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Treball Final de Grau

Ethylbenzene dehydrogenation: Reactor modeling and simulation.

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Hi ha una força motriu més poderosa que el vapor,
l'electricitat i l'energia atòmica: la voluntat.

Albert Einstein

Primer de tot agrair als meus tutors tot el treball i dedicació que ha suposat. Agrair-los-hi totes aquelles hores que han estat disponibles inclús fora d'horari laboral i sobretot la paciència que han tingut amb mi. També vull agrair al Dr. Curcó i en Dr. Llorenç l'ajut que m'han donat i el temps que m'han dedicat tot i no ser els meus tutors. Agrair als meus familiars el fet d'estar al meu costat totes aquelles hores que he passat treballant, d'intentar entendre el que estava fent i de donar-me suport amb aquesta tasca cada cop que obtenia un resultat fallit, que han estat molts. Finalment agrair a la meva parella el suport i els ànims que m'ha estat donant durant tot el procés que he tardat a fer aquest treball, agrair-li totes aquelles hores que m'ha estat sentint parlar d'aquest treball i l'esforç que ha fet per entendre'm.

Us agraeixo a tots tot el suport que m'heu donat.

A tots vosaltres, Gràcies.

CONTENTS

SUMMARY

Nowadays, Styrene is a product that takes part in the great majority of industrial processes to produce objects that we use in the daily life. Because it is a very affordable component, with which you can generate all kinds of polymers with very useful and manageable physical and chemical properties, its importance in the industrial world invites us to think if the conditions of the reactors step are the best to carry the ethylbenzene dehydrogenation on properly.

The purpose of this work is to generate a code from both theoretical and experimental sources of information, and simulate the ethylbenzene dehydrogenation reaction for the subsequent study of the evolution of the physical properties of the components, the profiles of the variables to be controlled and the kinetic parameters of the most important reactions, in different types of flow models with the aim of determining what is the flow model that gives us results closer to the real ones, and then analyse how the control variables of the process affect to the reactors system and the properties of the components, using the model of flow previously determined as closer to the real one

In order to develop the code, the 3 most relevant balances were used, from a mathematical point of view, such as: the mass balance, the energy balance and the motion balance; And from the point of view of the kinetics of the reactions, some expressions that follow the formalism of LHHW have been used to explain the mechanism of catalytic reaction, which considers a physicochemical reaction model divided into seven stages.

The results obtained have been dealt with through the Microsoft Excel program for a better understanding of these and subsequently represented, discussed and compared in order to extract a suitable conclusion.

Keywords: Catalytic reactors, Modeling, Programming, Simulation, Dehydrogenation, Styrene.

RESUM

Actualment l'Estirè és un producte que intervé en la gran majoria de processos industrials per a la producció d'objectes que usem en la vida quotidiana. A causa del fet que és un component molt assequible, amb el que es poden generar tota classe de polímers amb unes propietats físiques i químiques molt útils i manejables, la seva importància al món industrial ens invita a pensar si realment, a l'hora de produir-se, s'estan utilitzant les condicions més òptimes en els reactors químics, per a aconseguir la màxima quantitat d'estirè.

El propòsit d'aquest treball és generar un codi a partir de fonts d'informació, tant teòriques com experimentals, i simular la reacció de deshidrogenació de l'etilbenzè pel posterior estudi de l'evolució de les propietats físiques dels components, els perfils de les variables a controlar i els paràmetres cinètics de les reaccions més importants, en diferents tipus de models de flux amb l'objectiu de determinar quin és el model de flux que ens dóna uns resultats més pròxims als reals i, seguidament, analitzar com afecten les variables de control del procés sobre el rendiment dels reactors i les propietats dels components, utilitzant el model de flux determinat anteriorment com a més pròxim al real. Per a desenvolupar el codi s'han utilitzat, des d'un punt de vista matemàtic, els 3 balanços més rellevants tals com: el balanç de matèria, el balanç d'energia i el balanç de quantitat de moviment; I des del punt de vista de la cinètica de les reaccions, s'han utilitzat unes expressions que segueixen el formalisme de LHHW, per a explicar el mecanisme de reacció catalítica, el qual considera un model de reacció fisicoquímic dividit en set etapes.

Els resultats obtinguts han estat tractats mitjançant el programa Microsoft Excel per a un millor enteniment d'aquests i posteriorment representats, discutits i comparats amb la finalitat d'extreure una conclusió final adient.

Paraules clau: Reactors catalítics, Modelització, Programació, Simulació, Deshidrogenació, Estirè.

1. INTRODUCTION

1.1. STYRENE IN THE CHEMICAL INDUSTRY

Styrene, whose systematic name is ethenylbenzene and also known as vinyl benzene, is used to make rubbers, polymers, copolymers, polystyrene plastics, and resins. This liquid is a colorless, toxic one. It evaporates easily and at high concentrations its sweet odor suits to less pleasant odor. Its molecular formula is C_8H_8, Figure 1 and Table 1 show its structure and physical properties.

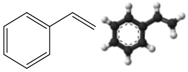


Figure 1: Molecular structure of styrene monomer.

Molecular weight	104,153 g/mol
Physical Form	A colorless, oily liquid
Boiling point	145,15 ºC
Freezing point	-30,6 ºC
Density (20 ºC)	0,9059 g/L
Vapor pressure at 20 ºC	5 mmHg
Critical temperature	362,1 ºC
Critical Volume	3,37 mL/g
Flammable limits in air	1,1-6,1 vol%
Flashpoint	31,1 ºC
Autoignition point	490 ºC

Table 1: Physical properties of styrene [Plastics Europe, (2018)]

Acute short-term exposure to styrene causes mucous membrane and eye irritation and gastrointestinal effects. A large exposure to it results in effects on the central nervous system. All effects can be found at safety data sheets. (See Appendixes III, IV)

The styrene production started in the 1930s by BASF (an agreement of different companies such as Bayer, Hoechst, and Agfa) in Germany and Dow Chemical in the USA. Many of those plants were built in Germany before World War II to make synthetic rubber. After the war, styrene demand kept growing to produce, mainly, polystyrene. Many factors contributed to its growth like the facility of being handled easily and safely, polymerized and copolymerized under a variety of conditions and because is one of the least expensive thermoplastics volumetrically. Polystyrene accounted for 65% of the total styrene demand.

In the 1970s the production of styrene was 2.0 million metric tons in the USA. In the 1980s its demand increased and, consequently, also the value of the production up to $3.2x10^6$ tons and $5.8x10^6$ tons in 2004. *[Kirk-Othmer. 5th Edition (2006)].*

As it can be seen in the figure 2, in 2012 the annual styrene production was over 26.4 million tons in all world and would reach the value of 29.7 million tons in 2015. That is why manufacturing styrene is one of the 10th most important industrial processes in the world. The production of styrene is expected to increase to 41 million tons in 2021 *[Ali, E. Et al. (2018)]*, as It can be seen in *Figure 2.*

The major commercial process to produce styrene is ethylbenzene dehydrogenation which involves 85% of the commercial production. There are other ways to produce styrene. The second most used process is from co-production of propylene oxide. Besides these two methods, there also are the Zeolite-Based Alkylation and the Aluminium Chloride-Based Alkylation. Both methods are not as common as ethylbenzene dehydrogenation or co-production of propylene oxide processes due to the catalyst's issues *[Kirk-Othmer. 5th Edition (2006)]*. Nowadays, most plants have the capacity to produce over 100.000 tons per year.

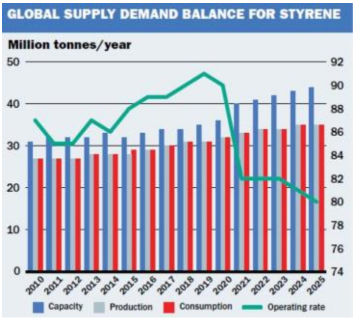


Figure 2: Styrene production through years [O'Connor Rhian, Global styrene shortage to persist (2018)]

1.1.1. Ethylbenzene dehydrogenation process

This method uses a series of catalytic fixed bed reactors to carry the reactions out, one distillation unit, and a boiler. Because of the reactions system has a parallel-series reaction, sometimes is preferable to avoid as much as possible the mix of all components. Using a perfect mix reactor will not be the best option for that job. For this situation, there is another way to carry on those reactions by using another reactor called plug flow reactor.

Steam goes through the heater [A] to reach the range temperature of 720-800 ºC. Afterward it is mixed [B] with ethylbenzene and the resultant stream is feed to the first reactor [C] at 620ºC. The steam is used to provide enough heat to the reaction due it is endothermic. Besides, steam cleans all carbon depositions of catalyst coming from cracking reactions. Once the mainstream went through the first reactor it goes to one reheater [D] to reach the temperature of 590ºC. After the reheater, the stream enters the second reactor [E] to end the reaction time. Finally, it goes to the distillation unit [F] to separate styrene from the impurities. The ethylbenzene that didn't react is recirculated and reheated [G] closer to 600ºC. We can see the process in *Figure 3*:

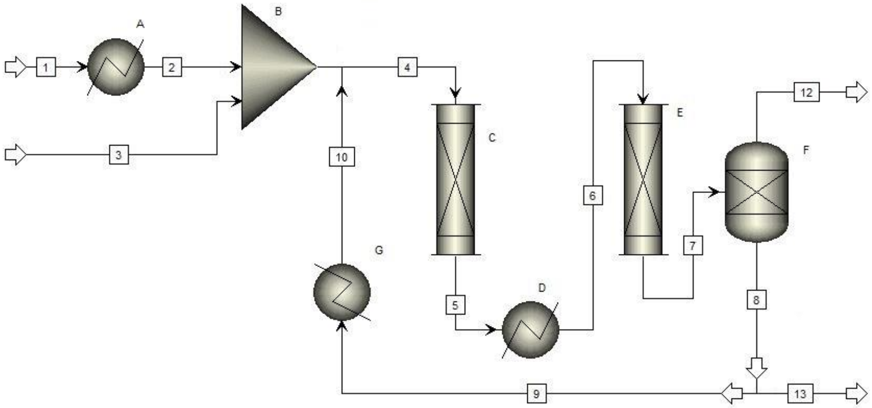


Figure 3: Ethylbenzene dehydrogenation scheme process. A, D, G) Heater. B) Mixer. C, D) Adiabatic fixed bed reactor. F) Distillation column. 1) Steam feed. 3) Ethylbenzene feed. 9) Ethylbenzene recirculation. 12) Styrene product. 13) Impurities.

Reactors used to carry out ethylbenzene dehydrogenation are elongated, cylindrical and vertical structures of very large size. Its diameter goes from 1,5 to 9 meters and its length from 2 to 30,5 meters where the size depends on the styrene demand *[James R.Butler. et.al. (2000)]*.

Sometimes the first reactor is about 50 % to 100 % bigger than the second one. There are, sometimes, processes that use 3 adiabatic fixed bed plug flow reactors instead of 2 due to their size. The bigger reactor is, the more ethylbenzene can react and consequently, the more conversion of it will be; making possible the use of only two reactors.

About feed stream, usually contain less than 6 moles of H_2O for each mole of ethylbenzene corresponding to 1 kg of water for each kg of ethylbenzene. The stream pressure is about 50 kPa to 300 kPa and the residence time goes from 0,05 h^{-1} to 2 h^{-1}. The first reactor's feed stream is at a temperature range of 600-640ºC and the second feed stream is reheated up to 590ºC [Armando Galeotti, et.al. (2015)].

1.1.2. Propylene oxide process

In the propylene oxide/styrene process ethylbenzene is reacted with oxygen to produce ethylbenzene hydroperoxide. Afterward, it reacts with propylene to form propylene oxide. There is one co-product of the main reaction named phenylmethylcarbinol which is dehydrated to give styrene. The process produces 2.25 tons of styrene for every tone of propylene oxide *[Rhian O'connor, (2017)]*. We can see the process in the following scheme of figure 4:

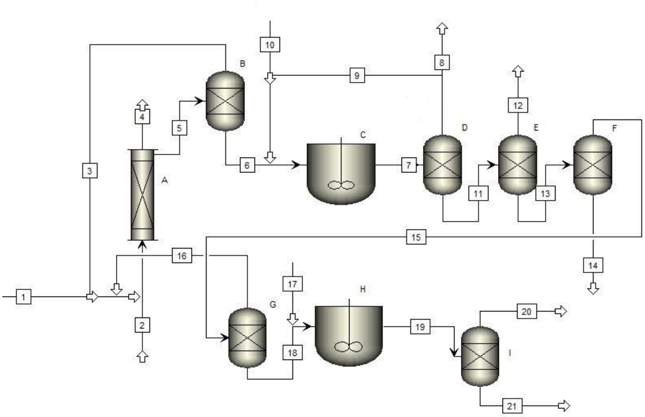


Figure 4: PO-SM scheme process. A) Peroxidation reactor. c) Epoxidation reactor. B, D, E, F, G, I) Distillation column. H) Dehydration reactor. 1) Ethylbenzene feeding stream. 2,4) Airstream. 10, 17) Catalyst feeding stream. 8) Propylene oxide product stream. 20) Styrene product.

There are some critical differences between both methods that makes ethylbenzene dehydrogenation the most used process worldwide to synthesize styrene. Up to 90% of the plants uses this method. *[Ali, Emad et.al, Polish Journal of Chemical Technology Vol. 20. Nº1 (2018)].*

Those differences are the following one:

- Although both ways use ethylbenzene as an intermediate product, the co-production with propylene oxide method is not as useful as the dehydrogenation process because of all the sub-products generated. The yield of the process is also important too. The yield of ethylbenzene dehydrogenation is higher than the other method.
- The catalyst price Is also an important aspect. Dehydrogenation process usually uses iron oxide/potassium oxide catalyst and co-production process uses a titanium-gold catalyst, silver or titanium silicate catalyst.
- The simplicity of the dehydrogenation process, compared to propylene oxide process, make it cheaper as well *[T.Alexander et.al. (2006)]*.

1.2. CHEMISTRY OF ETHYLBENZENE DEHYDROGENATION

Ethylbenzene dehydrogenates to styrene in the gas phase according to an endothermic reversible reaction. Generally, it takes place in a fixed-bed reactor at 600-680 ºC temperature range and with overheated steam *[Chen, Shiou-Shan. Kirk-Othmer. 5th Edition (2006)]*, using a potassium promoted-iron catalyst (usually, before oxidation contains a 40-90% Fe_2O_3 and a 5-30% K_2O) as a catalyst.

As can be deduced from the stoichiometry of the reaction, low pressure favors the reaction (eq. 1) due to the mole dissociation, one mole of ethylbenzene gives 1 mole of styrene and 1 of hydrogen. Nowadays, all reactors are designed to operate at 41 kPa or less.

Styrene and ethylbenzene also can react in a set of secondary reactions to give benzene and methane (eqs. 2, 3 & 4), phenylacetylene, toluene (3 & 4), and, from impurities of the ethylbenzene feedstock, carbon dioxide, α-methylstyrene, allylbenzene, vinyltoluene, xylenes, cumene, n-propylbenzene, ethyltoluene, butylbenzenes, and heavy aromatics *[Chen, Shiou-Shan. Kirk-Othmer. 5th Edition (2006)]*. Dehydrogenation is an endothermic reaction, so that, high temperature favors it both kinetically and thermodynamically. However, high temperature increases by-products from side reactions and reduces styrene selectivity. Toluene formation accounts for the biggest yield loss, up to 2% of styrene produced and benzene formation accounts up to 1% of ethylbenzene reacted. So, toluene and benzene are considered the main by-products and it is considered all the others insignificant in terms of the yield losses. As a consequence, the reaction scheme to be considered is the following one:

1- $C_6H_5C_2H_5 \leftrightarrows C_6H_5C_2H_3 + H_2 \qquad \Delta H_r(298°C) = 117.690\ \frac{kJ}{mol}$

2- $C_6H_5C_2H_5 \rightarrow C_6H_6 + C_2H_4 \qquad \Delta H_r(298\ °C) = 105.510\ \frac{kJ}{mol}$

3- $C_6H_5C_2H_5 + H_2 \rightarrow C_6H_5CH_3 + CH_4 \qquad \Delta H_r(298°C) = -54.680\ \frac{kJ}{mol}$

4- $C_6H_5C_2H_3 + 2H_2 \rightarrow C_6H_5CH_3 + CH_4 \qquad \Delta H_r(298°C) = -172.370\ \frac{kJ}{mol}$

The reaction enthalpy, ΔH_r, is the enthalpy change associated with the mass transformation occurred in a chemical reaction. It is generated or absorbed depending on the enthalpy of reactants and products, and its value is calculated by using the formation heat of all components that participates into the reaction. The value of reaction enthalpy can be positive or negative. Being positive ($\Delta H_r > 0$) means that the reaction will absorb heat from its surroundings as the reactants convert into products. Consequently, the temperature will decrease (only in the adiabatic mode). On the other hand, if the reaction enthalpy is negative ($\Delta H_r < 0$) means that the reaction will release heat and consequently the temperature will increase. When a reaction has positive reaction enthalpy, it is called endothermic reaction, and, if a reaction has negative reaction enthalpy it is called exothermic reaction.

The next equation shows how to calculate the reaction enthalpy:

$$\Delta H_r\left(\frac{kJ}{mol}\right) = \sum \vartheta \cdot \Delta H_{f,p} - \sum \vartheta \cdot \Delta H_{f,r} = \sum_{j=1}^{S} \vartheta_j \cdot \Delta H_{f,j}$$

Where “ϑ” is the stoichiometric coefficient of the component “i”, $\Delta H_{f,p}$ is the formation heat of the products and $\Delta H_{f,r}$ is the formation heat of the reactants.

As it has been seen before, the first secondary associated reaction is endothermic and, as the main one, will decrease the temperature range as the reaction progresses. The second and third secondary associated reactions are both exothermic which means that the temperature range will increase as the reactions progress.

However, these ignored by-products provoke operational problems in the distillation unit *[Chen, Shiou-Shan. Kirk-Othmer. 5th Edition (2006)]*. By another side, phenylacetylene obtained by styrene dehydrogenation reacts with styrene provoking crosslinking in the product. Also, it generates free radical reactions increasing the dangerous nature of the process.

In the literature, you can also find this same reaction over other catalysts, as a commercial iron catalyst, Shell 105 (iron), Iron-alumina and KMS-1 (iron).

Some of these catalysts have more selectivity and require high temperature to affect the same ethylbenzene conversion. Despite having more selectivity, most of they contain chromium, which sublimes at a temperature range of 590-640ºC. So, the fast degradation of them is a drawback.

1.3. KINETICS OF ETHYLBENZENE DEHYDROGENATION.

Lee Won Jae. developed a kinetic model for this reaction system over a promoted potassium iron-catalyst by using experimental data, at temperature range of 600-640 K and at 1.2 Bar, documented by *Froment, G.F et al. (1990), Froment, G.F et al. (1975) and Weller, S. W. (1975).* The kinetic model is based on the LHHW mechanism where indicated that the controlling stage was the reaction on the catalyst surface.

The mechanism for catalytic reactions considers a physicochemical model of the process with seven stages that can be explained by the LHHW (Langmuir-Hinshelwood-Hougen-Watson) formalism, where the adsorption is determined by using the Langmuir isothermal and where, in this case, based on the Lee Won Jae article *[Lee, W. J. 2005]*, for a particle diameter of 0.0055 m, the reaction over the surface is the main stage. From that, the kinetic models formed by three terms are deduced.

The three parts of the kinetic expression of LHHW are the kinetic group, the driving force, and the adsorption group. For the main reaction, as the controlling step is the reaction on the catalyst surface, the kinetic group is $k_i \cdot K_a$ [where k_i is the rate constant and K_a is the adsorption equilibrium constant of the component "a"], the driving force will be expressed as $p_a - p_b p_c / K$ [where K is the equilibrium constant of the reaction and p_i are the partial pressures of the reaction elements], and the adsorption term of the kinetic expression will be $(1 + K_a P_a + K_b P_b + K_c P_c)^n$ where "n" is the adsorption group exponent and its value depends on the kind of interaction that occurs between the reactant and the catalyst. In this case, will get the value of 2. In addition, at the adsorption term of the kinetic expression, the adsorption equilibrium constants and partial pressures of the products of the secondary associated reactions are neglected due to their lower concentration than that of the main products.

The kinetic expressions for all reactions, in the same other as the mentioned reactions are the following one:

$$r_{c,1} = \frac{k_1 K_{EB}\left(P_{EB} - \frac{P_{ST}P_{H_2}}{K_{eq}}\right)}{(1 + K_{EB}P_{EB} + K_{H_2}P_{H_2} + K_{ST}P_{ST})^2}\left[\frac{kmol}{kg\ cat \cdot\ h}\right]$$

$$r_{c,2} = \frac{k_2 K_{EB}P_{EB}}{(1 + K_{EB}P_{EB} + K_{H_2}P_{H_2} + K_{ST}P_{ST})^2}\left[\frac{kmol}{kg\ cat \cdot\ h}\right]$$

$$r_{c,3} = \frac{k_3 K_{EB}P_{EB}K_{H_2}P_{H_2}}{(1 + K_{EB}P_{EB} + K_{H_2}P_{H_2} + K_{ST}P_{ST})^2}\left[\frac{kmol}{kg\ cat \cdot\ h}\right]$$

$$r_{c,4} = \frac{k_4 K_{ST}P_{ST}K_{H_2}P_{H_2}}{(1 + K_{EB}P_{EB} + K_{H_2}P_{H_2} + K_{ST}P_{ST})^2}\left[\frac{kmol}{kg\ cat \cdot\ h}\right]$$

In this case all these expressions will be modified by changing the partial pressure for the equivalence of total pressure multiplied by the molar fraction. The resulting kinetic expressions are:

$$r_{c,1} = \frac{k_1 K_{EB}\left(P \cdot y_{EB} - \frac{P \cdot y_{ST} \cdot P \cdot y_{H_2}}{K_{eq}}\right)}{(1 + K_{EB}P \cdot y_{EB} + K_{H_2}P \cdot y_{ST} + K_{ST}P \cdot y_{H_2})^2}\left[\frac{kmol}{kg\ cat \cdot\ h}\right]$$

$$r_{c,2} = \frac{k_2 K_{EB}P \cdot y_{EB}}{(1 + K_{EB}P \cdot y_{EB} + K_{H_2}P \cdot y_{ST} + K_{ST}P \cdot y_{H_2})^2}\left[\frac{kmol}{kg\ cat \cdot\ h}\right]$$

$$r_{c,3} = \frac{k_3 K_{EB}P \cdot y_{EB}K_{H_2}P \cdot y_{H_2}}{(1 + K_{EB}P \cdot y_{EB} + K_{H_2}P \cdot y_{ST} + K_{ST}P \cdot y_{H_2})^2}\left[\frac{kmol}{kg\ cat \cdot\ h}\right]$$

$$r_{c,4} = \frac{k_4 K_{ST}P \cdot y_{ST}K_{H_2}P \cdot y_{H_2}}{(1 + K_{EB}P \cdot y_{EB} + K_{H_2}P \cdot y_{ST} + K_{ST}P \cdot y_{H_2})^2}\left[\frac{kmol}{kg\ cat \cdot\ h}\right]$$

The rate and adsorption constants depend on temperature according to an Arrhenius type one:

$$k_i = A_i e^{\left(\frac{-Ea_i}{R\,T}\right)} \qquad i = 1{,}2{,}3{,}4$$

$$K_j = e^{\left(\frac{\Delta S_{a,j}}{R}\right)} e^{\left(\frac{-\Delta H_{a,j}}{RT}\right)} \qquad j = EB, ST, H_2$$

Where A_i is the pre-exponential factor and E_i is the activation energy of reaction *'i'*, and $\Delta H_{a,j}$ is the adsorption enthalpy of species *"j"* and A_j the pre-exponential factor of adsorption's constant. *Table 2* shows all the values the set of the considered reactions.

Rate coefficient	**Ea (Activation energy) (kJ/mol)**	**A_i (Pre-exponential factor of rate coefficient) (kmol/kg cat·h)**
k_1	175,38	$4{,}594\text{x}10^{9}$
k_2	296,29	$1{,}060\text{x}10^{15}$
k_3	474,76	$1{,}246\text{x}10^{26}$
k_4	213,78	$8{,}024\text{x}10^{10}$
Adsorption equilibrium constant	**$\Delta H_{a,}$ (Adsorption enthalpy) (kJ/mol)**	**$\Delta S_{a,j}$ (Pre-exponential factor of adsorption equilibrium constant) (1/Bar)**
K_{EB}	-102,22	$1{,}014\text{x}10^{-5}$
K_{ST}	-104,56	$2{,}678\text{x}10^{-5}$
K_{H2}	-117,95	$4{,}519\text{x}10^{-7}$

Table 2: Activation energies, adsorption enthalpies and pre-exponential factor for the Hougen-Watson kinetic model [Lee Jae, Won et.al. (2005)].

The main reaction, dehydrogenation reaction, is limited thermodynamically, and the temperature dependence of the equilibrium constant extracted by *Jenson, V. G. et.al. (1977)* where he documented it from *Wenner, R. R. (1948)*:

$$K_{EQ}(T) = 0.027 \cdot e^{[0.021\cdot(T(K)-773)]}$$

Heeding the activation energies of the reactions, the second reaction is more important when there is a high-temperature range. High activation energy, more than the main reaction, means that the reaction will be favored and, as a consequence, the styrene selectivity of the main reaction will be reduced.

The third reaction has the highest activation energy of the system. Due to it, will only take important at the start of the reactor where the highest range of temperature is.

Finally, the fourth reaction is the most problematic because as more styrene is generated, higher will be the reaction rate and then the styrene will react faster. Consequently, the global conversion of ethylbenzene to styrene will decrease considerably.

2. OBJECTIVES

In this Final Degree Project, the main objective is to create a mathematical code by using the Mathematica program to simulate the two reactors needed to produce styrene monomer by dehydrogenating ethylbenzene. Mathematica program allows you to create, through pre-created mathematical sentences, any kind of code, graph all obtained results and export all data to any other data processor easily.

The mathematical model developed in the code will assume 2 different hypotheses:

- The reactors will follow the plug flow model.
- The reactors will follow the dispersion model only with axial gradients into it.

At the first hypothesis, all parameters will be considered constant because, as will be seen in the following sections will not change enough to consider them variable.

The second hypothesis will be divided into two parts. In the first one, as in the first hypothesis, will be considered that will not be any variation of some physical parameters along the reactor whereas while in the second one it will be considered variable almost every parameter of balance.

The characteristics of the reactors system are based on the real industrial reactors. They consist of a series of two catalytic fixed bed reactors with an intermediate temperature exchanger. The volume of those reactors is, usually, around 9-10 m^3 for each reactor.

The exchanger is needed to provide to the fluid enough temperature, to carry on with the reactions. Therefore, the temperature range is increased to 893.15 K one more time (in all simulations) with the objective of reaching the highest reaction rates.

The properties of the catalyst used can be seen in the next table:

Apparent density (kg cat/m^3)	Particle density (kg cat/m^3)	Empty fraction (-)	Particle diameter (m)
1422	2500	0,4312	0,0055

Table 3: Properties of catalyst bed.

At the real industrial process, the characteristics of the flow are the following ones: Temperature range is 893.15 K and the linear velocity of the fluid is 12 m/s. Pressure is set at 0.501 Bar with a molar ration in the fluid ((Ethylbenzene to water) of $1\,mol\,Eb/6\,mol\,H_2O$ which gives an initial concentration of 0.963 mol/m^3 of ethylbenzene and 5,777 mol/m^3 of steam.

In addition, the value of the reactor yield is usually around 60-70 %. Finally, in this simulation, the feed flow is considered to be free of products.

In addition, there would be two secondary objectives. These objectives are the following ones:

First secondary objective will be analysing the results from the three hypothesis (ideal model, dispersion model with constant physical parameters and dispersion model without constant physical parameters) and compare them aiming to determine which are the results that are closest to the real ones.

Once the most real simulation is chosen there is the second secondary objective. This objective is to evaluate the pressure effect over the system, the temperature effect, the composition effect and the Length/Diameter ratio of the reactor and determine which are the best conditions to hold the ethylbenzene dehydrogenation.

3. MATHEMATICAL MODEL

The mathematical model of a unit operation consists in all the necessary equations to describe its reality and is basically constituted by the mass balances, enthalpy balance, and motion balance *[López C. et.al (2000)]*. The microscopic approach to the system requires the microscopic ones, which have the forms showed in *Table 4:*

Mass balance	
$\varepsilon \cdot \frac{\partial C_A}{\partial t} + \varepsilon \cdot \left(u_r \frac{\partial C_A}{\partial r} + \frac{u_\theta}{r} \cdot \frac{\partial C_A}{\partial \theta} + u_z \cdot \frac{\partial C_A}{\partial z}\right) = \varepsilon \cdot Deff_{m,i} \left(\frac{1}{r} \cdot \frac{\partial}{\partial r}\left(r \cdot \frac{\partial C_A}{\partial r}\right) + \frac{1}{r^2} \cdot \frac{\partial^2 C_A}{\partial \theta^2} + \frac{\partial^2 C_A}{\partial z^2}\right) + (1-\varepsilon) \cdot \sum_{i=1}^{R} \nu_{A,i} \cdot r_i\,(T,c)$	(1)
Enthalpy balance:	
$\frac{\partial T}{\partial t} + \left(G_r \cdot Cp_{m,r} \frac{\partial T}{\partial r} + \frac{G_\theta \cdot Cp_{m,\theta}}{r} \cdot \frac{\partial T}{\partial \theta} + G_z \cdot Cp_{m,z} \cdot \frac{\partial T}{\partial z}\right) = k_{m,i} \left(\frac{1}{r} \cdot \frac{\partial}{\partial r}\left(r \cdot \frac{\partial T}{\partial r}\right) + \frac{1}{r^2} \cdot \frac{\partial^2 T}{\partial \theta^2} + \frac{\partial^2 T}{\partial z^2}\right) + \sum_{i=1}^{R} r_i(T,c) \cdot \Delta H_{\,i} + Q$	(2)
Motion balance:	
$\frac{dP}{dz} 10^5 = -\frac{G}{\rho_m(T,c) d'_p} \left(\frac{1-\varepsilon}{\varepsilon^3}\right) \left[\frac{150\,(1-\varepsilon)\mu_m(T,c)}{d'_p} + 1.75\,G\right]$	(3)

Table 4: Microscopic balances in cylindrical coordinates. (The meaning of each symbol can be seen in the Acronyms page)

In these balances appears some physical parameters, some of them are in implicit form, that change along the reactor because they are dependent on the temperature and concentration. These parameters are listed in *Table 5*. There is also another kind of parameters that change along the reactor due their dependence to the temperature and concentration as well. Those parameters are called chemical parameters and consists of the group of catalytic reactions that have been seen previously in section 1.3. Finally, bed porosity will be considered a constant value.

Physical parameter	Symbol
Linear velocity	u_z
Molar flow	q
Mass flow	w
Medium molar mass	M_m
Mix density	ρ_m
Mix viscosity	μ_m
Diffusion coefficient of the mix	$Deff_{m,i}$
Specific heat of the mix	$Cp_{m,i}$
Thermal conductivity of the mix	$k_{m,i}$
Pressure	P

Table 5: Non-constant physical parameters of the balances.

3.1. ASSUMING PLUG FLOW REACTOR.

When the fluid is flowing at different circulation regimes according to its velocity and the tube ratio between the diameter and the length sometimes the frontline of the fluid becomes totally flat. It happens, also, if the fluid flows across a tube with high turbulence or through a very large tube. The particle diameter also affects at the model because it influences the preferential paths and the shortcut. Having a flat frontline means that there is not any mix in the axial direction but, in the radial or angular direction, is considered that there is a uniform physical and chemical composition representing, then, each volume differential can be considered as a perfect mix reactor.

A plug flow reactor can be simulated by many perfect mix reactors in series, and each perfect mix reactor works in his own operation point.

Attending to the Mass Balance, equation number 1, can be modified according to the next considerations:

- Considering that there will only be concentration gradient due to the flow movement and not by the diffusivity, the first term of the right of the equation will become 0.

- Since there is no evaluation at the radial axis and angular axis, the concentration on these directions will be homogeneous and, so that, the corresponding terms are equal to 0.
- And finally, the catalytic reactions of each mass balance must be considered.

In order to match the units, the last term must be multiplied by the density of the bed because in catalytic reactions, the reaction rate is usually given as a function of the amount of catalyst used.

The resulting mass balance for a component A is:

$$\varepsilon \cdot u_z \cdot \frac{\partial C_A}{\partial z} = (1-\varepsilon) \cdot \sum_{i=1}^{R} \nu_{A,i} \cdot r_{c,i}\,(T,c) \tag{4}$$

As is well known, it must be considered the mass balance for all the components presents in the system. Thus the 8 mass balances to be considered are the following ones:

$$\varepsilon \cdot u_z \cdot \frac{\partial C_{EB}}{\partial z} = (1-\varepsilon) \cdot \rho_L \cdot (\nu_{EB,1} \cdot r_{c,1}(T,c) + \nu_{EB,2} \cdot r_{c,2}(T,c) + \nu_{EB,3} \cdot r_{c,3}(T,c)) \tag{5}$$

$$\varepsilon \cdot u_z \cdot \frac{\partial C_{ST}}{\partial z} = (1-\varepsilon) \cdot \rho_L \cdot (\nu_{ST,1} \cdot r_{c,1}(T,c) + \nu_{ST,4} \cdot r_{c,4}(T,c)) \tag{6}$$

$$\varepsilon \cdot u_z \cdot \frac{\partial C_{H_2}}{\partial z} = (1-\varepsilon) \cdot \rho_L \cdot (\nu_{H_2,1} \cdot r_{c,1}(T,c) + \nu_{H_2,3}(T,c) \cdot r_{c,3} + \nu_{H_2,4} \cdot r_{c,4}(T,c)) \tag{7}$$

$$\varepsilon \cdot u_z \cdot \frac{\partial C_{Be}}{\partial z} = (1-\varepsilon) \cdot \rho_L \cdot (\nu_{Be,2} \cdot r_{c,2}(T,c)) \tag{8}$$

$$\varepsilon \cdot u_z \cdot \frac{\partial C_{Ethyl}}{\partial z} = (1-\varepsilon) \cdot \rho_L \cdot (\nu_{Ethyl,2} \cdot r_{c,2}(T,c)) \tag{9}$$

$$\varepsilon \cdot u_z \cdot \frac{\partial C_{Tol}}{\partial z} = (1-\varepsilon) \cdot \rho_L \cdot (\nu_{Tol,3} \cdot r_{c,3}(T,c) + \nu_{Tol,4} \cdot r_{c,4}(T,c)) \tag{10}$$

$$\varepsilon \cdot u_z \cdot \frac{\partial C_{Met}}{\partial z} = (1-\varepsilon) \cdot \rho_L \cdot (\nu_{Met,3} \cdot r_{c,3}(T,c) + \nu_{Met,4} \cdot r_{c,4}(T,c)) \tag{11}$$

$$\varepsilon \cdot u_z \cdot \frac{\partial C_{H_2O}}{\partial z} = 0 \tag{12}$$

The Enthalpy balance is

$$G_z \cdot Cp_{m,z} \cdot \frac{\partial T}{\partial z} = \rho_L \cdot \Big(r_{c,1}(T,c) \cdot (-\Delta H_{\ 1}) + r_{c,2}(T,c) \cdot (-\Delta H_{\ 2}) + r_{c,3}(T,c) \cdot (-\Delta H_{\ 3}) + r_{c,4}(T,c) \cdot (-\Delta H_{\ 4}) \Big) + Q \tag{13}$$

Where "G", the mass velocity, is the result of multiplying the density of the mix by the linear velocity $G\left(\frac{mol}{h \cdot m^2}\right) = \frac{u_z \cdot \rho_m}{M_m}$. And it is considered that:

1. The industrial production unit is adiabatic and thus, the last term of the energy balance, Q, will become 0, and all term dependent of the time will become 0 at steady state.
2. There will only be temperature gradient due to the flow movement and not by the thermal conductivity, the 3rd term of the equation number 2 will become 0.
3. There is no evaluation at the radial axis and angular axis, the temperature on those directions will be homogeneous and, so that, its derivates are equal to 0.
4. The last term must be multiplied by the catalyst bulk density.

In the above-mentioned balances appears those physical parameters mentioned in section 3. Assuming a temperature decrease of 80 K and ethylbenzene conversion of 80%, [values based on some experiments data from *Lee Jae, Won et.al. (2005) and Nijhuis, T. A., et.al. (2006)],* the variations of the physical parameters are closer to the 10% (Table 6). So that, as a first approximation they will be considered constant. All initial physical parameters are shown in table 3 of section 2.

Parameter	simbol	units	Average value	variation (%)
Linear velocity	uz	m·h-1	12,0780	1,300
Volumetric flow rate	q	m3·h-1	76827,4320	1,320
Massic flow rate	w	kmol·h-1	544,0985	11,290
Average molar mass	Mm	kg·mol-1	0,0290	10,240
Mix density	ρm	kg·m-3	0,1955	10,260
Specific heat of the mix	Cpm	kJ·(mol·K)-1	0,0768	5,910
Pressure	P	Bar	0,5120	4,390

Table 6: Variation of physical parameters

In addition, when the concentrations of the components of a reactions system are low and the operational pressure is low too, the drop pressure may be neglected. At section 2 is said that the initial concentration of ethylbenzene is about 0.963 mol/m^3. That value is considered low concentration, so that, the pressure of the system will be assumed constant.

3.2. ASSUMING DISPERSION MODEL.

One of the typical deviations of the plug flow model, which occurs on the stuffed beds, is called axial dispersion. The axial dispersion means that all components will disperse into the reactor and every differential stage will mix with its adjacent differential stages given, then, a false concentration in the current differential stage compared with the concentration that would be in ideal conditions. In addition, this mix usually provokes the reduction of the yield of the reactor by reducing the conversion of the main reaction and favours the secondary reactions increasing then the production of by-products.

Also, thermal conductivity is related to the axial diffusion because it depends on the temperature and composition. Consequently, if there is some mix into the reactor, there will be a temperature dispersion through the adjacent differential stages producing then a little deviation of the temperature profile that can reduce the conversion of the main reaction, generate some thermal problems and destabilize the reactor.

In this section, after the following considerations:

1. All term dependent of the time will become 0 at steady state.
2. Since there is no evaluation at the radial axis and angular axis, the concentration on these directions will be homogeneous and, so that, its derivates are equal to 0.
3. The last term must be multiplied by the catalyst bulk density.
4. And finally, the catalytic reactions of each mass balance must be considered.

The equation (1) is the following one:

$$\varepsilon \cdot Deff_{m,z} \frac{d^2 C_A}{dz^2} - \varepsilon \cdot u_z \cdot \frac{dC_A}{dz} + (1-\varepsilon) \cdot \rho_L \cdot \sum_{i=1}^{R} \nu_{A,i} \cdot r_{c,i}(T,c) = 0 \tag{14}$$

As in the above section, it must be considered the mass balance for all the components presents in the system. Thus the 8 mass balances to be considered are the following ones:

$$\varepsilon \cdot Deff_{m,z}\frac{d^2C_{EB}}{dz^2} - \varepsilon \cdot u_z \cdot \frac{dC_{EB}}{dz} + (1-\varepsilon)\cdot\rho_L \cdot \left(\nu_{EB,1}\cdot r_{c,1}(T,c) + \nu_{EB,2}\cdot r_{c,2}(T,c) + \nu_{EB,3}\cdot r_{c,3}(T,c)\right) = 0 \tag{15}$$

$$\varepsilon \cdot Deff_{m,z}\frac{d^2C_{ST}}{dz^2} - \varepsilon \cdot u_z \cdot \frac{dC_{ST}}{dz} + (1-\varepsilon)\cdot\rho_L \cdot \left(\nu_{ST,1}\cdot r_{c,1}(T,c) + \nu_{ST,4}\cdot r_{c,4}(T,c)\right) = 0 \tag{16}$$

$$\varepsilon \cdot Deff_{m,z}\frac{d^2C_{H_2}}{dz^2} - \varepsilon \cdot u_z \cdot \frac{dC_{H_2}}{dz} + (1-\varepsilon)\cdot\rho_L \cdot \left(\nu_{H_2,1}\cdot r_{c,1}(T,c) + \nu_{H_2,3}\cdot r_{c,3}(T,c) + \nu_{H_2,4}\cdot r_{c,4}(T,c)\right) = 0 \tag{17}$$

$$\varepsilon \cdot Deff_{m,z}\frac{d^2C_{Be}}{dz^2} - \varepsilon \cdot u_z \cdot \frac{dC_{Be}}{dz} + (1-\varepsilon)\cdot\rho_L \cdot \left(\nu_{Be,2}\cdot r_{c,2}(T,c)\right) = 0 \tag{18}$$

$$\varepsilon \cdot Deff_{m,z}\frac{d^2C_{Ethyl}}{dz^2} - \varepsilon \cdot u_z \cdot \frac{dC_{Ethyl}}{dz} + (1-\varepsilon)\cdot\rho_L \cdot \left(\nu_{Ethyl,2}\cdot r_{c,2}(T,c)\right) = 0 \tag{19}$$

$$\varepsilon \cdot Deff_{m,z}\frac{d^2C_{Tol}}{dz^2} - \varepsilon \cdot u_z \cdot \frac{dC_{Tol}}{dz} + (1-\varepsilon)\cdot\rho_L \cdot \left(\nu_{Tol,3}\cdot r_{c,3}(T,c) + \nu_{Tol,4}\cdot r_{c,4}(T,c)\right) = 0 \tag{20}$$

$$\varepsilon \cdot Deff_{m,z}\frac{d^2C_{Met}}{dz^2} - \varepsilon \cdot u_z \cdot \frac{dC_{Met}}{dz} + (1-\varepsilon)\cdot\rho_L \cdot \left(\nu_{Met,3}\cdot r_{c,3}(T,c) + \nu_{Met,4}\cdot r_{c,4}(T,c)\right) = 0 \tag{21}$$

$$\varepsilon \cdot Deff_{m,z}\frac{d^2C_{H_2O}}{dz^2} - \varepsilon \cdot u_z \cdot \frac{dC_{H_2O}}{dz} = 0 \tag{22}$$

For the Enthalpy balance, equation (2), and using the same simplifications as before, but only, for the temperature, the resulting balance is:

$$k_{m,i}\cdot\frac{\partial^2T}{\partial z^2} - G_z \cdot Cp_{m,z}\cdot\frac{\partial T}{\partial z} + \rho_L \cdot \left(r_{c,1}(T,c)\cdot(-\Delta H_1) + r_{c,2}(T,c)\cdot(-\Delta H_2) + r_{c,3}(T,c)\cdot(-\Delta H_3) + r_{c,4}(T,c)\cdot(-\Delta H_4)\right) = 0 \tag{23}$$

3.2.1. Assuming Constant physical parameters.

To justify that constancy, as in the above section the value of each parameter is compared assuming that the temperature has decreased 80 K and there is 80% conversion of ethylbenzene. In addition, there must be added two new parameters. These parameters are the Diffusion coefficient and the thermal conductivity. As the pressure is assumed constant, diffusion coefficient will be considered constant too. These variations are listed in Table 7.

Parameter	symbol	units	Average Value	variation (%)
Diffusion coefficient of the mix	Deffm	m2·h-1	0,0805	0,004
Thermal conductivity of the mix	km	J·(m·K·h)-1	0,0434	6,000

Table 7: Variation of physical parameters

As in section 3.1, the microscopic balances are needed to simulate the profile of concentration and temperature inside the reactor. In this case, the balances shown in section 3.2 will be used.

So, for each component, the expression of the mass balance is:

$$\varepsilon \cdot Deff_{m,z} \frac{d^2C_A}{dz^2} - \varepsilon \cdot u_z \cdot \frac{dC_A}{dz} + (1-\varepsilon) \cdot \rho_L \cdot \sum_{i=1}^{R} \nu_{A,i} \cdot r_{c,i}(T,c) = 0 \tag{24}$$

Substituting the last term of the mass balance of each component with their respective reactions:

$$\varepsilon \cdot Deff_{m,z} \frac{d^2C_{EB}}{dz^2} - \varepsilon \cdot u_z \cdot \frac{dC_{EB}}{dz} + (1-\varepsilon) \cdot \rho_L \cdot \left(\nu_{EB,1} \cdot r_{c,1}(T,c) + \nu_{EB,2} \cdot r_{c,2}(T,c) + \nu_{EB,3} \cdot r_{c,3}(T,c)\right) = 0 \tag{25}$$

$$\varepsilon \cdot Deff_{m,z} \frac{d^2C_{ST}}{dz^2} - \varepsilon \cdot u_z \cdot \frac{dC_{ST}}{dz} + (1-\varepsilon) \cdot \rho_L \cdot \left(\nu_{ST,1} \cdot r_{c,1}(T,c) + \nu_{ST,4} \cdot r_{c,4}(T,c)\right) = 0 \tag{26}$$

$$\varepsilon \cdot Deff_{m,z} \frac{d^2C_{H_2}}{dz^2} - \varepsilon \cdot u_z \cdot \frac{dC_{H_2}}{dz} + (1-\varepsilon) \cdot \rho_L \cdot \left(\nu_{H_2,1} \cdot r_{c,1}(T,c) + \nu_{H_2,3} \cdot r_{c,3}(T,c) + \nu_{H_2,4} \cdot r_{c,4}(T,c)\right) = 0 \tag{27}$$

$$\varepsilon \cdot Deff_{m,z} \frac{d^2C_{Be}}{dz^2} - \varepsilon \cdot u_z \cdot \frac{dC_{Be}}{dz} + (1-\varepsilon) \cdot \rho_L \cdot \left(\nu_{Be,2} \cdot r_{c,2}(T,c)\right) = 0 \tag{28}$$

$$\varepsilon \cdot Deff_{m,z}\frac{d^2C_{Ethyl}}{dz^2} - \varepsilon \cdot u_z \cdot \frac{dC_{Ethyl}}{dz} + (1-\varepsilon)\cdot\rho_L \cdot \left(\nu_{Ethyl,2}\cdot r_{c,2}(T,c)\right) = 0 \tag{29}$$

$$\varepsilon \cdot Deff_{m,z}\frac{d^2C_{Tol}}{dz^2} - \varepsilon \cdot u_z \cdot \frac{dC_{Tol}}{dz} + (1-\varepsilon)\cdot\rho_L \cdot \left(\nu_{Tol,3}\cdot r_{c,3}(T,c) + \nu_{Tol,4}\cdot r_{c,4}(T,c)\right) = 0 \tag{30}$$

$$\varepsilon \cdot Deff_{m,z}\frac{d^2C_{Met}}{dz^2} - \varepsilon \cdot u_z \cdot \frac{dC_{Met}}{dz} + (1-\varepsilon)\cdot\rho_L \cdot \left(\nu_{Met,3}\cdot r_{c,3}(T,c) + \nu_{Met,4}\cdot r_{c,4}(T,c)\right) = 0 \tag{31}$$

$$\varepsilon \cdot Deff_{m,z}\frac{d^2C_{H_2O}}{dz^2} - \varepsilon \cdot u_z \cdot \frac{dC_{H_2O}}{dz} = 0 \tag{32}$$

And for the enthalpy balance:

$$k_{m,i}\cdot\frac{\partial^2 T}{\partial z^2} - G_z\cdot Cp_{m,z}\cdot\frac{\partial T}{\partial z} + \rho_L \cdot\left(r_{c,1}(T,c)\cdot(-\Delta H_{\,1}) + r_{c,2}(T,c)\cdot(-\Delta H_{\,2}) + r_{c,3}(T,c)\cdot(-\Delta H_{\,3}) + r_{c,4}(T,c)\cdot(-\Delta H_{\,4})\right) = 0 \tag{33}$$

3.2.2. Assuming Variable physical parameters

In this section, all three balances raised in section 3, Mass balance, Enthalpy balance, and Motion balance will be used. The developing of Mass balance and Enthalpy balance is done in section 3.2.

When fluid passes through the catalyst bed, appears friction between the fluid and the bed. This friction provokes a pressure loss on the fluid since part of the amount of movement energy that it carries dissipates due to the force exerted by that friction. To study this pressure drop a motion balance is applied. This balance relates de pressure drop with the length of the reactor:

$$\frac{dP}{dz}10^5 = -\frac{G}{\rho_m(T,c)d_p'}\left(\frac{1-\varepsilon}{\varepsilon^3}\right)\left[\frac{150\,(1-\varepsilon)\mu_m(T,c)}{d_p'} + 1.75\,G\right] \tag{34}$$

Where d_p' is the effective particle diameter.

All parameters that were considered constants at the above section are now variables that change along the reactor. These variables depend on the temperature and the composition of the fluid and their expressions can be seen at section 4.

As in the above sections, it must be considered the mass balance for all the components present in the system:

$$\varepsilon \cdot Deff_{m,z}(T,c)\frac{d^2C_{EB}}{dz^2} - \varepsilon \cdot u_z(T,c)\cdot\frac{dC_{EB}}{dz} + (1-\varepsilon)\cdot\rho_L \cdot \left(\nu_{EB,1}\cdot r_{c,1}(T,c) + \nu_{EB,2}\cdot r_{c,2}(T,c) + \nu_{EB,3}\cdot r_{c,3}(T,c)\right) = 0 \tag{35}$$

$$\varepsilon \cdot Deff_{m,z}(T,c)\frac{d^2C_{ST}}{dz^2} - \varepsilon \cdot u_z(T,c)\cdot\frac{dC_{ST}}{dz} + (1-\varepsilon)\cdot\rho_L \cdot \left(\nu_{ST,1}\cdot r_{c,1}(T,c) + \nu_{ST,4}\cdot r_{c,4}(T,c)\right) = 0 \tag{36}$$

$$\varepsilon \cdot Deff_{m,z}(T,c)\frac{d^2C_{H_2}}{dz^2} - \varepsilon \cdot u_z(T,c)\cdot\frac{dC_{H_2}}{dz} + (1-\varepsilon)\cdot\rho_L \cdot \left(\nu_{H_2,1}\cdot r_{c,1}(T,c) + \nu_{H_2,3}\cdot r_{c,3}(T,c) + \nu_{H_2,4}\cdot r_{c,4}(T,c)\right) = 0 \tag{37}$$

$$\varepsilon \cdot Deff_{m,z}(T,c)\frac{d^2C_{Be}}{dz^2} - \varepsilon \cdot u_z(T,c)\cdot\frac{dC_{Be}}{dz} + (1-\varepsilon)\cdot\rho_L \cdot \left(\nu_{Be,2}\cdot r_{c,2}(T,c)\right) = 0 \tag{38}$$

$$\varepsilon \cdot Deff_{m,z}(T,c)\frac{d^2C_{Ethyl}}{dz^2} - \varepsilon \cdot u_z(T,c)\cdot\frac{dC_{Ethyl}}{dz} + (1-\varepsilon)\cdot\rho_L \cdot \left(\nu_{Ethyl,2}\cdot r_{c,2}(T,c)\right) = 0 \tag{39}$$

$$\varepsilon \cdot Deff_{m,z}(T,c)\frac{d^2C_{Tol}}{dz^2} - \varepsilon \cdot u_z(T,c)\cdot\frac{dC_{Tol}}{dz} + (1-\varepsilon)\cdot\rho_L \cdot \left(\nu_{Tol,3}\cdot r_{c,3}(T,c) + \nu_{Tol,4}\cdot r_{c,4}(T,c)\right) = 0 \tag{40}$$

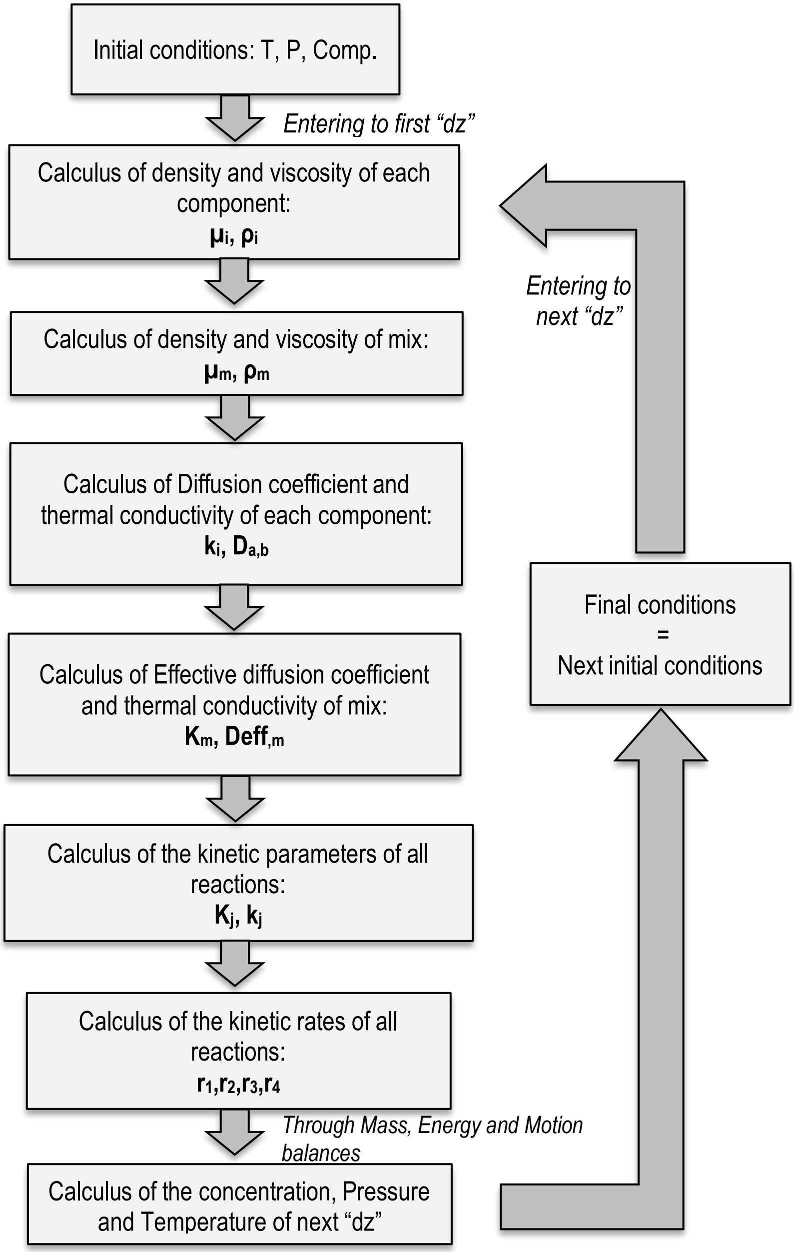
$$\varepsilon \cdot Deff_{m,z}(T,c)\frac{d^2C_{Met}}{dz^2} - \varepsilon \cdot u_z(T,c)\cdot\frac{dC_{Met}}{dz} + (1-\varepsilon)\cdot\rho_L \cdot \left(\nu_{Met,3}\cdot r_{c,3}(T,c) + \nu_{Met,4}\cdot r_{c,4}(T,c)\right) = 0 \tag{41}$$

$$\varepsilon \cdot Deff_{m,z}(T,c)\frac{d^2C_{H_2O}}{dz^2} - \varepsilon \cdot u_z(T,c)\cdot\frac{dC_{H_2O}}{dz} = 0 \tag{42}$$

As in section 3.2, the Enthalpy balance is the following one:

$$k_{m,i}(T,c)\cdot\frac{\partial^2 T}{\partial z^2} - G_z(T,c)\cdot Cp_{m,z}(T,c)\cdot\frac{\partial T}{\partial z} + \rho_L \cdot \left(r_{c,1}(T,c)\cdot(-\Delta H_{\,1}) + r_{c,2}(T,c)\cdot(-\Delta H_{\,2}) + r_{c,3}(T,c)\cdot(-\Delta H_{\,3}) + r_{c,4}(T,c)\cdot(-\Delta H_{\,4})\right) = 0 \tag{43}$$

Finally, next scheme shows the general resolution of all simulations:



4. RESULTS

The next table will show the scheme of the different simulations that have been done.

Nº	Model	Properties constancy	P (Bar)	Composition		T (K)	L/D
				Mol EB/Mol H_2O	$C_{Eb,O}$ (mol/m^3)		
1	Ideal	Constant	0,501	1/6	0,963	893,15	5/1,5
2	Dispersion	Constant	0,501	1/6	0,963	893,15	5/1,5
3	Dispersion	Non-constant	0,501	1/6	0,963	893,15	5/1,5
4	Dispersion	Non-constant	0,501	1/6	0,963	893,15	2,5/1,5
5	Dispersion	Non-constant	0,501	1/6	0,963	893,15	10/1,5
6	Dispersion	Non-constant	0,501	1/6	0,963	793,15	5/1,5
7	Dispersion	Non-constant	0,501	1/6	0,963	943,15	5/1,5
8	Dispersion	Non-constant	1,5	1/6	0,963	893,15	5/1,5
9	Dispersion	Non-constant	0,501	1/6	2	893,15	5/1,5
10	Dispersion	Non-constant	0,501	1/3	0,963	893,15	5/1,5
11	Dispersion	Non-constant	0,501	1/10	0,963	893,15	5/1,5

Table 8: Summary of simulations.

With these initial parameters, the mass flow and all physical parameters can be defined before starting the simulations. These parameters are listed in table 10.

Temperature reference of 893,15 K	Ethylbenzene	Water steam	Styrene	Hydrogen
Density, ρ (kg/m^3)	0,7164	0,1215	0,7028	0,0135
Viscosity, μ (Pa·s)	1,86E-05	3,58E-05	1,90E-05	1,32E-05
Diffusion coefficient, D (m^2/h)	0,0347	1,321	0,0361	18,767
Specific heat, C_p (kJ/mol·K)	**	*	**	***
a	-	143,05	-	56,505
b	-	-183,54	-	-702,24
b	-	82,751	-	1165
d	-	-3,6989	-	-560,7
Thermal diffusivity, k_m (kJ/m·h·K)	0,00547	0,06197	0,00569	0,20595

*Table 9: Initial physical properties. *, **, ***, each equation used can be seen in the appendix 3.*

Apart from the properties of the above table, in the appendix 3 are calculated all properties of the mixture. Each method to calculate the value of each property of the mixture is raised and explained.

4.1. SIMULATION DISCRIMINATION

In this section it will be discussed which is the simulation model that approaches more to the real process.

In the figure 19 of the appendix 5 the simulation profiles can be seen. At the first reactor, temperature decreases reaching the value of 780 K due the dehydrogenation of ethylbenzene. The concentration of ethylbenzene and styrene at the end of the reactor are, respectively, 0.64 mol/m^3 and 0.31 mol/m^3. The selectivity of styrene, that is the relation of the styrene produced front ethylbenzene reacted, at the end of the reactor is 98.88% and the value of yield is 32.88% as can be seen in the figure 5.

At the second reactor, as at the first reactor, the temperature decreases, in less quantity, due the dehydrogenation of ethylbenzene reaching the value of 816 K. The final concentration of ethylbenzene and styrene are 0.40 mol/m^3 and 0.53 mol/m^3. The selectivity of styrene, at the end of this second reactor, is 88.98% and the final yield is 52.14%. The ethylbenzene conversion is up to 59% at the end of the second reactor.

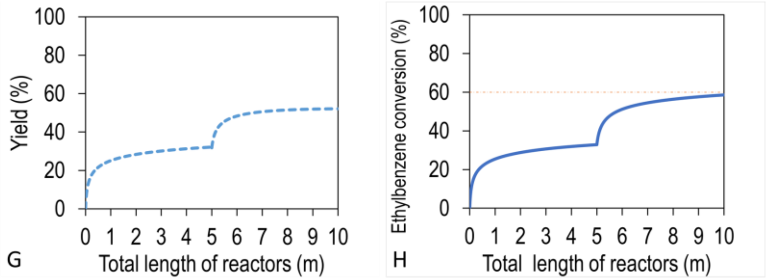


Figure 5: Simulation Nº1. 893.15 K, 0.501 Bar, 1/6 mol Eb/H$_2$O, 5/1.5 L/D
G) Yield of reactors; H) Total conversion of ethylbenzene

The results of this simulation do not approximate to the real values. Therefore, a simulation with dispersion model and constant physical parameters is done below.

The figure 20 of appendix 5 shows the profiles of simulation number 2. At the first reactor, as the main reaction is endothermic, the temperature has decreased up to 100 K. The concentration of ethylbenzene at the end of the reactor is 0.65 mol/m^3. This value of concentration remained almost the same since the fourth meter of the reactor meaning then that the main reaction is closer to the equilibrium.

The selectivity of styrene, at the end of the reactor, is around 97.86% and the yield of the reactor, at the end of it is 32.26%.

The temperature of the second reactor decreased up to 80 K. The conversion of this second reactor reaches the value of 38% with a total conversion of ethylbenzene of 59%. The final concentration of ethylbenzene is 0.40 mol/m^3 and final styrene concentration is up to 0.53 mol/m^3. The selectivity of styrene is up to 88.82% and total yield has the value of 52.18%.

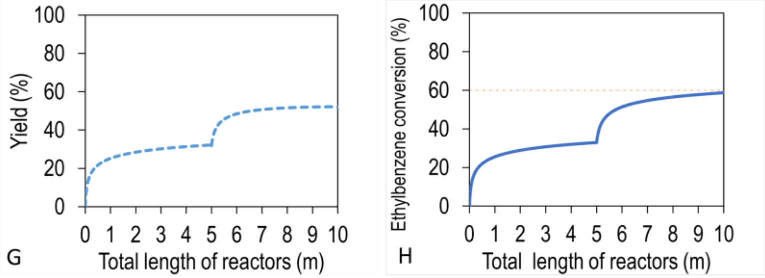


Figure 6: Simulation Nº2. 893.15 K, 0.501 Bar, 1/6 mol Eb/H_2O, 5/1.5 L/D
G) Yield of reactors; H) Total conversion of ethylbenzene

This time the results are more similar to the industrial values than the results of simulation number 1. However, they are still far to real ones. Therefore, a final simulation with dispersion model and non-constant parameters will be done to see if the non-constancy of the parameters affects the values.

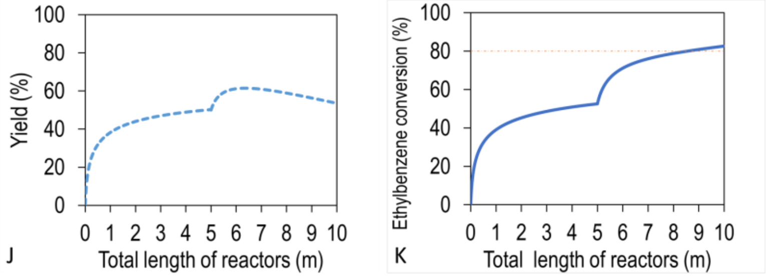


Figure 7: Simulation Nº3. 893.15 K, 0.501 Bar, 1/6 mol Eb/H_2O, 5/1.5 L/D
J) Yield of reactors; K) Total conversion of ethylbenzene

As can be seen in the graphics of figure number 21 of the appendix 5, at the first reactor, while the reaction progresses, the temperature decreases up to 820 K. It happens because the endothermic dehydrogenation of ethylbenzene. In addition, the density of the mix decreases provoking then an increment of the flow rate and, consequently, a pressure loss.

The diffusion coefficient also decreases due the temperature decreasing. The same happens with the specific heat of the mix. However, the thermal conductivity of the mix increases its value because of the formation of all products, which have more thermal conductivity by themselves.

The conversion of ethylbenzene is up to 50% and its concentration at the end of the reactor is 0.46 mol/m^3. This result is quite acceptable due the bibliographic value of the total ethylbenzene conversion is around of 88%. In addition, the selectivity of styrene is also a good result compared to the bibliographic value, which is around of 95%. The associated reactions and the low range temperature at the end of the reactor cause the selectivity decrease.

Finally, the yield of the reactor is quite constant, and its value is up to 52% and can be seen in figure 7.

In the second reactor, the temperature range decreases as well but not as much as in the first reactor. This is because the concentration of ethylbenzene is less and, consequently, the main reaction rate is lower. The value of all physical parameters, mentioned at the first reactor, decrease following the same way. However, approximately at half reactor length, as the fourth secondary associated reaction is quite exothermic the temperature range increases considerably because it becomes higher than the rate of the main reaction. This temperature change makes a pressure gain provoking then, a decrease of the flow rate and the volumetric flow. In addition, as the pressure modifies all molar fractions, all physical parameters change another time, increasing its value. This change provokes a selectivity loss respect the styrene reaching the value of 64.18%, loss of the styrene produced and in general, loss of the total yield of the reactor. The total yield is up to 53.61%, and the conversion of ethylbenzene is around of 82,65%.

The results of this last simulation are the closest to the real one. So that, it can be said that the non-constancy of the physical parameters affects considerably to the yield of the reactors. In addition, seeing that decrease of the selectivity and of the yield in general at the middle of the second reactor it should be contemplated to cut this second reactor and check if this change will improve the results.

4.2. DETERMINATION THE PROCESS VARIABLES EFFECT

In this section will be discussed how affects the temperature, pressure, composition and reactor dimension to the total yield. All parameters than appears at the tables are the accumulated value respect the system entry.

4.2.1. Effect of reactor dimension L/D

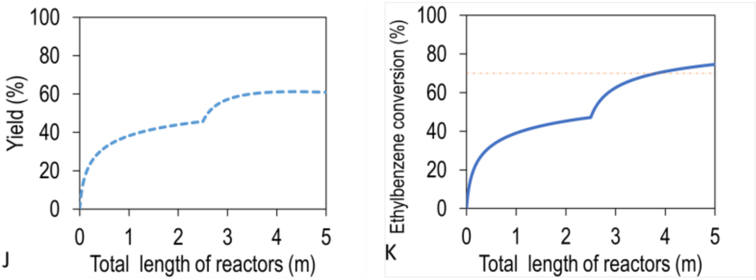


Figure 8: Simulation Nº4. 893.15 K, 0.501 Bar, 1/6 mol Eb/H_2O, 2.5/1.5 L/D
J) Yield of reactors; K) Total conversion of ethylbenzene

In this simulation (number 4) only the size of the reactors has been changed. All profiles can be seen in figure 22 of appendix 5. The pattern of all parameters is like the simulation with the L/D of 3,33 but with some differences. First, respect the first reactor, using a reduced length provokes a decreasing of the conversion reaching the value of 47,15%. In addition, the styrene selectivity value is up to 96.92% and consequently the yield has lower value than the simulation number 3 with 45.69%.

At the second reactor there is not the temperature increasing produced by the 4th associated secondary reaction and consequently the selectivity if styrene reaches the value of 81.64%. Value that is clearly higher than the styrene selectivity of the simulation number 3 which have a value lower than 40%. About the conversion, the final conversion of ethylbenzene is 74.63%, and the total yield of the simulation is quite high with a value of 60.93%. However, as It can be seen at the graphic “J”, the yield of the simulation starts to decrease slowly (like the simulation number 3) and so, that 60.93% of yield is not the higher value that has been reached into the simulation.

At the simulation number 5, as the above one, only the size has been changed. All its simulation profiles can be seen in the appendix 5 at figure 23. Respect the physical parameters, the dynamic of all parameters is like the simulation number 3 and 4. However, there are some differences in the reactor number 2. As it can be seen, the diffusion coefficient of mix of the simulation 5, at the second reactor, increases its value since the start meanwhile at the second reactor of simulations 3 and 4 this term also increases its value but not with such a considerable gradient. Respect the flow rate, after increasing its value, the decreasing gradient of the simulation number 5 is so huge meanwhile the respective flow rate gradients of simulations 3 and 4 are almost null. The styrene selectivity of the second reactor at the start is quite good with a value of 98,42%. However, the styrene selectivity at the end of it is so bad with a value of 34,14 %.

Respect the conversion, the total conversion of ethylbenzene is so high reaching the value of 93.04 %. Although the ethylbenzene conversion is very high, the styrene selectivity is very low and that makes the yield of the reactor decrease considerably, reaching the value of 28,57%, causing less production of styrene and more production of undesired by-products.

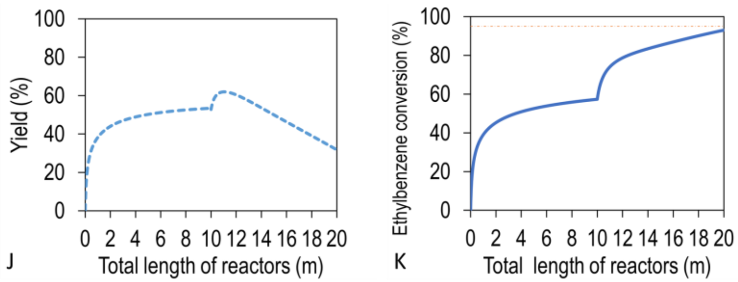


Figure 9: Simulation Nº 5. 893.15 K, 0.501 Bar, 1/6 mol Eb/H_2O, 10/1.5 L/D
J) Yield of reactors; K) Total conversion of ethylbenzene

But what can we say about the global concentration, selectivity and concentration? Simulations number 3,4 and 5 are the same but modifying the length of the reactor. This change affects a little bit to these variables. The following graphics shows the differences of all 3 simulations:

		Reactor 1			Reactor 2		
Nº	Parameter: L/D	Styrene selectivity	Ethylbenzene conversion	Total yield	Styrene selectivity	Ethylbenzene conversion	Total yield
3	5/1,5	95,56%	52,57%	50,23%	64,86%	82,65%	53,61%
4	2,5/1,5	96,92%	47,15%	45,70%	81,64%	74,62%	60,92%
5	10/1,5	93,21%	57,35%	53,46%	34,14%	93,04%	31,77%

Table 10: Results comparison of simulations 3,4,5

As it can be seen in the above table, the highest yield of the reactor 1 is at simulation 5 even being the selectivity the lowest. It means that at the conditions of the first reactor, using a biggest reactor will increase our results, only a 3% but it still is an improve to the final value.

Respect the reactor number 2, using a bigger reactor is quite bad because even the conversion of ethylbenzene is the highest, the selectivity drops to a 34 % decreasing then the yield and favouring the production of non-desired by-products. However, the highest selectivity is at simulation number 3 which a value of 81,64% that added to the ethylbenzene conversion which has a value of 74,62% results in a higher yield where its value is about 60.92%.

Seeing these results, it can be determined that carry the reaction on a bigger reactor in the first step and a smaller reactor in the second step will probably increase our results making the yield higher and then optimizing the process.

4.2.2. Effect of temperature

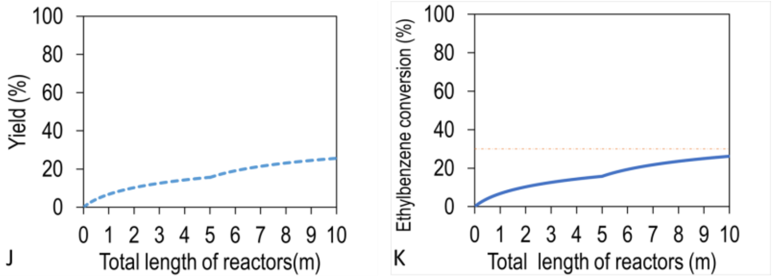


Figure 10: Simulation Nº6. 793.15 K, 0.501 Bar, 1/6 mol Eb/H_2O, 5/1.5 L/D
J) Yield of reactors; K) Total conversion of ethylbenzene

All graphics of this simulation can be seen in figure 24 of appendix 5. The conduct of all parameters is like the above simulations because the composition does not change. In addition, as the temperature range is lower than the above and below simulations, physical parameters will not be affected as much as the other simulations neither.

With this low temperature range the reactions are not able to react properly and so there are low changes of the composition. Furthermore, this simulation was carried on with even more low temperature range and nothing reacted. Therefore, there is only this simulation with low temperature range. The same behaviour is repeated at the second reactor.

With these conditions the final concentration of ethylbenzene takes the value of 0.71 mol/m^3. It means that less than 30 % reacted. The selectivity of styrene is closer to the 100% on both reactors because, if it is hard to react for the main reaction, will be quite impossible to react for the secondary associated reactions.

The yield of the first reactor is up to 15,70% and the ethylbenzene conversion has the value of 15,77%. Both results are quite low and therefore quite bad. At the second reactor, the final ethylbenzene conversion is up to 26,20% and the total yield reaches the value of 25,53 %.

Seeing these results, you can say that low temperature issue makes more difficult to carry on the reaction and consequently this process would be impossible to do with any economic benefit.

At figure number 25 of the appendix 5 are the profiles of simulation number 7. As it can be seen, the temperature range has been increased 50 K. This increment was selected with the objective to simulate the same reactions with more temperature but without overstate the increment.

First of all, physical parameters of reactor number 1 follow the same pattern as the other. The conversion of the first reactor is clearly the best of all simulations with a value of 71,40%. However, you cannot say the same for the styrene selectivity because its value is around 89,95 % at the end of the reactor. That does not mean that this value is bad. By seeing the graphic 'J', the yield of the reactor number 1 is clearly one of the highest of all simulations with a value of 57,78%.

On the other hand, the reactor number 2 has so bad results. There is an increment of pressure that makes the flow rate decrease considerably. Additionally, most of the values of physical parameters remains quite uniform. The big difference appears at selectivity. The selectivity of styrene is practically null from the 8th meter of the reactor because at that temperature range, 2nd, 3rd and 4th secondary associated reactions are so favoured and then, the main reaction is in the background. The value of styrene selectivity at the end of the second reactor is up to 0,0016%. The ethylbenzene conversion of this reaction is almost 100%. As is said before, having a 100% conversion does not mean that is good if the selectivity is almost 0.

Finally, the total yield reaches the value of 0,0016%.

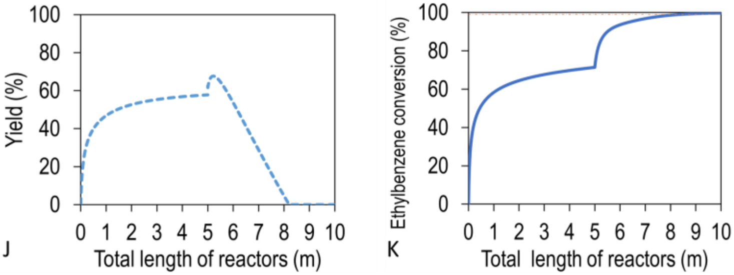


Figure 11: Simulation Nº7. 943.15 K, 0.501 Bar, 1/6 mol Eb/H_2O, 5/1.5 L/D
J) Yield of reactors; K) Total conversion of ethylbenzene

In table 10 the values of each simulation done with a different temperature can be seen to compare the results:

		Reactor 1			Reactor 2		
Nº	Parameter (Temperature)	Styrene selectivity	Ethylbenzene conversion	Total yield	Styrene selectivity	Ethylbenzene conversion	Total yield
3	893,15 K	95,56%	52,57%	50,23%	64,86%	82,65%	53,61%
6	793,15 K	99,49%	15,77%	15,69%	97,81%	26,20%	25,62%
7	943,15 K	89,95%	71,39%	57,79%	0,00%	99,75%	0,00%

Table 11: Results comparison of simulations 3,6,7

As it can be seen in the above table, increasing the temperature at first reactor will increase considerably the production of styrene and all its by-products. Even so, the selectivity of styrene keeps having a high value. However, at simulation number 3, even the temperature is 50 K lower, the yield of the first reactor is almost the same as the yield of simulation number 7. Respect simulation number 6, low temperature gives so bad results.

At second reactor high temperature affects negatively to the styrene production reducing its selectivity almost to 0 and so, reducing its yield to 0.0016%. Running the reactions at medium temperature range (893,15K) will give a styrene selectivity of 64,86% and ethylbenzene conversion of 82%. Even the conversion is high, selectivity of styrene is low and so a high number of by-products will be generated. These values will give a total yield of 53.61%. At low temperature range the selectivity will be higher but the conversion quite low and so a final yield with a value of 25,62%.

Respect physical parameters, temperature range affects considerably to them. In the below table the last value of each parameter in each reactor will be shown to see their differences:

	Reactor 1			Reactor 2		
Parameter	893,15 K	793,15 K	943,15 K	893,15 K	793,15 K	943,15 K
Diffusion coefficient of the mix [m^2/h]	0,071	0,07	0,073	0,076	0,07	0,1
Specific heat of the mix [kJ/mol·K]	0,074	0,077	0,072	0,069	0,076	0,056
Thermal conductivity of the mix [kJ/m·h·K]	1,51	1,27	1,64	1,73	1,33	1,93
Pressure [Bar]	0,488	0,44	0,517	0,536	0,451	0,6

Table 12: Physical parameters at different temperature range

As it can be seen, at first reactor comparing parameters between simulations 3 and 6, their values do not change so much. It happens because at simulation number 3 the final temperature range is up to 820 K value that is closer to the temperature of the simulation number 6. So that, the diffusion coefficient is almost the same. Specific heat follows the same pattern as well. Seeing that values you can say that in both parameters the temperature affects much more than pressure or composition. However, the value of thermal conductivity is quite different. So that, in that case not only the temperature is important.

Composition also affects the value of this parameter. Comparing the values of simulations 3 and 7, as the final temperature of both simulations are around values of 840-820 K diffusion coefficient and specific heat do not change so much. However, thermal conductivity is affected by composition and temperature and as the yield of simulation 7 is higher, the composition is more different and then, the value of the thermal conductivity reaches a higher value. About pressure, all 3 values do not change so much. Therefore, you can say that pressure do not affect the parameters as much as temperature does.

At second reactor values of simulation number 6 are almost the same as the reactor number 1. The big differences appear between simulations 3 and 7. All values are increased due in both simulations appear a temperature increase. However, the increasing of simulation 7 is higher than simulation 3 and therefore, the value of thermal conductivity and diffusion of simulation 7 is higher. Finally, as the conversion of simulation 7 is almost 100%, all by-products generated makes the value of specific heat lower than the simulation 3.

4.2.3. Effect of pressure

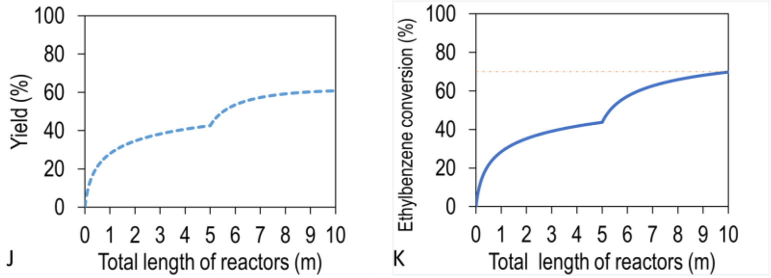


Figure 12: Simulation Nº8. 893.15 K, 1.501 Bar, 1/6 mol Eb/H_2O, 5/1.5 L/D
J) Yield of reactors; K) Total conversion of ethylbenzene

In this case the temperature range is not the problem. The problem is the pressure. As it can be seen in the figure 26 at the appendix 5, increased pressure increases the flow rate and consequently the volumetric rate. The starting pressure has the value of 1.5 Bar but when the fluid interacts with the catalyst bed, appear a pressure drop and consequently a flow rate increase.

At the above simulations the flow rate was around of 12 m/s while in this one the flow rate is up to 36 m/s. As is said before, the pattern of all parameters is decrease due all parameters are very influenced by the temperature. However, the composition of the mix affects quite more at the physical parameters than the temperature. Therefore, there is little difference between the physical parameters of the above simulations.

The final concentration of ethylbenzene is 0.29 mol/m^3. As it can be seen, increasing the pressure makes a decrease on the conversion of ethylbenzene because the main reaction produces 2 mol of products for every mol of reactant and, by applying the Le Châtelier law, low pressure favours those reactions which the mol produced/reacted fraction is higher than 1.

The selectivity of styrene of the first reaction is considerably higher than the second one due the difference of concentrations and the yield of the first reactor have a value of 40%. The conversion of ethylbenzene is around the 70% of maximum.

4.2.4. Effect of concentration

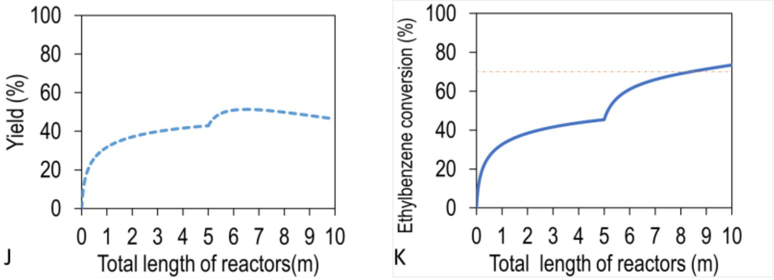


Figure 13: Simulation Nº9. 893.15 K, 0.501 Bar, 1/6 mol Eb/H_2O, 5/1.5 L/D
J) Yield of reactors; K) Total conversion of ethylbenzene

In this simulation the composition has been changed. That means that all physical parameters changed as well. As can be seen on the figure 27 of the appendix 5, respect the other simulations, all physical parameters are completely different. The trend of all parameters remains the same but with the difference of the range value.

Respect the first reactor, ethylbenzene conversion reaches the value of 45,38% and the styrene selectivity 94,47% With these values, the resultant yield is 42,88%. At the second reactor the total ethylbenzene conversion is 73,46% but its styrene selectivity decreases to 63,22% provoking then a descend of the total yield which reaches the value of 46,44%.

With these results It can be determined that increasing the concentration of ethylbenzene keeping the same mole relation between steam and ethylbenzene do not modifies considerably the values of the parameters.

4.2.5. Effect of composition

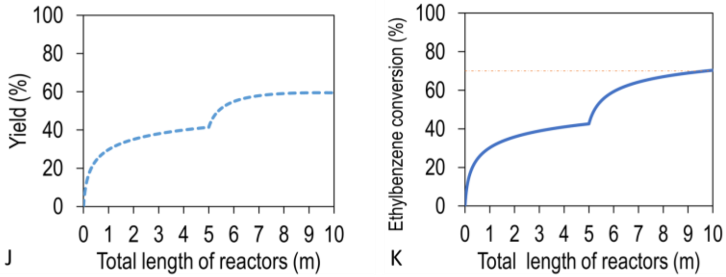


Figure 14: Simulation Nº10. 893.15 K, 0.501 Bar, 1/3 mol Eb/H2O, 5/1.5 L/D
J) Yield of reactors; K) Total conversion of ethylbenzene

In this simulation the relation of ethylbenzene and steam has been reduced provoking then a less heat input to the reaction. Graphics of figure 28 of the appendix 5 shows that in the first reactor all physical parameters follow, as the other simulations, the same tendency. The styrene selectivity reaches the value of 97,31 % at the end of the reactor and the conversion of ethylbenzene is around 42,59%. The yield of the first reactor is 41,45%.

Respect the second reactor, there is a pressure increment due all reactor. The selectivity of it is worse than the selectivity of the first reactor with a value of 84,49%. The conversion, in this case, reaches the value of 48,41%. Finally, the yield of the reactor is pretty alike the first one with a value of 40,90%.

In this final simulation, number 11, the conditions are the same as the above one with only the difference of the mol relation. In this case, mol relation between ethylbenzene and steam is 1/10. As it can be seen in figure 29, at the first reactor, all parameters follow the same tendency. The styrene selectivity is 92,37% at the end of the reactor and the conversion of ethylbenzene reaches the value of 62,56%. The yield of this reactor is 57,79% making that value the highest of all simulations.

The second reaction does not follow the same way as the first one. As the steam ratio is higher there is more heat input to the reactor and then there is a high temperature and pressure increase provoking then a decrease of the styrene selectivity and the total yield. Before talking about the yield, there is a decrease of the flow rate and increase of the diffusion coefficient due the temperature increasing. Now, the value of styrene selectivity is 27,97% and the total conversion of ethylbenzene is the 82,36%. The total yield of the second reactor is 23,03% making then one of the worsts results.

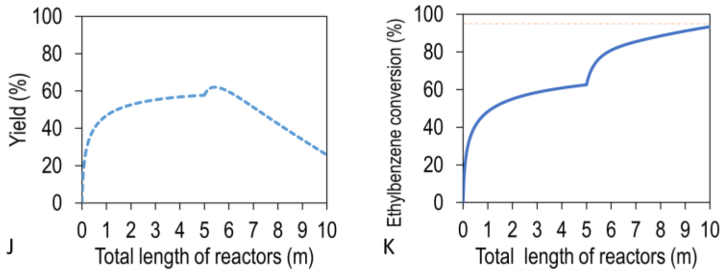


Figure 15: Simulation N°11. 893.15 K, 0.501 Bar, 1/10 mol Eb/H_2O, 5/1.5 L/D
J) Yield of reactors; K) Total conversion of ethylbenzene

In the below table It can be seen all values of different simulations done with a modified initial composition:

		Reactor 1			Reactor 2		
Nº	Parameter Mol ratio Eb/H_2O	Styrene selectivity	Ethylbenzene conversion	Total yield	Styrene selectivity	Ethylbenzene conversion	Total yield
3	1/6	95,56%	52,57%	50,23%	64,86%	82,65%	53,61%
10	1/3	97,31%	42,59%	41,45%	84,49%	70,38%	59,47%
11	1/10	92,37%	62,56%	57,79%	27,97%	93,39%	26,12%

Table 13: Results comparison of simulations 3,10,11

As can be seen, respect the first reactor of each simulation, the best styrene selectivity appears at simulation 10 but due its conversion is low, the total yield became the worst with a value of 41,45%. On the other hand, simulation 11 has the worst selectivity but as it has the best conversion the total yield reaches the highest value with 57,79%. This difference is made by the provided heat from steam. More steam means more heat and consequently more conversion. In addition, as the simulation number 3 has de medium mol ratio respect other two, its yield value has a higher value than simulation 10 but lower value respect simulation 11.

About reactor number 2, provide the reactions with too much heat is self-defeating. As it can be seen, simulation number 11 has the lower values in styrene selectivity and yield. However, ethylbenzene conversion is the highest because secondary associated reactions are favoured with high temperature. On the other hand, as the concentration of ethylbenzene is low in this second reactor, provide the system with low heat will contribute more efficiently avoiding favouring secondary reactions. So that, the simulation number 10 has the highest yield and the highest styrene selectivity.

4.3. BETTER CONDITIONS OF THE PROCESS VARIABLES

To determine which is the best modelling the yield of all simulations are shown in the figure 16.

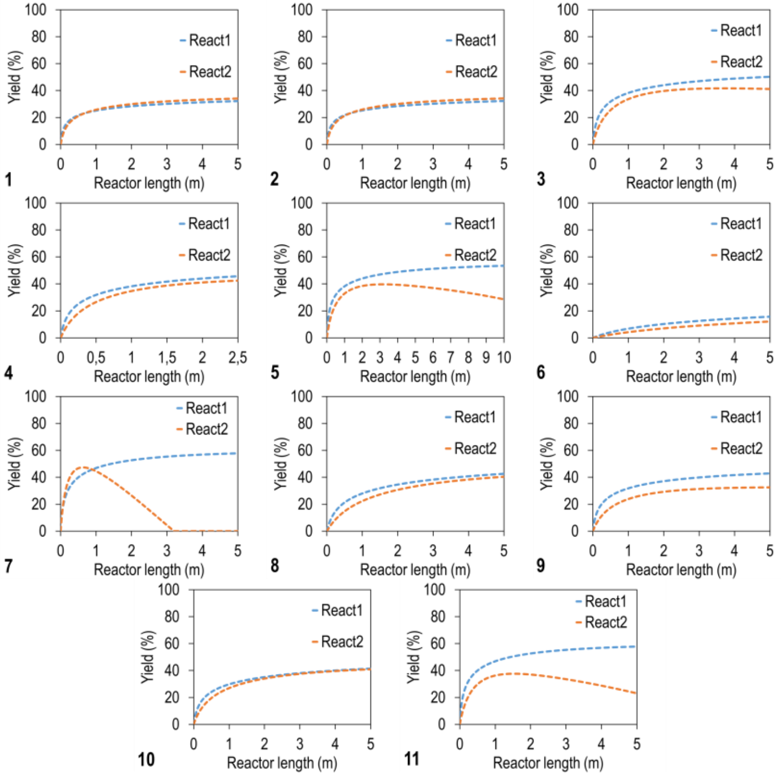


Figure 16: ***1)*** *Ideal model simulation;* ***2)*** *Dispersion model with constant physical parameters;* ***3)*** *Dispersion model with non-constant physical parameters.* ***4)*** *Dispersion model with non-constant physical parameters and length reduced;* ***5)*** *Dispersion model with non-constant physical parameters and length increased;* ***6)*** *Dispersion model with non-constant physical parameters and temperature decreased;* ***7)*** *Dispersion model with non-constant physical parameters and temperature increased;* ***8)*** *Dispersion model with non-constant physical parameters and pressure increased;* ***9)*** *Dispersion model with non-constant physical parameters and concentration increased;* ***10*** *Dispersion model with non-constant physical parameters and EB/H2O mol relation reduced;* ***11)*** *Dispersion model with non-constant physical parameters and EB/H2O mol relation increased.*

As It can be seen, in each graphic appears both reactors of the simulations. Respect the first reactor, the best modelling is which have number 11 with a yield value of 57,79 %. However, there is another simulation that have almost the same yield. This simulation is the number 7 where the temperature range has increased. Its yield is 57,78%. Respect the second reactor, the best yield is at the simulation number 4 with a value of 42,44%.

With that results It can't be determined which is the best modelling because even one reactor could be the best, the other one fails. So that, to determine the best modelling is still needed to compare the final concentration of styrene, which is the desired product, of each simulation. In the following figure all final concentrations of styrene can be seen.

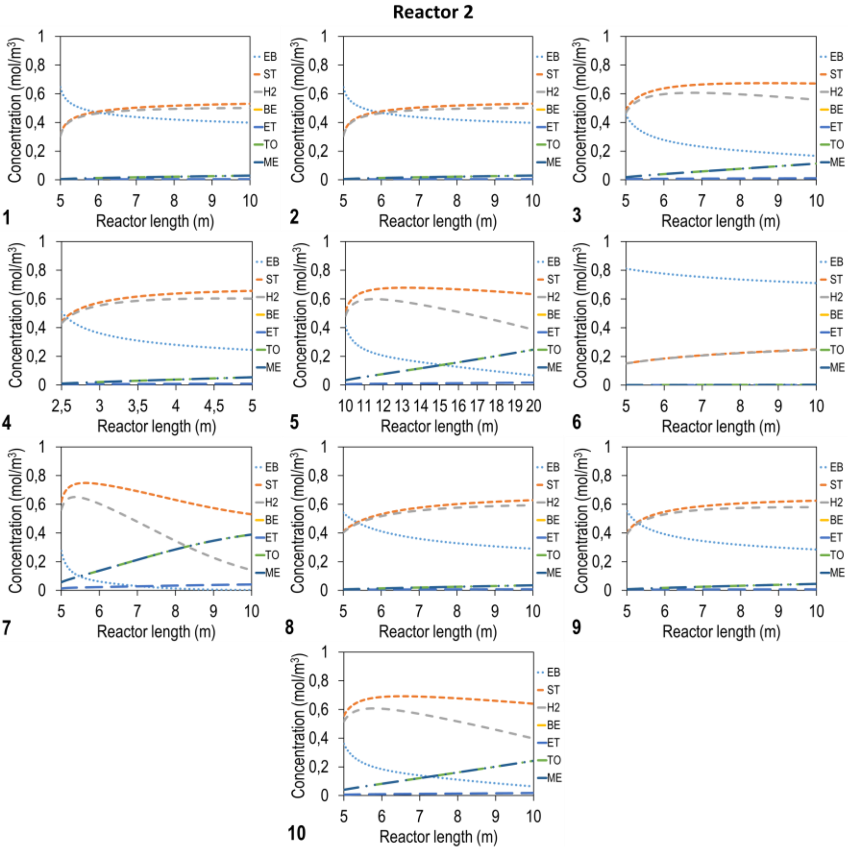


Figure 17: ***1)*** *Ideal model simulation;* ***2)*** *Dispersion model with constant physical parameters;* ***3)*** *Dispersion model with non-constant physical parameters.* ***4)*** *Dispersion model with non-constant physical parameters and length reduced;* ***5)*** *Dispersion model with non-constant physical parameters and length increased;* ***6)*** *Dispersion model with non-constant physical parameters and temperature decreased;* ***7*** *Dispersion model with non-constant physical parameters and temperature increased;* ***8*** *Dispersion model with non-constant physical parameters and pressure increased;* ***9*** *Dispersion model with non-constant physical parameters and EB/H2O mol relation reduced;* ***10)*** *Dispersion model with non-constant physical parameters and EB/H2O mol relation increased.*

As It can be seen above, there are one simulation that has not been shown. This simulation is the number 9 of table 8. It has been decided to not show It due the increasing of ethylbenzene concentration. On the other hand, the highest concentrations at the end of the simulation are the concentrations of the simulations 3 and 4 which its respective values are 0.67 and 0.65 mol/m^3.

At the below graphics, are shown all yields respect each parameter that is wanted to be analysed. Graphic 1 shows how yield varies front temperature. This variation has a maximum that is localized around the value of 893,15 K. Casually, that value is usually used at industrial production of styrene because is the optimum temperature to carry the reaction on.

Graphic 2 shows how yield varies front the length/diameter relation. As it can be seen, at lower value higher is the yield. That result can be related to the secondary associated reactions. If the reactor is shorter, there probably will not be any chance to increase the reaction rates of secondary reactions and so the yield will be increased.

Graphic 3 shows the same relation but this time respect the initial composition. This graphics shows that at higher relation between ethylbenzene and steam, the yield is increased. The simulation that have better results is which has a 1/3 mol ratio. It means that if there is less heat provided to the reactor better will be the results but, if the reaction is an exothermic, how it could be possible? As is said at section 1.2., more heat favours the ethylbenzene dehydrogenation. Therefore, more heat should improve the results. The fact is that if the reactor is too long and is provided with too heat, at the end of the process there will be a yield drop because secondary associated reactions will be much more favoured than the main reaction. So that, at less quantity of heat steam and a shorter reactor the yield is increased.

At graphic 4, yield vs pressure, at less pressure the reaction rate will be better (according to LeChâtelier law) but as it can be seen is the opposite. At higher pressure yield increases its value a little bit. Why it happens? This time Is not about the length. As the pressure is higher, reaction rates are lower and with a length of 5 meters, all reactions are not able to react properly and consequently there is less quantity of reacted styrene reaching then a higher value of the yield.

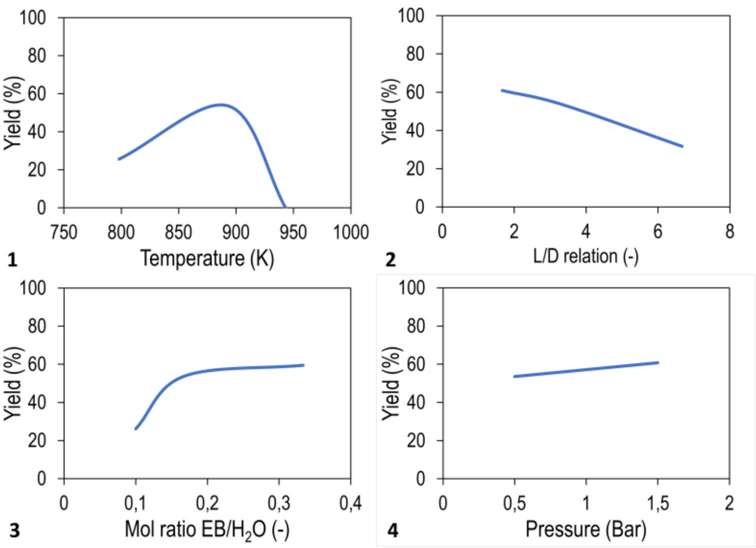


Figure 18: Yield front variables to control.

Finally, that information shows that the best conditions to produce styrene are those of the simulation number 4.

Conditions	
$C_{Eb,o}$ (mol/m^3)	0,963
T_0 (K)	893,15
P_0 (Bar)	0,501
L/D (-)	1,67
Mol relation (-) Eb/H_2O	1/6

Table 14: Best conditions to dehydrogenate ethylbenzene

5. CONCLUSIONS

Ethylbenzene dehydrogenation and its secondary associated reactions make a very sensitive system. So that, even in all physical parameters do not change so much, the little variation is quite important to change completely all system. Consequently, is assumed that running the reactor considering that all parameters do no change is not correct due the big differences between constant and non-constant parameters. In addition, the ideal flow gives similar results respect the non-ideal simulation with constant parameters meaning then than the results are also not acceptable.

Respect the initial conditions, as can be seen above, temperature have a very important role. As all activation energies have a high value, low temperature will not help the reactor. In this case, temperature must stay at range of 900 K otherwise the reaction will never run. However, too high temperature will be bad as well because at that range, secondary associations will increase its rate and then, the yield of all reactor will descend considerably.

Pressure, like temperature, is important to consider. As the reactions generates more quantity of mol than the reacted ones, low pressure will favour the direct reaction. Running the reaction with high pressure will end with a lousy yield because the indirect reaction will be favoured.

The relation of L/D is as important as temperature or pressure. As can be seen in the graphics, the second reactor of the simulation number 3 increases its temperature at half of it due the 4th secondary reaction and this is a problem. However, the second reactor of the simulation number 4 does not have that problem because the length of the reactor is shorter. In addition, yield of the second reactor of simulation 4 is higher than the yield of the simulation 3. Therefore, running the reaction on a first reactor with L/D of 1,67 and EB/H2O mol relation of 1/6 and the second reactor with L/D of 1,67 should improve the results, increase the total yield of the reactors system and increase the styrene production.

To sum up this section, model a reactors system for ethylbenzene dehydrogenation is not easy due its complexity even without considering the radial gradient.

The values obtained at simulations 3-11 can be considered acceptable due the similarity respect the bibliographic values. The other 2 simulations (ideal and non-ideal with constant physical parameters) are considered not correct due their values do not have any similarity with the bibliographic values.

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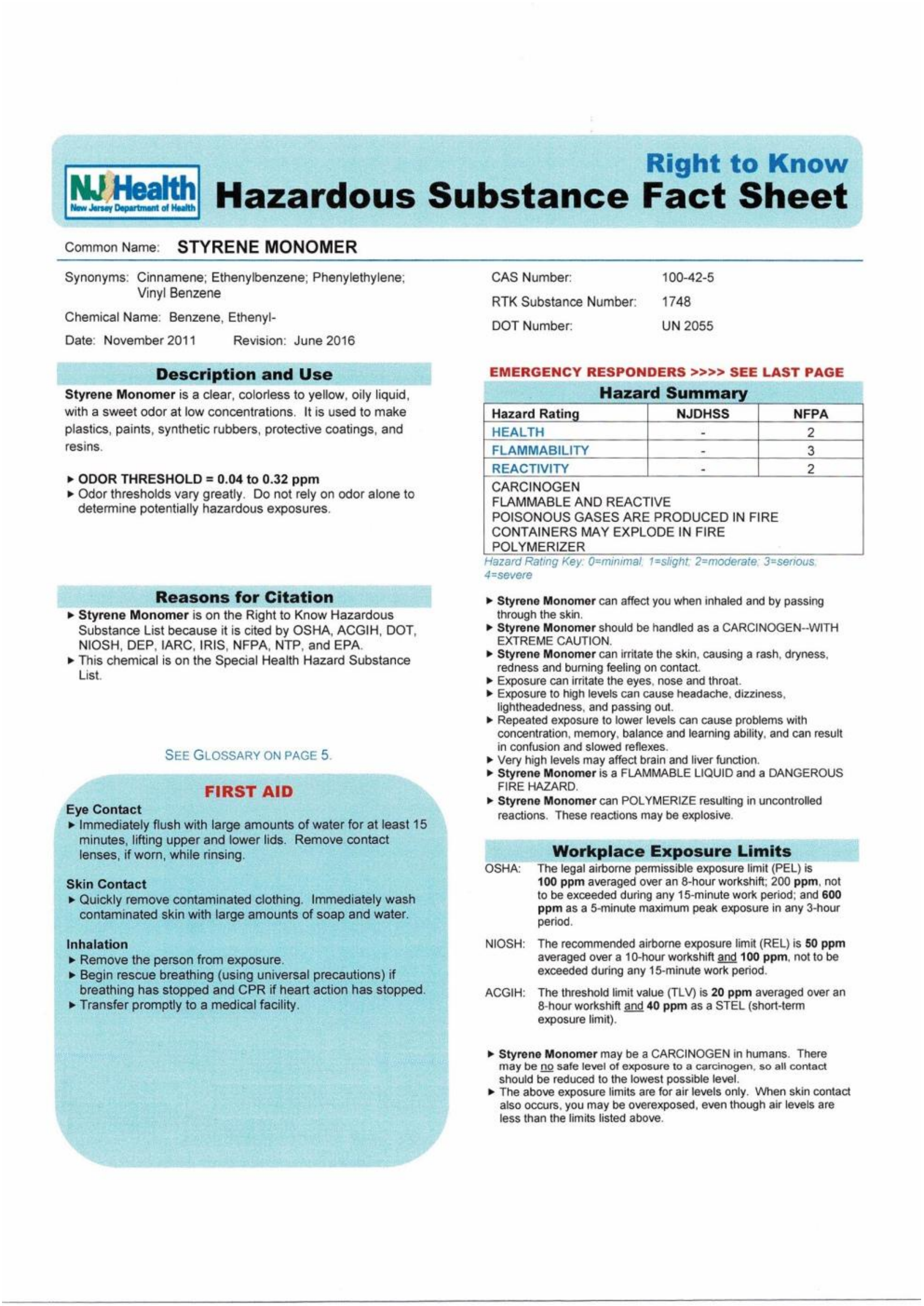
ACRONYMS

A_i	Pre-exponential factor of rate coefficient [kmol/(kg cat·h)]
$\Delta H_{r,i}$	Reaction enthalpy of reaction n° ‘*i*’’ [kJ/mol]
$\Delta S_{a,j}$	Pre-exponential factor of adsorption equilibrium constant [Bar^{-1}]
C_i	Concentration of component ‘*i*’ [mol/m^3]
Cp_m	Specific heat of mix [kJ/(mol·K)]
$C_{p,i}$	Specific heat of the component ‘*i*’ [kJ/(mol·K)]
$D_{A,B}$	Binary diffusion coefficient [cm^2/s]
$D_{A,m}$	Diffusion coefficient of mix [cm^2/s]
$Deff_{m,i}$	Efective diffusion coefficient of mix [cm^2/s]
d'_p	Particle diameter [m]
ρ_m	Density of the mix [kg/m^3]
ρ_m	Density of the component ‘*i*’ [kg/m^3]
ρ_L	Bulk density [kg cat/m^3]
Ea_i	Activation energy of reaction n° ‘*i*’[kJ/mol]
ε	Porosity [-]
G_r	Mass velocity [$mol/(h \cdot m^2)$]
K_j	Adsorption equilibrium constant of component ‘*j*’ [Bar^{-1}]
k_m	Thermal conductivity of the mix [kJ/m·h·K]
k_i	Rate coefficient of reaction n° ‘*i*’ [kmol/(kg cat·h)]
k_j	Thermal conductivity of component ‘*i*’ [kJ/m·h·K]
M_i	Molar weight [kg/kmol]
Ω_v	Lennard-Jones potential parameter [-]
P	Total pressure [Bar]

P_i	Partial pressure [Bar]
Q	Heat flow [kJ]
R	Ideal gas constant [(Bar·m^3)/(mol·K)]
r	Radius [m]
r_i	Intensive rate of reaction nº ‘*i*’ [kmol/(kgcat·h)]
σ_i	Atomic length of component ‘*i*’ [Ǻ]
T	Temperature [K]
$T_{b,i}$	Critical temperature at boiling point of component ‘*i*’ [K]
u	Lineal velocity [m/s]
μ_m	Viscosity of the mix [Pa·s]
μ_i	Viscosity of the component ‘*i*’ [Pa·s]
$\mu_{p,i}$	Dipolar moment of component ‘*i*’ [Debeye,D]
$V_{b,i}$	Molar volume at boiling point of component ‘*i*’ [m^3/mol]
$\nu_{A,i}$	Stochiometric value of component ‘*i*’ [-]
y_i	Molar fraction of component ‘*i*’ [-]
$\sum v$	Atomic diffusion volume [-]

APPENDICES

APPENDIX 1: SAFETY DATA SHEET



NJ Health
New Jersey Department of Health

Right to Know
Hazardous Substance Fact Sheet

Common Name: **STYRENE MONOMER**

Synonyms: Cinnamene; Ethenylbenzene; Phenylethylene; Vinyl Benzene

Chemical Name: Benzene, Ethenyl-

Date: November 2011 Revision: June 2016

CAS Number:	100-42-5
RTK Substance Number:	1748
DOT Number:	UN 2055

Description and Use

Styrene Monomer is a clear, colorless to yellow, oily liquid, with a sweet odor at low concentrations. It is used to make plastics, paints, synthetic rubbers, protective coatings, and resins.

- **ODOR THRESHOLD = 0.04 to 0.32 ppm**
- Odor thresholds vary greatly. Do not rely on odor alone to determine potentially hazardous exposures.

Reasons for Citation

- **Styrene Monomer** is on the Right to Know Hazardous Substance List because it is cited by OSHA, ACGIH, DOT, NIOSH, DEP, IARC, IRIS, NFPA, NTP, and EPA.
- This chemical is on the Special Health Hazard Substance List.

SEE GLOSSARY ON PAGE 5.

FIRST AID

Eye Contact

- Immediately flush with large amounts of water for at least 15 minutes, lifting upper and lower lids. Remove contact lenses, if worn, while rinsing.

Skin Contact

- Quickly remove contaminated clothing. Immediately wash contaminated skin with large amounts of soap and water.

Inhalation

- Remove the person from exposure.
- Begin rescue breathing (using universal precautions) if breathing has stopped and CPR if heart action has stopped.
- Transfer promptly to a medical facility.

EMERGENCY RESPONDERS >>>> SEE LAST PAGE

Hazard Summary

Hazard Rating	NJDHSS	NFPA
HEALTH	-	2
FLAMMABILITY	-	3
REACTIVITY	-	2

CARCINOGEN
FLAMMABLE AND REACTIVE
POISONOUS GASES ARE PRODUCED IN FIRE
CONTAINERS MAY EXPLODE IN FIRE
POLYMERIZER

Hazard Rating Key: 0=minimal; 1=slight; 2=moderate; 3=serious; 4=severe

- **Styrene Monomer** can affect you when inhaled and by passing through the skin.
- **Styrene Monomer** should be handled as a CARCINOGEN--WITH EXTREME CAUTION.
- **Styrene Monomer** can irritate the skin, causing a rash, dryness, redness and burning feeling on contact.
- Exposure can irritate the eyes, nose and throat.
- Exposure to high levels can cause headache, dizziness, lightheadedness, and passing out.
- Repeated exposure to lower levels can cause problems with concentration, memory, balance and learning ability, and can result in confusion and slowed reflexes.
- Very high levels may affect brain and liver function.
- **Styrene Monomer** is a FLAMMABLE LIQUID and a DANGEROUS FIRE HAZARD.
- **Styrene Monomer** can POLYMERIZE resulting in uncontrolled reactions. These reactions may be explosive.

Workplace Exposure Limits

OSHA:	The legal airborne permissible exposure limit (PEL) is **100 ppm** averaged over an 8-hour workshift; 200 **ppm**, not to be exceeded during any 15-minute work period; and **600 ppm** as a 5-minute maximum peak exposure in any 3-hour period.
NIOSH:	The recommended airborne exposure limit (REL) is **50 ppm** averaged over a 10-hour workshift and **100 ppm**, not to be exceeded during any 15-minute work period.
ACGIH:	The threshold limit value (TLV) is **20 ppm** averaged over an 8-hour workshift and **40 ppm** as a STEL (short-term exposure limit).

- **Styrene Monomer** may be a CARCINOGEN in humans. There may be no safe level of exposure to a carcinogen, so all contact should be reduced to the lowest possible level.
- The above exposure limits are for air levels only. When skin contact also occurs, you may be overexposed, even though air levels are less than the limits listed above.

Determining Your Exposure

- Read the product manufacturer's Material Safety Data Sheet (MSDS) and the label to determine product ingredients and important safety and health information about the product mixture.
- For each individual hazardous ingredient, read the New Jersey Department of Health and Senior Services Hazardous Substance Fact Sheet, available on the RTK Program website (http://www.state.nj.us/health/workplacehealthandsafety/right-to-know/) or in your facility's RTK Central File or Hazard Communication Standard file.
- You have a right to this information under the New Jersey Worker and Community Right to Know Act and the Public Employees Occupational Safety and Health (PEOSH) Act if you are a public worker in New Jersey, and under the federal Occupational Safety and Health Act (OSHA) if you are a private worker.
- The New Jersey Right to Know Act requires most employers to label chemicals in the workplace and requires public employers to provide their employees with information concerning chemical hazards and controls. The federal OSHA Hazard Communication Standard (29 CFR 1910.1200) and the PEOSH Hazard Communication Standard (N.J.A.C. 12:100-7) require employers to provide similar information and training to their employees.

This Fact Sheet is a summary of available information regarding the health hazards that may result from exposure. Duration of exposure, concentration of the substance and other factors will affect your susceptibility to any of the potential effects described below.

Health Hazard Information

Acute Health Effects

The following acute (short-term) health effects may occur immediately or shortly after exposure to **Styrene Monomer**:

- **Styrene Monomer** can irritate the skin, causing a rash, dryness, redness and burning feeling on contact.
- Exposure can irritate the eyes, nose and throat.
- Exposure can cause headache, dizziness, lightheadedness, and passing out.

Chronic Health Effects

The following chronic (long-term) health effects can occur at some time after exposure to **Styrene Monomer** and can last for months or years:

Cancer Hazard

- **Styrene Monomer** may be a CARCINOGEN in humans since it has been shown to cause lung cancer in animals.
- Many scientists believe there is no safe level of exposure to a carcinogen.

Reproductive Hazard

- There is no evidence that **Styrene Monomer** affects reproduction. This is based on test results presently available to the NJDHSS from published studies.

Other Effects

- Repeated exposure to lower levels can cause problems with concentration, memory, balance and learning ability, and can result in confusion and slowed reflexes.
- Very high levels may affect brain and liver function.

Medical

Medical Testing

For frequent or potentially high exposure (half of the TLV or greater), the following are recommended before beginning work and at regular times after that:

- Exam of the nervous system
- Liver function tests

If symptoms develop or overexposure is suspected, the following is recommended:

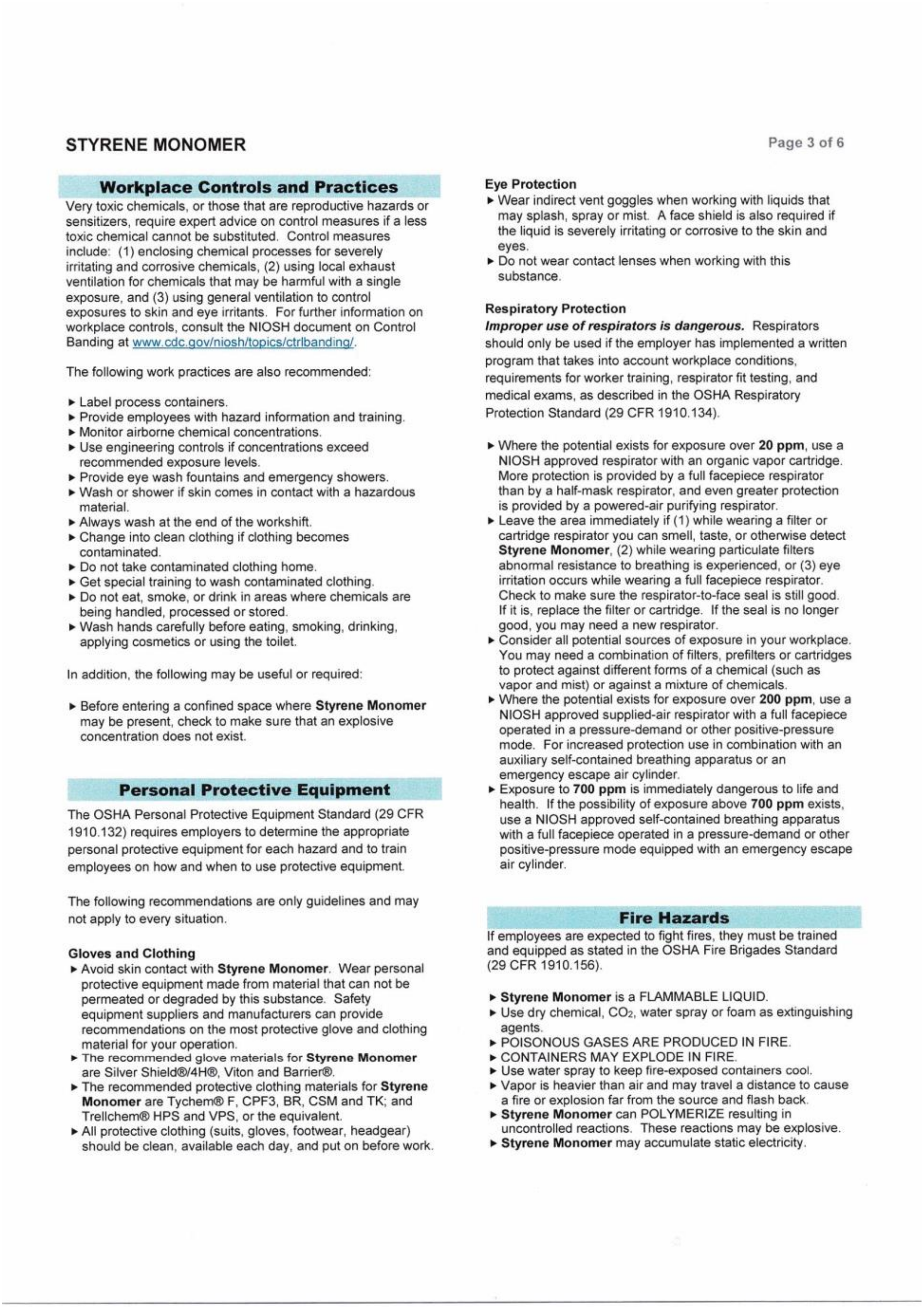
- EEG (brain wave study)

Any evaluation should include a careful history of past and present symptoms with an exam. Medical tests that look for damage already done are not a substitute for controlling exposure.

You have a legal right to request copies of your medical testing under the OSHA Access to Employee Exposure and Medical Records Standard (29 CFR 1910.1020).

Mixed Exposures

- More than light alcohol consumption can cause liver damage. Drinking alcohol may increase the liver damage caused by **Styrene Monomer**.



STYRENE MONOMER

Workplace Controls and Practices

Very toxic chemicals, or those that are reproductive hazards or sensitizers, require expert advice on control measures if a less toxic chemical cannot be substituted. Control measures include: (1) enclosing chemical processes for severely irritating and corrosive chemicals, (2) using local exhaust ventilation for chemicals that may be harmful with a single exposure, and (3) using general ventilation to control exposures to skin and eye irritants. For further information on workplace controls, consult the NIOSH document on Control Banding at www.cdc.gov/niosh/topics/ctrlbanding/.

The following work practices are also recommended:

- Label process containers.
- Provide employees with hazard information and training.
- Monitor airborne chemical concentrations.
- Use engineering controls if concentrations exceed recommended exposure levels.
- Provide eye wash fountains and emergency showers.
- Wash or shower if skin comes in contact with a hazardous material.
- Always wash at the end of the workshift.
- Change into clean clothing if clothing becomes contaminated.
- Do not take contaminated clothing home.
- Get special training to wash contaminated clothing.
- Do not eat, smoke, or drink in areas where chemicals are being handled, processed or stored.
- Wash hands carefully before eating, smoking, drinking, applying cosmetics or using the toilet.

In addition, the following may be useful or required:

- Before entering a confined space where **Styrene Monomer** may be present, check to make sure that an explosive concentration does not exist.

Personal Protective Equipment

The OSHA Personal Protective Equipment Standard (29 CFR 1910.132) requires employers to determine the appropriate personal protective equipment for each hazard and to train employees on how and when to use protective equipment.

The following recommendations are only guidelines and may not apply to every situation.

Gloves and Clothing

- Avoid skin contact with **Styrene Monomer**. Wear personal protective equipment made from material that can not be permeated or degraded by this substance. Safety equipment suppliers and manufacturers can provide recommendations on the most protective glove and clothing material for your operation.
- The recommended glove materials for **Styrene Monomer** are Silver Shield®/4H®, Viton and Barrier®.
- The recommended protective clothing materials for **Styrene Monomer** are Tychem® F, CPF3, BR, CSM and TK; and Trellchem® HPS and VPS, or the equivalent.
- All protective clothing (suits, gloves, footwear, headgear) should be clean, available each day, and put on before work.

Eye Protection

- Wear indirect vent goggles when working with liquids that may splash, spray or mist. A face shield is also required if the liquid is severely irritating or corrosive to the skin and eyes.
- Do not wear contact lenses when working with this substance.

Respiratory Protection

Improper use of respirators is dangerous. Respirators should only be used if the employer has implemented a written program that takes into account workplace conditions, requirements for worker training, respirator fit testing, and medical exams, as described in the OSHA Respiratory Protection Standard (29 CFR 1910.134).

- Where the potential exists for exposure over **20 ppm**, use a NIOSH approved respirator with an organic vapor cartridge. More protection is provided by a full facepiece respirator than by a half-mask respirator, and even greater protection is provided by a powered-air purifying respirator.
- Leave the area immediately if (1) while wearing a filter or cartridge respirator you can smell, taste, or otherwise detect **Styrene Monomer**, (2) while wearing particulate filters abnormal resistance to breathing is experienced, or (3) eye irritation occurs while wearing a full facepiece respirator. Check to make sure the respirator-to-face seal is still good. If it is, replace the filter or cartridge. If the seal is no longer good, you may need a new respirator.
- Consider all potential sources of exposure in your workplace. You may need a combination of filters, prefilters or cartridges to protect against different forms of a chemical (such as vapor and mist) or against a mixture of chemicals.
- Where the potential exists for exposure over **200 ppm**, use a NIOSH approved supplied-air respirator with a full facepiece operated in a pressure-demand or other positive-pressure mode. For increased protection use in combination with an auxiliary self-contained breathing apparatus or an emergency escape air cylinder.
- Exposure to **700 ppm** is immediately dangerous to life and health. If the possibility of exposure above **700 ppm** exists, use a NIOSH approved self-contained breathing apparatus with a full facepiece operated in a pressure-demand or other positive-pressure mode equipped with an emergency escape air cylinder.

Fire Hazards

If employees are expected to fight fires, they must be trained and equipped as stated in the OSHA Fire Brigades Standard (29 CFR 1910.156).

- **Styrene Monomer** is a FLAMMABLE LIQUID.
- Use dry chemical, CO_2, water spray or foam as extinguishing agents.
- POISONOUS GASES ARE PRODUCED IN FIRE.
- CONTAINERS MAY EXPLODE IN FIRE.
- Use water spray to keep fire-exposed containers cool.
- Vapor is heavier than air and may travel a distance to cause a fire or explosion far from the source and flash back.
- **Styrene Monomer** can POLYMERIZE resulting in uncontrolled reactions. These reactions may be explosive.
- **Styrene Monomer** may accumulate static electricity.

Spills and Emergencies

If employees are required to clean-up spills, they must be properly trained and equipped. The OSHA Hazardous Waste Operations and Emergency Response Standard (29 CFR 1910.120) may apply.

If **Styrene Monomer** is spilled or leaked, take the following steps:

- Evacuate personnel and secure and control entrance to the area.
- Eliminate all ignition sources.
- Absorb liquids in vermiculite, dry sand, earth, or a similar material and place into sealed containers for disposal.
- Ventilate area of spill or leak.
- Keep **Styrene Monomer** out of confined spaces, such as sewers, because of the possibility of an explosion.
- DO NOT wash into sewer.
- It may be necessary to contain and dispose of **Styrene Monomer** as a HAZARDOUS WASTE. Contact your state Department of Environmental Protection (DEP) or your regional office of the federal Environmental Protection Agency (EPA) for specific recommendations.

Handling and Storage

Prior to working with **Styrene Monomer** you should be trained on its proper handling and storage.

- *Unstabilized* **Styrene Monomer** can POLYMERIZE VIOLENTLY on exposure to HEAT; LIGHT; OXIDIZING AGENTS (such as PERCHLORATES, PERMANGANATES, CHLORATES, NITRATES, CHLORINE, BROMINE and FLUORINE); OXYGEN; and PEROXIDES (such as *Dibenzoyl Peroxide*) or when CONTAMINATED.
- **Styrene Monomer** can form unstable *Peroxides* in AIR that may explode spontaneously.
- **Styrene Monomer** reacts violently with STRONG ACIDS (such as HYDROCHLORIC, SULFURIC, NITRIC and OLEUM) and METAL SALTS (such as IRON CHLORIDE and ALUMINUM CHLORIDE).
- **Styrene Monomer** attacks RUBBER, COPPER and COPPER ALLOYS.
- Store in tightly closed containers in a cool, well-ventilated area away from HEAT SOURCES and protect from SUNLIGHT and CONTAMINATION.
- Store **Styrene Monomer** with an inhibitor such as *p-tert-Butyl Catechol* and *Hydroquinone*.
- Sources of ignition, such as smoking and open flames, are prohibited where **Styrene Monomer** is used, handled, or stored.
- Metal containers involving the transfer of **Styrene Monomer** should be grounded and bonded.
- Use explosion-proof electrical equipment and fittings wherever **Styrene Monomer** is used, handled, manufactured, or stored.
- Use only non-sparking tools and equipment, especially when opening and closing containers of **Styrene Monomer**.
- **Styrene Monomer** may accumulate static electricity.

Occupational Health Information Resources

The New Jersey Department of Health and Senior Services, Occupational Health Service, offers multiple services in occupational health. These services include providing informational resources, educational materials, public presentations, and industrial hygiene and medical investigations and evaluations.

The Right to Know Hazardous Substance Fact Sheets are not intended to be copied and sold for commercial purposes.

STYRENE MONOMER

Page 5 of 6

GLOSSARY

ACGIH is the American Conference of Governmental Industrial Hygienists. They publish guidelines called Threshold Limit Values (TLVs) for exposure to workplace chemicals.

Acute Exposure Guideline Levels (AEGLs) are established by the EPA. They describe the risk to humans resulting from once-in-a lifetime, or rare, exposure to airborne chemicals.

Boiling point is the temperature at which a substance can change its physical state from a liquid to a gas.

A **carcinogen** is a substance that causes cancer.

The **CAS number** is unique, identifying number, assigned by the Chemical Abstracts Service, to a specific chemical.

CFR is the Code of Federal Regulations, which are the regulations of the United States government.

A **combustible** substance is a solid, liquid or gas that will burn.

A **corrosive** substance is a gas, liquid or solid that causes destruction of human skin or severe corrosion of containers.

The **critical temperature** is the temperature above which a gas cannot be liquefied, regardless of the pressure applied.

DEP is the New Jersey Department of Environmental Protection.

DOT is the Department of Transportation, the federal agency that regulates the transportation of chemicals.

EPA is the Environmental Protection Agency, the federal agency responsible for regulating environmental hazards.

ERG is the Emergency Response Guidebook. It is a guide for emergency responders for transportation emergencies involving hazardous substances.

Emergency Response Planning Guideline (ERPG) values provide estimates of concentration ranges where one reasonably might anticipate observing adverse effects.

A **fetus** is an unborn human or animal.

A **flammable** substance is a solid, liquid, vapor or gas that will ignite easily and burn rapidly.

The **flash point** is the temperature at which a liquid or solid gives off vapor that can form a flammable mixture with air.

IARC is the International Agency for Research on Cancer, a scientific group.

Ionization Potential is the amount of energy needed to remove an electron from an atom or molecule. It is measured in electron volts.

IRIS is the Integrated Risk Information System database on human health effects that may result from exposure to various chemicals, maintained by federal EPA.

LEL or **Lower Explosive Limit**, is the lowest concentration of a combustible substance (gas or vapor) in the air capable of continuing an explosion.

mg/m^3 means milligrams of a chemical in a cubic meter of air. It is a measure of concentration (weight/volume).

A **mutagen** is a substance that causes mutations. A **mutation** is a change in the genetic material in a body cell. Mutations can lead to birth defects, miscarriages, or cancer.

NFPA is the National Fire Protection Association. It classifies substances according to their fire and explosion hazard.

NIOSH is the National Institute for Occupational Safety and Health. It tests equipment, evaluates and approves respirators, conducts studies of workplace hazards, and proposes standards to OSHA.

NTP is the National Toxicology Program which tests chemicals and reviews evidence for cancer.

OSHA is the federal Occupational Safety and Health Administration, which adopts and enforces health and safety standards.

PEOSHA is the New Jersey Public Employees Occupational Safety and Health Act, which adopts and enforces health and safety standards in public workplaces.

Permeated is the movement of chemicals through protective materials.

ppm means parts of a substance per million parts of air. It is a measure of concentration by volume in air.

Protective Action Criteria (PAC) are values established by the Department of Energy and are based on AEGLs and ERPGs. They are used for emergency planning of chemical release events.

A **reactive** substance is a solid, liquid or gas that releases energy under certain conditions.

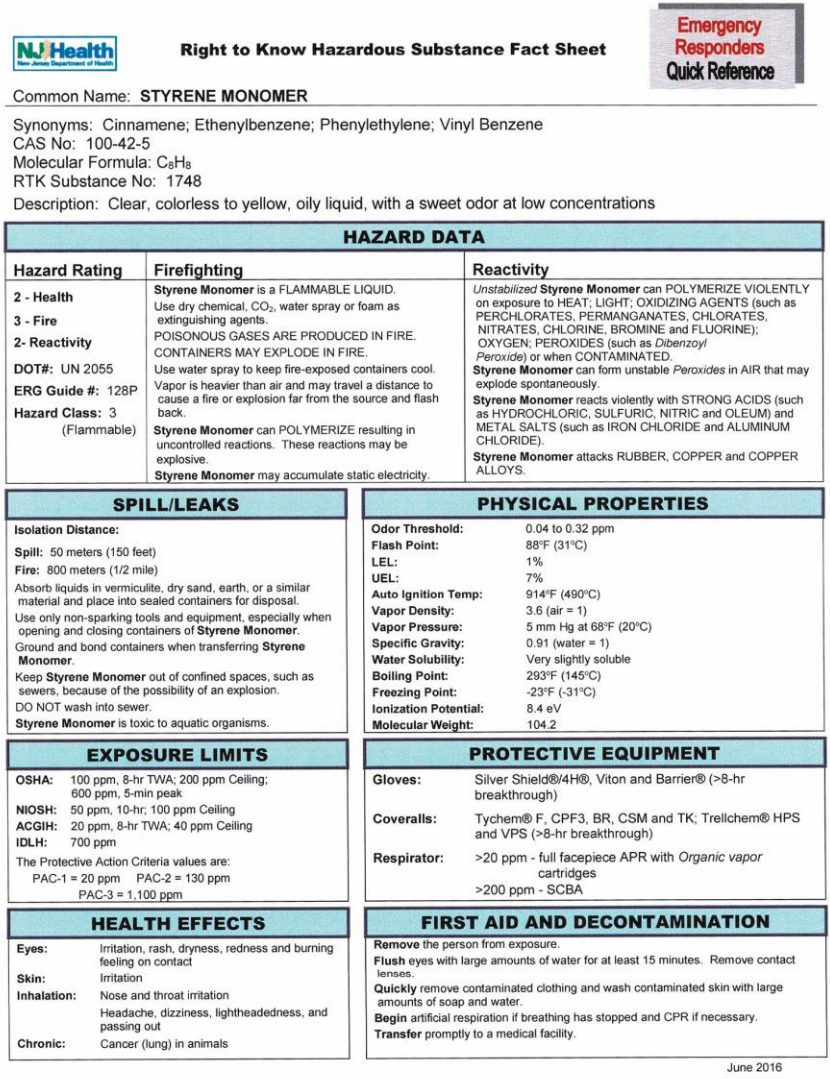
STEL is a Short Term Exposure Limit which is usually a 15-minute exposure that should not be exceeded at any time during a work day.

A **teratogen** is a substance that causes birth defects by damaging the fetus.

UEL or **Upper Explosive Limit** is the highest concentration in air above which there is too much fuel (gas or vapor) to begin a reaction or explosion.

Vapor Density is the ratio of the weight of a given volume of one gas to the weight of another (usually *Air*), at the same temperature and pressure.

The **vapor pressure** is a force exerted by the vapor in equilibrium with the solid or liquid phase of the same substance. The higher the vapor pressure the higher concentration of the substance in air.



NJ Health New Jersey Department of Health

Right to Know Hazardous Substance Fact Sheet

Emergency Responders Quick Reference

Common Name: **STYRENE MONOMER**

Synonyms: Cinnamene; Ethenylbenzene; Phenylethylene; Vinyl Benzene
CAS No: 100-42-5
Molecular Formula: C_8H_8
RTK Substance No: 1748
Description: Clear, colorless to yellow, oily liquid, with a sweet odor at low concentrations

HAZARD DATA

Hazard Rating

2 - Health

3 - Fire

2- Reactivity

DOT#: UN 2055

ERG Guide #: 128P

Hazard Class: 3 (Flammable)

Firefighting

Styrene Monomer is a FLAMMABLE LIQUID.

Use dry chemical, CO_2, water spray or foam as extinguishing agents.

POISONOUS GASES ARE PRODUCED IN FIRE.

CONTAINERS MAY EXPLODE IN FIRE.

Use water spray to keep fire-exposed containers cool.

Vapor is heavier than air and may travel a distance to cause a fire or explosion far from the source and flash back.

Styrene Monomer can POLYMERIZE resulting in uncontrolled reactions. These reactions may be explosive.

Styrene Monomer may accumulate static electricity.

Reactivity

Unstabilized **Styrene Monomer** can POLYMERIZE VIOLENTLY on exposure to HEAT; LIGHT; OXIDIZING AGENTS (such as PERCHLORATES, PERMANGANATES, CHLORATES, NITRATES, CHLORINE, BROMINE and FLUORINE); OXYGEN; PEROXIDES (such as *Dibenzoyl Peroxide*) or when CONTAMINATED.

Styrene Monomer can form unstable *Peroxides* in AIR that may explode spontaneously.

Styrene Monomer reacts violently with STRONG ACIDS (such as HYDROCHLORIC, SULFURIC, NITRIC and OLEUM) and METAL SALTS (such as IRON CHLORIDE and ALUMINUM CHLORIDE).

Styrene Monomer attacks RUBBER, COPPER and COPPER ALLOYS.

SPILL/LEAKS

Isolation Distance:

Spill: 50 meters (150 feet)

Fire: 800 meters (1/2 mile)

Absorb liquids in vermiculite, dry sand, earth, or a similar material and place into sealed containers for disposal.

Use only non-sparking tools and equipment, especially when opening and closing containers of **Styrene Monomer**.

Ground and bond containers when transferring **Styrene Monomer**.

Keep **Styrene Monomer** out of confined spaces, such as sewers, because of the possibility of an explosion.

DO NOT wash into sewer.

Styrene Monomer is toxic to aquatic organisms.

PHYSICAL PROPERTIES

Odor Threshold:	0.04 to 0.32 ppm
Flash Point:	88°F (31°C)
LEL:	1%
UEL:	7%
Auto Ignition Temp:	914°F (490°C)
Vapor Density:	3.6 (air = 1)
Vapor Pressure:	5 mm Hg at 68°F (20°C)
Specific Gravity:	0.91 (water = 1)
Water Solubility:	Very slightly soluble
Boiling Point:	293°F (145°C)
Freezing Point:	-23°F (-31°C)
Ionization Potential:	8.4 eV
Molecular Weight:	104.2

EXPOSURE LIMITS

OSHA:	100 ppm, 8-hr TWA; 200 ppm Ceiling; 600 ppm, 5-min peak
NIOSH:	50 ppm, 10-hr; 100 ppm Ceiling
ACGIH:	20 ppm, 8-hr TWA; 40 ppm Ceiling
IDLH:	700 ppm

The Protective Action Criteria values are:
PAC-1 = 20 ppm PAC-2 = 130 ppm
PAC-3 = 1,100 ppm

PROTECTIVE EQUIPMENT

Gloves:	Silver Shield®/4H®, Viton and Barrier® (>8-hr breakthrough)
Coveralls:	Tychem® F, CPF3, BR, CSM and TK; Trellchem® HPS and VPS (>8-hr breakthrough)
Respirator:	>20 ppm - full facepiece APR with *Organic vapor* cartridges >200 ppm - SCBA

HEALTH EFFECTS

Eyes:	Irritation, rash, dryness, redness and burning feeling on contact
Skin:	Irritation
Inhalation:	Nose and throat irritation Headache, dizziness, lightheadedness, and passing out
Chronic:	Cancer (lung) in animals

FIRST AID AND DECONTAMINATION

Remove the person from exposure.

Flush eyes with large amounts of water for at least 15 minutes. Remove contact lenses.

Quickly remove contaminated clothing and wash contaminated skin with large amounts of soap and water.

Begin artificial respiration if breathing has stopped and CPR if necessary.

Transfer promptly to a medical facility.

June 2016

APPENDIX 2: BALANCE NUMERICAL RESOLUTION.

In this section, it will be explained all the processes to solve the above equations. These processes will be solved by programming code into the “Mathematica” program.

First, a simplified general expression of the Mass and Enthalpy balance will be used to explain the basic solving processes. So, the general expression for ideal plug flow model is:

$$-b \cdot \frac{dy}{dx} + c = 0$$

Reorganizing it, the resultant equation is:

$$dy = \frac{c}{b} \cdot dx$$

Integrating and reorganizing the above expression:

$$y_{i+1} = y_i + \frac{c}{b} \cdot (x_{i+1} - x_i)$$

For the non-ideal plug flow model, the expression is:

$$a \cdot \frac{d^2y}{dx^2} - b \cdot \frac{dy}{dx} + c = 0$$

This equation is not as easy as the above one, so that, to solve it must be done a variable change and a simplification, as it shows below:

$$m' = \frac{d^2y}{dx^2}\ ; m = \frac{dy}{dx};$$

$$m'' - \frac{b}{a} \cdot m' = -\frac{c}{a}$$

The next step is to pose an integral factor $\mu(x)$, where:

$$\mu(x) = e^{\int -\frac{b}{a} \cdot dx}$$

And use it to solve the expression:

$$m = \frac{1}{\mu(x)} \cdot \left(\int \mu(x) \cdot \left(-\frac{c}{a}\right) \cdot dx \right)$$

Using the definition of the exponential derivate, the resultant equation is:

$$m = \frac{1}{e^{-\frac{b}{a}x}} \cdot \left(\frac{e^{-\frac{b}{a}x}}{-\frac{b}{a}} \cdot \left(-\frac{c}{a}\right) + C_1 \right)$$

Reorganizing the above equation, the final expression of "m" is:

$$m = C_1 \cdot e^{\frac{b}{a}x} + \frac{c}{b} = \frac{dy}{dx}$$

Integrating the resultant equation, the function of "y" is encountered:

$$\int \frac{dy}{dx} = \int \left(C_1 \cdot e^{\frac{b}{a}x} + \frac{c}{b} \right)$$

$$\int dy = \int \left(C_1 \cdot e^{\frac{b}{a} \cdot x} + \frac{c}{b} \right) \cdot dx$$

$$y = \frac{a}{b} \cdot C_1 \cdot e^{\frac{b}{a}x} + \frac{c}{b} \cdot x + C_2$$

As it can be seen, there are 2 constants that must be found. To get them, the boundary conditions will be applied. In this case, at the start of the reactor there is an initial concentration of each component. Thus:

$$y(0) = y_0$$

At the end of the reactor is considered that there is not contribution of the axial dispersion or thermal conductivity over the outflow. So:

$$\left.\frac{dy}{dx}\right|_{x=L} = 0$$

With these boundary conditions and the above equations, the values of both constants are:

$$C_1 = -\frac{c}{b} \cdot e^{-\frac{b}{a}x}$$

$$C_2 = y_0 + \frac{a \cdot c}{b^2} \cdot e^{-\frac{b}{a} \cdot L}$$

Substituting both constants at the main equation, the resultant function for every volume differential is:

$$\mathrm{y}(x) = \frac{\mathrm{a} \cdot \mathrm{c}}{\mathrm{b}^2} \cdot \left(\mathrm{e}^{-\frac{\mathrm{b}}{\mathrm{a}} \cdot \mathrm{L}} - \mathrm{e}^{\frac{\mathrm{b}}{\mathrm{a}} \cdot (x - \mathrm{L})}\right) + \frac{\mathrm{c}}{\mathrm{b}} \cdot x + \mathrm{y}_0$$

Appling the above expression into the mass and enthalpy balances, the equations used into the code are respectively:

$$C_A = \frac{\mathrm{Deff}_m \cdot \rho_L \cdot \sum_{i=1}^{R}(\nu_{A,i} \cdot r_{c,i}(T,c)) \cdot (1-\varepsilon)}{\varepsilon \cdot u^2} (e^{-\frac{u}{\mathrm{Deff}_m} \cdot L} - e^{\frac{u}{\mathrm{Deff}_m}(h-L)}) + \frac{\rho_L \cdot \sum_{i=1}^{R}(\nu_{A,i} \cdot r_{c,i}(T,c)) \cdot (1-\varepsilon)}{\varepsilon \cdot u} h + \mathrm{C}_{A,0}$$

$$\mathrm{T} = \frac{\mathrm{k}_m \cdot \rho_L \cdot \sum_{i=1}^{R}(r_{c,i}(T,c) \cdot \Delta H_i)}{(G \cdot \mathrm{Cp}_m)^2} \left(e^{\frac{G \cdot \mathrm{Cp}_m}{\mathrm{k}_m}(h-L)} - e^{-\frac{G \cdot \mathrm{Cp}_m}{\mathrm{k}_m} \cdot L}\right) - \frac{\rho_L \cdot \sum_{i=1}^{R}(r_{c,i}(T,c) \cdot \Delta H_i)}{G \cdot \mathrm{Cp}_m} h + \mathrm{T}_0;$$

The above expressions are only true into current volume differential. So that, “h” is the length of that current differential. Every time a differential is evaluated, the initial conditions will change, and the value of all parameters will change as well.

APPENDIX 3: MIXTURE'S PHYSICAL PARAMETERS CALCULUS.

In the studied system, we have eight components interacting between them. Four of them are in greater quantity so all physical parameters will be more influenced by those four components.

Since in the reactions the number of moles varies, the density of the mix will vary as well. It means that the viscosity, diffusivity, specific heat and thermal diffusion will change along the reactor. Due to this variation, it has been determined some expressions to analyse these parameters in each differential volume.

3.1. DENSITY'S CALCULUS

To calculate the density of the mix is used the ideal equation of gases. The density of each component has been calculated and, by using the molar fraction of the fluid, the density of the mix has been calculated. The equations used can be seen below:

$$\rho_i = \frac{P\ M_i}{R\ 1.013\ T}$$

Where M_i is the molar mass of each component in kg/mol.

$$\rho_m = \sum_{i=1}^{n} \rho_i \cdot y_i$$

Where ρ_i is the density of each component and y_i is the molar fraction of each component.

3.2. DIFFUSIVITY'S CALCULUS

To determine the effective diffusivity of the mix there is calculated 2 different diffusivities. One of them is the mix diffusivity caused by the interaction of each component with each one and the other one is the binary diffusivity of each component with each other. The equation used in the binary diffusivity was carried out by Fuller et al. 1965. This equation uses the atomic diffusion volumes. These atomic parameters were determined by a regression analysis of many experimental data.[1]

$$D_{A,B} = \frac{0{,}00143 \cdot T^{1{,}75}}{P \cdot {M_{A,B}}^{0{,}5}\left[{(\sum v)_A}^{1/3} + {(\sum v)_B}^{1/3}\right]^2}$$

T is the temperature in Kelvin, P is the pressure in Bar, M_A and M_B are the molar weights if respective component where:

$$M_{A,B} = 2 \cdot \left[\frac{1}{M_A} + \frac{1}{M_B}\right]^{-1}$$

And $\sum v$ is the sum of the atomic diffusion volumes of each component. In our case, those components of all system are C, H, O. The units of $D_{A,B}$ are given in cm²/s.

The other diffusivity parameter, $D_{i,m}$ uses the binary diffusivity and the mix composition to determine the diffusivity of the component "i" into the mixture. The equation used was extracted from Stefan-Maxwell equations considering the following reaction: $aA + bB \rightleftharpoons rR + sS$

$$\frac{1}{D_{A,m}} = \frac{1}{1 + \theta_A \cdot y_A} \cdot \left[\begin{matrix} \frac{1}{D_{A,B}} \cdot \left(y_B - \frac{b}{a} \cdot y_A\right) + \frac{1}{D_{A,R}} \cdot \left(y_R + \frac{r}{a} \cdot y_A\right) \\ + \frac{1}{D_{A,S}} \cdot \left(y_S + \frac{s}{a} \cdot y_A\right) \end{matrix}\right]$$

Where $\theta_A = (r + s - a - b)/a$ and y_i is the molar fraction of each component. The units of ${D_{A,m}}^{-1}$ are s/cm² *[Froment, G.F et.al (1990)].*

In our case, the reaction will have only 3 components, but the reactions are carried out with a fourth component that is in excess. For that component, is considered that its molar fraction does not change along the reactor.

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[1] Bruce E.Poling, John M.Prauznitz, John P.O'connell, (2001). *The properties of Gases and Liquids.* 5th Edition. New York. McGraw-hill international editions*. p. 11.1. Documented at 12/11/2018 from University of Barcelona.*

Finally, the axial effective diffusivity equation uses the diffusivity of the mixture and two constants. Those constants depend on the catalyst form and the fluid phase *[F.Cunill et.al (2013)]*:

	Liquids		**Gases**	
	spherical particle	**Irregular particle**	**spherical particle**	**Irregular particle**
C_1 (longitudinal)	2,5	2,5	0,7	4
C_1 (radial)	0,08	0,08	0,12	0,12
C_2 (longitudinal)	8,8	7,7	5,8	5,1
C_2 (radial)	-	-	78±20	-

Table 15: Parameter values of effective diffusivity.

The equation used is the following one:

$$Deff_{m,z} = u \cdot d_p \cdot \left(\frac{0,7}{M} + \frac{C_1}{1 + M \cdot C_2}\right)$$

Where M is a function of the particle Reynolds and the Schmidt number.

$$M = \left(\frac{u \cdot \rho \cdot d_p}{\mu_f}\right) \cdot \left(\frac{\mu_f}{\rho \cdot D_{A,m}}\right)$$

This equation only works if the fraction $L/d_p > 50$ and the particle Reynolds number is higher than 1. In our case, the two constants that have been taken are C_1 and C_2 for a longitudinal reactor with gas phase and irregular catalyst.

3.3. MIXTURE'S VISCOSITY CALCULUS

To calculate the mixture's viscosity for gases, it must consider that the temperature and the composition change along the reactor's length due to the reaction system.

First, the viscosity of each component is calculated by the next equation:

$$\mu_i = 26,69x10^{-6} \cdot \frac{(M_i \cdot T)^{1/2}}{{\sigma_i}^2 \cdot \Omega_v}$$

Where μ_i is the viscosity given in Pa·s, M_i is the molar mass of component "i", σ_i is the characteristic length of each component in Å which is calculated using the next equation:

$$\sigma_i = \left(\frac{1,585 \cdot V_{b,i}}{1 + 1,3 \cdot {\delta_i}^2}\right)^{1/3}$$

Where $V_{b,i}$ is the molar liquid volume at boiling temperature and at 1 atm and δ_i is a dimensionless parameter calculated with the dipole moment of each component:

$$\delta_i = \frac{1940 \cdot {\mu_p}^2}{V_{b,i} \cdot T_{b,i}}$$

The last parameter of single viscosity equation is Ω_v. This is an expression given by Lennar-Jones like Lennard-Jones potentials equation. Its form is the following one:

$$\Omega_v = [A \cdot (T^*)^{-b}] + C \cdot e^{-(D \cdot T^*)} + E \cdot e^{-(F \cdot T^*)}$$

Where the values of parameters A, B, C, D, E, F are in the next table:

A	**B**	**C**	**D**	**E**	**F**
1,16145	0,14874	0,52487	0,7732	2,16178	2,43787

Table 16: Constant values of Lennar-Jhon potentials.

And T* is determined by $\frac{\kappa \cdot T}{\varepsilon_i}$ where $\frac{\kappa}{\varepsilon_i} = 1{,}18 \cdot \left(1 + 1{,}3 \cdot {\delta_i}^2\right) \cdot\ T_{b,i}$

This expression can be only used if 0,3≤T*≤100 *[Bruce E.Poling et.al (2001)]*.

Once the viscosity of all components at the same temperature is calculated there must be calculated the mix's viscosity. To get this is used the Wilke approximation method where it uses the viscosity of each component as the following equation shows:

$$\mu_m = \sum_{i=1}^{N} \frac{\mu_i \cdot y_i}{\sum_{j=1}^{N} y_j \cdot \Phi_{ij}} \ [Pa \cdot s]$$

This parameter, Φ_{ij}, is determined by using the next expression *[Davidson, T. A. 1993]*:

$$\Phi_{ij} = \frac{1}{\sqrt{8}} \cdot \left(1 + \frac{M_i}{M_j}\right)^{-1/2} \cdot \left[1 + \left(\frac{\mu_i}{\mu_j}\right)^{\frac{1}{2}} \cdot \left(\frac{M_j}{M_i}\right)^{\frac{1}{4}}\right]^2$$

If j=i, Φ_{ij} is equal to 1.

3.4. MIXTURE'S HEAT CONDUCTIVITY CALCULUS

The last parameter it must be calculated to develop heat balance is mix heat conductivity. Is considered that there is no radial heat conductivity gradient due it is assumed that only exists temperature gradient in "z" axis. In addition, the reaction takes place on the catalyst surface that it means there will not be any conduction heat transfer through the catalyst so there will not be any temperature gradient in the catalyst particle.

Therefore, once the heat conductivity is determined, we will use it as effective thermal conductivity. To calculate the thermal conductivity value will be used the Wilke approximation method with the Chapman-Enskog model equations and the force constants for the Lennar-Jones Potential model *[Bruce E.Poling et.al (2001)]*.

First, it must be calculated the specific heat at constant volume of each component. Due to the temperature changes through the reactor length, are used Chapman-Enskog equations that relate the specific heat with the temperature. Moreover, for the simplest molecules, there are empirical equations to determine specific heat with less than 2% of error. Starting from the simplest molecules *[Van Wylen, G.J et.al (1994)]*:

***Hydrogen:

$$C_{p,H2} = 56{,}505 - 702{,}74 \cdot \beta^{-0{,}75} + 1165{,}0 \cdot \beta^{-1} - 560{,}70 \cdot \beta^{-1{,}5}$$

*Water (g)

$$C_{p,H2O} = 143{,}05 - 183{,}54 \cdot \beta^{0{,}25} + 82{,}751 \cdot \beta^{0{,}5} - 3{,}6989 \cdot \beta$$

Where β is the fraction of $\frac{T(K)}{100}$ and the units of specific heat are kJ/kmol·K.
For complex molecules is used another expression as we can see next:

$$** \; C_{p,i} = (5 + N_r) \cdot (0{,}5) \cdot \left(\frac{R_u}{M_i}\right)$$

Where R_u is the ideal gas constant in kJ/kmol·K, M_i is the molar weight and N_r is the number of rotational degrees of freedom. In this case, all molecules are nonlinear so that N_r takes the value of 3.

Once all specific heats are calculated, there must be determined the heat conductivity of each component. In this case, is used the next equation:

$$k_i = 8{,}3127x10^{-2} \cdot \frac{\sqrt{T \cdot M_i}}{{\sigma_i}^2 \cdot \Omega_k} + 1{,}32 \cdot \left(C_{p,i} - \frac{5}{2} \cdot \frac{R_u}{M_i}\right) \cdot \left(2{,}6709x10^{-6} \cdot \frac{\sqrt{M_i \cdot T}}{{\sigma_i}^2 \cdot \Omega_k}\right)$$

Where $\Omega_k = \Omega_v$.

The last step of getting the mix thermal conductivity is approximating it by using the Wilke method:

$$k_m = \sum_{i=1}^{N} \frac{k_i \cdot x_i}{\sum_{j=1}^{N} x_j \cdot \Phi_{ij}}$$

$$\Phi_{ij} = \frac{1}{\sqrt{8}} \cdot \left(1 + \frac{M_i}{M_j}\right)^{-1/2} \cdot \left[1 + \left(\frac{\mu_i}{\mu_j}\right)^{\frac{1}{2}} \cdot \left(\frac{M_j}{M_i}\right)^{\frac{1}{4}}\right]^2$$

Where $x_{j,i}$ is the molar fraction and if j=i, Φ_{ij} is equal to 1 *[Van Wylen,G.J et.al (1994)]*.

APPENDIX 4: SIMULATION CODE

PLUG FLOW MODEL

```
Quit[];
```

Initial Conditions of the fluid.

```
P=0.501;(*Bar*) u=43200;(*m/h*)
x0=0.963;x1=0;x2=0;x3=0;x4=0;x5=0;x6=0;x7=5.777; (*mol/m^3*)
T1=893.15;
ϵ=0.4312;(*Subscript[m, b]^3/Subscript[m, r]^3*)ρB=1442; (*(kg cat)/m^3*)
dp=0.0055;
nn=50000;
L=5;
h=N[L/nn];
Ceb[0]=x0; Cw[0]=x7; Cst[0]=x1;Ch2[0]=x2;CBe[0]=x3; CEthyl[0]=x4;CTol[0]=x5;CMet[0]=x6;
Ceb[1]=x0; Cw[1]=x7; Cst[1]=x1;Ch2[1]=x2;CBe[1]=x3; CEthyl[1]=x4;CTol[1]=x5;CMet[1]=x6;(*mol/m^3*)
T[0]=893.15;
T[1]=893.15;
```

Physical Properties of the fluid.

```
Mmeb=106.17; Mmw=18; Mmst=104.15; Mmh2=2;Mmbe=78.11; Mmet=28.05;
Mmto=92.14;Mmme=16.04; (*g/mol*)
R=0.08206 1.013/1000;
ru=8.314;
M1=Mmeb;M2=Mmw;M3=Mmst;M4=Mmh2;M5=Mmbe;M6=Mmet;M7=Mmto;M8=Mmme;
y1=x0/(x7+x0+x1+x2+x3+x4+x5+x6);
y2=x7/(x7+x0+x1+x2+x3+x4+x5+x6);
y3=x1/(x7+x0+x1+x2+x3+x4+x5+x6);
y4=x2/(x7+x0+x1+x2+x3+x4+x5+x6);
x=0;
Do[x=x+1; ρx= (P Mx/1000)/(R T1),8];
Density=∑_{i=1}^{4} ρi yi;
MM= ∑_{i=1}^{4} Mi yi/1000
G=(u*Density)/MM; (*mol/(m^2·h)*)
Cp1=(8) (1/2) ((8.314/1000) /(M1/1000));
Cp2=(143.05-183.54 (T1/100)^0.25+82.751 (T1/100)^0.5-3.6989 (T1/100)^1)/1000;
Cp3=(8)*(1/2) ((8.314/1000) /(M3/1000) );
Cp4=(56.505-702.24 (T1/100)^-0.75+1165.0 (T1/100)^-1-560.70 (T1/100)^-1.5)/1000;
Cpm = Cp1 y1+Cp2 y2+Cp3 y3+Cp4 y4;
Cpm=Cpm;
```

Initial conditions of the reactions and values of the rate constants and adsorption equilibrium constants

$\Delta H*_1$=117.690; $\Delta H*_2$=105.510; $\Delta H*_3$=-54.680; $\Delta H*_4$=-172.370; (*kJ/mol*)
Ea_1=175.38; Ea_2=296.29;Ea_3=474.76; Ea_4=213.78; (*kJ/mol*)
A_1=5.594*10^9; A_2=1.060*10^{15}; A_3=1.246*10^{26}; A_4=8.024*10^{10}; (*kmol/(kg cat·h)*)
ΔH_{EB}=-102.22; ΔH_{ST}=-104.56;ΔH_{H2}=-117.95; (*kJ/mol*)
A_{EB}=1.014*10^{-5}; A_{ST}=2.678*10^{-5};A_{H2}=4.519*10^{-7}; (*1/Bar*)
kc1= A_1Exp[-Ea_1/(ru/1000 T1)];kc2= A_2 Exp[-Ea_2/(ru/1000 T1)];kc3= A_3 Exp[-Ea_3/(ru/1000 T1)];kc4= A_4 Exp[-Ea_4/(ru/1000 T1)];
Keb=A_{EB} Exp[-ΔH_{EB}/(ru/1000 T1)] ; Kst=A_{ST} Exp[-ΔH_{ST}/(ru/1000 T1)];Kh2=A_{H2} Exp[-ΔH_{H2}/(ru/1000 T1)];
Keq=0.027*Exp[0.021 (T1-773)];
Rr1=(kc1 Keb (y_1 P-(y_3 y_4 P^2)/Keq)*1000)/(1+Keb Subscript[y, 1] P+Kst Subscript[y, 3] P+Kh2 Subscript[y, 4] P)^2;
r1=Rr1;
Rr2=(kc2 Keb y_1 P 1000)/(1+Keb Subscript[y, 1] P+Kst Subscript[y, 3] P+Kh2 Subscript[y, 4] P)^2;
r2=Rr2;
Rr3=(kc3 Keb y_1 P Kh2 y_4 P 1000)/(1+Keb Subscript[y, 1] P+Kst Subscript[y, 3] P+Kh2 Subscript[y, 4] P)^2;
r3=Rr3;
Rr4=(kc4 Kst y_3 P Kh2 y_4 P 1000)/(1+Keb Subscript[y, 1] P+Kst Subscript[y, 3] P+Kh2 Subscript[y, 4] P)^2;
r4=Rr4;
r_1[0]=Rr1; r_2[0]=Rr2;r_3[0]=Rr3; r_4[0]=Rr4;
r_1[1]=Rr1; r_2[1]=Rr2;r_3[1]=Rr3; r_4[1]=Rr4;(*mol/(kg cat·h)*)
i=0;

Do[i=i+1;
C_{eb}[i+1]= h/u ρ_B (1-ϵ)/ϵ (-r_1[i]-r_2[i]-r_3[i])+ C_{eb}[i];
C_w[i+1]= C_w[i-1];
C_{st}[i+1]= h/u ρ_B (1-ϵ)/ϵ (r_1[i]-r_4[i])+ C_{st}[i];
C_{h2}[i+1]= h/u ρ_B (1-ϵ)/ϵ (r_1[i]-r_3[i]-2r_4[i])+ C_{h2}[i];
C_{Be}[i+1]= h/u ρ_B (1-ϵ)/ϵ r_2[i]+ C_{Be}[i];
C_{Ethyl}[i+1]=h/u ρ_B (1-ϵ)/ϵ r_2[i]+ C_{Ethyl}[i];
C_{Tol}[i+1]= h/u ρ_B (1-ϵ)/ϵ (r_3[i]+r_4[i])+ C_{Tol}[i];
C_{Met}[i+1]= h/u ρ_B (1-ϵ)/ϵ (r_3[i]+r_4[i])+ C_{Met}[i];
T[i+1]= h/(G Cpm) ρ_B(r_1[i] (-$\Delta H*_1$)+ r_2[i](-$\Delta H*_2$)+ r_3[i] (-$\Delta H*_3$)+r_4[i] (-$\Delta H*_4$))+T[i] ;
y_{eb}[i+1]=C_{eb}[i+1]/(C_{eb}[i+1]+C_{st}[i+1]+C_{h2}[i+1]+C_{Be}[i+1]+C_{Ethyl}[i+1]+C_{Tol}[i+1]+C_{Met}[i+1]+C_w[i+1]);
y_w[i+1]=C_w[i+1]/(C_{eb}[i+1]+C_{st}[i+1]+C_{h2}[i+1]+C_{Be}[i+1]+C_{Ethyl}[i+1]+C_{Tol}[i+1]+C_{Met}[i+1]+C_w[i+1]);
y_{st}[i+1]=C_{st}[i+1]/(C_{eb}[i+1]+C_{st}[i+1]+C_{h2}[i+1]+C_{Be}[i+1]+C_{Ethyl}[i+1]+C_{Tol}[i+1]+C_{Met}[i+1]+C_w[i+1]);
y_{h2}[i+1]=C_{h2}[i+1]/(C_{eb}[i+1]+C_{st}[i+1]+C_{h2}[i+1]+C_{Be}[i+1]+C_{Ethyl}[i+1]+C_{Tol}[i+1]+C_{Met}[i+1]+C_w[i+1]);

y_{Be}[i+1]=C_{Be}[i+1]/(C_{eb}[i+1]+C_{st}[i+1]+C_{h2}[i+1]+C_{Be}[i+1]+C_{Ethyl}[i+1]+C_{Tol}[i+1]+C_{Met}[i+1]+C_w[i+1]);
y_{Ethyl}[i+1]=C_{Ethyl}[i+1]/(C_{eb}[i+1]+C_{st}[i+1]+C_{h2}[i+1]+C_{Be}[i+1]+C_{Ethyl}[i+1]+C_{Tol}[i+1]+C_{Met}[i+1]+C_w[i+1]);
y_{Tol}[i+1]=C_{Tol}[i+1]/(C_{eb}[i+1]+C_{st}[i+1]+C_{h2}[i+1]+C_{Be}[i+1]+C_{Ethyl}[i+1]+C_{Tol}[i+1]+C_{Met}[i+1]+C_w[i+1]);
y_{Met}[i+1]=C_{Met}[i+1]/(C_{eb}[i+1]+C_{st}[i+1]+C_{h2}[i+1]+C_{Be}[i+1]+C_{Ethyl}[i+1]+C_{Tol}[i+1]+C_{Met}[i+1]+C_w[i+1]);
kc_1[i+1]= A_1Exp[-Ea_1/(ru/1000 T[i+1])];kc_2[i+1]= A_2Exp[-Ea_2/(ru/1000 T[i+1])];kc_3[i+1]= A_3Exp[-Ea_3/(ru/1000 T[i+1])];kc_4[i+1]= A_4Exp[-Ea_4/(ru/1000 T[i+1])];
K_{EB}[i+1]=A_{EB}Exp[-ΔH_{EB}/(ru/1000 T[i+1])] ; K_{ST}[i+1]=A_{ST}Exp[-ΔH_{ST}/(ru/1000 T[i+1])];K_{H2}[i+1]=A_{H2}Exp[-ΔH_{H2}/(ru/1000 T[i+1])];
K_{EQ}[i+1]=0.027*Exp[0.021 (T[i+1]-773)];
r_1[i+1]=(kc_1[i+1] K_{EB}[i+1] (y_{eb}[i+1] P-(y_{st}[i+1] P y_{h2}[i+1] P)/K_{EQ}[i+1])*1000)/(1+Subscript[K, EB][i+1] Subscript[y, eb][i+1] P+Subscript[K, H2][i+1] Subscript[y, h2][i+1]P+Subscript[K, ST][i+1] Subscript[y, st][i+1]P)^2;
r_2[i+1]=(kc_2[i+1] K_{EB}[i+1] y_{eb}[i+1] P *1000)/(1+Subscript[K, EB][i+1] Subscript[y, eb][i+1] P+Subscript[K, H2][i+1] Subscript[y, h2][i+1]P+Subscript[K, ST][i+1] Subscript[y, st][i+1]P)^2;
r_3[i+1]=(kc_3[i+1] K_{EB}[i+1] y_{eb}[i+1] P K_{H2}[i+1] y_{h2}[i+1]P*1000)/(1+Subscript[K, EB][i+1] Subscript[y, eb][i+1] P+Subscript[K, H2][i+1] Subscript[y, h2][i+1]P+Subscript[K, ST][i+1] Subscript[y, st][i+1]P)^2;
r_4[i+1]=(kc_4[i+1] K_{ST}[i+1] y_{st}[i+1] P K_{H2}[i+1] y_{h2}[i+1]P *1000)/(1+Subscript[K, EB][i+1] Subscript[y, eb][i+1] P+Subscript[K, H2][i+1] Subscript[y, h2][i+1]P+Subscript[K, ST][i+1] Subscript[y, st][i+1]P)^2;
,nn];

Layout of the Graphics 1;

Graphics of Concentration;

CEthylbenzene=Table[C_{eb}[a],{a,0,i}]; CStyrene=Table[C_{st}[a],{a,0,i}]; CHydrogen=Table[C_{h2}[a],{a,0,i}]; CBenzene=Table[C_{Be}[a],{a,0,i}]; CEthylene=Table[C_{Ethyl}[a],{a,0,i}];CToluene=Table[C_{Tol}[a],{a,0,i}]; CMethane=Table[C_{Met}[a],{a,0,i}];
Concentrations=Join[{CEthylbenzene,CStyrene,CHydrogen, CBenzene,CEthylene,CToluene,CMethane}];

Graphic of Temperature;

Temperature=Table[T[a],{a,0,i}];

Graphics of reactions rate;

Reaction1=Table[r_1[a],{a,0,i}]; Reaction2=Table[r_2[a],{a,0,i}];Reaction3=Table[r_3[a],{a,0,i}]; Reaction4=Table[r_4[a],{a,0,i}];
Reactions=Join[{Reaction1,Reaction2,Reaction3,Reaction4}];

Graphics of reactions rate constants;

RRConstant1=Table[kc_1[a],{a,0,i}];RRConstant2=Table[kc_2[a],{a,0,i}];RRConstant3=Table[kc_3[a],{a,0,i}];RRConstant4=Table[kc_4[a],{a,0,i}];
RRConstants=Join[{RRConstant1,RRConstant2,RRConstant3,RRConstant4}];

Graphics of adsorption equilibrium constants and reaction equilibrium;

```
AECEthylbenzene=Table[KEB[a],{a,0,i}];AECStyrene=Table[KST[a],{a,0,i}];AECHydrogen=Table[
KH2[a],{a,0,i}]; ReactionEquilibrium=Table[KEQ[a],{a,0,i}];
AEConstants=Join[{AECEthylbenzene,AECStyrene,AECHydrogen}];
ListPlot[Concentrations,AxesLabel->{"Reactor's length (m·10^5)","Concentration
(mol/m^3)"},PlotLegends-
>{"Ethylbenzene","Styrene","Hydrogen","Benzene","Ethylene","Toluene","Methane"},PlotRange-
>{{0,nn},{0,1}}]
ListPlot[Temperature,AxesLabel->{"Reactor's length (m·10^5)","Temperature (K)"},PlotRange-
>{{0,nn},{750,900}}]
ListPlot[Reactions,AxesLabel->{"Reactor's length (m·10^5)","Reaction rate (mol/(kg
cat·h))"},PlotLegends->{"r1","r2","r3","r4"}]
ListPlot[RRConstants,AxesLabel->{"Reactor's length (m·10^5)","Reaction rate constant (mol/(kg
cat·h))"},PlotLegends->{"k1","k2","k3","k4"}]
ListPlot[AEConstants,AxesLabel->{"Reactor's length (m·10^5)","Adsorption equilibrium constant
(1/Bar)"},PlotLegends->{"KEB","KST","KH2"}]
ListPlot[ReactionEquilibrium,AxesLabel->{"Reactor's length (m·10^5)","reaction equilibrium
constant (-)"},PlotRange->{{0,nn},{0,0.4}}]

T[i+1]=893.15;
Ceb[i+1]=Ceb[i];
Cw[i+1]=Cw[i];
Cst[i+1]=Cst[i];
Ch2[i+1]=Ch2[i];
CBe[i+1]=CBe[i];
CEthyl[i+1]=CEthyl[i];
CTol[i+1]=CTol[i];
CMet[i+1]=CMet[i];
yeb[i+1]=Ceb[i+1]/(Ceb[i+1]+Cst[i+1]+Ch2[i+1]+CBe[i+1]+CEthyl[i+1]+CTol[i+1]+CMet[i+1]+Cw[i+1]);
yw[i+1]=Cw[i+1]/(Ceb[i+1]+Cst[i+1]+Ch2[i+1]+CBe[i+1]+CEthyl[i+1]+CTol[i+1]+CMet[i+1]+Cw[i+1]);
yst[i+1]=Cst[i+1]/(Ceb[i+1]+Cst[i+1]+Ch2[i+1]+CBe[i+1]+CEthyl[i+1]+CTol[i+1]+CMet[i+1]+Cw[i+1]);
yh2[i+1]=Ch2[i+1]/(Ceb[i+1]+Cst[i+1]+Ch2[i+1]+CBe[i+1]+CEthyl[i+1]+CTol[i+1]+CMet[i+1]+Cw[i+1]);
yBe[i+1]=CBe[i+1]/(Ceb[i+1]+Cst[i+1]+Ch2[i+1]+CBe[i+1]+CEthyl[i+1]+CTol[i+1]+CMet[i+1]+Cw[i+1]);
yEthyl[i+1]=CEthyl[i+1]/(Ceb[i+1]+Cst[i+1]+Ch2[i+1]+CBe[i+1]+CEthyl[i+1]+CTol[i+1]+CMet[i+1]+Cw[i+1]);
yTol[i+1]=CTol[i+1]/(Ceb[i+1]+Cst[i+1]+Ch2[i+1]+CBe[i+1]+CEthyl[i+1]+CTol[i+1]+CMet[i+1]+Cw[i+1]);
yMet[i+1]=CMet[i+1]/(Ceb[i+1]+Cst[i+1]+Ch2[i+1]+CBe[i+1]+CEthyl[i+1]+CTol[i+1]+CMet[i+1]+Cw[i+1]);
kc1[i+1]= A1Exp[-Ea1/(ru/1000 T[i+1])];kc2[i+1]= A2Exp[-Ea2/(ru/1000 T[i+1])];kc3[i+1]= A3Exp[-
Ea3/(ru/1000 T[i+1])];kc4[i+1]= A4Exp[-Ea4/(ru/1000 T[i+1])];
KEB[i+1]=AEBExp[-ΔHEB/(ru/1000 T[i+1])] ; KST[i+1]=ASTExp[-ΔHST/(ru/1000
T[i+1])];KH2[i+1]=AH2Exp[-ΔHH2/(ru/1000 T[i+1])];
KEQ[i+1]=0.027*Exp[0.021 (T[i+1]-773)];
```

r_1[i+1]=(kc_1[i+1] K_{EB}[i+1] (y_{eb}[i+1] P-(y_{st}[i+1] P y_{h2}[i+1] P)/K_{EQ}[i+1])*1000)/(1+Subscript[K, EB][i+1] Subscript[y, eb][i+1] P+Subscript[K, H2][i+1] Subscript[y, h2][i+1]P+Subscript[K, ST][i+1] Subscript[y, st][i+1]P)^2;

r_2[i+1]=(kc_2[i+1] K_{EB}[i+1] y_{eb}[i+1] P *1000)/(1+Subscript[K, EB][i+1] Subscript[y, eb][i+1] P+Subscript[K, H2][i+1] Subscript[y, h2][i+1]P+Subscript[K, ST][i+1] Subscript[y, st][i+1]P)^2;

r_3[i+1]=(kc_3[i+1] K_{EB}[i+1] y_{eb}[i+1] P K_{H2}[i+1] y_{h2}[i+1]P*1000)/(1+Subscript[K, EB][i+1] Subscript[y, eb][i+1] P+Subscript[K, H2][i+1] Subscript[y, h2][i+1]P+Subscript[K, ST][i+1] Subscript[y, st][i+1]P)^2;

r_4[i+1]=(kc_4[i+1] K_{ST}[i+1] y_{st}[i+1] P K_{H2}[i+1] y_{h2}[i+1]P *1000)/(1+Subscript[K, EB][i+1] Subscript[y, eb][i+1] P+Subscript[K, H2][i+1] Subscript[y, h2][i+1]P+Subscript[K, ST][i+1] Subscript[y, st][i+1]P)^2;

Do[i=i+1;

C_{eb}[i+1]= h/u ρ_B (1-ϵ)/ϵ (-r_1[i]-r_2[i]-r_3[i])+ C_{eb}[i];

C_w[i+1]= C_w[i-1];

C_{st}[i+1]= h/u ρ_B (1-ϵ)/ϵ (r_1[i]-r_4[i])+ C_{st}[i];

C_{h2}[i+1]= h/u ρ_B (1-ϵ)/ϵ (r_1[i]-r_3[i]-2r_4[i])+ C_{h2}[i];

C_{Be}[i+1]= h/u ρ_B (1-ϵ)/ϵ r_2[i]+ C_{Be}[i];

C_{Ethyl}[i+1]=h/u ρ_B (1-ϵ)/ϵ r_2[i]+ C_{Ethyl}[i];

C_{Tol}[i+1]= h/u ρ_B (1-ϵ)/ϵ (r_3[i]+r_4[i])+ C_{Tol}[i];

C_{Met}[i+1]= h/u ρ_B (1-ϵ)/ϵ (r_3[i]+r_4[i])+ C_{Met}[i];

T[i+1]= h/(G Cpm) ρ_B(r_1[i] (-ΔH^*$_1$)+ r_2[i](-ΔH^*$_2$)+ r_3[i] (-ΔH^*$_3$)+r_4[i] (-ΔH^*$_4$))+T[i] ;

y_{eb}[i+1]=C_{eb}[i+1]/(C_{eb}[i+1]+C_{st}[i+1]+C_{h2}[i+1]+C_{Be}[i+1]+C_{Ethyl}[i+1]+C_{Tol}[i+1]+C_{Met}[i+1]+C_w[i+1]);

y_w[i+1]=C_w[i+1]/(C_{eb}[i+1]+C_{st}[i+1]+C_{h2}[i+1]+C_{Be}[i+1]+C_{Ethyl}[i+1]+C_{Tol}[i+1]+C_{Met}[i+1]+C_w[i+1]);

y_{st}[i+1]=C_{st}[i+1]/(C_{eb}[i+1]+C_{st}[i+1]+C_{h2}[i+1]+C_{Be}[i+1]+C_{Ethyl}[i+1]+C_{Tol}[i+1]+C_{Met}[i+1]+C_w[i+1]);

y_{h2}[i+1]=C_{h2}[i+1]/(C_{eb}[i+1]+C_{st}[i+1]+C_{h2}[i+1]+C_{Be}[i+1]+C_{Ethyl}[i+1]+C_{Tol}[i+1]+C_{Met}[i+1]+C_w[i+1]);

y_{Be}[i+1]=C_{Be}[i+1]/(C_{eb}[i+1]+C_{st}[i+1]+C_{h2}[i+1]+C_{Be}[i+1]+C_{Ethyl}[i+1]+C_{Tol}[i+1]+C_{Met}[i+1]+C_w[i+1]);

y_{Ethyl}[i+1]=C_{Ethyl}[i+1]/(C_{eb}[i+1]+C_{st}[i+1]+C_{h2}[i+1]+C_{Be}[i+1]+C_{Ethyl}[i+1]+C_{Tol}[i+1]+C_{Met}[i+1]+C_w[i+1]);

y_{Tol}[i+1]=C_{Tol}[i+1]/(C_{eb}[i+1]+C_{st}[i+1]+C_{h2}[i+1]+C_{Be}[i+1]+C_{Ethyl}[i+1]+C_{Tol}[i+1]+C_{Met}[i+1]+C_w[i+1]);

y_{Met}[i+1]=C_{Met}[i+1]/(C_{eb}[i+1]+C_{st}[i+1]+C_{h2}[i+1]+C_{Be}[i+1]+C_{Ethyl}[i+1]+C_{Tol}[i+1]+C_{Met}[i+1]+C_w[i+1]);

kc_1[i+1]= A_1Exp[-Ea_1/(ru/1000 T[i+1])];kc_2[i+1]= A_2Exp[-Ea_2/(ru/1000 T[i+1])];kc_3[i+1]= A_3Exp[-Ea_3/(ru/1000 T[i+1])];kc_4[i+1]= A_4Exp[-Ea_4/(ru/1000 T[i+1])];

K_{EB}[i+1]=A_{EB}Exp[-ΔH_{EB}/(ru/1000 T[i+1])] ; K_{ST}[i+1]=A_{ST}Exp[-ΔH_{ST}/(ru/1000 T[i+1])];K_{H2}[i+1]=A_{H2}Exp[-ΔH_{H2}/(ru/1000 T[i+1])];

K_{EQ}[i+1]=0.027*Exp[0.021 (T[i+1]-773)];

r_1[i+1]=(kc_1[i+1] K_{EB}[i+1] (y_{eb}[i+1] P-(y_{st}[i+1] P y_{h2}[i+1] P)/K_{EQ}[i+1])*1000)/(1+Subscript[K, EB][i+1] Subscript[y, eb][i+1] P+Subscript[K, H2][i+1] Subscript[y, h2][i+1]P+Subscript[K, ST][i+1] Subscript[y, st][i+1]P)^2;

r_2[i+1]=(kc_2[i+1] K_{EB}[i+1] y_{eb}[i+1] P *1000)/(1+Subscript[K, EB][i+1] Subscript[y, eb][i+1] P+Subscript[K, H2][i+1] Subscript[y, h2][i+1]P+Subscript[K, ST][i+1] Subscript[y, st][i+1]P)^2;

r_3[i+1]=(kc_3[i+1] K_{EB}[i+1] y_{eb}[i+1] P K_{H2}[i+1] y_{h2}[i+1]P*1000)/(1+Subscript[K, EB][i+1] Subscript[y, eb][i+1] P+Subscript[K, H2][i+1] Subscript[y, h2][i+1]P+Subscript[K, ST][i+1] Subscript[y, st][i+1]P)^2;

r_4[i+1]=(kc_4[i+1] K_{ST}[i+1] y_{st}[i+1] P K_{H2}[i+1] y_{h2}[i+1]P *1000)/(1+Subscript[K, EB][i+1] Subscript[y, eb][i+1] P+Subscript[K, H2][i+1] Subscript[y, h2][i+1]P+Subscript[K, ST][i+1] Subscript[y, st][i+1]P)^2;
,nn];

Layout of the Graphics 2;

Graphics of Concentration;

CEthylbenzene2=Table[C_{eb}[a],{a,nn+1,i}]; CStyrene2=Table[C_{st}[a],{a,nn+1,i}];
CHydrogen2=Table[C_{h2}[a],{a,nn+1,i}]; CBenzene2=Table[C_{Be}[a],{a,nn+1,i}];
CEthylene2=Table[C_{Ethyl}[a],{a,nn+1,i}];CToluene2=Table[C_{Tol}[a],{a,nn+1,i}];
CMethane2=Table[C_{Met}[a],{a,nn+1,i}];
Concentrations2=Join[{CEthylbenzene2,CStyrene2,CHydrogen2,
CBenzene2,CEthylene2,CToluene2,CMethane2}];
ListPlot[Concentrations2]

Graphic of Temperature;

Temperature2=Table[T[a],{a,nn+1,i}];
ListPlot[Temperature2]

Graphics of reactions rate;

Reaction12=Table[r_1[a],{a,nn+1,i}];
Reaction22=Table[r_2[a],{a,nn+1,i}];Reaction32=Table[r_3[a],{a,nn+1,i}];
Reaction42=Table[r_4[a],{a,nn+1,i}];
Reactions2=Join[{Reaction12,Reaction22,Reaction32,Reaction42}];
Reactionss2=Join[{Reaction22,Reaction32,Reaction42}];
ListPlot[Reactions2]
ListPlot[Reactionss2]

Graphics of reactions rate constants;

RRConstant12=Table[kc_1[a],{a,nn+1,i}];RRConstant22=Table[kc_2[a],{a,nn+1,i}];RRConstant32= Table[kc_3[a],{a,nn+1,i}];RRConstant42=Table[kc_4[a],{a,nn+1,i}];
RRConstants2=Join[{RRConstant12,RRConstant22,RRConstant32,RRConstant42}];
ListPlot[RRConstants2]

Graphics of adsorption equilibrium constants and reaction equilibrium;

AECEthylbenzene2=Table[K_{EB}[a],{a,nn+1,i}];AECStyrene2=Table[K_{ST}[a],{a,nn+1,i}];AECHydrogen2=Table[K_{H2}[a],{a,nn+1,i}]; ReactionEquilibrium2=Table[K_{EQ}[a],{a,nn+1,i}];
AEConstants2=Join[{AECEthylbenzene2,AECStyrene2,AECHydrogen2}];

DISPERSION MODEL WITH CONSTANT PHYSICAL PARAMETERS

```
Quit[];
```

Initial conditions of the fluid

```
P=0.501; (*Bar*) u=43200; ui=43200; (*m/h*) T1=893.15; (*K*) L=5; (*m*)
x0=0.963;x1=0;x2=0;x3=0;x4=0;x5=0;x6=0;x7=5.777; (*mol/m^3*)
ϵ=0.4312;(*Subscript[m, b]^3/Subscript[m, r]^3*)ρ=1442; (*(kg cat)/m^3*)
dp=0.0055;
nn=50000;
h=N[L/nn];
```

Physical Properties of the fluid

```
y1=x0/(x0+x1+x2+x3+x4+x5+x6+x7);
y2=x7/(x0+x1+x2+x3+x4+x5+x6+x7);
y3=x1/(x0+x1+x2+x3+x4+x5+x6+x7);
y4=x2/(x0+x1+x2+x3+x4+x5+x6+x7);
R=0.08206 1.013/1000;
ru=8.314;
Mmeb=106.17; Mmw=18; Mmst=104.15; Mmh2=2;Mmbe=78.11; Mmet=28.05;
Mmto=92.14;Mmme=16.04; (*g/mol*)
M1=Mmeb;M2=Mmw;M3=Mmst;M4=Mmh2;M5=Mmbe;M6=Mmet;M7=Mmto;M8=Mmme;
Teb=409.15; Tw=373.15; Tst=418.15; Th2=20.27; Tbe= 353.25; Tet=169.5; Tto= 384.00; Tme=111.65;
Tb1=Teb; Tb2=Tw; Tb3=Tst; Tb4=Th2; Tb5=Tbe; Tb6=Tet; Tb7=Tto; Tb8=Tme;
Veb=139.24; Vw=18.789; Vst=131.27; Vh2=28.16; Vbe= 96.017; Vet=49.29; Vto= 118.29; Vme=35.64;
Vm1=Veb; Vm2=Vw; Vm3=Vst; Vm4=Vh2; Vm5=Vbe; Vm6=Vet; Vm7=Vto; Vm8=Vme;
Deb=0.58; Dw=1.8546; Dst=0.13; Dh2=0; Dbe=0; Det=0; Dto=0.36; Dme=0;
Dp1=Deb;Dp2=Dw; Dp3=Dst;Dp4=Dh2;Dp5=Dbe;Dp6=Det;Dp7=Dto;Dp8=Dme;
Daeb:= 8*15.9+10*2.31; Daw:=4.54+2*2.31; Dast:=8*15.9+8*2.31;Dah2:=2*2.31;
da1=Daeb;da2=Daw;da3=Dast;da4=Dah2;
aa=1; bb=0; cc=1; dd=1;
ζa:=(cc+dd-aa-bb)/aa;
j=0;
Do[i=1;j=j+1;
  Mji,j=2 (1/Subscript[M, i]+1/Subscript[M, j])^-1,4];
i=0;
Do[i=i+1;
```

δ_i=(1940 Subscript[Dp, i]^2)/(Vm$_i$ Tb$_i$); σ_i=((1.585 Subscript[Vm, i])/(1+1.3 Subscript[δ, i]^2))$^{1/3}$; $\epsilon\kappa_i$=1.18 (1+1.3 Subscript[δ, i]^2) Tb$_i$; $\Omega_{V,i}$=(1.16145 (T1/Subscript[ϵκ, i])$^{-0.14874}$)+0.52487 (Exp[-0.77320 (T1/$\epsilon\kappa_i$)])+2.16178 (Exp[-2.43787 (T1/$\epsilon\kappa_i$)]);

μ_i=(2.6709 10^{-6}) $\sqrt{M_i\ T1}$ /(Subscript[σ, i]^2 $\Omega_{V,i}$),8];

i=0;

j=0;

Do[i=i+1;

$\Phi_{i,i}$=1;

Do[j=j+1;

$\Phi_{i\_,j\_}$:=1/ $\sqrt{8}$ (1+Subscript[M, i]/Subscript[M, j])$^{-0.5}$ (1+(Subscript[μ, i]/Subscript[μ, j])^0.5 (Subscript[M, j]/Subscript[M, i])^0.25)^2,8],8];

$\mu_m=\sum_{i=1}^{4}\left(\frac{y_i\ \mu_i}{\sum_{j=1}^{4} y_j\ \Phi_{i,j}}\right)$;

x=0;

Do[x=x+1; ρ_x= (P M$_x$/1000)/(R T1),8];

Density= $\sum_{i=1}^{4} \rho_i\ y_i$;

MM= $\sum_{i=1}^{4} M_i\ y_i$ /1000;

G=(u Density)/MM;

jj=1;j=1;

Do[j=j+1;

$D_{jj,j}$=(0.00143T1$^{1.75}$)/(P M$_{jj,j}$ ($da_{jj}^{\frac{1}{3}}$ +$da_j^{\frac{1}{3}}$)^2); ,4];

D_m=0.36/(1/(1+y_1) (1/$D_{1,2}$ (y_2)+1/$D_{1,3}$ (y_3+y_1)+1/$D_{1,4}$ (y_4+y_1)));

d=D_m;

MmM=((u ρm dp)/μ_m) (μ_m/(ρm d));

Deff= u dp (0.7/MmM+4/(1+MmM 5.1));

Cp_1=(8) (1/2) ((8.314/1000) /(M_1/1000));

Cp_2=(143.05-183.54 (T1/100)$^{0.25}$+82.751 (T1/100)$^{0.5}$-3.6989 (T1/100)^1)/1000;

Cp_3=(8)*(1/2) ((8.314/1000) /(M_3/1000));

Cp_4=(56.505-702.24 (T1/100)$^{-0.75}$+1165.0 (T1/100)$^{-1}$-560.70 (T1/100)$^{-1.5}$)/1000;

Cp_m = Cp_1 y_1+Cp_2 y_2+Cp_3 y_3+Cp_4 y_4;

Cpm=Cp_m;

k_1=8.3127*10^{-2} $\sqrt{\frac{T1}{M_1}}$ /(Subscript[σ, 1]^2 $\Omega_{V,1}$)+1.32 (Cp_1-5/2 8.314/1000/M_1) 2.6709*10^{-6} $\sqrt{M_1\ T1}$ /(Subscript[σ, 1]^2 $\Omega_{V,1}$);

k_2=8.3127*10^{-2} $\sqrt{\frac{T1}{M_2}}$ /(Subscript[σ, 2]^2 $\Omega_{V,2}$)+1.32 (Cp_2-5/2 8.314/1000/M_2) 2.6709*10^{-6} $\sqrt{M_2\ T1}$ /(Subscript[σ, 2]^2 $\Omega_{V,1}$);

k_3=8.3127*10^{-2} $\sqrt{\frac{T1}{M_3}}$ /(Subscript[σ, 3]^2 $\Omega_{V,3}$)+1.32 (Cp_3-5/2 8.314/1000/M_3) 2.6709*10^{-6} $\sqrt{M_3\ T1}$ /(Subscript[σ, 3]^2 $\Omega_{V,3}$);

k_4=8.3127*10^{-2} $\sqrt{\frac{T1}{M_4}}$ /(Subscript[σ, 4]^2 $\Omega_{V,4}$)+1.32 (Cp_4-5/2 8.314/1000/M_4) 2.6709*10^{-6} $\sqrt{M_4\ T1}$ /(Subscript[σ, 4]^2 $\Omega_{V,4}$);

k_m=(y_1 k_1)/(y_1 $\Phi_{1,1}$+y_2 $\Phi_{1,2}$+y_3 $\Phi_{1,3}$+y_4 $\Phi_{1,4}$)+(y_2 k_2)/(y_1 $\Phi_{2,1}$+y_2 $\Phi_{2,2}$+y_3 $\Phi_{2,3}$+y_4 $\Phi_{2,4}$)+(y_3 k_3)/(y_1 $\Phi_{3,1}$+y_2 $\Phi_{3,2}$+y_3 $\Phi_{3,3}$+y_4 $\Phi_{3,4}$)+(y_4 k_4)/(y_1 $\Phi_{4,1}$+y_2 $\Phi_{4,2}$+y_3 $\Phi_{4,3}$+y_4 $\Phi_{4,4}$);
km=k_m;

Initial conditions of the reactions and values of the rate constants and adsorption equilibrium constants

r1=74.74838; r2=1.20136;r3=0;r4=0; (*mol/(kg cat·h)*)
ΔH^*$_1$=117.690;ΔH^*$_2$=105.510;ΔH^*$_3$=-54.680;ΔH^*$_4$=-172.370; (*kJ/mol*)
Ea1=175.38; Ea2=296.29;Ea3=474.76; Ea4=213.78; (*kJ/mol*)
A1=5.594*10^{9}; A2=1.060*10^{15}; A3=1.246*10^{26}; A4=8.024*10^{10}; (*kmol/(kg cat·h)*)
ΔHeb=-102.22; ΔHst=-104.56;ΔHh2=-117.95; (*kJ/mol*)
Aeb=1.014*10^{-5}; Ast=2.678*10^{-5};Ah2=4.519*10^{-7}; (*1/Bar*)
kc1= A1 Exp[-Ea1/(ru/1000 T1)];kc2= A2 Exp[-Ea2/(ru/1000 T1)];kc3= A3 Exp[-Ea3/(ru/1000 T1)];kc4= A4 Exp[-Ea4/(ru/1000 T1)];
Keb=Aeb Exp[-ΔHeb/(ru/1000 T1)] ; Kst=Ast Exp[-ΔHst/(ru/1000 T1)];Kh2=Ah2 Exp[-ΔHh2/(ru/1000 T1)];
Keq=0.027*Exp[0.021 (T1-773)];
Rr1=(kc1 Keb (y_1 P-(y_3 y_4 P^2)/Keq)*1000)/(1+Keb Subscript[y, 1] P+Kst Subscript[y, 3] P+Kh2 Subscript[y, 4] P)^2;
r1=Rr1;

Rr2=(kc2 Keb y_1 P 1000)/(1+Keb Subscript[y, 1] P+Kst Subscript[y, 3] P+Kh2 Subscript[y, 4] P)^2;
r2=Rr2;
Rr3=(kc3 Keb y_1 P Kh2 y_4 P 1000)/(1+Keb Subscript[y, 1] P+Kst Subscript[y, 3] P+Kh2 Subscript[y, 4] P)^2;
r3=Rr3;

Rr4=(kc4 Kst y_3 P Kh2 y_4 P 1000)/(1+Keb Subscript[y, 1] P+Kst Subscript[y, 3] P+Kh2 Subscript[y, 4] P)^2;

r4=Rr4;

```
i=0;
Do[i=i+1;
 xx0=(Deff  ρ(-r1-r2-r3)(1-ϵ) )/(ϵ u^2) (Exp[-u/Deff L]-Exp[u/Deff (h-L)])+(ρ(-r1-r2-r3)(1-ϵ))/(ϵ u) h+x0;
 x0=xx0;
 fx0[i+1]=xx0;
 xx1=(Deff  ρ(r1-r4)(1-ϵ) )/(ϵ u^2) (Exp[-u/Deff L]-Exp[u/Deff (h-L)])+(ρ(r1-r4)(1-ϵ))/(ϵ u) h+x1;
 x1=xx1;
 fx1[i+1]=xx1;

 xx2=(Deff  ρ(r1-r3-2r4)(1-ϵ) )/(ϵ u^2) (Exp[-u/Deff L]-Exp[u/Deff (h-L)])+(ρ(r1-r3-2r4)(1-ϵ))/(ϵ u) h+x2;
 x2=xx2;
 fx2[i+1]=xx2;
 xx3=(Deff  ρ(r2)(1-ϵ) )/(ϵ u^2) (Exp[-u/Deff L]-Exp[u/Deff (h-L)])+(ρ(r2)(1-ϵ))/(ϵ u) h+x3;
 x3=xx3;
 fx3[i+1]=xx3;
 xx4=(Deff  ρ(r2)(1-ϵ) )/(ϵ u^2) (Exp[-u/Deff L]-Exp[u/Deff (h-L)])+(ρ(r2)(1-ϵ))/(ϵ u) h+x4;
 x4=xx4;
 fx4[i+1]=xx4;
 xx5=(Deff  ρ(r3+r4)(1-ϵ) )/(ϵ u^2) (Exp[-u/Deff L]-Exp[u/Deff (h-L)])+(ρ(r3+r4)(1-ϵ))/(ϵ u) h+x5;
 x5=xx5;
 fx5[i+1]=xx5;
 xx6=(Deff  ρ(r3+r4)(1-ϵ) )/(ϵ u^2) (Exp[-u/Deff L]-Exp[u/Deff (h-L)])+(ρ(r3+r4)(1-ϵ))/(ϵ u) h+x6;
 x6=xx6;
 fx6[i+1]=xx6;
 TT=(km  ρ (r1 ΔH^*_1+r2 ΔH^*_2+r3 ΔH^*_3+r4 ΔH^*_4) )/(G Cpm)^2 (-Exp[(-G Cpm)/km L]+Exp[(G Cpm)/km (h-L)])-(ρ (r1 ΔH^*_1+r2 ΔH^*_2+r3 ΔH^*_3+r4 ΔH^*_4))/(G Cpm ) h+T1;
 T1=TT;
 fT[i+1]=TT;

 y0=x0 /(x0+x1+x2+x3+x4+x5+x6+x7);
 yy0[i+1]=y0;
 y1=x1 /(x0+x1+x2+x3+x4+x5+x6+x7);
 yy1[i+1]=y1;
 y2=x2 /(x0+x1+x2+x3+x4+x5+x6+x7);
 yy2[i+1]=y2;
 y3=x3/(x0+x1+x2+x3+x4+x5+x6+x7);
 yy3[i+1]=y3;
 y4=x4/(x0+x1+x2+x3+x4+x5+x6+x7);
 yy4[i+1]=y4;
 y5=x5/(x0+x1+x2+x3+x4+x5+x6+x7);
```

```
 yy5[i+1]=y5;
 y6=x6/(x0+x1+x2+x3+x4+x5+x6+x7);
 yy6[i+1]=y6;
 y7=x7/(x0+x1+x2+x3+x4+x5+x6+x7);
 yy7[i+1]=y7;

 kc1= A1 Exp[-Ea1/(ru/1000 T1)];kc2= A2 Exp[-Ea2/(ru/1000 T1)];kc3= A3 Exp[-Ea3/(ru/1000
T1)];kc4= A4 Exp[-Ea4/(ru/1000 T1)];
 kc_1[i+1]=kc1;kc_2[i+1]=kc2;kc_3[i+1]=kc3;kc_4[i+1]=kc4;
 Keb=Aeb Exp[-ΔHeb/(ru/1000 T1)] ; Kst=Ast Exp[-ΔHst/(ru/1000 T1)];Kh2=Ah2 Exp[-
ΔHh2/(ru/1000 T1)];
 K_EB[i+1]=Keb;K_ST[i+1]=Kst;K_H2[i+1]=Kh2;
 Keq=0.027*Exp[0.021 (T1-773)];
 K_EQ[i+1]=Keq;

 Rr1=(kc1 Keb (y0 P-(y1 y2  P^2)/Keq )*1000)/(1+Keb y0 P+Kst y1 P+Kh2 y2 P)^2;
 r1=Rr1;
 r_1[i+1]=r1;
 Rr2=(kc2 Keb y0 P 1000)/(1+Keb y0 P+Kst y1 P+Kh2 y2 P)^2;
 r2=Rr2;
 r_2[i+1]=r2;
 Rr3=(kc3 Keb y0 P Kh2 y2 P 1000)/(1+Keb y0 P+Kst y1 P+Kh2 y2 P)^2;
 r3=Rr3;
 r_3[i+1]=r3;
 Rr4=(kc4 Kst y1 P Kh2 y2 P 1000)/(1+Keb y0 P+Kst y1 P+Kh2 y2 P)^2;
 r4=Rr4;
 r_4[i+1]=r4;
 ,nn];
```

Layout of the Graphics 1;

Graphics of Concentration;

```
CEthylbenzene=Table[fx0[a],{a,1,i}];CStyrene=Table[fx1[a],{a,1,i}];CHydrogen=Table[fx2[a],{a,1,
i}];CBenzene=Table[fx3[a],{a,1,i}];CEthylene=Table[fx4[a],{a,1,i}];CToluene=Table[fx5[a],{a,1,i}];
CMethane=Table[fx6[a],{a,1,i}];
Concentrations=Join[{CEthylbenzene,CStyrene,CHydrogen,CBenzene,CEthylene,CToluene,C
Methane}];
```

Graphic of Temperature;

```
Temperature=Table[fT[a],{a,1,i}];
```

Graphics of reactions rate;

```
Reaction1=Table[r_1[a],{a,0,i}];        Reaction2=Table[r_2[a],{a,0,i}];Reaction3=Table[r_3[a],{a,0,i}];
Reaction4=Table[r_4[a],{a,0,i}];
Reactions=Join[{Reaction1,Reaction2,Reaction3,Reaction4}];
Reactionss=Join[{Reaction2,Reaction3,Reaction4}];
```

Graphics of reactions rate constants;

```
RRConstant1=Table[kc1[a],{a,0,i}];RRConstant2=Table[kc2[a],{a,0,i}];RRConstant3=Table[kc3[a]
,{a,0,i}];RRConstant4=Table[kc4[a],{a,0,i}];
RRConstants=Join[{RRConstant1,RRConstant2,RRConstant3,RRConstant4}];
```

Graphics of adsorption equilibrium constants and reaction equilibrium;

```
AECEthylbenzene=Table[KEB[a],{a,0,i}];AECStyrene=Table[KST[a],{a,0,i}];AECHydrogen=Table[
KH2[a],{a,0,i}]; ReactionEquilibrium=Table[KEQ[a],{a,0,i}];
AEConstants=Join[{AECEthylbenzene,AECStyrene,AECHydrogen}];
```

Plotting graphics;

```
ListPlot[Concentrations,AxesLabel->{"Reactor's length (m·10^5)","Concentration
(mol/m^3)"},PlotLegends-
>{"Ethylbenzene","Styrene","Hydrogen","Benzene","Ethylene","Toluene","Methane"},PlotRange-
>{{0,nn},{0,1}}]
ListPlot[Temperature,AxesLabel->{"Reactor's length (m·10^5)","Temperature (K)"},PlotRange-
>{{0,nn},{750,900}}]
ListPlot[Reactions,AxesLabel->{"Reactor's length (m·10^5)","Reaction rate (mol/(kg
cat·h))"},PlotLegends->{"r1","r2","r3","r4"}]
ListPlot[Reaction1,AxesLabel->{"Reactor's length (m·10^5)","Reaction rate 1 (mol/(kg
cat·h))"},PlotRange->{{0,nn},{0,75}}]
ListPlot[Reactionss,AxesLabel->{"Reactor's length (m·10^5)","Reaction rate (mol/(kg
cat·h))"},PlotLegends->{"r2","r3","r4"}]
ListPlot[RRConstants,AxesLabel->{"Reactor's length (m·10^5)","Reaction rate constant (mol/(kg
cat·h))"},PlotLegends->{"k1","k2","k3","k4"}]
ListPlot[AEConstants,AxesLabel->{"Reactor's length (m·10^5)","Adsorption equilibrium constant
(1/Bar)"},PlotLegends->{"KEB","KST","KH2"}]
ListPlot[ReactionEquilibrium,AxesLabel->{"Reactor's length (m·10^5)","reaction equilibrium
constant (-)"},PlotRange->{{0,nn},{0,0.4}}]
```

Heat exchange step

```
Clear[T1];
T1=893.15;
kc1= A1 Exp[-Ea1/(ru/1000 T1)];kc2= A2 Exp[-Ea2/(ru/1000 T1)];kc3= A3 Exp[-Ea3/(ru/1000
T1)];kc4= A4 Exp[-Ea4/(ru/1000 T1)];
kc1[i+1]=kc1;kc2[i+1]=kc2;kc3[i+1]=kc3;kc4[i+1]=kc4;
Keb=Aeb Exp[-ΔHeb/(ru/1000 T1)] ; Kst=Ast Exp[-ΔHst/(ru/1000 T1)];Kh2=Ah2 Exp[-
ΔHh2/(ru/1000 T1)];
KEB[i+1]=Keb;KST[i+1]=Kst;KH2[i+1]=Kh2;
Keq=0.027*Exp[0.021 (T1-773)];
```

```
KEQ[i+1]=Keq;
Rr1=(kc1 Keb (y0 P-(y1 y2  P^2)/Keq )*1000)/(1+Keb y0 P+Kst y1 P+Kh2 y2 P)^2;
r1=Rr1;
r1[i+1]=r1;

Rr2=(kc2 Keb y0 P 1000)/(1+Keb y0 P+Kst y1 P+Kh2 y2 P)^2;
r2=Rr2;
r2[i+1]=r2;
Rr3=(kc3 Keb y0 P Kh2 y2 P 1000)/(1+Keb y0 P+Kst y1 P+Kh2 y2 P)^2;
r3=Rr3;
r3[i+1]=r3;
Rr4=(kc4 Kst y1 P Kh2 y2 P 1000)/(1+Keb y0 P+Kst y1 P+Kh2 y2 P)^2;
r4=Rr4;
r4[i+1]=r4;
Do[i=i+1;
 xx0=(Deff  ρ(-r1-r2-r3)(1-ϵ) )/(ϵ u^2) (Exp[-u/Deff L]-Exp[u/Deff (h-L)])+(ρ(-r1-r2-r3)(1-ϵ))/(ϵ u)
h+x0;
 x0=xx0;
 fx0[i+1]=xx0;
 xx1=(Deff  ρ(r1-r4)(1-ϵ) )/(ϵ u^2) (Exp[-u/Deff L]-Exp[u/Deff (h-L)])+(ρ(r1-r4)(1-ϵ))/(ϵ u) h+x1;
 x1=xx1;
 fx1[i+1]=xx1;
 xx2=(Deff  ρ(r1-r3-2r4)(1-ϵ) )/(ϵ u^2) (Exp[-u/Deff L]-Exp[u/Deff (h-L)])+(ρ(r1-r3-2r4)(1-ϵ))/(ϵ u)
h+x2;
 x2=xx2;
 fx2[i+1]=xx2;
 xx3=(Deff  ρ(r2)(1-ϵ) )/(ϵ u^2) (Exp[-u/Deff L]-Exp[u/Deff (h-L)])+(ρ(r2)(1-ϵ))/(ϵ u) h+x3;
 x3=xx3;
 fx3[i+1]=xx3;
 xx4=(Deff  ρ(r2)(1-ϵ) )/(ϵ u^2) (Exp[-u/Deff L]-Exp[u/Deff (h-L)])+(ρ(r2)(1-ϵ))/(ϵ u) h+x4;
 x4=xx4;
 fx4[i+1]=xx4;
 xx5=(Deff  ρ(r3+r4)(1-ϵ) )/(ϵ u^2) (Exp[-u/Deff L]-Exp[u/Deff (h-L)])+(ρ(r3+r4)(1-ϵ))/(ϵ u) h+x5;
 x5=xx5;
 fx5[i+1]=xx5;
 xx6=(Deff  ρ(r3+r4)(1-ϵ) )/(ϵ u^2) (Exp[-u/Deff L]-Exp[u/Deff (h-L)])+(ρ(r3+r4)(1-ϵ))/(ϵ u) h+x6;
 x6=xx6;
 fx6[i+1]=xx6;
 TT=(km  ρ (r1 ΔH^*1+r2 ΔH^*2+r3 ΔH^*3+r4 ΔH^*4) )/(G Cpm)^2 (-Exp[(-G Cpm)/km L]+Exp[(G
Cpm)/km (h-L)])-(ρ (r1 ΔH^*1+r2 ΔH^*2+r3 ΔH^*3+r4 ΔH^*4))/(G Cpm ) h+T1;
 T1=TT;
 fT[i+1]=TT;

 y0=x0 /(x0+x1+x2+x3+x4+x5+x6+x7);
 yy0[i+1]=y0;
```

```
y1=x1 /(x0+x1+x2+x3+x4+x5+x6+x7);
yy1[i+1]=y1;
y2=x2 /(x0+x1+x2+x3+x4+x5+x6+x7);
yy2[i+1]=y2;
y3=x3/(x0+x1+x2+x3+x4+x5+x6+x7);
yy3[i+1]=y3;
y4=x4/(x0+x1+x2+x3+x4+x5+x6+x7);
yy4[i+1]=y4;
y5=x5/(x0+x1+x2+x3+x4+x5+x6+x7);
yy5[i+1]=y5;
y6=x6/(x0+x1+x2+x3+x4+x5+x6+x7);
yy6[i+1]=y6;
y7=x7/(x0+x1+x2+x3+x4+x5+x6+x7);
yy7[i+1]=y7;
kc1= A1 Exp[-Ea1/(ru/1000 T1)];kc2= A2 Exp[-Ea2/(ru/1000 T1)];kc3= A3 Exp[-Ea3/(ru/1000 T1)];kc4= A4 Exp[-Ea4/(ru/1000 T1)];
kc1[i+1]=kc1;kc2[i+1]=kc2;kc3[i+1]=kc3;kc4[i+1]=kc4;
Keb=Aeb Exp[-ΔHeb/(ru/1000 T1)] ; Kst=Ast Exp[-ΔHst/(ru/1000 T1)];Kh2=Ah2 Exp[-ΔHh2/(ru/1000 T1)];
KEB[i+1]=Keb;KST[i+1]=Kst;KH2[i+1]=Kh2;
Keq=0.027*Exp[0.021 (T1-773)];
KEQ[i+1]=Keq;

Rr1=(kc1 Keb (y0 P-(y1 y2  P^2)/Keq )*1000)/(1+Keb y0 P+Kst y1 P+Kh2 y2 P)^2;
r1=Rr1;
r1[i+1]=r1;
Rr2=(kc2 Keb y0 P 1000)/(1+Keb y0 P+Kst y1 P+Kh2 y2 P)^2;
r2=Rr2;
r2[i+1]=r2;
Rr3=(kc3 Keb y0 P Kh2 y2 P 1000)/(1+Keb y0 P+Kst y1 P+Kh2 y2 P)^2;
r3=Rr3;
r3[i+1]=r3;
Rr4=(kc4 Kst y1 P Kh2 y2 P 1000)/(1+Keb y0 P+Kst y1 P+Kh2 y2 P)^2;
r4=Rr4;
r4[i+1]=r4;
,  nn];
```

Layout of the Graphics 2;

Graphics of Concentration;

```
CEthylbenzene2=Table[fx0[a],{a,nn+1,i}];CStyrene2=Table[fx1[a],{a,nn+1,i}];CHydrogen2=Table[fx2[a],{a,nn+1,i}];CBenzene2=Table[fx3[a],{a,nn+1,i}];CEthylene2=Table[fx4[a],{a,nn+1,i}];CToluene2=Table[fx5[a],{a,nn+1,i}];CMethane2=Table[fx6[a],{a,nn+1,i}];
Concentrations2=Join[{CEthylbenzene2,CStyrene2,CHydrogen2,CBenzene2,CEthylene2,CToluene2,CMethane2}];
ListPlot[Concentrations2]
```

Graphic of Temperature;

```
Temperature2=Table[fT[a],{a,nn+1,i}];
ListPlot[Temperature2]
```

Graphics of reactions rate;

```
Reaction12=Table[r1[a],{a,nn+1,i}];
Reaction22=Table[r2[a],{a,nn+1,i}];Reaction32=Table[r3[a],{a,nn+1,i}];
Reaction42=Table[r4[a],{a,nn+1,i}];
Reactions2=Join[{Reaction12,Reaction22,Reaction32,Reaction42}];
Reactionss2=Join[{Reaction22,Reaction32,Reaction42}];
ListPlot[Reactions2]
ListPlot[Reactionss2]
```

Graphics of reactions rate constants;

```
RRConstant12=Table[kc1[a],{a,nn+1,i}];RRConstant22=Table[kc2[a],{a,nn+1,i}];RRConstant32=Table[kc3[a],{a,nn+1,i}];RRConstant42=Table[kc4[a],{a,nn+1,i}];
RRConstants2=Join[{RRConstant12,RRConstant22,RRConstant32,RRConstant42}];
ListPlot[RRConstants2]
```

Graphics of adsorption equilibrium constants and reaction equilibrium;

```
AECEthylbenzene2=Table[KEB[a],{a,nn+1,i}];AECStyrene2=Table[KST[a],{a,nn+1,i}];AECHydrogen2=Table[KH2[a],{a,nn+1,i}]; ReactionEquilibrium2=Table[KEQ[a],{a,nn+1,i}];
AEConstants2=Join[{AECEthylbenzene2,AECStyrene2,AECHydrogen2}];
ListPlot[AEConstants2]
ListPlot[ReactionEquilibrium2]
```

DISPERSION MODEL WITH NON-CONSTANT PHYSICAL PARAMETERS

Quit[];

Initial conditions of the fluid and reactor

P=0.501; (*Bar*) u=43200; ui=43200; (*m/h*) T1=893.15; (*K*) L=5; (*m*)
x0=0.963;x1=0;x2=0;x3=0;x4=0;x5=0;x6=0;x7=5.777; (*mol/m^3*)
ϵ=0.4312;(*Subscript[m, b]^3/Subscript[m, r]^3*)ρ=1442; (*(kg cat)/m^3*)
dp=0.0055;
nn=50000;
h=N[L/nn];

Physical Properties of the fluid

y_1=x0/(x7+x0+x1+x2+x3+x4+x5+x6);
y_2=x7/(x7+x0+x1+x2+x3+x4+x5+x6);
y_3=x1/(x7+x0+x1+x2+x3+x4+x5+x6);
y_4=x2/(x7+x0+x1+x2+x3+x4+x5+x6);
y_5=x3/(x7+x0+x1+x2+x3+x4+x5+x6);
y_6=x4/(x7+x0+x1+x2+x3+x4+x5+x6);
y_7=x5/(x7+x0+x1+x2+x3+x4+x5+x6);
y_8=x6/(x7+x0+x1+x2+x3+x4+x5+x6);
R=0.08206 1.013/1000;
ru=8.314;
Mm_{eb}=106.17; Mm_{w}=18; Mm_{st}=104.15; Mm_{h2}=2;Mm_{be}=78.11; Mm_{et}=28.05; Mm_{to}=92.14;Mm_{me}=16.04; (*g/mol*)
M_1=Mm_{eb};M_2=Mm_{w};M_3=Mm_{st};M_4=Mm_{h2};M_5=Mm_{be};M_6=Mm_{et};M_7=Mm_{to};M_8=Mm_{me};
T_{eb}=409.15; T_{w}=373.15; T_{st}=418.15; T_{h2}=20.27; T_{be}= 353.25; T_{et}=169.5; T_{to}= 384.00; T_{me}=111.65;
Tb_1=T_{eb}; Tb_2=T_{w}; Tb_3=T_{st}; Tb_4=T_{h2}; Tb_5=T_{be}; Tb_6=T_{et}; Tb_7=T_{to}; Tb_8=T_{me};
V_{eb}=139.24; V_{w}=18.789; V_{st}=131.27; V_{h2}=28.16; V_{be}= 96.017; V_{et}=49.29; V_{to}= 118.29; V_{me}=35.64;
Vm_1=V_{eb}; Vm_2=V_{w}; Vm_3=V_{st}; Vm_4=V_{h2}; Vm_5=V_{be}; Vm_6=V_{et}; Vm_7=V_{to}; Vm_8=V_{me};
D_{eb}=0.58; D_{w}=1.8546; D_{st}=0.13; D_{h2}=0; D_{be}=0; D_{et}=0; D_{to}=0.36; D_{me}=0;
Dp_1=D_{eb};Dp_2=D_{w}; Dp_3=D_{st};Dp_4=D_{h2};Dp_5=D_{be};Dp_6=D_{et};Dp_7=D_{to};Dp_8=D_{me};
Da_{eb}:= 8*15.9+10*2.31; Da_{w}:=4.54+2*2.31; Da_{st}:=8*15.9+8*2.31;Da_{h2}:=2*2.31;
da_1=Da_{eb};da_2=Da_{w};da_3=Da_{st};da_4=Da_{h2};
aa=1; bb=0; cc=1; dd=1;
ζa:=(cc+dd-aa-bb)/aa;
j=0;
Do[i=1;j=j+1;
  $Mj_{i,j}$=2 (1/Subscript[M, i]+1/Subscript[M, j])$^{-1}$,4];
i=0;
Do[i=i+1;

δ_i=(1940 Subscript[Dp, i]^2)/(Vm$_i$ Tb$_i$); σ_i=((1.585 Subscript[Vm, i])/(1+1.3 Subscript[δ, i]^2))$^{1/3}$; ϵκ$_i$=1.18 (1+1.3 Subscript[δ, i]^2) Tb$_i$; $\Omega_{V,i}$=(1.16145 (T1/Subscript[ϵκ, i])$^{-0.14874}$)+0.52487 (Exp[-0.77320 (T1/ϵκ$_i$)])+2.16178 (Exp[-2.43787 (T1/ϵκ$_i$)]);

μ_i=(2.6709 10^{-6}) $\sqrt{M_i\ T1}$ /(Subscript[σ, i]^2 $\Omega_{V,i}$),8];

i=0;

j=0;

Do[i=i+1;

$\Phi_{i,i}$=1;

Do[j=j+1;

$\Phi_{i\_,j\_}$:=1/ $\sqrt{8}$ (1+Subscript[M, i]/Subscript[M, j])$^{-0.5}$ (1+(Subscript[μ, i]/Subscript[μ, j])^0.5 (Subscript[M, j]/Subscript[M, i])^0.25)^2,8],8];

$\mu_m=\sum_{i=1}^{4}\left(\frac{y_i\ \mu_i}{\sum_{j=1}^{4} y_j\ \Phi_{i,j}}\right)$;

x=0;

Do[x=x+1; ρ_x= (P M$_x$/1000)/(R T1),8];

Density= $\sum_{i=1}^{4} \rho_i\ y_i$;

MM= $\sum_{i=1}^{4} M_i\ y_i$/1000;

G=(u Density)/MM;

jj=1;j=1;

Do[j=j+1;

$D_{jj,j}$=(0.00143T1$^{1.75}$)/(P Mj$_{jj,j}$ ($da_{jj}^{\frac{1}{3}}+da_j^{\frac{1}{3}}$)^2); ,4];

D$_m$=0.36/(1/(1+y$_1$) (1/D$_{1,2}$ (y$_2$)+1/D$_{1,3}$ (y$_3$+y$_1$)+1/D$_{1,4}$ (y$_4$+y$_1$)));

d=D$_m$;

MmM=((u ρm dp)/μ$_m$) (μ$_m$/(ρm d));

Deff= u dp (0.7/MmM+4/(1+MmM 5.1))

Cp$_1$=(8) (1/2) ((8.314/1000) /(M$_1$/1000));

Cp$_2$=(143.05-183.54 (T1/100)$^{0.25}$+82.751 (T1/100)$^{0.5}$-3.6989 (T1/100)^1)/1000;

Cp$_3$=(8)*(1/2) ((8.314/1000) /(M$_3$/1000));

Cp$_4$=(56.505-702.24 (T1/100)$^{-0.75}$+1165.0 (T1/100)$^{-1}$-560.70 (T1/100)$^{-1.5}$)/1000;

Cp$_m$ = Cp$_1$ y$_1$+Cp$_2$ y$_2$+Cp$_3$ y$_3$+Cp$_4$ y$_4$

Cpm=Cp$_m$;

k$_1$=8.3127*10^{-2} $\sqrt{\frac{T1}{M_1}}$ /(Subscript[σ, 1]^2 $\Omega_{V,1}$)+1.32 (Cp$_1$-5/2 8.314/1000/M$_1$) 2.6709*10^{-6} $\sqrt{M_1\ T1}$ /(Subscript[σ, 1]^2 $\Omega_{V,1}$);

k$_2$=8.3127*10^{-2} $\sqrt{\frac{T1}{M_2}}$ /(Subscript[σ, 2]^2 $\Omega_{V,2}$)+1.32 (Cp$_2$-5/2 8.314/1000/M$_2$) 2.6709*10^{-6} $\sqrt{M_2\ T1}$ /(Subscript[σ, 2]^2 $\Omega_{V,1}$);

k_3=8.3127*10^{-2} $\sqrt{\frac{T1}{M_3}}$ /(Subscript[σ, 3]^2 $\Omega_{V,3}$)+1.32 (Cp_3-5/2 8.314/1000/M_3) 2.6709*10^{-6} $\sqrt{M_3\ T1}$ /(Subscript[σ, 3]^2 $\Omega_{V,3}$);

k_4=8.3127*10^{-2} $\sqrt{\frac{T1}{M_4}}$ /(Subscript[σ, 4]^2 $\Omega_{V,4}$)+1.32 (Cp_4-5/2 8.314/1000/M_4) 2.6709*10^{-6} $\sqrt{M_4\ T1}$ /(Subscript[σ, 4]^2 $\Omega_{V,4}$);

k_m=(y_1 k_1)/(y_1 $\Phi_{1,1}$+y_2 $\Phi_{1,2}$+y_3 $\Phi_{1,3}$+y_4 $\Phi_{1,4}$)+(y_2 k_2)/(y_1 $\Phi_{2,1}$+y_2 $\Phi_{2,2}$+y_3 $\Phi_{2,3}$+y_4 $\Phi_{2,4}$)+(y_3 k_3)/(y_1 $\Phi_{3,1}$+y_2 $\Phi_{3,2}$+y_3 $\Phi_{3,3}$+y_4 $\Phi_{3,4}$)+(y_4 k_4)/(y_1 $\Phi_{4,1}$+y_2 $\Phi_{4,2}$+y_3 $\Phi_{4,3}$+y_4 $\Phi_{4,4}$)

km=k_m;

Initial conditions of the reactions and values of the rate constants and adsorption equilibrium constants

ΔH^*$_1$=117.690;ΔH^*$_2$=105.510;ΔH^*$_3$=-54.680;ΔH^*$_4$=-172.370; (*kJ/mol*)

Ea1=175.38; Ea2=296.29;Ea3=474.76; Ea4=213.78; (*kJ/mol*)

A1=5.594*10^9; A2=1.060*10^{15}; A3=1.246*10^{26}; A4=8.024*10^{10}; (*kmol/(kg cat·h)*)

ΔHeb=-102.22; ΔHst=-104.56;ΔHh2=-117.95; (*kJ/mol*)

Aeb=1.014*10^{-5}; Ast=2.678*10^{-5};Ah2=4.519*10^{-7}; (*1/Bar*)

kc1= A1 Exp[-Ea1/(ru/1000 T1)];kc2= A2 Exp[-Ea2/(ru/1000 T1)];kc3= A3 Exp[-Ea3/(ru/1000 T1)];kc4= A4 Exp[-Ea4/(ru/1000 T1)];

Keb=Aeb Exp[-ΔHeb/(ru/1000 T1)] ; Kst=Ast Exp[-ΔHst/(ru/1000 T1)];Kh2=Ah2 Exp[-ΔHh2/(ru/1000 T1)];

Keq=0.027*Exp[0.021 (T1-773)];

Rr1=(kc1 Keb (y_1 P-(y_3 y_4 P^2)/Keq)*1000)/(1+Keb Subscript[y, 1] P+Kst Subscript[y, 3] P+Kh2 Subscript[y, 4] P)^2

r1=Rr1;

Rr2=(kc2 Keb y_1 P 1000)/(1+Keb Subscript[y, 1] P+Kst Subscript[y, 3] P+Kh2 Subscript[y, 4] P)^2

r2=Rr2;

Rr3=(kc3 Keb y_1 P Kh2 y_4 P 1000)/(1+Keb Subscript[y, 1] P+Kst Subscript[y, 3] P+Kh2 Subscript[y, 4] P)^2

r3=Rr3;

Rr4=(kc4 Kst y_3 P Kh2 y_4 P 1000)/(1+Keb Subscript[y, 1] P+Kst Subscript[y, 3] P+Kh2 Subscript[y, 4] P)^2

r4=Rr4;

i=0;

Do[i=i+1;

xx0=(Deff ρ(-r1-r2-r3)(1-ϵ))/(ϵ u^2) (Exp[-u/Deff L]-Exp[u/Deff (h-L)])+(ρ(-r1-r2-r3)(1-ϵ))/(ϵ u) h+x0;

x0=xx0;

```
 fx0[i+1]=xx0;
 xx1=(Deff  ρ(r1-r4)(1-ϵ) )/(ϵ u^2) (Exp[-u/Deff L]-Exp[u/Deff (h-L)])+(ρ(r1-r4)(1-ϵ))/(ϵ u) h+x1;
 x1=xx1;
 fx1[i+1]=xx1;
 xx2=(Deff  ρ(r1-r3-2r4)(1-ϵ) )/(ϵ u^2) (Exp[-u/Deff L]-Exp[u/Deff (h-L)])+(ρ(r1-r3-2r4)(1-ϵ))/(ϵ u)
h+x2;
 x2=xx2;
 fx2[i+1]=xx2;
 xx3=(Deff  ρ(r2)(1-ϵ) )/(ϵ u^2) (Exp[-u/Deff L]-Exp[u/Deff (h-L)])+(ρ(r2)(1-ϵ))/(ϵ u) h+x3;
 x3=xx3;
 fx3[i+1]=xx3;
 xx4=(Deff  ρ(r2)(1-ϵ) )/(ϵ u^2) (Exp[-u/Deff L]-Exp[u/Deff (h-L)])+(ρ(r2)(1-ϵ))/(ϵ u) h+x4;
 x4=xx4;
 fx4[i+1]=xx4;
 xx5=(Deff  ρ(r3+r4)(1-ϵ) )/(ϵ u^2) (Exp[-u/Deff L]-Exp[u/Deff (h-L)])+(ρ(r3+r4)(1-ϵ))/(ϵ u) h+x5;
 x5=xx5;
 fx5[i+1]=xx5;
 xx6=(Deff  ρ(r3+r4)(1-ϵ) )/(ϵ u^2) (Exp[-u/Deff L]-Exp[u/Deff (h-L)])+(ρ(r3+r4)(1-ϵ))/(ϵ u) h+x6;
 x6=xx6;
 fx6[i+1]=xx6;
 xx7=x7;
 Ct=xx0+xx1+xx2+xx3+xx4+xx5+xx6+xx7;
 TT=(km  ρ (r1 ΔH^*_1+r2 ΔH^*_2+r3 ΔH^*_3+r4 ΔH^*_4) )/(G Cpm)^2 (-Exp[(-G Cpm)/km L]+Exp[(G
Cpm)/km (h-L)])-(ρ (r1 ΔH^*_1+r2 ΔH^*_2+r3 ΔH^*_3+r4 ΔH^*_4))/(G Cpm ) h+T1;
 T1=TT;
 fT[i+1]=TT;

 y0=x0 /(x0+x1+x2+x3+x4+x5+x6+x7);
 yy0[i+1]=y0;
 y1=x1 /(x0+x1+x2+x3+x4+x5+x6+x7);
 yy1[i+1]=y1;
 y2=x2 /(x0+x1+x2+x3+x4+x5+x6+x7);
 yy2[i+1]=y2;
 y3=x3/(x0+x1+x2+x3+x4+x5+x6+x7);
 yy3[i+1]=y3;
 y4=x4/(x0+x1+x2+x3+x4+x5+x6+x7);
 yy4[i+1]=y4;
 y5=x5/(x0+x1+x2+x3+x4+x5+x6+x7);
 yy5[i+1]=y5;
 y6=x6/(x0+x1+x2+x3+x4+x5+x6+x7);
 yy6[i+1]=y6;
 y7=x7/(x0+x1+x2+x3+x4+x5+x6+x7);
 yy7[i+1]=y7;
```

kc1= A1 Exp[-Ea1/(ru/1000 T1)];kc2= A2 Exp[-Ea2/(ru/1000 T1)];kc3= A3 Exp[-Ea3/(ru/1000 T1)];kc4= A4 Exp[-Ea4/(ru/1000 T1)];

kc$_1$[i+1]=kc1;kc$_2$[i+1]=kc2;kc$_3$[i+1]=kc3;kc$_4$[i+1]=kc4;

Keb=Aeb Exp[-ΔHeb/(ru/1000 T1)] ; Kst=Ast Exp[-ΔHst/(ru/1000 T1)];Kh2=Ah2 Exp[-ΔHh2/(ru/1000 T1)];

K$_{EB}$[i+1]=Keb;K$_{ST}$[i+1]=Kst;K$_{H2}$[i+1]=Kh2;

Keq=0.027*Exp[0.021 (T1-773)];

K$_{EQ}$[i+1]=Keq;

$\Omega_{V,1}$=(1.16145 (T1/Subscript[ϵκ, 1])$^{-0.14874}$)+0.52487 (Exp[-0.77320 (T1/ϵκ$_1$)])+2.16178 (Exp[-2.43787 (T1/ϵκ$_1$)]);μ$_1$=(2.6709 10^{-6}) $\sqrt{M_1\ T1}$ /(Subscript[σ, 1]^2 $\Omega_{V,1}$) ;

$\Omega_{V,2}$=(1.16145 (T1/Subscript[ϵκ, 3])$^{-0.14874}$)+0.52487 (Exp[-0.77320 (T1/ϵκ$_2$)])+2.16178 (Exp[-2.43787 (T1/ϵκ$_2$)]);μ$_2$=(2.6709 10^{-6}) $\sqrt{M_2\ T1}$ /(Subscript[σ, 2]^2 $\Omega_{V,2}$) ;

$\Omega_{V,3}$=(1.16145 (T1/Subscript[ϵκ, 3])$^{-0.14874}$)+0.52487 (Exp[-0.77320 (T1/ϵκ$_3$)])+2.16178 (Exp[-2.43787 (T1/ϵκ$_3$)]);μ$_3$=(2.6709 10^{-6}) $\sqrt{M_3\ T1}$ /(Subscript[σ, 3]^2 $\Omega_{V,3}$) ;

$\Omega_{V,4}$=(1.16145 (T1/Subscript[ϵκ, 4])$^{-0.14874}$)+0.52487 (Exp[-0.77320 (T1/ϵκ$_4$)])+2.16178 (Exp[-2.43787 (T1/ϵκ$_4$)]);μ$_4$=(2.6709 10^{-6}) $\sqrt{M_4\ T1}$ /(Subscript[σ, 4]^2 $\Omega_{V,4}$) ;

Φ[1,1]=1;

Φ[1,2]=1/$\sqrt{8}$ (1+Subscript[M, 1]/Subscript[M, 2])$^{-0.5}$ (1+(Subscript[μ, 1]/Subscript[μ, 2])^0.5 (Subscript[M, 2]/Subscript[M, 1])^0.25)^2; Φ[1,3]=1/$\sqrt{8}$ (1+Subscript[M, 1]/Subscript[M, 3])$^{-0.5}$ (1+(Subscript[μ, 1]/Subscript[μ, 3])^0.5 (Subscript[M, 3]/Subscript[M, 1])^0.25)^2; Φ[1,4]=1/$\sqrt{8}$ (1+Subscript[M, 1]/Subscript[M, 4])$^{-0.5}$ (1+(Subscript[μ, 1]/Subscript[μ, 4])^0.5 (Subscript[M, 4]/Subscript[M, 1])^0.25)^2;

Φ[2,1]=1/$\sqrt{8}$ (1+Subscript[M, 2]/Subscript[M, 1])$^{-0.5}$ (1+(Subscript[μ, 2]/Subscript[μ, 1])^0.5 (Subscript[M, 1]/Subscript[M, 2])^0.25)^2; Φ[2,2]=1; Φ[2,3]=1/$\sqrt{8}$ (1+Subscript[M, 2]/Subscript[M, 3])$^{-0.5}$ (1+(Subscript[μ, 2]/Subscript[μ, 3])^0.5 (Subscript[M, 3]/Subscript[M, 2])^0.25)^2; Φ[2,4]=1/$\sqrt{8}$ (1+Subscript[M, 2]/Subscript[M, 4])$^{-0.5}$ (1+(Subscript[μ, 2]/Subscript[μ, 4])^0.5 (Subscript[M, 4]/Subscript[M, 2])^0.25)^2;

Φ[3,1]=1/$\sqrt{8}$ (1+Subscript[M, 3]/Subscript[M, 1])$^{-0.5}$ (1+(Subscript[μ, 3]/Subscript[μ, 1])^0.5 (Subscript[M, 1]/Subscript[M, 3])^0.25)^2; Φ[3,2]=1/$\sqrt{8}$ (1+Subscript[M, 3]/Subscript[M, 2])$^{-0.5}$ (1+(Subscript[μ, 3]/Subscript[μ, 2])^0.5 (Subscript[M, 2]/Subscript[M, 3])^0.25)^2; Φ[3,3]=1; Φ[3,4]=1/$\sqrt{8}$ (1+Subscript[M, 3]/Subscript[M, 4])$^{-0.5}$ (1+(Subscript[μ, 3]/Subscript[μ, 4])^0.5 (Subscript[M, 4]/Subscript[M, 3])^0.25)^2;

Φ[4,1]=1/$\sqrt{8}$ (1+Subscript[M, 4]/Subscript[M, 1])$^{-0.5}$ (1+(Subscript[μ, 4]/Subscript[μ, 1])^0.5 (Subscript[M, 1]/Subscript[M, 4])^0.25)^2;Φ[4,2]=1/$\sqrt{8}$ (1+Subscript[M, 4]/Subscript[M, 2])$^{-0.5}$ (1+(Subscript[μ, 4]/Subscript[μ, 2])^0.5 (Subscript[M, 2]/Subscript[M, 4])^0.25)^2; Φ[4,3]=1/$\sqrt{8}$ (1+Subscript[M, 4]/Subscript[M, 3])$^{-0.5}$ (1+(Subscript[μ, 4]/Subscript[μ, 3])^0.5 (Subscript[M, 3]/Subscript[M, 4])^0.25)^2; Φ[4,4]=1;

```
 μm=(y0  μ1)/(y0  Φ[1,1]+y7  Φ[1,2]+y1  Φ[1,3]+y2  Φ[1,4])+(y7  μ2)/(y0  Φ[2,1]+y7  Φ[2,2]+y1
Φ[2,3]+y2  Φ[2,4])+(y1  μ3)/(y0  Φ[3,1]+y7  Φ[3,2]+y1  Φ[3,3]+y2  Φ[3,4])+(y2  μ4)/(y0  Φ[4,1]+y7
Φ[4,2]+y2 Φ[4,3]+y3 Φ[4,4]); (*Pa·s*)
 MM=(M1y0+M2y7+M3y1+M4y2+M5y3+M6y4+M7y5+M8y6)/1000;

 Pp[i]=P;
 Pp[i+1]=Ct R T1;
 Pn=100;

 If[Pp[i+1]!=Pn,
   ρm= (Pp[i+1] MM)/(R T1);
  ux=(Density ui/3600)/ ρm;
  Pn=-((ux  ρm)/( ρm dp))((1-ϵ)/ϵ3) ((150 (1-ϵ)μm )/dp+1.75 ux  ρm) h/10^5+P; ];
 u=ux 3600;
 v[i+1]=u;
 P=Pp[i+1];
 ρm= (Pp[i+1] MM)/(R T1);

 Rr1=(kc1 Keb (y0 P-(y1 y2  P^2)/Keq )*1000)/(1+Keb y0 P+Kst y1 P+Kh2 y2 P)^2;
 r1=Rr1;
 r1[i+1]=r1;
 Rr2=(kc2 Keb y0 P 1000)/(1+Keb y0 P+Kst y1 P+Kh2 y2 P)^2;
 r2=Rr2;
 r2[i+1]=r2;
 Rr3=(kc3 Keb y0 P Kh2 y2 P 1000)/(1+Keb y0 P+Kst y1 P+Kh2 y2 P)^2;
 r3=Rr3;
 r3[i+1]=r3;
 Rr4=(kc4 Kst y1 P Kh2 y2 P 1000)/(1+Keb y0 P+Kst y1 P+Kh2 y2 P)^2;
 r4=Rr4;
 r4[i+1]=r4;
 G=(u ρm)/MM;

 jj=1;j=1;
 Do[j=j+1;

  Djj,j=(0.00143T1^1.75)/(P  Mjjj,j (dajj^(1/3) +daj^(1/3) )^2); ,4];
 Dm=0.36/(1/(1+y0) (1/D1,2  (y7)+1/D1,3 (y1+y0)+1/D1,4 (y2+y0)));
 d=Dm;
 MmM=((u ρm dp )/μm) (μm/(ρm d));
 Deff= u dp (0.7/MmM+4/(1+MmM 5.1));
 DD[i+1]=Deff;

 Cp1=(8) (1/2) ((8.314/1000) /(M1/1000));
 Cp2=(143.05-183.54 (T1/100)^0.25+82.751 (T1/100)^0.5-3.6989 (T1/100)^1)/1000;
 Cp3=(8)*(1/2) ((8.314/1000) /(M3/1000) );
```

Cp_4=(56.505-702.24 (T1/100)$^{-0.75}$+1165.0 (T1/100)$^{-1}$-560.70 (T1/100)$^{-1.5}$)/1000;
Cp_m = Cp_1 y0+Cp_2 y7+Cp_3 y1+Cp_4 y2;
Cpm=Cp_m;
CCP[i+1]=Cpm;

$k_1=8.3127*10^{-2}\sqrt{\frac{T1}{\frac{M_1}{1000}}}$ /(Subscript[σ, 1]^2 $\Omega_{V,1}$)+1.32 (Cp_1-5/2 8.314/1000/(M_1/1000)) 2.6709*$10^{-6}\sqrt{\frac{M_1}{1000}T1}$ /(Subscript[σ, 1]^2 $\Omega_{V,1}$);

$k_2=8.3127*10^{-2}\sqrt{\frac{T1}{\frac{M_2}{1000}}}$ /(Subscript[σ, 2]^2 $\Omega_{V,2}$)+1.32 (Cp_2-5/2 8.314/1000/(M_2/1000)) 2.6709*$10^{-6}\sqrt{\frac{M_2}{1000}T1}$ /(Subscript[σ, 2]^2 $\Omega_{V,1}$);

$k_3=8.3127*10^{-2}\sqrt{\frac{T1}{\frac{M_3}{1000}}}$ /(Subscript[σ, 3]^2 $\Omega_{V,3}$)+1.32 (Cp_3-5/2 8.314/1000/(M_3/1000)) 2.6709*$10^{-6}\sqrt{\frac{M_3}{1000}T1}$ /(Subscript[σ, 3]^2 $\Omega_{V,3}$);

$k_4=8.3127*10^{-2}\sqrt{\frac{T1}{\frac{M_4}{1000}}}$ /(Subscript[σ, 4]^2 $\Omega_{V,4}$)+1.32 (Cp_4-5/2 8.314/1000/(M_4/1000)) 2.6709*$10^{-6}\sqrt{\frac{M_4}{1000}T1}$ /(Subscript[σ, 4]^2 $\Omega_{V,4}$);

k_m=(y0 k_1)/(y0 Φ[1,1]+y7 Φ[1,2]+y1 Φ[1,3]+y2 Φ[1,4])+(y7 k_2)/(y0 Φ[2,1]+y7 Φ[2,2]+y1 Φ[2,3]+y2 Φ[2,4])+(y1 k_3)/(y0 Φ[3,1]+y7 Φ[3,2]+y1 Φ[3,3]+y2 Φ[3,4])+(y2 k_4)/(y0 Φ[4,1]+y7 Φ[4,2]+y2 Φ[4,3]+y3 Φ[4,4]);
km=k_m;
kkm[i+1]=km;
q[i+1]=v[i+1] Pi 0.75^2;,50000];

Layout of the Graphics 1;

Graphics of Concentration;

CEthylbenzene=Table[fx0[a],{a,1,i}];
CStyrene=Table[fx1[a],{a,1,i}];CHydrogen=Table[fx2[a],{a,1,i}];CBenzene=Table[fx3[a],{a,1,i}];CEthylene=Table[fx4[a],{a,1,i}];CToluene=Table[fx5[a],{a,1,i}];CMethane=Table[fx6[a],{a,1,i}];
Concentrations=Join[{CEthylbenzene,CStyrene,CHydrogen,CBenzene,CEthylene,CToluene,CMethane}];

Graphic of temperature and physical parameters;

```
Temperature=Table[fT[a],{a,1,i}];
Pressure=Table[Pp[a],{a,1,i}];
Vflow=Table[q[a],{a,1,i}];
Velocity=Table[v[a]/3600,{a,1,i}];
CDifusion=Table[DD[a],{a,1,i}];
SHeat=Table[CCP[a],{a,1,i}];
TConduct= Table[kkm[a],{a,1,i}];
```

Graphics of reactions rate;

```
Reaction1=Table[r1[a],{a,0,i}];Reaction2=Table[r2[a],{a,0,i}];Reaction3=Table[r3[a],{a,0,i}];
Reaction4=Table[r4[a],{a,0,i}];
Reactions=Join[{Reaction1,Reaction2,Reaction3,Reaction4}];
Reactionss=Join[{Reaction2,Reaction3,Reaction4}];
```

Graphics of reactions rate constants;

```
RRConstant1=Table[kc1[a],{a,0,i}];RRConstant2=Table[kc2[a],{a,0,i}];RRConstant3=Table[kc3[a]
,{a,0,i}];RRConstant4=Table[kc4[a],{a,0,i}];
RRConstants=Join[{RRConstant1,RRConstant2,RRConstant3,RRConstant4}];
```

Graphics of adsorption equilibrium constants and reaction equilibrium;

```
AECEthylbenzene=Table[KEB[a],{a,0,i}];AECStyrene=Table[KST[a],{a,0,i}];AECHydrogen=Table[
KH2[a],{a,0,i}]; ReactionEquilibrium=Table[KEQ[a],{a,0,i}];
AEConstants=Join[{AECEthylbenzene,AECStyrene,AECHydrogen}];
```

Plotting graphics;

```
ListPlot[Concentrations,AxesLabel->{"Reactor's length (m·10^5)","Concentration
(mol/m^3)"},PlotLegends-
>{"Ethylbenzene","Styrene","Hydrogen","Benzene","Ethylene","Toluene","Methane"},PlotRange-
>{{0,nn},{0,1}}]
ListPlot[Temperature,AxesLabel->{"Reactor's length (m·10^5)","Temperature (K)"},PlotRange-
>{{0,nn},{750,900}}]
ListPlot[Pressure]
ListPlot[Vflow]
ListPlot[Velocity]
ListPlot[CDifusion]
ListPlot[SHeat]
ListPlot[TConduct]
ListPlot[Reactions,AxesLabel->{"Reactor's length (m·10^5)","Reaction rate (mol/(kg
cat·h))"},PlotLegends->{"r1","r2","r3","r4"}]
ListPlot[Reaction1,AxesLabel->{"Reactor's length (m·10^5)","Reaction rate 1 (mol/(kg
cat·h))"},PlotRange->{{0,nn},{0,75}}]
ListPlot[Reactionss,AxesLabel->{"Reactor's length (m·10^5)","Reaction rate (mol/(kg
cat·h))"},PlotLegends->{"r2","r3","r4"}]
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ListPlot[RRConstants,AxesLabel->{"Reactor's length (m·10^5)","Reaction rate constant (mol/(kg cat·h))"},PlotLegends->{"k_1","k_2","k_3","k_4"}]
ListPlot[AEConstants,AxesLabel->{"Reactor's length (m·10^5)","Adsorption equilibrium constant (1/Bar)"},PlotLegends->{"K_{EB}","K_{ST}","K_{H2}"}]
ListPlot[ReactionEquilibrium,AxesLabel->{"Reactor's length (m·10^5)","reaction equilibrium constant (-)"},PlotRange->{{0,nn},{0,0.4}}]

Heat exchange step;

Clear[T1,P,u,L];
L=5;
T1=893.15;
P=0.501;
u=43200;
kc1= A1 Exp[-Ea1/(ru/1000 T1)];kc2= A2 Exp[-Ea2/(ru/1000 T1)];kc3= A3 Exp[-Ea3/(ru/1000 T1)];kc4= A4 Exp[-Ea4/(ru/1000 T1)];
kc_1[i+1]=kc1;kc_2[i+1]=kc2;kc_3[i+1]=kc3;kc_4[i+1]=kc4;
Keb=Aeb Exp[-ΔHeb/(ru/1000 T1)] ; Kst=Ast Exp[-ΔHst/(ru/1000 T1)];Kh2=Ah2 Exp[-ΔHh2/(ru/1000 T1)];
K_{EB}[i+1]=Keb;K_{ST}[i+1]=Kst;K_{H2}[i+1]=Kh2;
Keq=0.027*Exp[0.021 (T1-773)];
K_{EQ}[i+1]=Keq;

Rr1=(kc1 Keb (y0 P-(y1 y2 P^2)/Keq)*1000)/$(1+\text{Keb y0 P+Kst y1 P+Kh2 y2 P})^2$;
r1=Rr1;
r_1[i+1]=r1;
Rr2=(kc2 Keb y0 P 1000)/$(1+\text{Keb y0 P+Kst y1 P+Kh2 y2 P})^2$;
r2=Rr2;
r_2[i+1]=r2;
Rr3=(kc3 Keb y0 P Kh2 y2 P 1000)/$(1+\text{Keb y0 P+Kst y1 P+Kh2 y2 P})^2$;
r3=Rr3;
r_3[i+1]=r3;
Rr4=(kc4 Kst y1 P Kh2 y2 P 1000)/$(1+\text{Keb y0 P+Kst y1 P+Kh2 y2 P})^2$;
r4=Rr4;
r_4[i+1]=r4;

$\Omega_{V,1}$=(1.16145 $(\text{T1/Subscript}[\epsilon\kappa, 1])^{-0.14874}$)+0.52487 (Exp[-0.77320 (T1/$\epsilon\kappa_1$)])+2.16178 (Exp[-2.43787 (T1/$\epsilon\kappa_1$)]);μ_1=(2.6709 10^{-6}) $\sqrt{M_1\ T1}$ /(Subscript[σ, 1]^2 $\Omega_{V,1}$) ;
$\Omega_{V,2}$=(1.16145 $(\text{T1/Subscript}[\epsilon\kappa, 3])^{-0.14874}$)+0.52487 (Exp[-0.77320 (T1/$\epsilon\kappa_2$)])+2.16178 (Exp[-2.43787 (T1/$\epsilon\kappa_2$)]);μ_2=(2.6709 10^{-6}) $\sqrt{M_2\ T1}$ /(Subscript[σ, 2]^2 $\Omega_{V,2}$) ;
$\Omega_{V,3}$=(1.16145 $(\text{T1/Subscript}[\epsilon\kappa, 3])^{-0.14874}$)+0.52487 (Exp[-0.77320 (T1/$\epsilon\kappa_3$)])+2.16178 (Exp[-2.43787 (T1/$\epsilon\kappa_3$)]);μ_3=(2.6709 10^{-6}) $\sqrt{M_3\ T1}$ /(Subscript[σ, 3]^2 $\Omega_{V,3}$) ;

$\Omega_{V,4}$=(1.16145 (T1/Subscript[ϵκ, 4])$^{-0.14874}$)+0.52487 (Exp[-0.77320 (T1/ϵκ_4)])+2.16178 (Exp[-2.43787 (T1/ϵκ_4)]);μ_4=(2.6709 10^{-6}) $\sqrt{M_4\ T1}$ /(Subscript[σ, 4]^2 $\Omega_{V,4}$) ;

Φ[1,1]=1;

Φ[1,2]=1/$\sqrt{8}$ (1+Subscript[M, 1]/Subscript[M, 2])$^{-0.5}$ (1+(Subscript[μ, 1]/Subscript[μ, 2])^0.5 (Subscript[M, 2]/Subscript[M, 1])^0.25)^2; Φ[1,3]=1/$\sqrt{8}$ (1+Subscript[M, 1]/Subscript[M, 3])$^{-0.5}$ (1+(Subscript[μ, 1]/Subscript[μ, 3])^0.5 (Subscript[M, 3]/Subscript[M, 1])^0.25)^2; Φ[1,4]=1/$\sqrt{8}$ (1+Subscript[M, 1]/Subscript[M, 4])$^{-0.5}$ (1+(Subscript[μ, 1]/Subscript[μ, 4])^0.5 (Subscript[M, 4]/Subscript[M, 1])^0.25)^2;

Φ[2,1]=1/$\sqrt{8}$ (1+Subscript[M, 2]/Subscript[M, 1])$^{-0.5}$ (1+(Subscript[μ, 2]/Subscript[μ, 1])^0.5 (Subscript[M, 1]/Subscript[M, 2])^0.25)^2; Φ[2,2]=1; Φ[2,3]=1/$\sqrt{8}$ (1+Subscript[M, 2]/Subscript[M, 3])$^{-0.5}$ (1+(Subscript[μ, 2]/Subscript[μ, 3])^0.5 (Subscript[M, 3]/Subscript[M, 2])^0.25)^2; Φ[2,4]=1/$\sqrt{8}$ (1+Subscript[M, 2]/Subscript[M, 4])$^{-0.5}$ (1+(Subscript[μ, 2]/Subscript[μ, 4])^0.5 (Subscript[M, 4]/Subscript[M, 2])^0.25)^2;

Φ[3,1]=1/$\sqrt{8}$ (1+Subscript[M, 3]/Subscript[M, 1])$^{-0.5}$ (1+(Subscript[μ, 3]/Subscript[μ, 1])^0.5 (Subscript[M, 1]/Subscript[M, 3])^0.25)^2; Φ[3,2]=1/$\sqrt{8}$ (1+Subscript[M, 3]/Subscript[M, 2])$^{-0.5}$ (1+(Subscript[μ, 3]/Subscript[μ, 2])^0.5 (Subscript[M, 2]/Subscript[M, 3])^0.25)^2; Φ[3,3]=1; Φ[3,4]=1/$\sqrt{8}$ (1+Subscript[M, 3]/Subscript[M, 4])$^{-0.5}$ (1+(Subscript[μ, 3]/Subscript[μ, 4])^0.5 (Subscript[M, 4]/Subscript[M, 3])^0.25)^2;

Φ[4,1]=1/$\sqrt{8}$ (1+Subscript[M, 4]/Subscript[M, 1])$^{-0.5}$ (1+(Subscript[μ, 4]/Subscript[μ, 1])^0.5 (Subscript[M, 1]/Subscript[M, 4])^0.25)^2;Φ[4,2]=1/$\sqrt{8}$ (1+Subscript[M, 4]/Subscript[M, 2])$^{-0.5}$ (1+(Subscript[μ, 4]/Subscript[μ, 2])^0.5 (Subscript[M, 2]/Subscript[M, 4])^0.25)^2; Φ[4,3]=1/$\sqrt{8}$ (1+Subscript[M, 4]/Subscript[M, 3])$^{-0.5}$ (1+(Subscript[μ, 4]/Subscript[μ, 3])^0.5 (Subscript[M, 3]/Subscript[M, 4])^0.25)^2; Φ[4,4]=1;

μ_m=(y0 μ_1)/(y0 Φ[1,1]+y7 Φ[1,2]+y1 Φ[1,3]+y2 Φ[1,4])+(y7 μ_2)/(y0 Φ[2,1]+y7 Φ[2,2]+y1 Φ[2,3]+y2 Φ[2,4])+(y1 μ_3)/(y0 Φ[3,1]+y7 Φ[3,2]+y1 Φ[3,3]+y2 Φ[3,4])+(y2 μ_4)/(y0 Φ[4,1]+y7 Φ[4,2]+y2 Φ[4,3]+y3 Φ[4,4]);

MM=(M_1y0+M_2y7+M_3y1+M_4y2+M_5y3+M_6y4+M_7y5+M_8y6)/1000;

Pp[i+1]=P;

ρm= (Pp[i+1] MM)/(R T1);

G=(u ρm)/MM;

jj=1;j=1;

Do[j=j+1;

$D_{jj,j}$=(0.00143T1$^{1.75}$)/(P $Mj_{jj,j}$ ($da_{jj}{}^{\frac{1}{3}}$ +$da_j{}^{\frac{1}{3}}$)^2); ,4];

D_m=0.36/(1/(1+y0) (1/$D_{1,2}$ (y7)+1/$D_{1,3}$ (y1+y0)+1/$D_{1,4}$ (y2+y0)));

d=D_m;

MmM=((u ρm dp)/μ_m) (μ_m/(ρm d));

Deff= u dp (0.7/MmM+4/(1+MmM 5.1));

Cp_1=(8) (1/2) ((8.314/1000) /(M_1/1000));
Cp_2=(143.05-183.54 $(T1/100)^{0.25}$+82.751 $(T1/100)^{0.5}$-3.6989 $(T1/100)^{1}$)/1000;
Cp_3=(8)*(1/2) ((8.314/1000) /(M_3/1000));
Cp_4=(56.505-702.24 $(T1/100)^{-0.75}$+1165.0 $(T1/100)^{-1}$-560.70 $(T1/100)^{-1.5}$)/1000;
Cp_m = Cp_1 y0+Cp_2 y7+Cp_3 y1+Cp_4 y2;
Cpm=Cp_m;

k_1=8.3127*10^{-2} $\sqrt{\frac{T1}{\frac{M_1}{1000}}}$ /(Subscript[σ, 1]^2 $\Omega_{V,1}$)+1.32 (Cp_1-5/2 8.314/1000/(M_1/1000)) 2.6709*10^{-6} $\sqrt{\frac{M_1}{1000}\,T1}$ /(Subscript[σ, 1]^2 $\Omega_{V,1}$);
k_2=8.3127*10^{-2} $\sqrt{\frac{T1}{\frac{M_2}{1000}}}$ /(Subscript[σ, 2]^2 $\Omega_{V,2}$)+1.32 (Cp_2-5/2 8.314/1000/(M_2/1000)) 2.6709*10^{-6} $\sqrt{\frac{M_2}{1000}\,T1}$ /(Subscript[σ, 2]^2 $\Omega_{V,1}$);
k_3=8.3127*10^{-2} $\sqrt{\frac{T1}{\frac{M_3}{1000}}}$ /(Subscript[σ, 3]^2 $\Omega_{V,3}$)+1.32 (Cp_3-5/2 8.314/1000/(M_3/1000)) 2.6709*10^{-6} $\sqrt{\frac{M_3}{1000}\,T1}$ /(Subscript[σ, 3]^2 $\Omega_{V,3}$);
k_4=8.3127*10^{-2} $\sqrt{\frac{T1}{\frac{M_4}{1000}}}$ /(Subscript[σ, 4]^2 $\Omega_{V,4}$)+1.32 (Cp_4-5/2 8.314/1000/(M_4/1000)) 2.6709*10^{-6} $\sqrt{\frac{M_4}{1000}\,T1}$ /(Subscript[σ, 4]^2 $\Omega_{V,4}$);
k_m=(y0 k_1)/(y0 Φ[1,1]+y7 Φ[1,2]+y1 Φ[1,3]+y2 Φ[1,4])+(y7 k_2)/(y0 Φ[2,1]+y7 Φ[2,2]+y1 Φ[2,3]+y2 Φ[2,4])+(y1 k_3)/(y0 Φ[3,1]+y7 Φ[3,2]+y1 Φ[3,3]+y2 Φ[3,4])+(y2 k_4)/(y0 Φ[4,1]+y7 Φ[4,2]+y2 Φ[4,3]+y3 Φ[4,4]);
km=k_m;

Do[i=i+1;
 xx0=(Deff ρ(-r1-r2-r3)(1-ϵ))/(ϵ u^2) (Exp[-u/Deff L]-Exp[u/Deff (h-L)])+(ρ(-r1-r2-r3)(1-ϵ))/(ϵ u) h+x0;
 x0=xx0;
 fx0[i+1]=xx0;
 xx1=(Deff ρ(r1-r4)(1-ϵ))/(ϵ u^2) (Exp[-u/Deff L]-Exp[u/Deff (h-L)])+(ρ(r1-r4)(1-ϵ))/(ϵ u) h+x1;
 x1=xx1;
 fx1[i+1]=xx1;

```
xx2=(Deff  ρ(r1-r3-2r4)(1-ϵ) )/(ϵ u^2) (Exp[-u/Deff L]-Exp[u/Deff (h-L)])+(ρ(r1-r3-2r4)(1-ϵ))/(ϵ u) h+x2;
x2=xx2;
fx2[i+1]=xx2;
xx3=(Deff  ρ(r2)(1-ϵ) )/(ϵ u^2) (Exp[-u/Deff L]-Exp[u/Deff (h-L)])+(ρ(r2)(1-ϵ))/(ϵ u) h+x3;
x3=xx3;
fx3[i+1]=xx3;
xx4=(Deff  ρ(r2)(1-ϵ) )/(ϵ u^2) (Exp[-u/Deff L]-Exp[u/Deff (h-L)])+(ρ(r2)(1-ϵ))/(ϵ u) h+x4;
x4=xx4;
fx4[i+1]=xx4;
xx5=(Deff  ρ(r3+r4)(1-ϵ) )/(ϵ u^2) (Exp[-u/Deff L]-Exp[u/Deff (h-L)])+(ρ(r3+r4)(1-ϵ))/(ϵ u) h+x5;
x5=xx5;
fx5[i+1]=xx5;
xx6=(Deff  ρ(r3+r4)(1-ϵ) )/(ϵ u^2) (Exp[-u/Deff L]-Exp[u/Deff (h-L)])+(ρ(r3+r4)(1-ϵ))/(ϵ u) h+x6;
x6=xx6;
fx6[i+1]=xx6;
xx7=x7;
Ct=xx0+xx1+xx2+xx3+xx4+xx5+xx6+xx7;

TT=(km  ρ (r1 ΔH^*_1+r2 ΔH^*_2+r3 ΔH^*_3+r4 ΔH^*_4) )/(G Cpm)^2 (-Exp[(-G Cpm)/km L]+Exp[(G Cpm)/km (h-L)])-(ρ (r1 ΔH^*_1+r2 ΔH^*_2+r3 ΔH^*_3+r4 ΔH^*_4))/(G Cpm ) h+T1;
T1=TT;
fT[i+1]=TT;

y0=x0 /(x0+x1+x2+x3+x4+x5+x6+x7);
yy0[i+1]=y0;
y1=x1 /(x0+x1+x2+x3+x4+x5+x6+x7);
yy1[i+1]=y1;
y2=x2 /(x0+x1+x2+x3+x4+x5+x6+x7);
yy2[i+1]=y2;
y3=x3/(x0+x1+x2+x3+x4+x5+x6+x7);
yy3[i+1]=y3;
y4=x4/(x0+x1+x2+x3+x4+x5+x6+x7);
yy4[i+1]=y4;
y5=x5/(x0+x1+x2+x3+x4+x5+x6+x7);
yy5[i+1]=y5;
y6=x6/(x0+x1+x2+x3+x4+x5+x6+x7);
yy6[i+1]=y6;
y7=x7/(x0+x1+x2+x3+x4+x5+x6+x7);
yy7[i+1]=y7;

kc1= A1 Exp[-Ea1/(ru/1000 T1)];kc2= A2 Exp[-Ea2/(ru/1000 T1)];kc3= A3 Exp[-Ea3/(ru/1000 T1)];kc4= A4 Exp[-Ea4/(ru/1000 T1)];
kc1[i+1]=kc1;kc2[i+1]=kc2;kc3[i+1]=kc3;kc_4[i+1]=kc4;
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Keb=Aeb Exp[-ΔHeb/(ru/1000 T1)] ; Kst=Ast Exp[-ΔHst/(ru/1000 T1)];Kh2=Ah2 Exp[-ΔHh2/(ru/1000 T1)];
K_{EB}[i+1]=Keb;K_{ST}[i+1]=Kst;K_{H2}[i+1]=Kh2;
Keq=0.027*Exp[0.021 (T1-773)];
K_{EQ}[i+1]=Keq;

$\Omega_{V,1}$=(1.16145 (T1/Subscript[ϵκ, 1])$^{-0.14874}$)+0.52487 (Exp[-0.77320 (T1/$\epsilon\kappa_1$)])+2.16178 (Exp[-2.43787 (T1/$\epsilon\kappa_1$)]);μ_1=(2.6709 10^{-6}) $\sqrt{M_1\ T1}$ /(Subscript[σ, 1]^2 $\Omega_{V,1}$) ;
$\Omega_{V,2}$=(1.16145 (T1/Subscript[ϵκ, 3])$^{-0.14874}$)+0.52487 (Exp[-0.77320 (T1/$\epsilon\kappa_2$)])+2.16178 (Exp[-2.43787 (T1/$\epsilon\kappa_2$)]);μ_2=(2.6709 10^{-6}) $\sqrt{M_2\ T1}$ /(Subscript[σ, 2]^2 $\Omega_{V,2}$) ;
$\Omega_{V,3}$=(1.16145 (T1/Subscript[ϵκ, 3])$^{-0.14874}$)+0.52487 (Exp[-0.77320 (T1/$\epsilon\kappa_3$)])+2.16178 (Exp[-2.43787 (T1/$\epsilon\kappa_3$)]);μ_3=(2.6709 10^{-6}) $\sqrt{M_3\ T1}$ /(Subscript[σ, 3]^2 $\Omega_{V,3}$) ;
$\Omega_{V,4}$=(1.16145 (T1/Subscript[ϵκ, 4])$^{-0.14874}$)+0.52487 (Exp[-0.77320 (T1/$\epsilon\kappa_4$)])+2.16178 (Exp[-2.43787 (T1/$\epsilon\kappa_4$)]);μ_4=(2.6709 10^{-6}) $\sqrt{M_4\ T1}$ /(Subscript[σ, 4]^2 $\Omega_{V,4}$) ;
Φ[1,1]=1;
Φ[1,2]=1/$\sqrt{8}$ (1+Subscript[M, 1]/Subscript[M, 2])$^{-0.5}$ (1+(Subscript[μ, 1]/Subscript[μ, 2])^0.5 (Subscript[M, 2]/Subscript[M, 1])^0.25)^2; Φ[1,3]=1/$\sqrt{8}$ (1+Subscript[M, 1]/Subscript[M, 3])$^{-0.5}$ (1+(Subscript[μ, 1]/Subscript[μ, 3])^0.5 (Subscript[M, 3]/Subscript[M, 1])^0.25)^2; Φ[1,4]=1/$\sqrt{8}$ (1+Subscript[M, 1]/Subscript[M, 4])$^{-0.5}$ (1+(Subscript[μ, 1]/Subscript[μ, 4])^0.5 (Subscript[M, 4]/Subscript[M, 1])^0.25)^2;
Φ[2,1]=1/$\sqrt{8}$ (1+Subscript[M, 2]/Subscript[M, 1])$^{-0.5}$ (1+(Subscript[μ, 2]/Subscript[μ, 1])^0.5 (Subscript[M, 1]/Subscript[M, 2])^0.25)^2; Φ[2,2]=1; Φ[2,3]=1/$\sqrt{8}$ (1+Subscript[M, 2]/Subscript[M, 3])$^{-0.5}$ (1+(Subscript[μ, 2]/Subscript[μ, 3])^0.5 (Subscript[M, 3]/Subscript[M, 2])^0.25)^2; Φ[2,4]=1/$\sqrt{8}$ (1+Subscript[M, 2]/Subscript[M, 4])$^{-0.5}$ (1+(Subscript[μ, 2]/Subscript[μ, 4])^0.5 (Subscript[M, 4]/Subscript[M, 2])^0.25)^2;
Φ[3,1]=1/$\sqrt{8}$ (1+Subscript[M, 3]/Subscript[M, 1])$^{-0.5}$ (1+(Subscript[μ, 3]/Subscript[μ, 1])^0.5 (Subscript[M, 1]/Subscript[M, 3])^0.25)^2; Φ[3,2]=1/$\sqrt{8}$ (1+Subscript[M, 3]/Subscript[M, 2])$^{-0.5}$ (1+(Subscript[μ, 3]/Subscript[μ, 2])^0.5 (Subscript[M, 2]/Subscript[M, 3])^0.25)^2; Φ[3,3]=1; Φ[3,4]=1/$\sqrt{8}$ (1+Subscript[M, 3]/Subscript[M, 4])$^{-0.5}$ (1+(Subscript[μ, 3]/Subscript[μ, 4])^0.5 (Subscript[M, 4]/Subscript[M, 3])^0.25)^2;
Φ[4,1]=1/$\sqrt{8}$ (1+Subscript[M, 4]/Subscript[M, 1])$^{-0.5}$ (1+(Subscript[μ, 4]/Subscript[μ, 1])^0.5 (Subscript[M, 1]/Subscript[M, 4])^0.25)^2;Φ[4,2]=1/$\sqrt{8}$ (1+Subscript[M, 4]/Subscript[M, 2])$^{-0.5}$ (1+(Subscript[μ, 4]/Subscript[μ, 2])^0.5 (Subscript[M, 2]/Subscript[M, 4])^0.25)^2; Φ[4,3]=1/$\sqrt{8}$ (1+Subscript[M, 4]/Subscript[M, 3])$^{-0.5}$ (1+(Subscript[μ, 4]/Subscript[μ, 3])^0.5 (Subscript[M, 3]/Subscript[M, 4])^0.25)^2; Φ[4,4]=1;

```
 μm=(y0  μ1)/(y0  Φ[1,1]+y7  Φ[1,2]+y1  Φ[1,3]+y2  Φ[1,4])+(y7  μ2)/(y0  Φ[2,1]+y7  Φ[2,2]+y1
Φ[2,3]+y2  Φ[2,4])+(y1  μ3)/(y0  Φ[3,1]+y7  Φ[3,2]+y1  Φ[3,3]+y2  Φ[3,4])+(y2  μ4)/(y0  Φ[4,1]+y7
Φ[4,2]+y2 Φ[4,3]+y3 Φ[4,4]); (*Pa·s*)
 MM=(M1y0+M2y7+M3y1+M4y2+M5y3+M6y4+M7y5+M8y6)/1000;

 Pp[i]=P;
 Pp[i+1]=Ct R T1;
 Pn=100;


 If[Pp[i+1]!=Pn,
   ρm= (Pp[i+1] MM)/(R T1);
  ux=(Density ui/3600)/ ρm;
  Pn=-((ux  ρm)/( ρm dp))((1-ϵ)/ϵ3) ((150 (1-ϵ)μm )/dp+1.75 ux  ρm) h/10^5+P; ];
 u=ux 3600;
 v[i+1]=u;
 P=Pp[i+1];
 ρm= (Pp[i+1] MM)/(R T1);

 Rr1=(kc1 Keb (y0 P-(y1 y2  P^2)/Keq )*1000)/(1+Keb y0 P+Kst y1 P+Kh2 y2 P)^2;
 r1=Rr1;
 r1[i+1]=r1;
 Rr2=(kc2 Keb y0 P 1000)/(1+Keb y0 P+Kst y1 P+Kh2 y2 P)^2;
 r2=Rr2;
 r2[i+1]=r2;
 Rr3=(kc3 Keb y0 P Kh2 y2 P 1000)/(1+Keb y0 P+Kst y1 P+Kh2 y2 P)^2;
 r3=Rr3;
 r3[i+1]=r3;
 Rr4=(kc4 Kst y1 P Kh2 y2 P 1000)/(1+Keb y0 P+Kst y1 P+Kh2 y2 P)^2;
 r4=Rr4;
 r4[i+1]=r4;

 G=(u ρm)/MM;

 jj=1;j=1;
 Do[j=j+1;

  Djj,j=(0.00143T1^1.75)/(P  Mjj,j (dajj^(1/3) +daj^(1/3) )^2); ,4];
 Dm=0.36/(1/(1+y0) (1/D1,2  (y7)+1/D1,3 (y1+y0)+1/D1,4 (y2+y0)));
 d=Dm;
 MmM=((u ρm dp )/μm) (μm/(ρm d));
 Deff= u dp (0.7/MmM+4/(1+MmM 5.1));

 DD[i+1]=Deff;
```

Cp_1=(8) (1/2) ((8.314/1000) /(M_1/1000));
Cp_2=(143.05-183.54 $(T1/100)^{0.25}$+82.751 $(T1/100)^{0.5}$-3.6989 $(T1/100)^{1}$)/1000;
Cp_3=(8)*(1/2) ((8.314/1000) /(M_3/1000));
Cp_4=(56.505-702.24 $(T1/100)^{-0.75}$+1165.0 $(T1/100)^{-1}$-560.70 $(T1/100)^{-1.5}$)/1000;
Cp_m = Cp_1 y0+Cp_2 y7+Cp_3 y1+Cp_4 y2;
Cpm=Cp_m;
CCP[i+1]=Cpm;

$k_1=8.3127*10^{-2}\sqrt{\frac{T1}{\frac{M_1}{1000}}}\,/(\text{Subscript}[\sigma,1]^2\ \Omega_{V,1})+1.32\,(Cp_1-5/2\ 8.314/1000/(M_1/1000))\ 2.6709*10^{-6}\sqrt{\frac{M_1}{1000}\,T1}\,/(\text{Subscript}[\sigma,1]^2\ \Omega_{V,1});$

$k_2=8.3127*10^{-2}\sqrt{\frac{T1}{\frac{M_2}{1000}}}\,/(\text{Subscript}[\sigma,2]^2\ \Omega_{V,2})+1.32\,(Cp_2-5/2\ 8.314/1000/(M_2/1000))\ 2.6709*10^{-6}\sqrt{\frac{M_2}{1000}\,T1}\,/(\text{Subscript}[\sigma,2]^2\ \Omega_{V,1});$

$k_3=8.3127*10^{-2}\sqrt{\frac{T1}{\frac{M_3}{1000}}}\,/(\text{Subscript}[\sigma,3]^2\ \Omega_{V,3})+1.32\,(Cp_3-5/2\ 8.314/1000/(M_3/1000))\ 2.6709*10^{-6}\sqrt{\frac{M_3}{1000}\,T1}\,/(\text{Subscript}[\sigma,3]^2\ \Omega_{V,3});$

$k_4=8.3127*10^{-2}\sqrt{\frac{T1}{\frac{M_4}{1000}}}\,/(\text{Subscript}[\sigma,4]^2\ \Omega_{V,4})+1.32\,(Cp_4-5/2\ 8.314/1000/(M_4/1000))\ 2.6709*10^{-6}\sqrt{\frac{M_4}{1000}\,T1}\,/(\text{Subscript}[\sigma,4]^2\ \Omega_{V,4});$

k_m=(y0 k_1)/(y0 Φ[1,1]+y7 Φ[1,2]+y1 Φ[1,3]+y2 Φ[1,4])+(y7 k_2)/(y0 Φ[2,1]+y7 Φ[2,2]+y1 Φ[2,3]+y2 Φ[2,4])+(y1 k_3)/(y0 Φ[3,1]+y7 Φ[3,2]+y1 Φ[3,3]+y2 Φ[3,4])+(y2 k_4)/(y0 Φ[4,1]+y7 Φ[4,2]+y2 Φ[4,3]+y3 Φ[4,4]);
km=k_m;

kkm[i+1]=km;

q[i+1]=v[i+1] Pi 0.75^2;,50000];

Layout of the Graphics 2;

Graphics of Concentration;

```
CEthylbenzene2=Table[fx0[a],{a,nn+1,i}];CStyrene2=Table[fx1[a],{a,nn+1,i}];CHydrogen2=Table[fx2[a],{a,nn+1,i}];CBenzene2=Table[fx3[a],{a,nn+1,i}];CEthylene2=Table[fx4[a],{a,nn+1,i}];CToluene2=Table[fx5[a],{a,nn+1,i}];CMethane2=Table[fx6[a],{a,nn+1,i}];
Concentrations2=Join[{CEthylbenzene2,CStyrene2,CHydrogen2,CBenzene2,CEthylene2,CToluene2,CMethane2}];
ListPlot[Concentrations2]
```

Graphic of Temperature and physical parameters;

```
Temperature2=Table[fT[a],{a,nn+1,i}];
Pressure2=Table[Pp[a],{a,nn+1,i}];
Vflow2=Table[q[a],{a,nn+1,i}];
Velocity2=Table[v[a]/3600,{a,nn+1,i}];
CDifusion2=Table[DD[a],{a,nn+1,i}];
SHeat2=Table[CCP[a],{a,nn+1,i}];
TConduct2= Table[kkm[a],{a,nn+1,i}];
ListPlot[Temperature2]
ListPlot[Pressure2]
ListPlot[Vflow2]
ListPlot[Velocity2]
ListPlot[CDifusion2]
ListPlot[SHeat2]
ListPlot[TConduct2]
```

Graphics of reactions rate;

```
Reaction12=Table[r1[a],{a,nn+1,i}];
Reaction22=Table[r2[a],{a,nn+1,i}];Reaction32=Table[r3[a],{a,nn+1,i}];
Reaction42=Table[r4[a],{a,nn+1,i}];
Reactions2=Join[{Reaction12,Reaction22,Reaction32,Reaction42}];
Reactionss2=Join[{Reaction22,Reaction32,Reaction42}];
ListPlot[Reactions2]
ListPlot[Reactionss2]
```

Graphics of reactions rate constants;

```
RRConstant12=Table[kc1[a],{a,nn+1,i}];RRConstant22=Table[kc2[a],{a,nn+1,i}];RRConstant32=Table[kc3[a],{a,nn+1,i}];RRConstant42=Table[kc4[a],{a,nn+1,i}];
RRConstants2=Join[{RRConstant12,RRConstant22,RRConstant32,RRConstant42}];
ListPlot[RRConstants2]
```

Graphics of adsorption equilibrium constants and reaction equilibrium;

```
AECEthylbenzene2=Table[KEB[a],{a,nn+1,i}];AECStyrene2=Table[KST[a],{a,nn+1,i}];AECHydrogen2=Table[KH2[a],{a,nn+1,i}]; ReactionEquilibrium2=Table[KEQ[a],{a,nn+1,i}];
```

```
AEConstants2=Join[{AECEthylbenzene2,AECStyrene2,AECHydrogen2}];
ListPlot[AEConstants2]
ListPlot[ReactionEquilibrium2]
```

APPENDIX 5: SIMULATION PROFILES

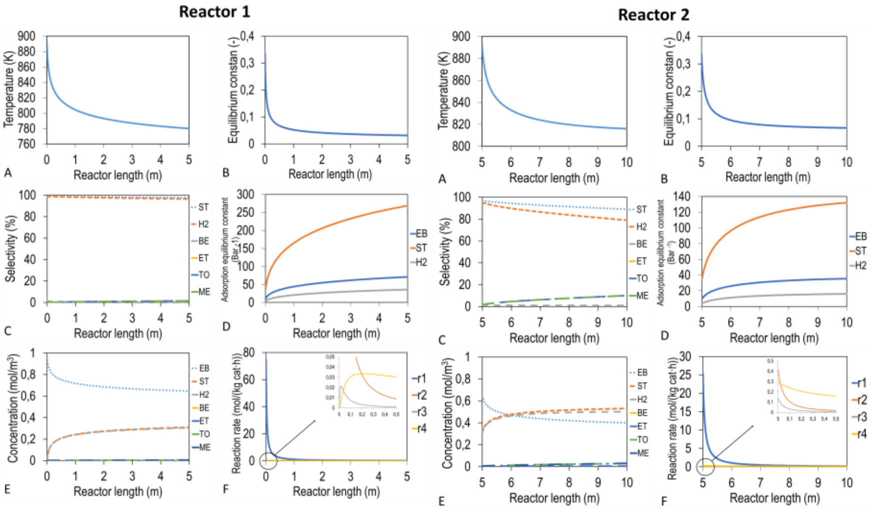


Figure 19: Simulation Nº 1.
A) Temperature; B) Equilibrium constant; C) Selectivity; D) Adsorption equilibrium constant; E) Concentrations; F) Reaction rates.

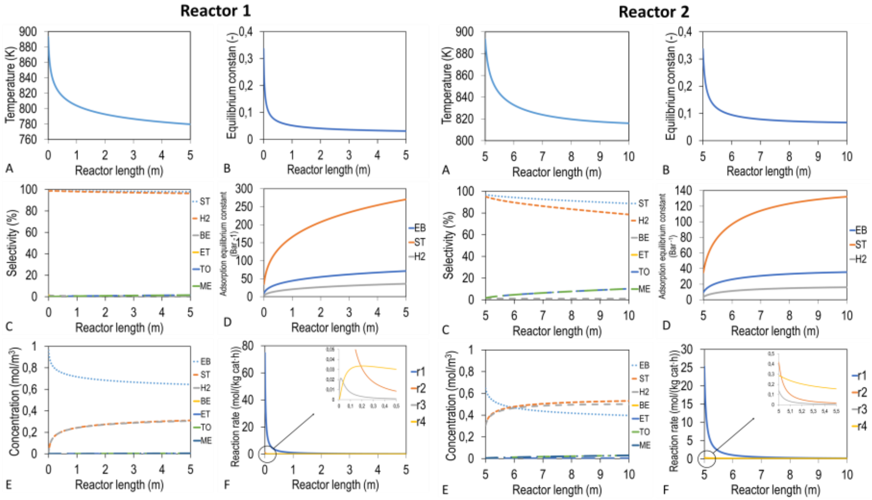


Figure 20: Simulation Nº2
A) Temperature; B) Equilibrium constant; C) Selectivity; D) Adsorption equilibrium constant; E) Concentrations; F) Reaction rates

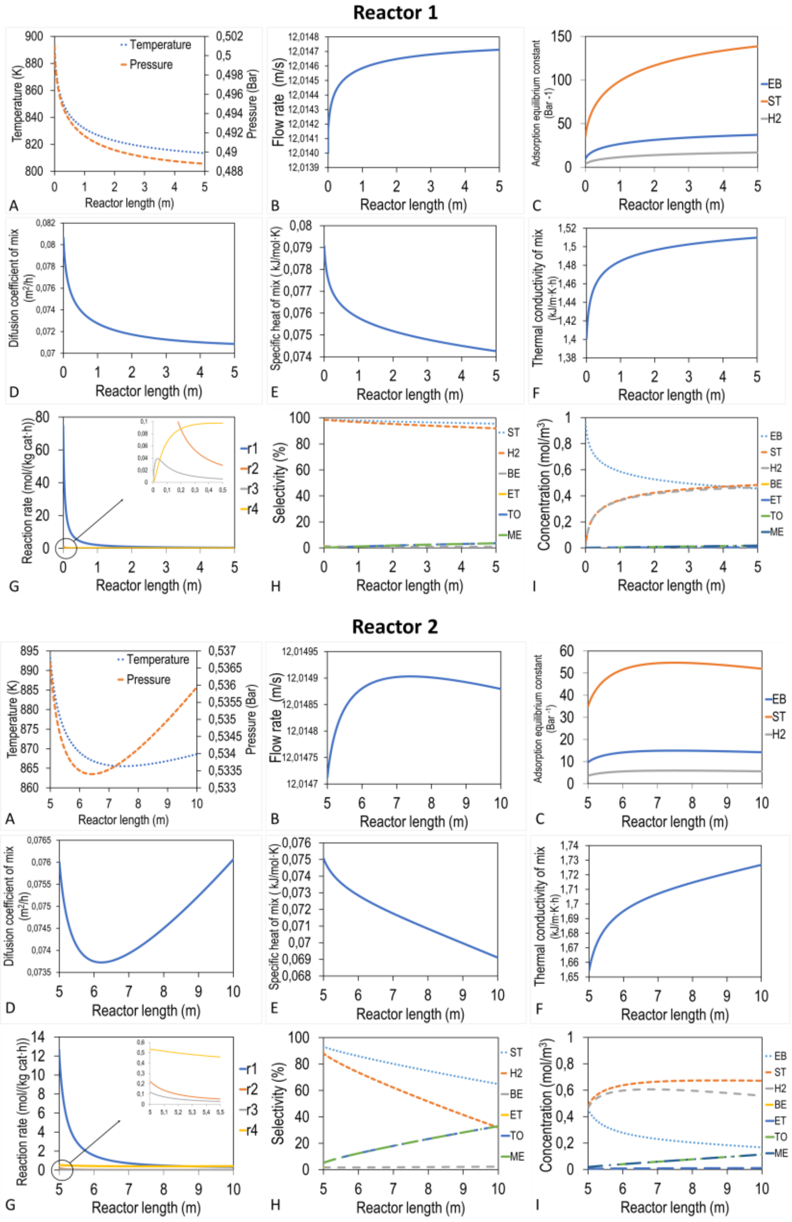


Figure 21: Simulation Nº3

A) Temperature; B) Flow Rate; C) Adsorption equilibrium constants; D) Diffusion coefficient; E) Specific heat of mix; F) Thermal conductivity; G) Reaction rates; H) Selectivity; I) Concentrations

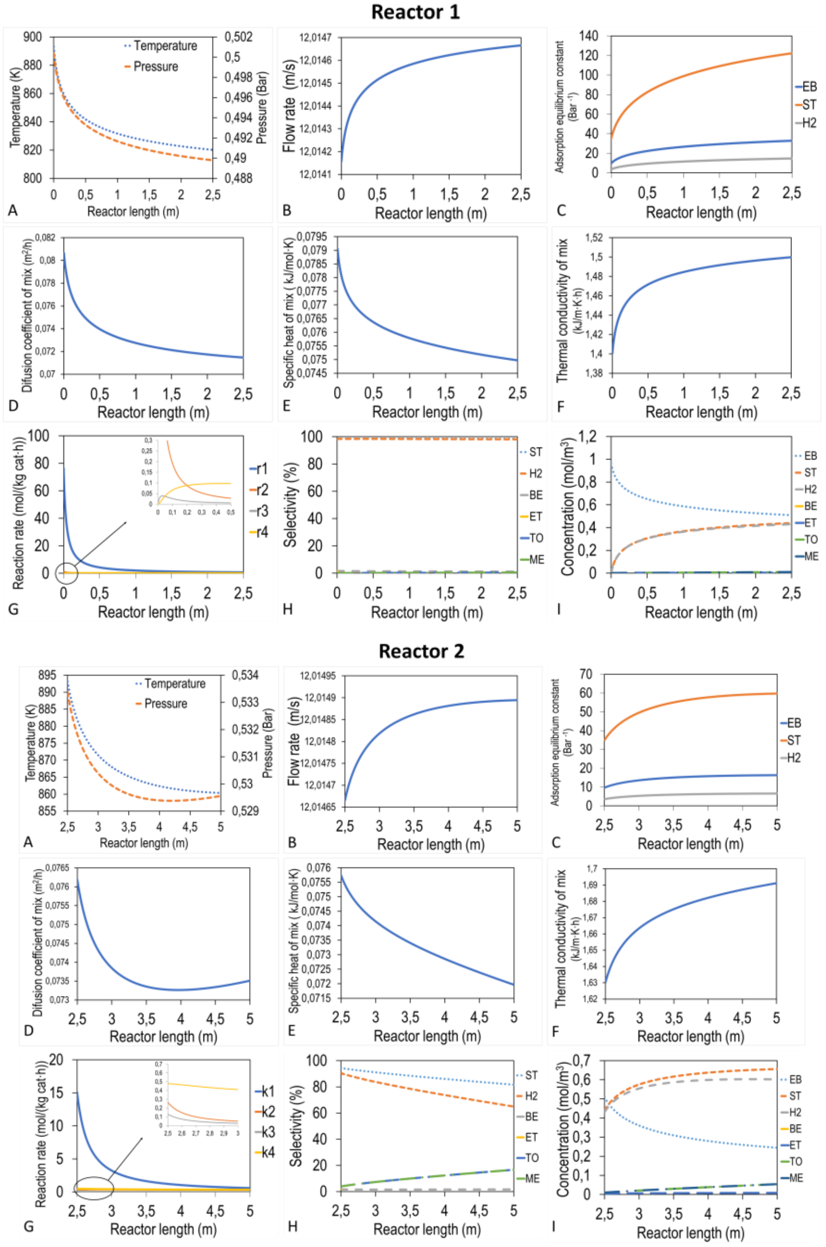


Figure 22: Simulation Nº4

A) Temperature; B) Flow Rate; C) Adsorption equilibrium constants; D) Diffusion coefficient; E) Specific heat of mix; F) Thermal conductivity; G) Reaction rates; H) Selectivity; I) Concentrations

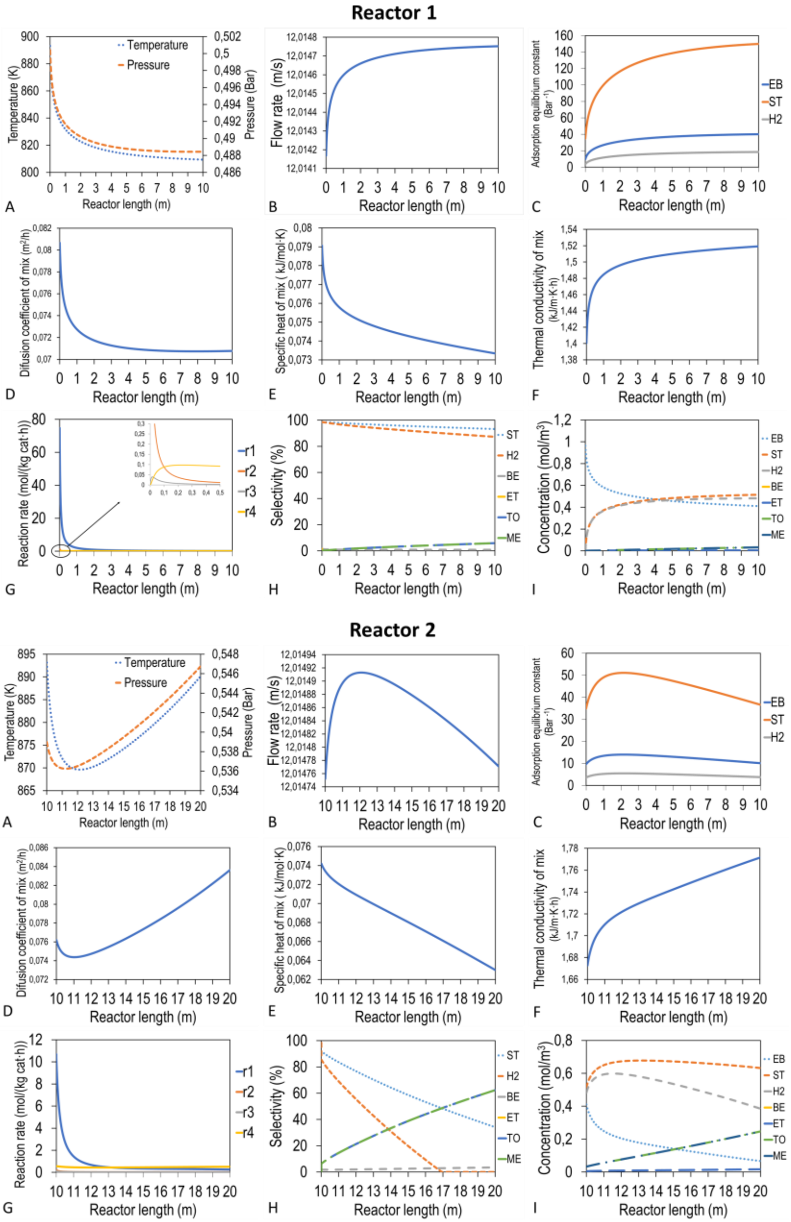
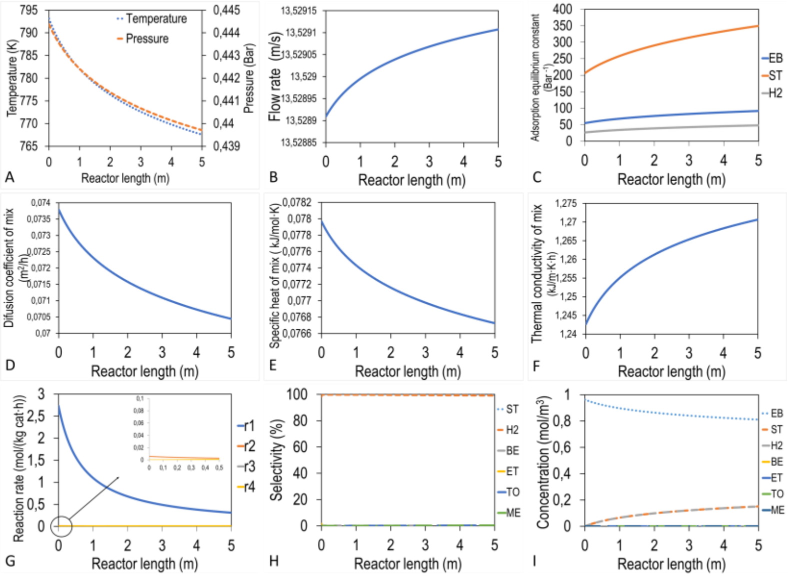


Figure 23: Simulation Nº5

A) Temperature; B) Flow Rate; C) Adsorption equilibrium constants; D) Diffusion coefficient; E) Specific heat of mix; F) Thermal conductivity; G) Reaction rates; H) Selectivity; I) Concentrations

Reactor 1



Reactor 2

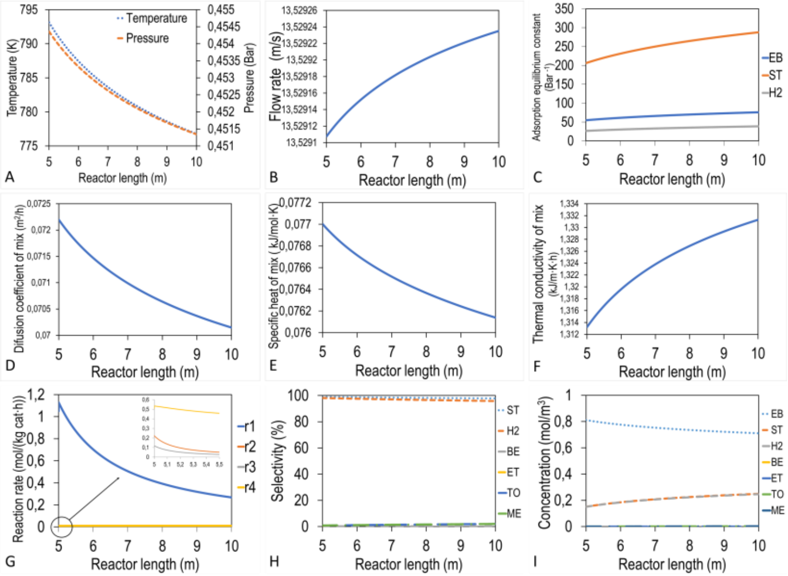


Figure 24: Simulation Nº6

A) Temperature; B) Flow Rate; C) Adsorption equilibrium constants; D) Diffusion coefficient; E) Specific heat of mix; F) Thermal conductivity; G) Reaction rates; H) Selectivity; I) Concentrations

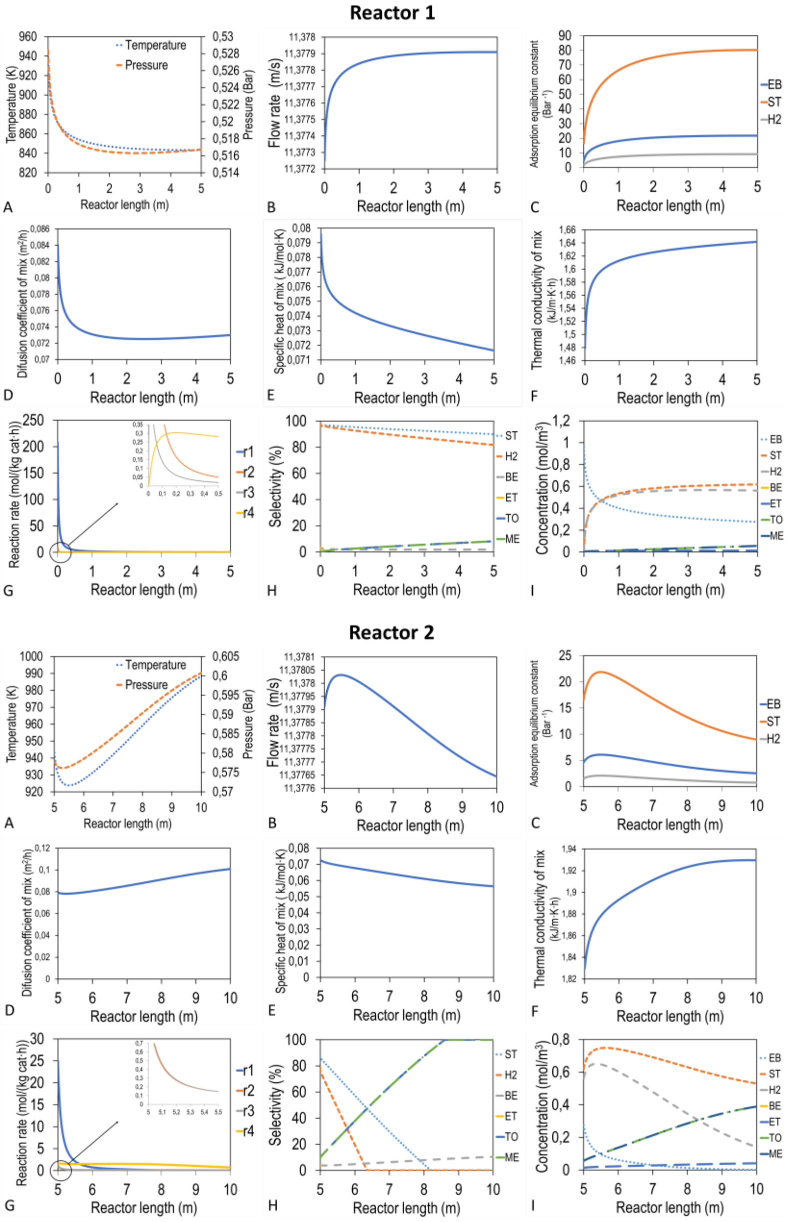


Figure 25: Simulation Nº7

A) Temperature; B) Flow Rate; C) Adsorption equilibrium constants; D) Diffusion coefficient; E) Specific heat of mix; F) Thermal conductivity; G) Reaction rates; H) Selectivity; I) Concentrations

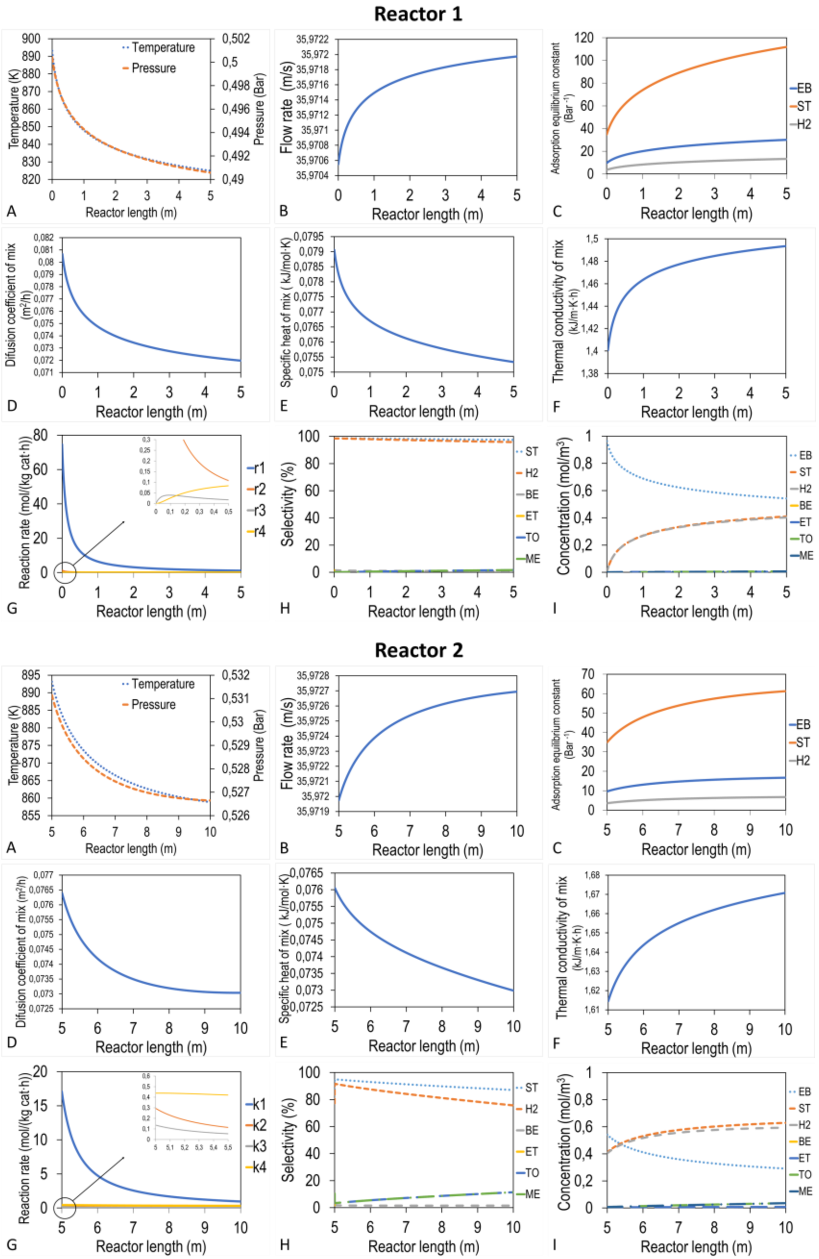


Figure 26: Simulation Nº8

A) Temperature; B) Flow Rate; C) Adsorption equilibrium constants; D) Diffusion coefficient; E) Specific heat of mix; F) Thermal conductivity; G) Reaction rates; H) Selectivity; I) Concentrations

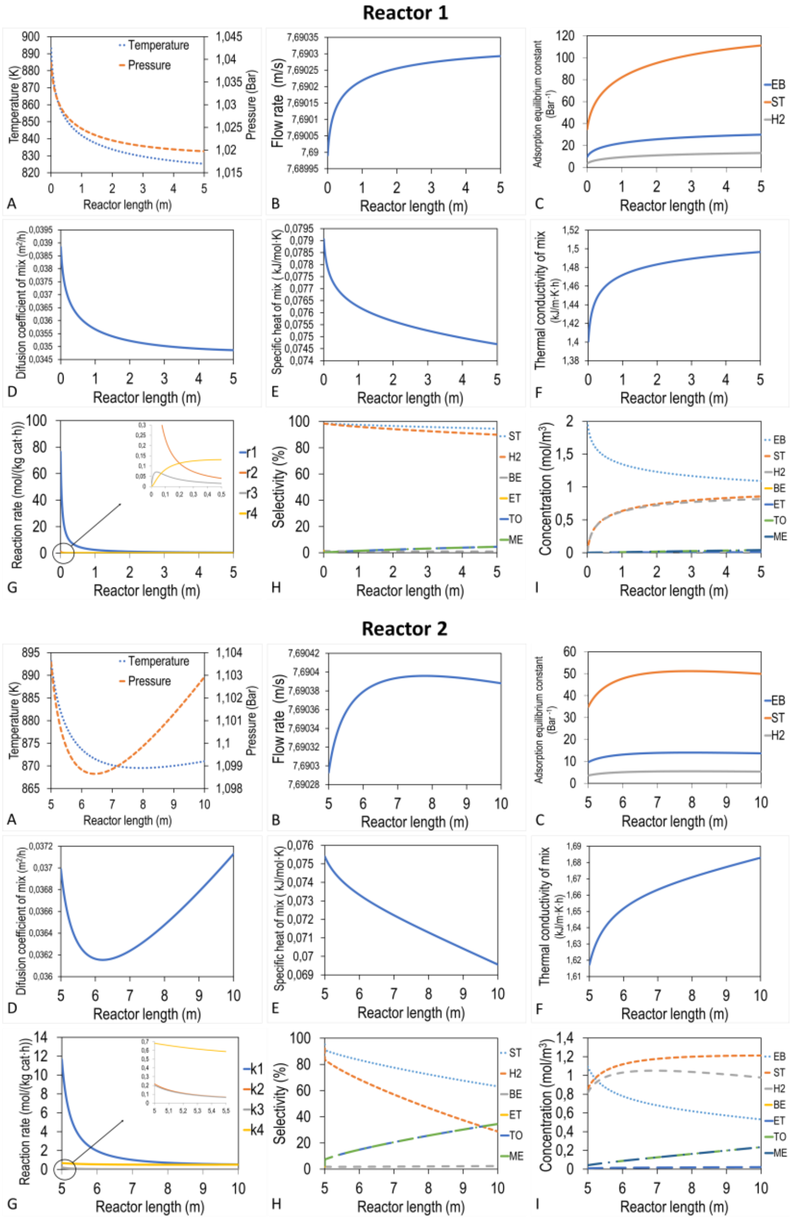


Figure 27: Simulation Nº9

A) Temperature; B) Flow Rate; C) Adsorption equilibrium constants; D) Diffusion coefficient; E) Specific heat of mix; F) Thermal conductivity; G) Reaction rates; H) Selectivity; I) Concentrations

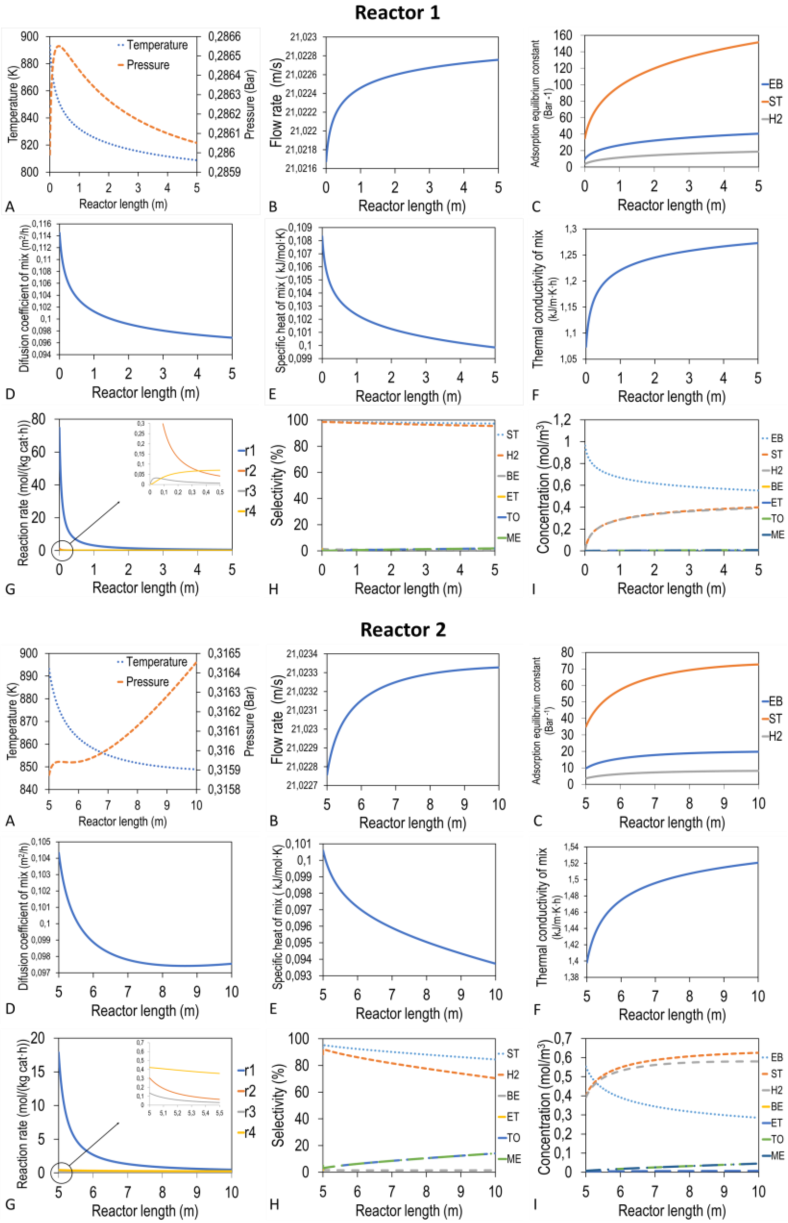


Figure 28: Simulation Nº10

A) Temperature; B) Flow Rate; C) Adsorption equilibrium constants; D) Diffusion coefficient; E) Specific heat of mix; F) Thermal conductivity; G) Reaction rates; H) Selectivity; I) Concentrations

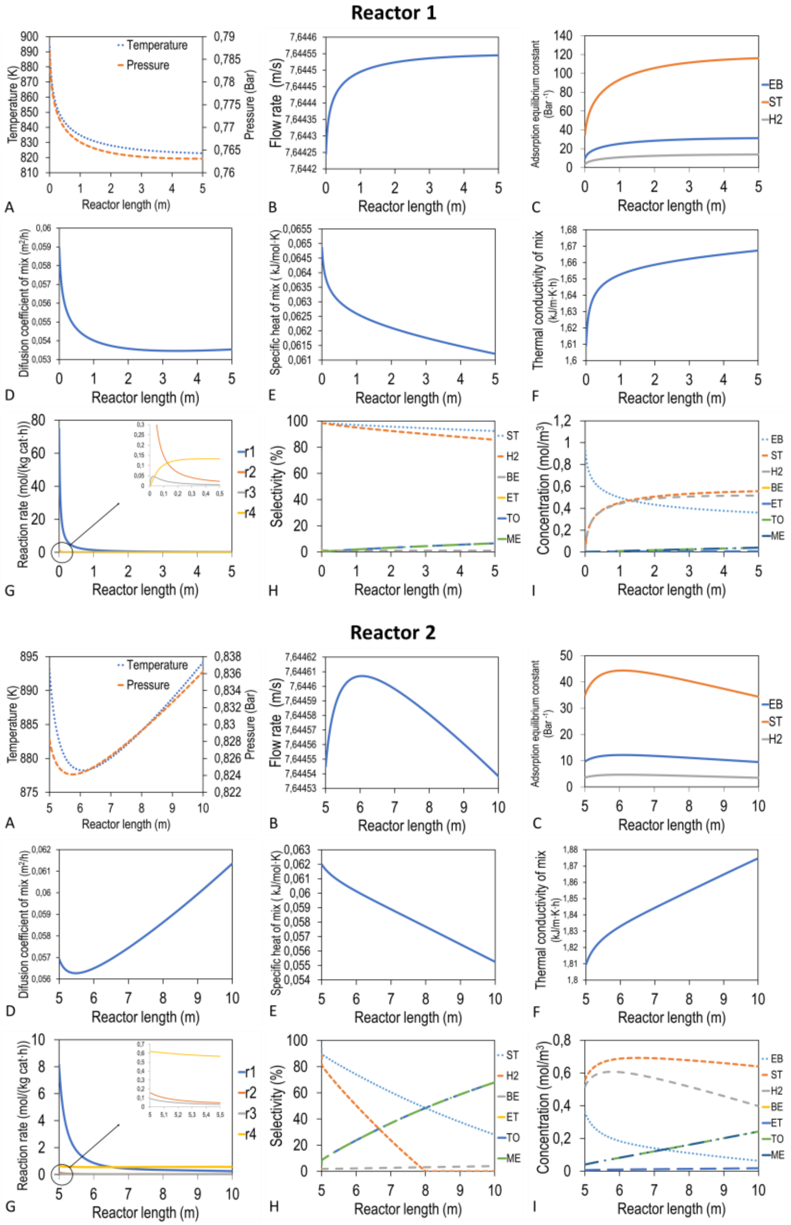


Figure 29: Simulation Nº11

A) Temperature; B) Flow Rate; C) Adsorption equilibrium constants; D) Diffusion coefficient; E) Specific heat of mix; F) Thermal conductivity; G) Reaction rates; H) Selectivity; I) Concentrations