creation of catalytic compositions with an increased mesoporous surface area, which allows the transalkylation process temperatures to be decreased and the catalytic activity of the catalysts to be increased.

A number of contemporary developments, including those in Russia, in the field of improving the process of liquid-phase transalkylation of benzene with DEB are devoted to the creation and use of zeolite [14, 15] and zeolite-containing [16, 17] catalysts based on Zeolite Y. Thus, starting from 2013 and up to the present time, the KT-BS-1 catalyst, a joint development of *NTC Salavatnefteorgsintez* and the Institute of Petrochemical Synthesis of the Russian Academy of Sciences (Moscow), has been successfully operated at the *Monomer* plant of the *Gazprom Neftekhim Salavat* enterprise. The KT-BS-1 catalyst is a deeply decationized Zeolite Y, containing no binders. The KT-BS-1 catalyst is produced in Russia (based on the set of necessary technological equipment) only by the *Ishimbay Catalyst Plant* (Ishimbay). The task of providing the necessary conditions for the production of a catalyst for benzene transalkylation with DEB to EB, comparable in quality to the KT-BS-1 brand catalyst, but using a fundamentally different technology, was set and successfully solved at the Scientific and Technical Center of *Gazprom Neftekhim Salavat* (hereinafter referred to as the STC).

As an alternative to the catalyst for benzene transalkylation with DEB of the KT-BS-1 brand, the STC developed a catalyst granulated with a binder [18] (hereinafter referred to as KT-SS). The catalyst contains 80 wt % of Zeolite Y in the acidic H⁺ form and 20 wt % of alumina as a binder. In comparison with the zeolite KT-BS-1, the KT-SS catalyst is obtained using the conventional technology for producing zeolite-containing catalysts with a binder. As a result, the catalyst has a developed secondary porous structure which plays a transport role in the supply of reactants to the active centers of the catalyst and the removal of reaction products. In addition, this catalyst can be produced in the required tonnage at any catalyst factory in Russia. The developed catalyst for the benzene transalkylation with DEB provides DEB conversion at the level of 82–83% with an EB yield of 21–22 wt % based on the passed feedstock. These indicators are comparable with the process indicators when using the KT-BS-1 catalyst. In 2023, a batch of the catalyst was produced and loaded into the transalkylation unit of workshop No. 46 of the *Monomer* plant.

The main contemporary technologies for producing EB are presented below.

1.1. Technip Energies/Badger Ethylbenzene EBMax technology

In parallel with the development of the gas-phase process for producing EB (since 1976) on the EM-3000 (ZSM-5) catalyst, *Mobil-Badger (ExxonMobil-Badger)* developed a liquid-phase alkylation process under the EBMax trademark. A significant advantage of this technology consists in the use of a new MCM-22 type zeolite developed by *ExxonMobil*, as a catalyst, which surpasses zeolite Beta and zeolite Y in terms of selectivity [19]. Today, the technologies developed by *Mobil-Badger* account for about 55% of all EB produced, with more than its half being produced using the EBMax technology [20]. Since 1995, the EBMax technology has been licensed 40 times, both for new plants and for the expansion and reconstruction of plants based on earlier technologies.¹³

ExxonMobil is one of the leading suppliers of EB catalysts in the world. Since 2001, nearly two-thirds

of all new and revamped EB capacity licensed by *Badger* has used *ExxonMobil* catalysts. As of 2017, *ExxonMobil* catalysts have been installed at approximately 35 EBMax customers. This enabled the construction of new plants, as well as the upgrading and expansion of EB production capacity at the world's largest plants. *ExxonMobil* catalysts account for more than 56% of the global EB production, exceeding 20 mln metric t/year, in the *Badger* EBMax (highly selective liquid phase) and *Badger* Vapor Phase (gas phase) processes.

The first commercial application of the process commenced in 1995 in Japan. Initially, the transalkylation process was carried out in the gas phase, using the ZSM-5 zeolite catalysis, in a manner similar to existing gas phase alkylation units.¹⁴ Later, following the emergence of catalysts based on MCM-22 zeolite, the process also became a liquid-phase one. Table 1 presents the main parameters of the EBMax process and the catalysts used.

Table 1. Key parameters of the EBMax process and the catalysts used

Key parameters	Alkylation	Transalkylation	Catalysts			
			Alkylation	Transalkylation		
Phase	Liquid	Liquid	EM-3300 (1995); EM-3210/EM-3310 (MSM-22 Zeolite)	EM-3700 ¹⁵ (MSM-22 Zeolite)		
Reaction temperature, °C	195–257	–				
Temperature of the feed mixture at the inlet to the transalkylation reactor, °C	–	200				
Reaction pressure, MPa	3.4	3.1				
Benzene/ethylene ratio (mol)	2.5–4	–				
Benzene/PEB ratio (wt)	–	2.0				
Ethylene conversion, %	100	–				
DEB conversion, %	–	62				
EB yield, wt %	99.5					
EB purity, vol %	min 99.8					
Cycle length between catalyst regenerations, years	More than 3					

¹³ https://www.badgerlicensing.com/sites/badger/files/2024-06/flysheet_ethylbenzene.pdf. Accessed January 10, 2025.

¹⁴ Koshkin S.A. Analysis and optimization of industrial technology for producing ethylbenzene on zeolite-containing catalysts. Cand. Sci. Thesis (Eng.). Tomsk. 2017.

¹⁵ Previously, a gas-phase process on ZSM-5 zeolite was used.

In the EBMax process, benzene is fed to the bottom of a liquid-filled multi-bed reactor. Ethylene is fed together with benzene at the reactor inlet and between the catalyst beds. The PEBs, which consist mainly of DEB, are transalkylated with benzene in a second reactor to form additional EB (Fig. 1). A special feature of the EBMax technology is the use of a catalytic reactive guard bed necessitated the need to employ expensive *ExxonMobil* zeolite-containing alkylation and transalkylation catalysts based on MWZ zeolite. These catalysts are sensitive to impurities of catalyst poisons in the feedstock. The presence of a highly selective catalyst based on MCM-22 in the technology allows the benzene to ethylene ratio to be decreased (from 2.5 to 4). This reduces the benzene circulation rate, increases efficiency, and reduces the throughput of the benzene extraction column. More than half of the EB produced in the world is obtained using the EBMax technology.

The cost of the steam produced in the process usually covers energy consumption and additional material costs. About 95% of the cost of EB production includes the cost of raw materials, with the remaining 5% being associated with energy and other costs [21]. Benzene accounts for the largest share of the cost of raw materials. In this context, the cost of EB production mainly depends on the price of benzene.

1.2. Lummus/UOP EBOne technology

The *Lummus/UOP* EBOne technology was first commercialized in 1990 by *Nippon Steel Chemical*

Company, Japan. The liquid-phase EBOne process uses a *UOP* zeolite-containing fixed-bed catalyst with a cycle length between regenerations of three to five years. This eliminates the need for regeneration equipment. The process requires low capital investments, provides high yields, and is energy-efficient. The formation of xylene impurities is virtually eliminated, which results in EB of excellent quality. The regenerated catalyst shows an efficiency equal to fresh catalyst, which is commercially proven. There are more than 45 projects worldwide with a capacity of 100000 to 1250000 t/year calculated for EB

The catalysts have undergone multiple regenerations without losing their mechanical strength or process characteristics. Q-Max catalysts are described in patents [22–24]. Initially, a Y-type zeolite was used at the alkylation stage. An USY-type zeolite was used at the transalkylation stage [11]. The technology development resulted in the use of new catalysts for alkylation and transalkylation catalysis under the trade names of *UOP* EBZ-500 (based on Beta zeolite) and EBZ-800 (based on USY zeolite) in 1996. Later, in the 2000s, *UOP* introduced a more contemporary alkylation catalyst, EBZ-800TL based on UZM-8 zeolite of the MWY structural type [25].

Table 2 presents the currently existing EB production plants operated based on the EBOne technology.

The process flow diagram of the EBOne process is shown in Fig. 2.

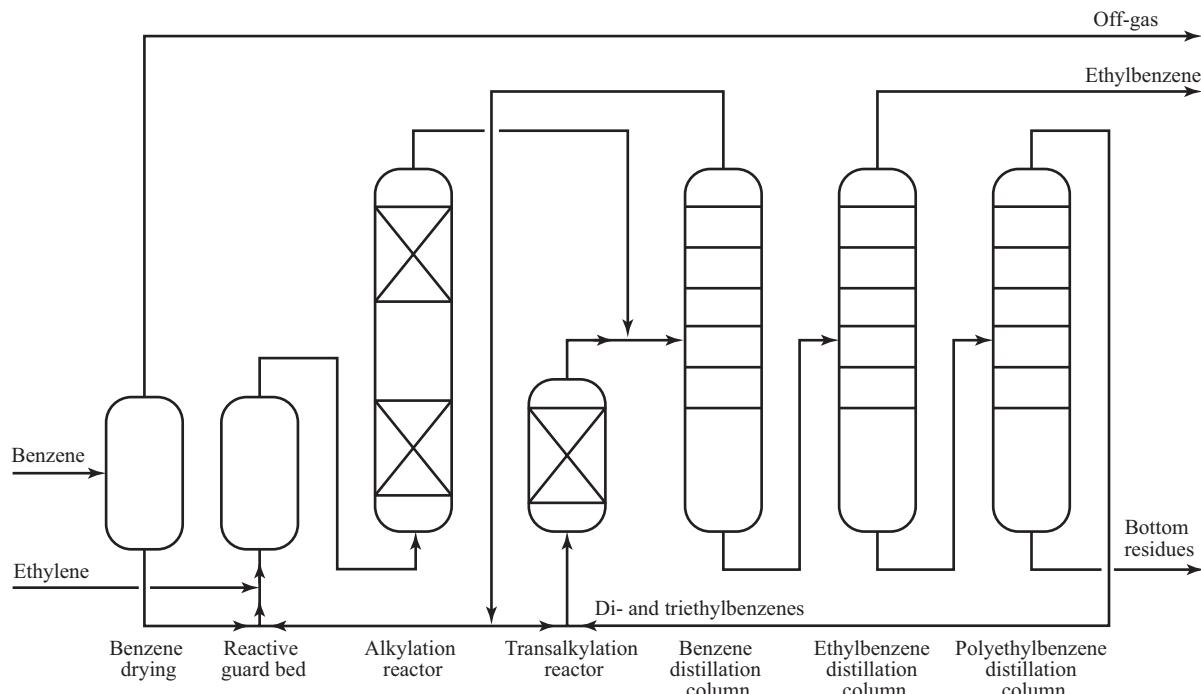


Fig. 1. Process flow diagram of the *Badger* EBMax process [19]

Table 2. Existing EB production plants using EBOne technology [26]

Company	Location	Capacity, t/year	Start
<i>Carbon Holdings</i>	Ain Sokhna, Egypt	424000	2020
<i>Tianjin Bohua Chemical Development Co.</i>	Tianjin, China	530000	2019
<i>PetroChina Jilin (No. 2)</i>	Jilin, China	342000	2012
<i>CNOOC/Shell Nanhai B.V.</i>	Huizhou, China	640000	2006
<i>PetroChina Daqing</i>	Daqing, China	95400	2005
<i>Asahi Kasei Corporation</i>	Mizushima, Japan	360000	2005
<i>SECCO (BP-SPC)</i>	Shanghai, China	719000 (695500) (535000)	2011 2009 2005
<i>Synthos Litvinov (Kaucuk)</i>	Litvinov, Czech Republic	300000	2004
<i>LG Chem I and II</i>	Yeosu, Republic of Korea	536472	2003
<i>Asahi Kasei Corporation</i>	Mizushima, Japan	355000	2003
<i>LyondellBasell (ARCO Chemical)</i>	Maasvlakte, The Netherlands	726000	2003
<i>Repsol</i>	Tarragona, Spain	505000 (380000)	2006 2000
<i>SADAF (Styrene II Project)</i>	Al Jubail, Saudi Arabia	530000	2000
<i>Trinseo (Styron, Dow/BSL)</i>	Böhlen, Germany	355000	1999
<i>PT Styrindo Mono Indonesia (SM No. 2)</i>	Merak, Indonesia	212000	1999
<i>IRPC (TPI)</i>	Rayong, Thailand	280000 (212000)	2013 1999
<i>PetroChina Jilin (JCI) (No. 1)</i>	Jilin, China	160000 (106000)	2002 1998
<i>Tabriz Petrochemical Co.</i>	Tabriz, Iran	106000	1998
<i>BASF-Sinopec YPC Company</i>	Nanjing, China	130000	1998
<i>Sinopec Maoming</i>	Maoming, China	106000	1996
<i>Shell Chemicals Seraya I</i>	Singapore	360000	1996
<i>Denka (Chiba Styrene Monomer)</i>	Chiba, Japan	265000	1994
<i>Taiyo Oil Company (Mitsui Toatsu Chemicals)</i>	Ube, Japan	288000	1993
<i>NS Styrene Monomer (Nippon Steel Chemical Co.) (SM No. 3)</i>	Oita, Japan	212000	1990

The EBOne process is essentially identical in design to the EBMax technology. It uses two reactors: one for benzene alkylation and one for DEB transalkylation. The reactors operate near the critical temperatures of the reaction mixtures to maximize EB yield.

The liquid-phase alkylation reactor comprises several zeolite catalyst beds operating adiabatically. The process conditions are selected such that to maintain the alkylation reaction mass in the liquid phase. Benzene is used in excess, and ethylene is introduced before each bed, which improves selectivity and increases the service life of the catalyst. Ethylene reacts completely in the alkylation reactor, thus leaving only inert components (ethane, etc.). These inert components pass through the reactor and are removed from the unit. The transalkylation reactor, similar in design to the alkylation reactor, also consists of several beds of zeolite catalyst. The conditions are also selected to conduct a liquid-phase process. The alkylation and transalkylation effluents are fed to a benzene column, where benzene is collected to the reactors as the top product for recirculation. The bottom part of the benzene column is fed to an EB column, where the product EB is obtained at the top. The distillation residue is withdrawn to a PAB (polyalkylbenzenes) column, from which DEB and TEB are withdrawn from the top as transalkylation feedstock. PAB resin is obtained from the bottom and is further used for fuel needs. The reboilers of the distillation columns can use hot oil, high-pressure steam, or direct heating. The

overhead vapors are condensed in waste heat boilers to form industrial steam.

A typical range of operating parameters for the EBOne process and the catalysts used are given in Table 3.

The EBOne technology is highly flexible. An increase in the efficiency of the process to about 70% can be achieved without economic losses. After reaching the 70% range, some losses in energy efficiency may be appeared in the distillation section. However, the reaction system efficiency can be at least 50% without any adverse technological or economic consequences.

1.3. CDTech EB technology

CDTech EB is an advanced technology developed by Catalytic Distillation Technologies Inc (CDTech) that produces high-purity EB from ethylene and benzene using a patented catalytic distillation process. The CDTech EB process flow diagram differs from EBOne technology only in the alkylation reactor system (Fig. 3).

The CDTech EB process is based on a patented catalytic distillation concept that combines the catalytic reaction and distillation in a single operation. Gaseous ethylene is introduced into the bottom of each reaction zone (either directly or via the overhead of the benzene column). The reaction takes place in the catalytic zones of the reactor, while distillation occurs throughout the column, which results in a counter-current of vapor and liquid throughout the reactor.

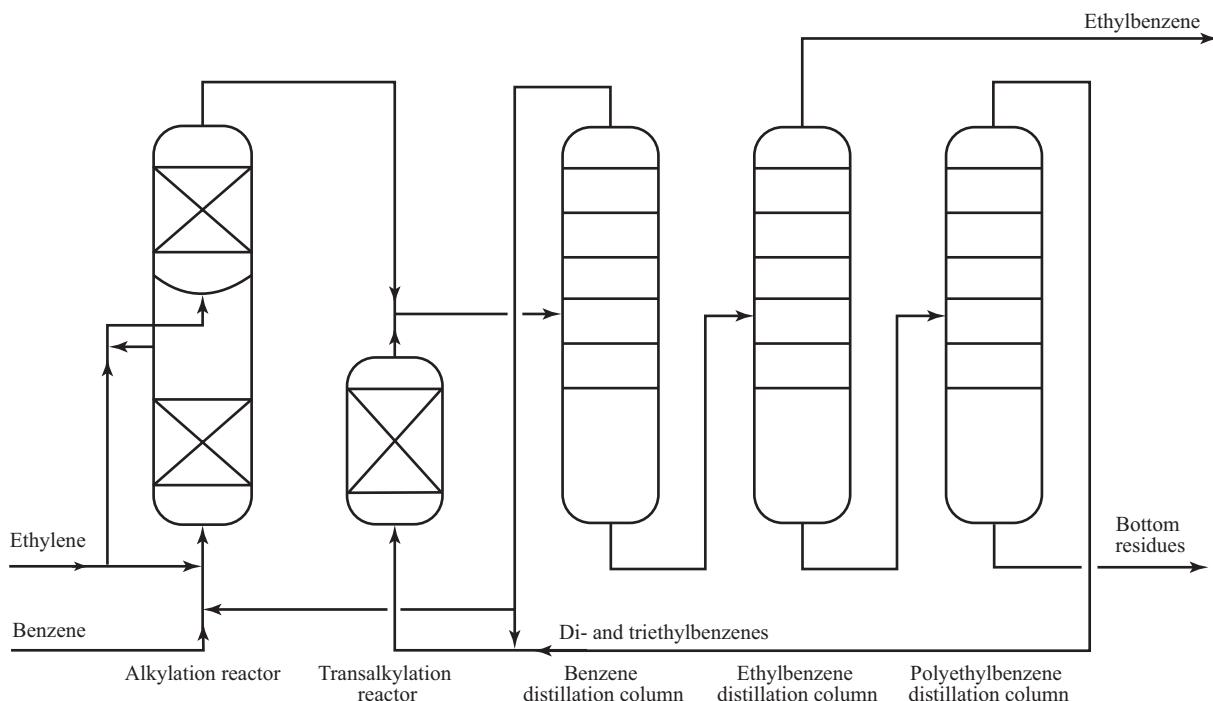


Fig. 2. Process flow diagram of the UOP EBOne process [25]

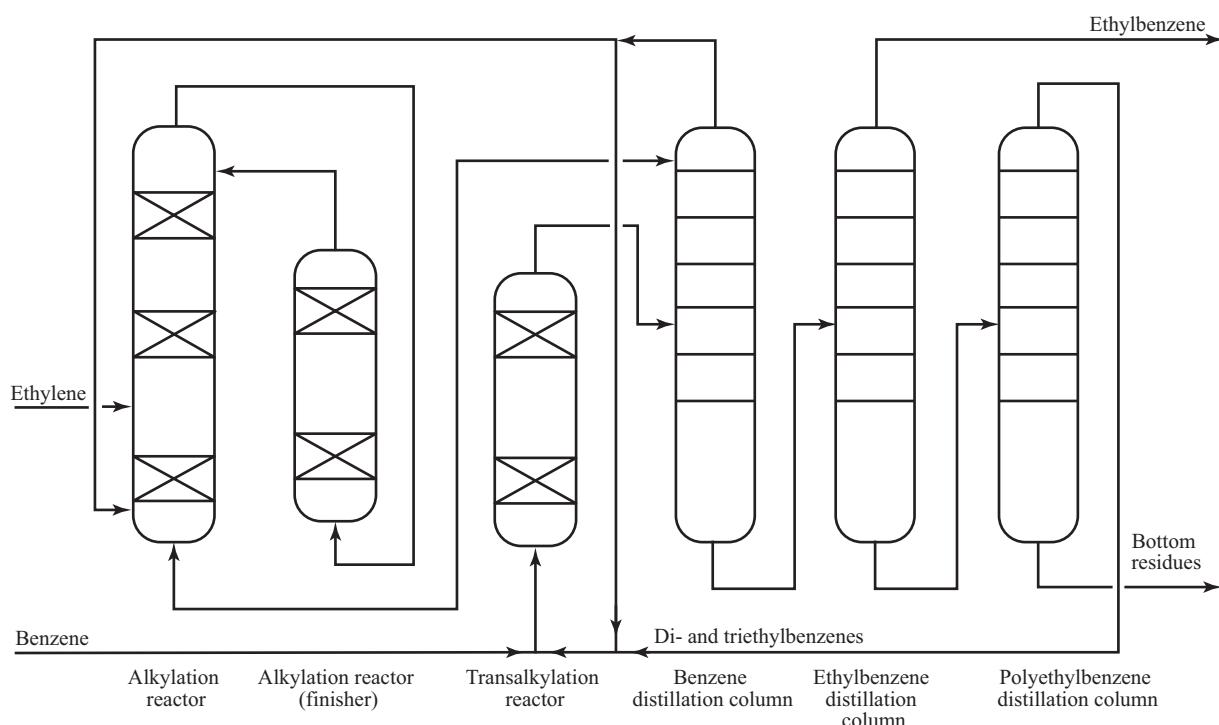


Fig. 3. Process flow diagram of the CDTech EB process [26]

Table 3. Key indicators of the EBOne process and the catalysts used

Key indicators of the process		Catalysts	
Phase	Liquid	Alkylation	Transalkylation
Reaction temperature, °C	~270	EBZ-800TL based on UZM-8 zeolite ¹⁶	EBZ-100 based on Zeolite Y
Alkylation temperature difference at the input and output, °C	200–270		
Reaction pressure, MPa (excess)	3.0–4.0		
Alkylation, benzene/ethylene ratio (mol)	2.0–4.0		
Transalkylation, benzene/PAB ratio (mol)	2.0–4.0		
EB yield, wt %	99.8		
EB purity, vol %	min 99.8%		
Cycle length between catalyst regenerations, years		More than 3	

¹⁶ UZM is a UOP zeolite material.

The reaction products are continuously removed from the catalytic zone by distillation, while any unreacted materials and other light components are removed from the top. The heat of the reaction is immediately removed due to evaporation of benzene, which allows the column to operate isothermally at the optimum reaction temperature. Ethylene vapor is introduced into the reactor at several points, coming into contact with liquid benzene entering from above. After that, the vapor is absorbed into the liquid phase. At equilibrium, most of the ethylene remains in the vapor phase. When a small amount of ethylene in the liquid comes into contact with the catalyst, it immediately reacts to form EB. This moves the ethylene concentration in the liquid phase away from equilibrium. The need for the vapor–liquid equilibrium results in “injection” of ethylene from the vapor phase into the liquid phase, thus restoring equilibrium. The alkylator can be designed to convert virtually all of the ethylene feedstock or only its part. In the latter case, an additional alkylator is provided to complete the ethylene conversion. Unreacted ethylene and benzene in the alkylator overhead are condensed and forwarded to an additional alkylator to ensure complete ethylene conversion.

The catalytic distillation column combines the alkylation and rectification processes in one stage. Alkylation occurs isothermally at reduced temperatures and pressures. In the catalytic distillation column, the products are removed from the reaction zone. These factors limit the formation of byproducts and increase the yield of the target product and its purity. Low reaction temperatures and pressures also reduce capital costs, increase plant safety, and minimize fugitive emissions. The multiphase environment of the catalytic distillation column maintains an extremely low ethylene concentration in the liquid phase (<0.1 wt %) due to its high volatility compared to benzene.

Configuring the EB synthesis unit as a catalytic distillation unit (instead of a separate alkylator and transalkylator) does not automatically result in a greater process efficiency. In order to achieve the desired efficiency, careful design of the reaction and separation conditions is required.

Since 1990, the CDTech EB technology has been selected for six projects worldwide. As shown in Table 4, three plants are currently in operation. The largest CDTech EB unit developed to date has been using a highly dilute ethylene feedstock containing less than 40 mol % of ethylene (the remainder consists primarily of hydrogen, methane, and ethane). Such a stream can be the products of the catalytic cracking process, which, according to the process thermodynamics, are characterized by a low yield of ethylene.

The CDTech EB process uses a specially developed zeolitic alkylation catalyst based on Y zeolite loaded into a catalytic distillation column. The catalyst is packed in specifically designed bags made of steel mesh and glass fiber fabric. The unique structure of the bags provides them with the necessary void fraction to allow steam to flow upward through the reactor. The glass fiber packing acts as a barrier preventing direct contact of the steam with the catalyst. The bags are approximately 30 cm in diameter and height, being easy to handle during loading operations. The CDTech proprietary bags containing the alkylation catalyst are stacked inside the alkylator similarly to the mode of structured packing (Fig. 4). This allows the alkylation reaction and distillation of the reactants and products to occur simultaneously. Multiple beds of stacked bags are used. The catalyst lifecycle is estimated to be over two years based on pilot tests (6000 h of continuous operation). At the same time, the high yield (99.7 wt %) and quality of the obtained EB (99.5 wt %) are maintained throughout the entire run [27].

The typical operating range for the CDTech EB process is shown in Table 5.

Thus, the low benzene/ethylene ratio makes the described process suitable for the reconstruction of obsolete plants. Among other things, it increases the capacity for EB production. The ratio of low process temperatures, pressures, as well as the simplicity and possibility of using carbon steel equipment makes this technology attractive in terms of minimal capital costs for construction as compared to competitors.

1.4. *Versalis* technology

Versalis offers contemporary technologies for producing EB on the basis of zeolite-containing PBE-1 (Polimeri Europa Beta zeolite¹⁷) catalysts for alkylation and PBE-2 for transalkylation based on Beta zeolite in the H-form. The technology has proven reliable following testing on an industrial scale at an EB plant with a capacity of 650000 t/year successfully launched in 2009. *Versalis* catalysts are described in the patent [28].

Specific features of the *Versalis* technology include the presence of primary benzene purification units to remove catalytic poisons, as well as preliminary mixing of benzene and ethylene (before the alkylation reactor). This increases the yield of target products. The catalyst used reduces the formation of ethylene oligomers and coke at high activity. This allows the process to be carried out under mild conditions, i.e., a temperature of 170–230°C and a relatively low pressure of 1–2 MPa. The benzene to ethylene ratio is at least 2 mol [11].

¹⁷ The Eni's chemical division, formerly *Polimeri Europa*, rebranded as *Versalis*.

Table 4. Existing installations for producing EB using CDTech EB technology

Company	Location	Capacity, t/year	Start
<i>S-Chem (JCP Company)</i>	Al Jubail, Saudi Arabia	>770000	2008
<i>INEOS Styrolution (Nova Chemicals Corp.)</i>	Sarnia, Canada	477000	1998
<i>Petroquimica Argentina SA. (PASA)</i>	Puerto San Martin, Argentina	140000	1997

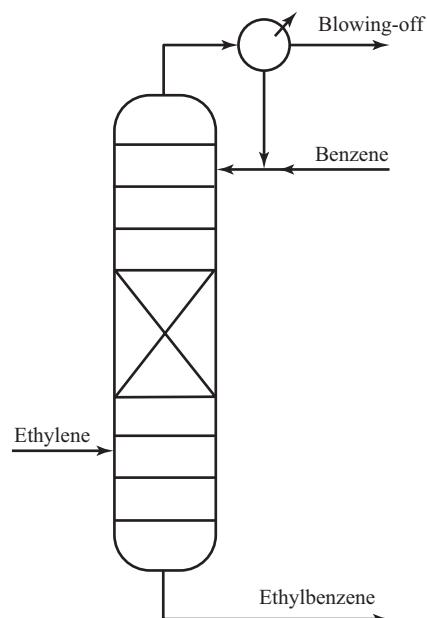


Fig. 4. Catalytic distillation column for EB synthesis [27]

Table 5. Operating range of the CDTech EB unit

Parameter	Value
Alkylation, benzene/ethylene ratio (mol)	2.0–4.0
Transalkylation, benzene/PAB ratio (mol)	2.0–4.0
Alkylation temperature range, °C	200 top, 240 bottom
Alkylator pressure, MPa	2.0–2.5
Ethylene consumption, kg/kg EB	0.264
Benzene consumption, kg/kg EB	0.738

The advantages of the *Versalis* technology are:

- high selectivity (at least 80%) and catalyst stability;
- high purity of EB (99.98%);
- 100% ethylene conversion and a total EB yield of 99.7% with an insignificant content of xylene byproducts (less than 10 ppmw);
- ease of operation;
- use of carbon steel;
- low capital investments and plant maintenance costs;
- easy handling of fresh catalyst and spent catalyst;
- catalyst regeneration intervals from 2 to 7 years;
- extended catalyst service life (up to five regenerations without performance degradation);
- efficient and reliable fresh benzene treatment to protect the catalyst from nitrogen contamination;
- low environmental impact;
- no acid waste stream and minimal gas emissions.

The PBE catalyst preparation procedures allow for optimum non-zeolitic porosity values, which increases the catalyst stability and reduces its deactivation rate.

The *Versalis* process does not generate liquid waste or gas emissions, with the exception of oil-containing water and vacuum pump vent emissions. The spent catalyst can be recycled after several regenerations.

The *Versalis* process flow diagram is shown in Fig. 5.

The *Versalis* technology includes adiabatic alkylation and transalkylation reactors with fixed catalyst beds, where the alkylation reactor contains several catalyst beds with fractional ethylene feed and is equipped with external intra-bed refrigerators to remove the exothermic reaction heat. The system for separating commercial EB and byproducts is virtually identical to that in the EBOne technology.

CONCLUSIONS

Ethylbenzene is a high-tonnage and high-margin product of petrochemical synthesis with a stable demand in the external and internal markets. More than 99% of EB is used in the production of styrene, a raw material for the production of polystyrene, ABS plastics¹⁸, and synthetic rubbers.

The presented review of contemporary technologies for the production of EB (*Badger EBMax*, *UOP EBOne*, *Versalis*, *CDTech EB*) shows the liquid-phase technology using contemporary zeolite-containing catalysts to be the most promising option at the present stage.

In comparison with the gas-phase process, the advantages of the liquid-phase process of benzene alkylation with ethylene include reduced energy costs due to relatively low process temperatures (below

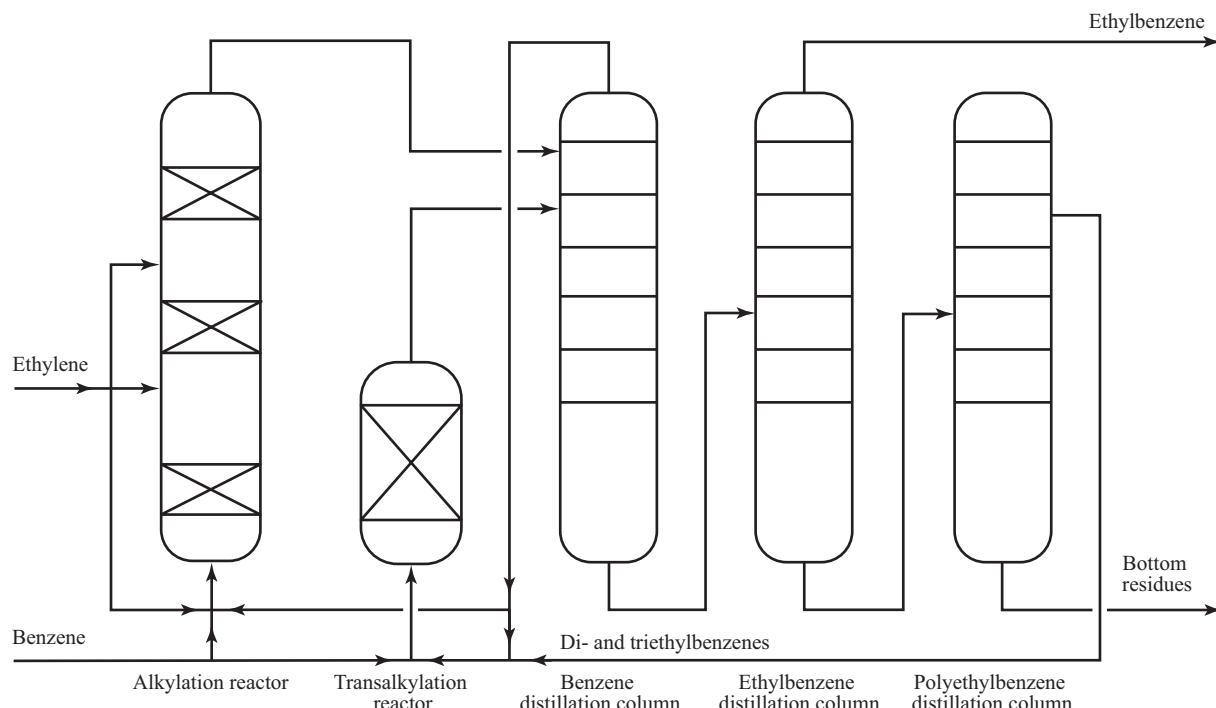


Fig. 5. Process flow diagram of the *Versalis* process [28]

¹⁸ ABS is an acrylonitrile butadiene styrene plastic.

270°C), reduced byproduct yield, increased EB yield, increased service life and inter-regeneration cycle of the catalyst. More than half of the EB produced in the world is obtained according to the EBMax technology using a catalyst based on an MWW family zeolite (MCM-22). This technology enables a low benzene to ethylene ratio (from 2.5 to 4), which reduces the benzene circulation rate, increases efficiency, and reduces the throughput of the benzene extraction column.

Zeolite-containing catalysts are highly active, stable, environmentally friendly, and regenerable as compared to liquid-phase alkylation catalysts (aluminum chloride). The use of such catalysts simplifies the process of preparing raw materials and designing the equipment.

The conventional technology for producing EB based on AlCl_3 does not provide adequate efficiency in converting benzene into EB. This is reflected in low raw material utilization rates, the formation of a large amount of highly polluted wastewater, and high corrosion.

Contemporary research in the field of benzene alkylation technology with ethylene into EB is associated with the creation and use of zeolite-containing catalysts as solid porous systems containing an active component and a binder. The active component is USY, Beta, mordenite, ZSM-5, ZSM-11, ZSM-12, ZSM-23, ZSM-35, ZSM-48, MCM-22, and MCM-49 zeolites. The preferred alkylation catalysts include Beta zeolite or a zeolite of the MCM-22 family. The binder is Al_2O_3 , SiO_2 , or amorphous aluminosilicate. After mixing the active component and the binder, the resulting mass is used to form granules followed by their drying and calcination. In individual cases, the catalyst can then be modified. Typically, the zeolite content in the catalysts ranges from 60 to 80 wt %.

A number of works have described various approaches to treating the original zeolites with the purpose of increasing their mesoporous surface area. This allows the transalkylation process temperature to be reduced and the catalytic activity of the resulting catalysts to be increased.

In 2022, the first industrial batch of the KT-GA-1 catalyst based on a zeolite of the MFI family (ZSM-5) for the process of gas-phase alkylation of benzene with ethylene in EB was released in Russia. Pilot industrial tests of the catalyst commenced on July 19, 2022, continuing up to the present time. The first year of

operation showed the Russian catalyst to be equivalent to its imported counterpart in all respects.

Contemporary developments in the field of catalysts for the process of transalkylation of benzene with DEB, including Russian ones, are devoted to the creation and use of zeolitic and zeolite-containing catalysts based on a FAU type zeolite (Zeolite Y).

The KT-BS-1 catalyst has been successfully operated in Russia at the *Monomer* plant of *Gazprom Neftekhim Salavat* starting from 2013 and up to the present time. This catalyst was developed jointly by *STC Salavatnefteorgsintez* and the Institute of Petrochemical Synthesis of the Russian Academy of Sciences (Moscow) on the basis of a deeply decationized Zeolite Y without binders. In addition, as an alternative to the catalyst for benzene transalkylation with DEB, KT-BS-1, the STC developed the KT-SS catalyst granulated with a binder: 80 wt % of Zeolite Y in the acidic H^+ form and 20 wt % of an alumina binder. The advantage of the KT-SS catalyst over the zeolitic KT-BS-1 is that the manufacture of the former uses conventional technology for producing zeolite-containing catalysts with a binder. As a result, the catalyst exhibits a developed secondary porous structure, which plays a transport role in the supply of reactants to the catalyst active centers as well as in the removal of reaction products. In addition, this catalyst can be produced in the required tonnage at any catalyst factory in Russia.

Thus, the advantages of the liquid-phase alkylation technology in the presence of contemporary highly active zeolite-containing catalysts make it the most preferable option in terms of minimal capital costs for construction as compared to other technologies for producing EB.

Authors' contributions

All authors contributed equally to the preparation of the article.

S.N. Potapova—analysis of the collected data, systematization of scientific literature, writing the text of the article.

L.A. Khakhin—planning the publication, writing and reviewing the article.

E.V. Korolev—data collection, preparing the tables, writing the text of the article.

S.M. Masoud—analysis of the collected data, data systematization, and preparing illustrations.

D.V. Svetikov—collecting the data, preparing the tables for the article.

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