

Kinetic modeling and packed-bed reactor simulation for ethylbenzene production process

Modelagem cinética e simulação de reator de leito empacotado para o processo de produção de etilbenzeno

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Abstract

Styrene is a monomer with numerous applications in the polymer industry which, in turn, is obtained through the ethylbenzene dehydrogenation. This work reports the ethylbenzene production process in an approach of the performance response of a Packed-Bed Reactor (PBR) based in β -zeolite catalytic. Three different strategies were simulated and evaluated under production operating in permanent regime: adiabatic PBR, PBR with thermal exchange and PBR with interstage cooling. Simulations were performed using the Matlab software's ODE45 method, by implementing the Runge-Kutta method, from the reactor design differential equations and the governing equations of the reversible reactions involved in the process. The results showed that the adoption of eight stages of thermal exchange with water at 298 K as coolant results in a good stabilization of the temperature in the catalytic bed reactor, favoring the continuity of the process and maintaining, besides good selectivity of the main reaction, conversion of approximately 90%.

Keywords: ethylbenzene, simulation, packed-bed reactor.

Resumo

O estireno, obtido através da desidrogenação do etilbenzeno, é um monômero com inúmeras aplicações na indústria de polímeros. Este trabalho aborda o desempenho de um reator de leito empacotado (PBR) baseado em catalisador β -zeólita para produção de etilbenzeno. Três estratégias diferentes foram simuladas e avaliadas sob operação em regime permanente: PBR adiabático, PBR com troca térmica e PBR com resfriamento interestágios. As simulações foram realizadas utilizando o método ODE45 do software Matlab, por implementação do método Runge-Kutta, a partir das equações diferenciais do projeto do reator e das equações governantes das reações reversíveis envolvidas no processo. Os resultados mostraram que a adoção de oito estágios de troca térmica com água a 298 K como fluido refrigerante resulta em uma boa estabilização da temperatura no reator de leito catalítico, favorecendo a continuidade do processo e mantendo, além de boa uma seletividade da reação principal, uma conversão de aproximadamente 90%.

Palavras-chave: etilbenzeno, simulação, reator de leito empacotado.

INTRODUCTION

The development of research related to the production of styrene has aroused the interest of researchers in the scientific community since the implementation of the first commercial process in 1930. Styrene, whose chemical formula is C_8H_8 is a non-saturated aromatic hydrocarbon which functions as the basis for the production of polystyrene. More than 80% of the styrene production is used for polymerization or copolymerization in the chemical industry, to produce thermoplastics, synthetic rubbers, and resins (JIE et al., 2017; LEITE, OLIVEIRA e RANGEL, 2004; ROMERO e DUARTE, 2016).

Styrene is obtained by dehydrogenation of ethylbenzene (C_8H_{10}), which in turn is synthesized from the catalytic alkylation of benzene (C_6H_6) with ethene (C_2H_4). Ethylbenzene, also known as ethylbenzol, is a colorless, flammable hydrocarbon, a chemical commodity. The reaction mechanism involved is a typical example of a process involving multiple reactions and depends on the ability to maximize the formation of the product of interest. After dehydrogenation, the product stream still contains a large fraction of unreacted ethylbenzene (20-40%). In addition, the reaction generates a secondary product - diethylbenzene ($C_{10}H_{14}$) - used in the production of divinylbenzene. Since the demand for styrene is much higher than for divinylbenzene, the current processes have been adjusted so that selectivity favors the production of ethylbenzene (HUSSAIN, MINH e LEE, 2017; JEWUR, 1984; JIE et al., 2017).

Currently, the homogeneous liquid alkylation process covers more than 24% of ethylbenzene production. Approximately 40% of the world production of C_8H_{10} is realized in the heterogeneous medium in the vapor phase. The remainder is produced in the heterogeneous liquid phase. The process also generates small amounts of impurities with similar boiling points, such as toluene (C_7H_8) and o-xylene (C_8H_{10}), which must also be removed from the product stream. Another unwanted product is formed due to the

presence of interferents in the feed stream. Commercial benzene, the reaction product of the reaction of the product of interest, contains a toluene fraction, which, when reacted with ethene, forms propylene (C_3H_6) (ANDRADE e CAMPOS, 2017; EBRAHIMI, et al., 2011; JIE et al, 2017).

Dehydrogenation of ethylbenzene is an equilibrium limited endothermic reaction with typically low conversions, even in processes conducted at elevated temperatures. Due to this endothermicity, the temperature of the catalytic bed decreases significantly in adiabatic reactors during the progress of the reaction, resulting in low conversions. This decrease in temperature also affects the selectivity for styrene, because, under equilibrium conditions, only undesirable reactions occur. Thus, it is necessary to maintain the temperature at a convenient value, in order to promote a high conversion level and high reaction rate (LEITE, OLIVEIRA e RANGEL, 2004).

Due to their excellent behavior and constructive simplicity, Packed-Bed Reactors (PBR) play a key role in chemical process engineering. They have been widely used for over 70 years, being applied in the chemical processes of gas absorption, etching, and catalytic conversion. Although new catalysts and structured reactors have been developed, packaged bed reactors will probably still be used in the coming decades, mainly because of their low cost (FERNENGEL, HABLA e HINRICHSEN, 2018; THIEODOROS e KENIG, 2009).

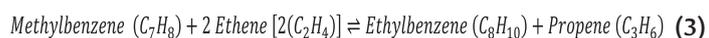
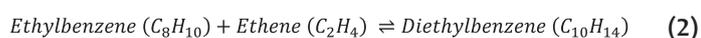
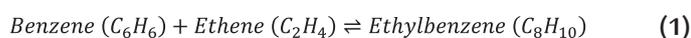
Many catalysts have already been tested for dehydrogenation of ethylbenzene with water vapor. Iron, aluminum, cobalt, tin, antimony oxides, various mixed oxides, zeolites, and mesoporous materials and supported catalysts were active and selective to styrene. Iron oxides are the most commercially employed because of their catalytic properties and their low cost. Early generations of acid catalysts (such as aluminum chloride or trifluoroborane in alumina) were highly corrosive and had very short lifetimes. More recently, zeolite based catalysts have demonstrated superior properties (ANDRADE e CAMPOS, 2017;

LEITE, OLIVEIRA e RANGEL, 2004; LUTTRELL e PETERSON, 2011).

In this context, based on the increasing worldwide demand for styrene, as well on the challenges associated to your chemical production routes involving multiple reactions, this article aiming to supply the attempt to provide subsidies capable to enrich the range of optimization strategies of the ethylbenzene production processes, following the emerging trend towards the improving of catalytic chemical processes in terms of efficiency, selectivity, and stability. For that, this work strives to delineate a new investigation of the performance of Packed-Bed Reactor with bed based on β -zeolite applicated to three software simulation strategies for ethylbenzene production operating in permanent regime: adiabatic PBR, PBR with thermal exchange and PBR with interstage cooling.

MODELING AND SIMULATION

The elaborated methodology was developed based on Andrade e Campos (2017). A kinetic study was realized for the production process of 80 thousand tons of ethylbenzene per year using benzene and ethene as raw materials. Simulation and optimization analyzes were developed for a Packed-Bed Reactor (PBR), modeled as a Plug-Flow Reactor (PFR). The differential equations of project for the PBR were solved by using the ODE45 method in the numerical solver Matlab, by implementing the Runge-Kutta method by means of the simultaneous modeling and resolution of the velocity equations of the main reaction (equation 1), secondary (equation 2) and impurity (equation 3) as well as equations of mass and energy balance involved in the process.



The kinetic and equilibrium parameters that describe the rates of the reversible reactions of the three governing reactions were provided by Andrade e Campos (2017) and were presented by equations 4 to 15. The thermodynamic data of the reagents involved in solving the equations were extracted from Smith, Van Ness e Abbott (2013), except for diethylbenzene (Haynes, Lide e Bruno, 2012), and can be consulted in Table 1. The kinetics of the main (1), secondary (2), and impurity (3) reactions were described and given by equations 16, 17, and 18.

$$k_1 = 255.3 * e^{\left(\frac{-42.496}{RT}\right)} \quad (4)$$

$$k_{-1} = 5.13 * e^{\left(\frac{-68.741}{RT}\right)} \quad (5)$$

$$k_2 = 52.41 * e^{\left(\frac{-53.148}{RT}\right)} \quad (6)$$

$$k_{-2} = 2.667 * e^{\left(\frac{-73.491}{RT}\right)} \quad (7)$$

$$k_3 = 44.32 * e^{\left(\frac{-50.132}{RT}\right)} \quad (8)$$

$$k_{-3} = 3.233 * e^{\left(\frac{-60.303}{RT}\right)} \quad (9)$$

$$K_E = 0.457 * e^{\left(\frac{7.769}{RT}\right)} \quad (10)$$

$$K_B = 6.77x10^{-3} * e^{\left(\frac{12.436}{RT}\right)} \quad (11)$$

$$K_{EB} = 3.19x10^{-3} * e^{\left(\frac{10.173}{RT}\right)} \quad (12)$$

$$K_{DEB} = 8.58x10^{-4} * e^{\left(\frac{14.059}{RT}\right)} \quad (13)$$

$$K_T = 4.63x10^{-3} * e^{\left(\frac{11.768}{RT}\right)} \quad (14)$$

$$K_P = 2.12x10^{-2} * e^{\left(\frac{8.354}{RT}\right)} \quad (15)$$

where: k_1 = rate constant of the main reaction for direct direction; k_{-1} = rate constant of the main reaction for inverse direction k_2 = rate constant of secondary reaction to direct; k_{-2} = rate constant of the secondary reaction in reverse direction; k_3 = constant of impurity reaction rate for direct sense; k_{-3} = constant of impurity reaction rate for inverse direction; K_E = equilibrium constant of ethene; K_B = equilibrium constant of benzene; K_{EB} = equilibrium constant of ethylbenzene; K_{DEB} = equilibrium constant of diethylbenzene;

K_T = equilibrium constant of methylbenzene; K_P = equilibrium constant of propene; R = universal constant of gases [8.314 J mol⁻¹ K⁻¹]; T = operating temperature [K].

$$r_1 = \frac{k_1 p_B p_E - k_{-1} p_{EB}}{(1 + K_B p_B + K_E p_E + K_{EB} p_{EB} + K_T p_T + K_P p_P)^2} \quad (16)$$

$$r_2 = \frac{k_2 p_{EB} p_E - k_{-2} p_{DEB}}{(1 + K_B p_B + K_E p_E + K_{EB} p_{EB} + K_{DEB} p_{DEB} + K_T p_T + K_P p_P)^2} \quad (17)$$

$$r_3 = \frac{k_3 p_T p_E - k_{-3} p_{DEB} p_P}{(1 + K_B p_B + K_E p_E + K_{EB} p_{EB} + K_{DEB} p_{DEB} + K_T p_T + K_P p_P)^2} \quad (18)$$

Where: r_1 = reaction rate of the reaction (1) [mol g⁻¹ min⁻¹]; r_2 = reaction rate of the reaction (2) [mol g⁻¹ min⁻¹]; r_3 = reaction rate of the reaction (3) [mol g⁻¹ min⁻¹]; P_E = partial pressure of ethane [MPa]; P_B = partial pressure of benzene [MPa]; P_{EB} = partial pressure of ethylbenzene [MPa]; P_{DEB} = partial pressure of diethylbenzene [MPa]; P_T = partial pressure of methylbenzene [MPa]; P_P = partial pressure of propene [Mpa].

Table 1

Standard enthalpies and constant-pressure heat capacities of the compounds (T = 298.15 K; R = 8.314 J mol⁻¹ K⁻¹)

Compound	Standard Enthalpies (ΔH_f°) (J mol ⁻¹)	Constant-Pressure Heat Capacities Equations in the Ideal-Gas State (C_p)
Ethene (E)	52.510	$C_{p,E}, R^{-1} = 1.424 + 14.394 \times 10^{-3} T - 4.392 \times 10^{-6} T^2$
Benzene (B)	82.930	$C_{p,B}, R^{-1} = -0.206 + 39.064 \times 10^{-3} T - 13.301 \times 10^{-6} T^2$
Ethylbenzene (EB)	29.920	$C_{p,EB}, R^{-1} = 1.124 + 55.380 \times 10^{-3} T - 18.476 \times 10^{-6} T^2$
Diethylbenzene (DEB)	-21.033	$C_{p,DEB}, R^{-1} = -33.93 + 85.563 \times 10^{-2} T - 543 \times 10^{-6} T^2 + 135.988 \times 10^{-9} T^3$
Methylbenzene (T)	50.170	$C_{p,T}, R^{-1} = 0.290 + 47.052 \times 10^{-3} T - 15.716 \times 10^{-6} T^2$
Propene (P)	19.710	$C_{p,P}, R^{-1} = 1.637 + 22.706 \times 10^{-3} T - 6.915 \times 10^{-6} T^2$

Source: Smith, Van Ness e Abbott (2013); Haynes, Lide e Bruno (2012).

In order to define the best reactor type, were performed simulations of the main variables of interest (temperature, molar flows of all species involved and reaction selectivity (X_{EB}) (equation 19) for three different conditions: PBR without thermal exchange (adiabatic), PBR with thermal exchange of cooling fluid (water at 298 K) and PBR with interstage cooling. The

selection of the best reactor strategy aimed to meet the operating conditions of feed of 10 MPa and 500 K and application of FX-02 catalyst, based on a β -zeolite capable of withstanding a maximum temperature of 723 K.

$$X_{EB} = \frac{F_{EB,out}}{F_{T,out}} \quad (19)$$

where: X_{EB} = selectivity of ethylbenzene production reaction; $F_{EB,out}$ = ethylbenzene outflow; $F_{T,out}$ = total outflow.

Ethene, benzene, and toluene molar flow rates were determined according to the proportions of ethene-benzene 3:1 and the purity of the benzene reagent (10% toluene and 90% benzene) and the other flows were taken as null at the reactor inlet. Table 2 exhibited the input parameters for the three PBR reactor simulated strategies.

Table 2

Input parameters of the PBR reactor for the three simulated strategies

Compound	Molar flow (mol min ⁻¹)
Ethene	1200
Benzene	400
Ethylbenzene	0
Diethylbenzene	0
Methylbenzene	38
Propene	0

RESULTS AND DISCUSSION

PBR without thermal exchange

The results obtained through simulation and modeling for the adiabatic PBR in the permanent regime were presented in Table 3 and illustrated by Figures 1 and 2. According to the output parameters found, the ethylbenzene annual production would be approximately 54 tons and the main reaction selectivity

in the output current of 0.13%. Beyond low selectivity and low annual production, the adoption of this strategy would be compromised due to another non-negligible factor. The results suggested that the operating temperature in the reactor would exceed the limit supported by the FX-02 β -zeolite catalyst, reaching 995 K. Zeolite catalysts, at high temperatures, tend to crack and deactivate its molecules can be to suffer poisonings or irreversible structural damages. Moreover, at 995 K the parallel reaction (equation 2) could be favored in the direct direction, culminating in consumption of the product of interest.

Table 3
Output parameters of adiabatic PBR

Temperature (K) = 995	
Compound	Molar flow (mol min ⁻¹)
Ethene	287
Benzene	0
Ethylbenzene	1
Diethylbenzene	437
Methylbenzene	0
Propene	38
<i>TOTAL</i>	<i>763</i>

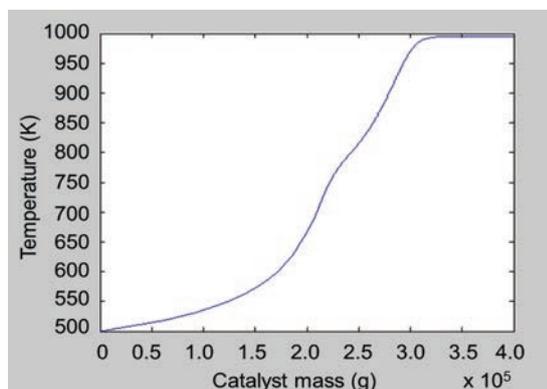


Figure 1: Temperature as a function of the mass of FX-02 in an adiabatic PBR.

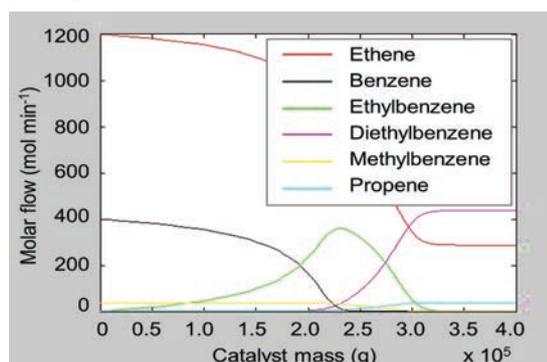


Figure 2: Molar flows as a function of the mass of FX-02 in an adiabatic PBR.

PBR with thermal exchange of cooling fluid

The results obtained for the steady-state operation of a PBR with coolant fluid (water, at 298 K) were presented in Table 4 and can be seen by Figures 3 and 4. For the output parameters found, the annual production of ethylbenzene would be 19424 tons and selectivity in the output current of 29.9%. Such results indicated that the strategy to adopt the referred thermal exchange for the ethylbenzene production process could stabilize the temperature of the reactor, keeping it below 723 K, respecting the maximum temperature supported by the catalyst as well as maintaining the selectivity of the reaction. Based on the benzene inlet and the ethylbenzene outlet molar flows and the formation of the product of interest only by the main reaction, considering benzene as a limiting reagent, approximately 90% conversion was achieved for this strategy.

Table 4
Output parameters of PBR with thermal exchange

Temperature (K) = 716	
Compound	Molar flow (mol min ⁻¹)
Ethene	771
Benzene	12
Ethylbenzene	363
Diethylbenzene	30
Methylbenzene	32
Propene	5
<i>TOTAL</i>	<i>1213</i>

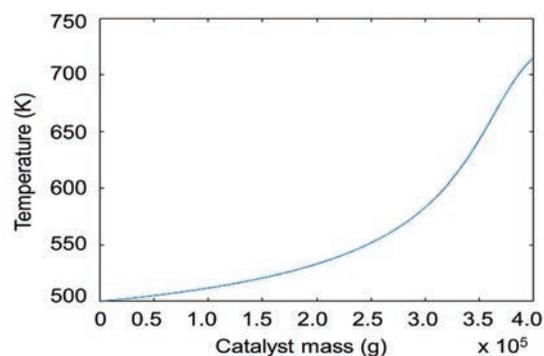


Figure 3: Temperature as a function of the mass of FX-02 in a PBR with thermal exchange.

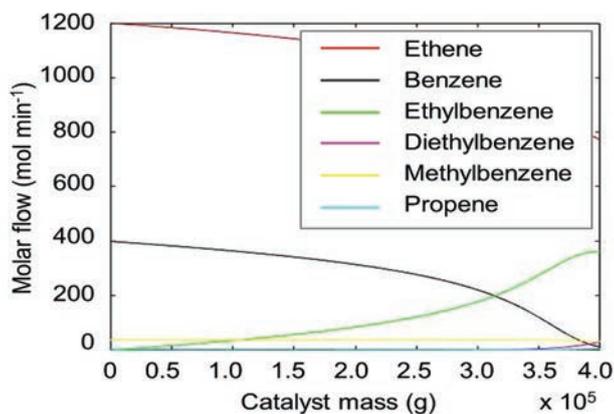


Figure 4: Molar flows as a function of the mass of FX-02 in a PBR with thermal exchange.

PBR with interstage cooling

The results obtained through simulation for the PBR with interstage cooling in the permanent regime were presented in Table 5 and illustrated by Figures 5 and 6. According to the output parameters found, the annual production of ethylbenzene would be 19638 tons and the selectivity of ethylbenzene in the current of the output of 30.2%. Compared to the other simulated strategies, it was the reactor that presented better performance. The adoption strategy of cooling stages in a fixed bed reactor showed that the operating temperature did not exceed the degradation temperature of the catalyst at any moment of the operation, favoring the continuity of the reaction and maintaining, besides great selectivity, a conversion of approximately 90%.

Table 5

Output parameters of PBR with interstage cooling

Temperature (K) = 652	
Compound	Molar flow (mol min ⁻¹)
Ethene	771
Benzene	10
Ethylbenzene	367
Diethylbenzene	28
Methylbenzene	33
Propene	5
<i>TOTAL</i>	<i>1214</i>

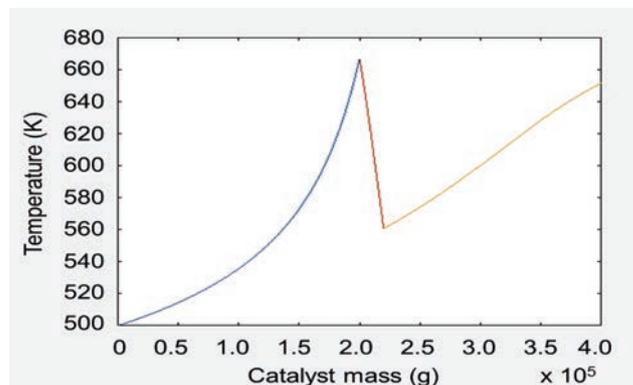


Figure 5: Temperature as a function of the mass of FX-02 in a PBR with interstage cooling.

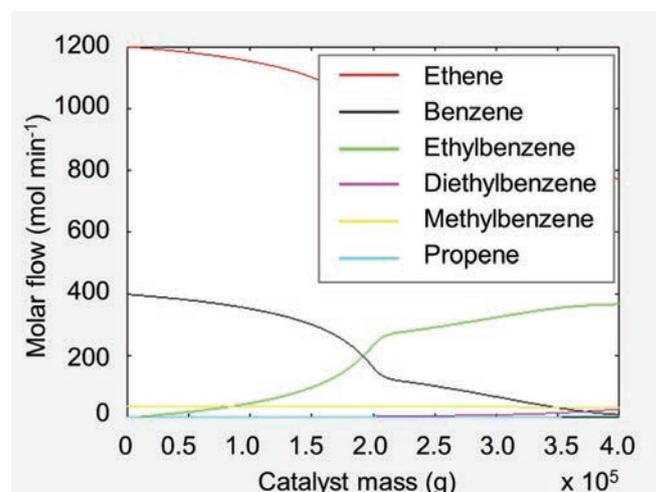


Figure 6: Molar flows as a function of the mass of FX-02 in a PBR with interstage cooling.

Optimization analysis

The simulation analysis of the best reactional operating conditions, where the parameters pressure, the number of heat exchangers in interstage and molar flow of each organic compound were individually varied, demonstrated the results presented in Tables 6 and 7 and shown in Figures 7 and 8. The strategy of adopting a fixed bed reactor with FX-02 catalyst and eight cooling stages was satisfactory for an ethylbenzene annual production of 80 thousand tons. The number of stages of thermal exchange with coolant was sufficient to stabilize the temperature in the reactor, keeping it below 600 K, respecting the degradation temperature of the catalyst. With the thermal changes in the reaction system, the temperature remained constant between 560 and 600 K, the values of the

reaction constants became relatively high, culminating in a high conversion to the mass of 550 kg of catalyst, besides a good selectivity for the main reaction.

Table 6

Operating reaction conditions of PBR with eight stages of cooling

Initial pressure (MPa)	Input temperature (K)	Catalyst mass (kg)	Stages of thermal exchange	Output temperature (K)
10	500	550	8	652

Table 7

Output parameters of PBR with eight stages of cooling

Compound	Molar flow (mol min ⁻¹)
Ethene	35
Benzene	26
Ethylbenzene	1493
Diethylbenzene	111
Methylbenzene	131
Propene	21
<i>TOTAL</i>	<i>1817</i>

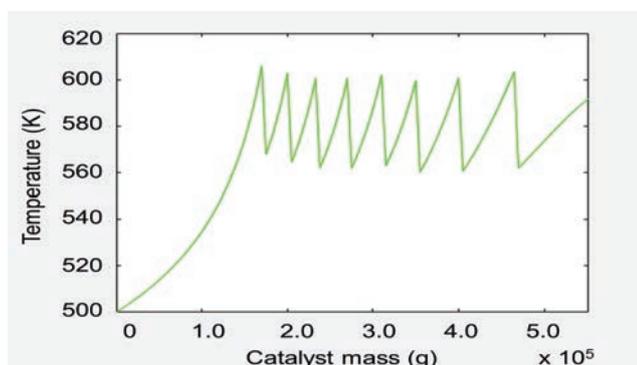


Figure 7: Temperature as a function of the mass of FX-02 in a PBR with eight cooling stages.

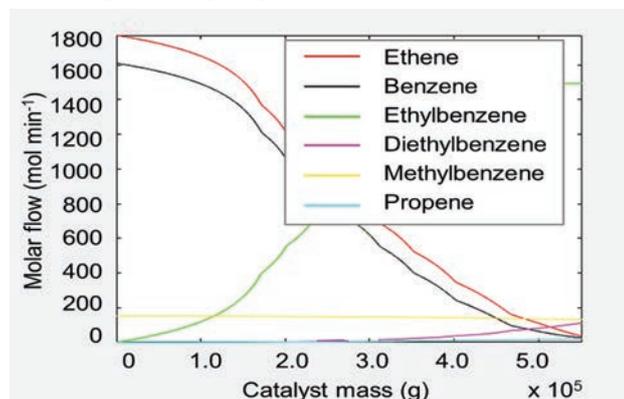


Figure 8: Molar flows as a function of the mass of FX-02 in a PBR with eight cooling stages.

CONCLUSIONS

The performance responses of three Packed-Bed Reactors with β -zeolite based catalytic bed for the production of ethylbenzene starting from benzene and ethene were analyzed by kinetic modeling and software simulation. Of the three simulated strategies, the PBR with interstage cooling under a permanent regime was defined as the best reactor topology for the process of interest. The simulation of optimization of operational parameters performed suggested the adoption of a PBR with eight stages of thermal exchange using water as coolant fluid in an optimization strategy of the catalytic chemical process in terms of production, selectivity, and stability.

REFERENCES

- ANDRADE, L. H.; CAMPOS, L. C.. **Cinética, cálculo de reatores, modelagem e simulação de processos**: trabalho prático. Belo Horizonte: PUC Minas, 2017.
- EBRAHIMI, A. N.; SHARAK, A. Z.; MOUSAVI, S. A.; AGHAZADEH, F.; SOLTANI, A.. Modification and optimization of benzene alkylation process for production of ethylbenzene, **Chemical Engineering and Processing: Process Intensification**, Tehran, v. 50, n. 1, p. 31-36, jan. 2011. Available in: <<https://doi.org/10.1016/j.cep.2010.10.011>>. Access in: 13 jun. 2019.
- FERNENGEL, J.; HABLA, F.; HINRICHSEN, O.. Scripting as an approach to automated CFD simulation for packed bed catalytic reactor modeling. **Chemie Ingenieur Technik**, Munique, v. 90, n. 5, p 685-689, feb. 2018. Available in: <<https://doi.org/10.1002/cite.201700153>>. Access in: 13 jun. 2019.
- HAYNES, W. M.; LIDE, D. R.; BRUNO, T. J.. **Handbook of Chemistry and Physics**. 93rd Edition. New York: CRC Press, 2012.
- HOSCH, W. L. **Styrene**. British Encyclopedia Inc., 2009.

HUSSAIN, A.; MINH, L. Q.; LEE, M.. Intensification of the ethylbenzene production process using a column configured with a side reactor. **Chemical Engineering and Processing: Process Intensification**, Gyeongsan, v. 122, s.n., p. 204-212, dec. 2017. Available in : <<http://dx.doi.org/10.1016/j.cep.2017.10.003>>. Access in: 13 jun. 2019.

JEWUR, S. S.. **Química de zeólitas e catálise**. Natal: UFRN, 1984.

JIE, K.; LIU, M.; ZHOU, Y.; LITTLE M. A.; BONAKALA, S.; CHONG, S. Y.; STEPHENSON, A.; CHEN, L.; HUANG, F.; COOPER, A. I.. Styrene purification by guest-induced restructuring of pillar[6]arene. **Journal of the American Chemical Society**, Hangzhou, v. 139, n. 8, p. 2908-2911, feb. 2017. Available in: <<https://pubs.acs.org/doi/10.1021/jacs.6b13300>>. Access in: 13 jun. 2019.

LEITE, H. E. B.; OLIVEIRA, A. C.; RANGEL, M. C.. The promoter action of zinc on catalysts for styrene synthesis. **Química Nova**, São Paulo, v. 27, n. 2, p. 247-250, apr. 2004. Available in: <<http://dx.doi.org/10.1590/S0100-40422004000200014>>. Access in: 13 jun. 2019.

LUTTRELL, W. E.; PETERSON, H. R.. Ethylbenzene. **Journal of Chemical Health and Safety**, Oklahoma City, v. 18, n. 1, p. 41-42, feb. 2011. Available in: <<https://doi.org/10.1016/j.jchas.2010.11.005>>. Access in: 13 jun. 2019.

ROMERO, G. R.; DUARTE, M. C.. **Simulação do processo de produção do estireno a partir da desidrogenação do etilbenzeno**. 2016. 81f. Trabalho de Conclusão de Curso (Graduação em Engenharia Química) - Escola de Engenharia, Universidade Federal Fluminense, Niterói, 2016. Available in: <<https://app.uff.br/riuff/handle/1/2157>>. Access in: 14 jun. 2019.

SMITH, J. M.; VAN NESS, H. C.; ABBOTT, M. M.. **Introdução à termodinâmica da engenharia química**. 7^a ed.. Rio de Janeiro: LTC, 2013.

THEODOROS, A.; KENIG, E.Y.. CFD-based analysis of the wall effect on the pressure drop in packed beds with moderate tube/particle diameter ratios in the laminar flow regime. **Chemical Engineering Journal**, Paderborn, v. 155, n. 1-2, p. 404-410, dec. 2009. Available in : <<https://doi.org/10.1016/j.cej.2009.07.057>>. Access in: 13 jun. 2019.