Hydrogenation of 2-Ethyl-3-Propylacrolein (EPA) in a Catalytic Reactor: Experimental, Modeling and Simulation

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ABSTRACT: *Hydrogenation of 2-Ethyl-3-Propylacrolein (EPA) in a three-phase fixed bed reactor is the most important part of 2-Ethyl-hexanol production in the Oxo process. In this research, hydrogenation of 2-Ethyl-3-Propylacrolein in a three-phase fixed bed reactor was modeling and simulated. The model equations including a set of partial differential equations were solved simultaneously using the method of lines and finite differences technique. The simulation with 80 elements of the hydrogenation reactor has 4.89 percent minimum deviation. Experimental data from laboratory scale reactor was used for evaluation of the hydrogenation reactor simulation results. The effect of operating conditions on 2-ethyl-hexanol yield was investigated in the temperature range of 130-160 °C, pressure range of 16-78 psi, hydrogen flow rate range of 150-220 mL/min, and 2-ethyl-hexenal flow rate in 0.04-0.11 mL/min. The results showed that increasing of temperature, pressure and hydrogen flow rate increases the EPA conversion whereas the variation of 2-ethyl-hexenal flow rate doesn't have any effect on the process yield.*

KEYWORDS: *Modeling; Simulation; Hydrogenation; 2-Ethyl-hexanol(2EH); Catalytic reactor.*

INTRODUCTION

The main use for 2-Ethyl-hexanol is the production of plasticizers, coatings, adhesives and other specialty chemicals. The largest market for 2-Ethyl-hexanol is plasticizer dioctyl phthalate which is used in the manufacture polyvinyl chloride products. A growing area for 2-Ethyl-hexanol is its use in the manufacture of acrylate and methacrylate esters [1]. *Yu et al.* (2016) used 2-Ethyl-hexanol as the surfactant to enhance boiling heat transfer of water, when the surfactant concentration was 1000 mg/L, enhancement was up to about 60% [2]. In addition, 2-ethylhexanol derivatives can be used as nonionic surfactants; studies show that the surfactants which are 2-ethylhexanol derivatives have more effect and less foaming [3]. Likewise, many other acrylates, 2-ethylhexyl acrylate is widely used in the production of homopolymers, which are applied in the manufacturing of elastomers, super absorbent polymers, fibers and plastics [4]. There are two main methods for producing 2-Ethyl-hexanol: Oxo and Guerbet reaction. *Gunther et al.* (1987) studied on 2-Ethyl-hexanol production process stages and conditions of each stage. In Gunther's work, the hydrogenation of the unsaturated aldehyde was carried out in two consecutive stages. In the first stage, the aldehyde is converted to a gas by heating and then hydrogenated

in the presence of a fixed bed copper-containing hydrogenation catalyst [5]. The catalyst contains approximately 60% by weight copper and about 10% by weight. The reaction was carried out at the temperature from 140 to 160° C, space velocity equal to 0.4 (liquid product volume/catalyst volume per hour) and pressure depends on temperature. The second hydrogenation step is carried out in the liquid phase. The applied catalyst is composed of 55% to 60% by weight Ni and about 30% by weight SiO_2. This hydrogenation is carried out under the temperature from 120 to 140 °C, pressure from 2 to 2.5 MPa and space velocity from 0.8 to 1.1 [5].

Miller and Bennett investigated producing 2-ethylhexanol by employing the Guerbet reaction [6]. In this process, the process reactions were carried out in temperature range of 218-228 °C and pressure range of 4.1-4.5 MPa. Poe presented a procedure for producing 2-ethylhexanol using the Guerbet reaction [7], which takes place at a temperature range of 200-300 ℃. The process, depending on the alcohol, the catalyst, and the presence of potassium hydroxide, occurs at a temperature range of 240-270℃. Since pressure is an essential controller of the process, primarily as a means of maintaining the reactants in the desired physical state, an adequate pressure is employed to maintain the starting alcohol in the liquid state. It has to be noted that this pressure will vary depending on the reaction temperature [7]. Regarding the lower output of this process and creation of different byproducts, producing 2-ethylhexanol is neither cost-effective nor applied industrially [7].

Kessen et al. investigated the synthesis of 2-ethylhexanol using the Oxo process, through which propane reacted with carbon monoxide and hydrogen in the presence of a catalyst containing Rhodium. The process was carried out under temperature and pressure ranges of 50-140℃ and 0.1 to 30 MPa, respectively. Ratio of Rhodium to sulfonated triaryl phosphine and ratio of organic phase to aqueous phase were adjusted between 1:3 to 1:300, and 1:1 to 1:100, respectively [8].

Thurman and Harris reduced the concentration of 2-ethyl-4-methylpentanol in the producing 2-ethylhexanol [9] by adding the distilled n-butyraldehyde to produce 2-ethylhex-2-enal and, eventually, hydrogenated with a catalyst to produce 2-ethylhexanol [9].

In the study has performed by *Lueken et al.* at 1990, the main purpose was studying on liquid phase hydrogenation of 2-ethyl-hexenal and the catalysts were used in this section of the process. The process was carried out at temperature range of 120 to 180℃ and at a pressure range of 10 to 100 bars. The applied catalyst is composed of nickel in an amount of from 15 to 0.3%, copper in an amount of from 15 to 0.3%, chromium in an amount of from 0.05 to 3.5%, and an alkali metal component in an amount of from 0.01 to 1.6% by weight [10]. In the invention of Thurman et al (1993), a process for producing 2-ethylhexanol having a reduced concentration of 2-ethyl-4-methyl-pentanol was provided. The water containing aldehyde mixture was introduced to a distillation zone with a residence time and at a temperature sufficient to hydrolyze the oligomeric contaminants and then distill substantially all of the isobutyraldehyde overhead [11]. In the Guerbet reaction, two molecules of an alcohol reacts and one molecule of an alcohol with increased number of carbon atoms will be produced. This reaction requires a catalyst and elevated temperatures.

Miller et al. 1961 studied on 2-ethyl-hexanol production from *Butanol* [6]. *Smedler* (1989) and *Collins* at 1983 studied on kinetic of 2-ethylhexenal hydrogenation process. *Collins et al.* studied on 2-Ethyl-2-hexenal hydrogenation over Raney Nickel and nickel boride in a batch slurry reactor. The reaction went to completion using Raney Nickel, and the formation of both 2-ethylhexanal and 2-ethylhexanol followed zero order kinetics [12]. Smedler studied on the kinetics of the consecutive hydrogenation reactions (2-ethyl-hexenal → 2-ethyl-hexanal → 2-ethyl-hexanol) in the liquid phase in presence of commercial Ni, Pd and Ni-S catalysts [12]. The hydrogenation can occur in liquid phase or in gas phase. Some of the drawbacks of the gas phase hydrogenation are the high energy consumption and the large dimension of the equipment but has an important advantage, the possibility to regenerate the catalyst. Regarding the liquid phase hydrogenation, the only drawback is the impossibility to regenerate the catalyst [13].

Both et al. (2013) studied mathematical modeling of the hydrogenation reactor of 2-Ethyl-3-Propylacrolein. In their developed model, the effect of catalyst deactivation on the rate of surface reaction was considered, catalyst internal efficiency factor was changed in range of 0.1 to 0.2 and the transferred hydrogen flow through the liquid film, on to the catalysts surface, by taking into consideration the internal diffusion resistance and the

Table 1: Comparison the yield of 2-Ethylhexanol production with the previous works.

Author	Year	Process	T (C)	P (Mpa)	Yield (%)	Ref.
Miller and Bennett	1961	Guerbet reaction	218-228	4.1-4.5	83.00	[6]
Poe	1987	Guerbet reaction	200-300	0.1	89.90	[7]
Kessen et al.	1987	Oxo process	50-140	0.1-30	97.70	[8]
Thurman and Harris	1993	Oxo process	70-90	-	99.80	[9]
Lueken et al.	1990	Oxo process	120-180	2-2.5	99.90	[10]
Ghaemi and Zerehsaz	2018	Oxo process	110-160	0.1-0.6	99.86	[15]

surface reaction rates, described by Langmuir–Hinshelwood expressions. The developed model was used for controlling the outlet temperature [14].

Ghaemi and Zerehsaz were studied hydrogenation of 2-Ethyl-3-Propylacrolein performance within temperature and pressure ranges of 110-160℃ and 1-6 bars, respectively. They showed that the optimum yield of 2-ethylhexanol production was achieved at a temperature of 155℃, the pressure of 4.4 bar, and hydrogen flow rate of 192.4 mL/min [15]. Table 1 shows the operating conditions of 2-ethylhexanol production by detail. It is clear that, in the Oxo method, the process occurs at a lower temperature and higher yield compared to that of the Guerbet method.

The hydrogenation process is complex, since adsorption, surface reactions, as well as product desorption, take place simultaneously on the surface of the solid catalyst. Therefore, modeling and simulation of this process is essential for predicting behavior of the hydrogenation processes. In this work, modeling and simulation of the 2-Ethyl-hexenal hydrogenation reactor were introduced. Also, the effects of some operating conditions on the process performance were investigated. The experimental data obtained from laboratory scale was applied for the evaluation of the simulation results.

THEORITICAL SECTION
Kinetic and mechanism

2-Ethyl-hexenal hydrogenation reaction pathways are shown in Fig. 1. If $r_1 >> r_3$, then B (2-Ethyl-hexanal) is the intermediate and if $r_3 >> r_1$, then D is the intermediate. In Smedler's work the kinetics of the consecutive hydrogenation reactions (2-ethyl-hexenal → 2-ethyl-hexanal → 2-ethyl-hexanol) were studied in the liquid phase in presence of commercial Ni, Pd and Ni-S catalysts [12].

$$2 - ethyl - hexenal + H_2 \rightarrow 2 - ethyl - hexanal \qquad (1)$$

$$2 - ethyl - hexanal + H_2 \rightarrow 2 - ethyl - hexanol \qquad (2)$$
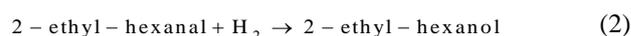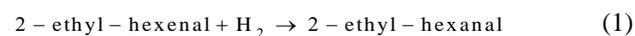
A Langmuir-Hinshelwood model was found to be the most probable model, for all three catalysts. The most probable reaction rate expressions are as follows [12]:

$$r_1 = \frac{k_1 \, K_A \, K_H \, C_A \, C_H}{\left(1 + K_A C_A + K_B C_B + \sqrt{K_H C_H}\right)^3} \qquad (3)$$

$$r_2 = \frac{k_2 \, K_B \, K_H \, C_B \, C_H}{\left(1 + K_A C_A + K_B C_B + \sqrt{K_H C_H}\right)^3} \qquad (4)$$

Where K_A is the adsorption equilibrium constant for 2-ethyl-hexenal, K_B is the adsorption equilibrium constant for 2-ethyl-hexanal, K_H is the adsorption equilibrium constant, k_1 and k_2 are the rate constants of surface reactions 1 and 2. k_1 and k_2 depend on temperature in order to following expressions [12]:

$$k_1 = \tau_1 . e^{-E_1 / RT} \qquad (5)$$

$$k_2 = \tau_2 . e^{-E_2 / RT} \qquad (6)$$

Where E_1 is the activation energy of reaction r_1, E_2 is activation energy of reaction r_2, T is the absolute temperature and R is the universal gas constant. τ_1 and τ_2 are the pre-exponential factors, constant for each chemical reaction. According to collision theory, τ_1 and τ_2 are the frequency of collisions in the correct orientation. The kinetics parameters was introduced in Table 2.

Process modeling

In order to modeling of hydrogenation process, the reactor is divided to several elements, and in each element the total and component mass balances for gas and liquid phases are written. To develop the dynamic model of

Table 2: Reaction rate parameters [12].

Parameter	Value	Unit
E_1	46	kJ/mol
E_2	77	kJ/mol
$_1\tau$	7.8×10^6	s^{-1}
$_2\tau$	9.6×10^9	s^{-1}
K_A	1.25×10^{-5}	m^3/mol
K_B	1.3×10^{-4}	m^3/mol
K_H	3.5×10^{-2}	m^3/mol
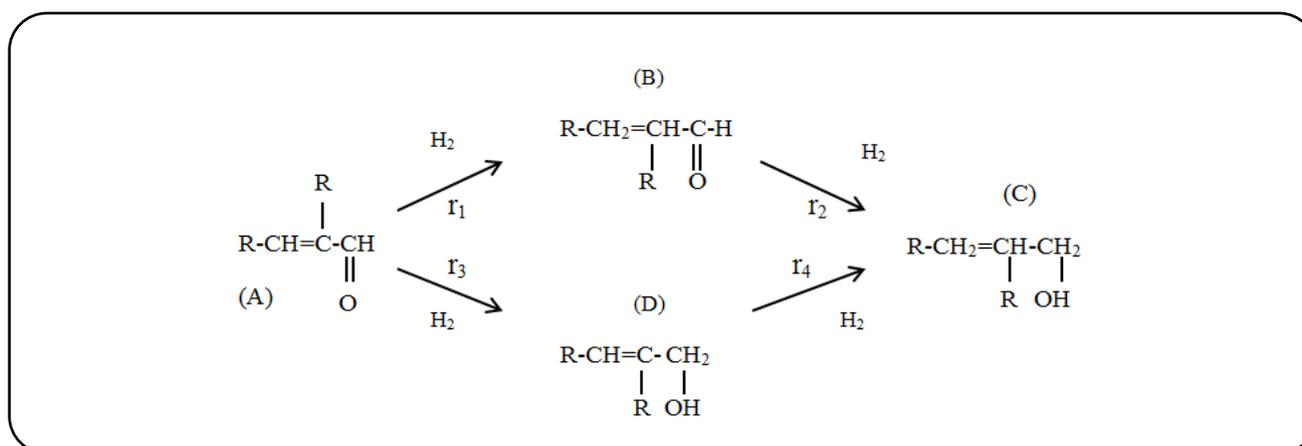
Fig. 1: 2-Ethyl-hexenal hydrogenation reaction pathways [12]

the reactor for the hydrogenation of 2-Ethyl-hexenal, the following assumptions have been considered:

• The reactor operates under isothermal and isobaric conditions.

• Reactions take place in the liquid phase.

• The catalyst particles are completely wetted with the liquid.

• Mass transfer resistance in catalyst pores is negligible ($\eta=1$).

• The gas and liquid phases flow in a plug flow condition.

• Components diffusion in axial direction is negligible.

• Axial dispersion in two phases is negligible.

• Components concentration in the catalyst particles and in the liquid phase is the same.

In Fig. 2, mass transfer at the phases interface as illustrated in Fig. 1 for one stage.

Based on the assumptions stated above, pseudo-homogeneous model is performed and the following
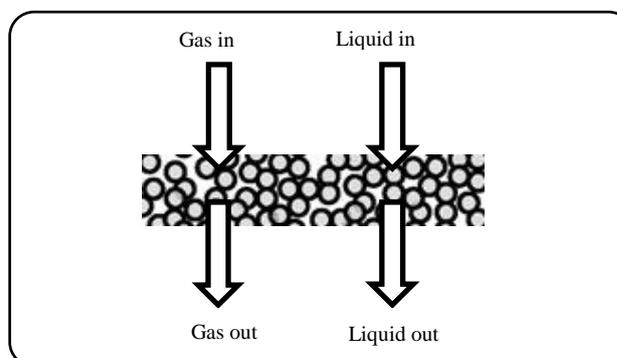
Fig. 2: An element of the trickle bed reactor.

equations are obtained [16]. The components in the gas phase are hydrogen and nitrogen. Nitrogen is an inert gas and its amount in gas phase is constant. The hydrogen transfers to the liquid phase and then reaches the catalyst surface and reaction occurred. There is no reaction in gas phase so changing the amount of hydrogen in gas phase is in order to hydrogen transfer to the liquid phase. The component mass balance in gas phase is:

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$$\frac{\partial \left(\varepsilon_G \ C_{G,H_2} \right)}{\partial t} = -\frac{\partial F_{G,H_2}}{\partial z} - N_{GL,H_2} \tag{7}$$

Where ε_G is the gas phase porosity, C_{G,H_2} is hydrogen concentration in the gas phase (mol. lit^{-1}), F_{G,H_2} is the hydrogen flow rate (mol/s), N_{GL,H_2} is the mass transfer rate of hydrogen in the gas phase (mol/m^2 s). The components mass balances in the liquid phase are:

$$\frac{\partial \left(\varepsilon_L \ C_{L,A} \right)}{\partial t} = -\frac{\partial F_{L,A}}{\partial z} - r_1 \cdot \rho_{bed} \tag{8}$$

$$\frac{\partial \left(\varepsilon_L \ C_{L,C} \right)}{\partial t} = -\frac{\partial F_{L,C}}{\partial z} + \left(r_1 - r_2 \right) \cdot \rho_{bed} \tag{9}$$

$$\frac{\partial \left(\varepsilon_L \ C_{L,H} \right)}{\partial t} = -\frac{\partial F_{L,H}}{\partial z} + N_{GL,H_2} - \left(r_1 + r_2 \right) \cdot \rho_{bed} \tag{10}$$

$$\frac{\partial \left(\varepsilon_L \ C_{L,B} \right)}{\partial t} = -\frac{\partial F_{L,B}}{\partial z} + r_2 \cdot \rho_{bed} \tag{11}$$

The components in the liquid phase are 2-Ethyl-hexenal (A), 2-Ethyl-hexanal (C), 2-Ethyl-hexanol (B), and hydrogen in the liquid phase (H). 2-Ethyl-hexanal is an intermediate component and its amount reaches to zero at the reactor outlet. $C_{L,i}$ is the liquid phase concentration of component i (mol/L), ρ_{bed} is the bed density, $F_{L,i}$ is the flow rate of component i in the liquid phase (mol/s) and ε_L is the liquid phase porosity. In order to hydrogen transfer to the liquid phase, gas flow rate decreases and liquid flow rate increases. Total mass balance for the gas and liquid phases are:

$$\frac{1}{v_L} \frac{\partial Q_L}{\partial t} = -\frac{\partial Q_L}{\partial z} + A \frac{M_H}{\rho_G} N_{GL,H_2} \tag{12}$$

$$\frac{1}{v_G} \frac{\partial Q_G}{\partial t} = -\frac{\partial Q_G}{\partial z} - A \frac{M_H}{\rho_G} N_{GL,H_2} \tag{13}$$

In above equations, $F_{L,i}$ is molar flow rate per unit surface area of component i in liquid phase (i=A, B, H, C) and $F_{G,H}$ is molar flow rate per unit surface area of hydrogen in the gas phase, so it can be written as follow:

$$F_{L,A} = \frac{C_{L,i} Q_L}{A} \qquad i = A, B, H, C \tag{14}$$

N_{GL,H_2} is hydrogen transfer flux from gas to the liquid phase and can be expressed as follows:

$$N_{GL,H_2} = K_{L,G} a_{L,G} \left(C_{L,H}{}^* - C_{L,H} \right) \tag{15}$$

Where $K_{L,G}$ is mass transfer coefficient of the liquid phase (m/s), $a_{L,G}$ is specific surface area of catalyst, $C_{L,H}$ is concentration of hydrogen in the liquid phase, $C_{L,H}{}^*$ represents the equilibrium concentration of hydrogen in the liquid phase and according to henery's law it can be expressed as follows:

$$C_{L,H}{}^* = H \ C_{G,H} \tag{16}$$

Where *H* is the Henery coefficient. After replacing the hydrogen transfer flux and molar flow rate per unit surface area of components in the model equations, the model equations can be written as follows:

$$\varepsilon_G \frac{\partial C_{G,H}}{\partial t} = -\frac{\partial \left(C_{G,H} Q_G \right)}{A \ \partial z} - \tag{17}$$
$$K_{L,G} a_{L,G} \left(H \cdot C_{G,H} - C_{L,H} \right)$$

$$\varepsilon_L \frac{\partial C_{L,A}}{\partial t} = -\frac{\partial \left(C_{L,A} Q_L \right)}{A \ \partial z} - r_1 \cdot \rho_{bed} \tag{18}$$

$$\varepsilon_L \frac{\partial C_{L,C}}{\partial t} = -\frac{\partial \left(C_{L,C} Q_L \right)}{A \ \partial z} + \left(r_1 - r_2 \right) \cdot \rho_{bed} \tag{19}$$

$$\varepsilon_L \frac{\partial C_{L,H}}{\partial t} = -\frac{\partial \left(C_{L,H} Q_L \right)}{A \ \partial z} + \tag{20}$$
$$K_{L,G} a_{L,G} \left(H \cdot C_{G,H} - C_{L,H} \right) - \left(r_1 + r_2 \right) \cdot \rho$$

$$\varepsilon_L \frac{\partial C_{L,B}}{\partial t} = -\frac{\partial \left(C_{L,B} Q_L \right)}{A \ \partial z} + r_2 \cdot \rho_{bed} \tag{21}$$

$$\frac{1}{v_L} \frac{\partial Q_L}{\partial t} = -\frac{\partial Q_L}{\partial z} + \tag{22}$$
$$A \frac{M_H}{\rho_G} K_{L,G} a_{L,G} \left(C_{L,H}{}^* - C_{L,H} \right)$$

$$\frac{1}{v_G} \frac{\partial Q_G}{\partial t} = -\frac{\partial Q_G}{\partial z} - \tag{23}$$
$$A \frac{M_H}{\rho_G} K_{L,G} a_{L,G} \left(C_{L,H}{}^* - C_{L,H} \right)$$

Where Q_L and Q_G are the liquid and gas phases flow rates, M_H is molecular weight of hydrogen, v_L and v_G are superficial liquid and gas velocities. The model equations were partial differential equations with respect to time and reactor length, so to solve the set of equations initial values and boundary conditions are needed. The initial values are:

$$@ \ t = 0, \forall z \ \Rightarrow C_{L,A} = C_{L,A0} \quad C_{G,H} = C_{G,H0} \tag{24}$$

$$C_{L,B} = 0 \quad C_{L,H_2} = 0 \quad C_{L,C} = 0$$

The boundary conditions are:

$$@ \ z = 0, \forall t \ \Rightarrow C_{L,A} = C_{L,A0} \tag{25}$$

$$C_{G,H} = C_{G,H0} \quad C_{L,B} = 0 \quad C_{L,H_2} = 0 \quad C_{L,C} = 0$$

Model parameters

The accuracy of the simulation results depends on model parameter computational methods. According to the model equations; chemical reaction rate constants, gas and liquid hold up and overall mass transfer coefficient between gas and liquid are process model parameters. In the hydrogenation reactor, one of the reactants is in the liquid phase and another is in the gas phase. Hydrogen transfers from gas phase to the gas-liquid interface, and then hydrogen transfers from the gas-liquid interface to the liquid phase. The overall mass transfer resistance between gas and liquid can be written as follow:

$$\frac{1}{K_{L,G} a_i} = \frac{1}{H k_G a_i} + \frac{1}{k_L a_i} \tag{26}$$

Where $k_L a_i$ is the liquid film mass transfer coefficient, $k_G a_i$ is the gas film mass transfer coefficient and H is the Henrry's constant. The overall mass transfer resistance between gas and liquid is the summation of gas side resistance and liquid side resistance. For slightly solution gases, such as hydrogen, the value of Henrry's constant exceeds unity and the gas film mass transfer resistance can be negligible. The overall mass transfer coefficient between gas and liquid is approximately equal to the liquid side mass transfer coefficient [17]:

$$\frac{1}{K_{L,G} a_i} = \frac{1}{k_L a_i} \tag{27}$$

The liquid side mass transfer coefficient is calculated using the following correlation [18]:

$$\frac{k_L a_i}{D_i} = 8.08 \left(\frac{G_L}{\mu}\right)^{0.41} Sc^{0.5} \tag{28}$$

Where, Sc is Schemit number, another important parameter in trickle bed reactor design is gas and liquid hold up. In this work, the liquid phase hold up is calculated using the following correlation reported by *Lange* [19]:

$$d\varepsilon_L = 0.16(1 - \varepsilon_S)\left(\frac{d_R}{d_P}\right)^{0.33} Re_L^{0.14} \tag{29}$$

Where Re_L is the liquid phase Reynolds number and ε_S is solid volume fraction, therefore:

$$Re_L = \frac{\rho_L u_L d_P}{\mu_L} \tag{30}$$

$$\varepsilon_S = 1 - \varepsilon \tag{31}$$

The summation of gas, liquid and solid fraction equal to 1 so, it can be written as:

$$1 = \varepsilon_S + \varepsilon_L + \varepsilon_G \tag{32}$$

Relative Deviation (RD) has been used as a criterion to compare the models. RD has been calculated using Eq. (33).

$$RD\% = \left|\frac{X_{Exp.} - X_{Cal.}}{X_{Exp.}}\right| \times 100 \tag{33}$$

Numerical solution

The model equations were a set of partial differential equations. In this work, the set of equations was solved using method of line and finite differences techniques [20]. The equations were discretized in the axial direction (reactor height) by dividing the reactor into several elements. Therefore, the process model equations were changed to a set of ordinary differential and algebraic equations. In the discretization of differential equations finite differences methods were applied. In the present process the reactor was divided into 80 elements.

RESULTS AND DISCUSSION

The operating conditions used in the process simulation is summarized in Table 3. The process simulation has performed for different number of elements and the amount of error for each number of elements is shown in Table 4. Based on the results in Table 4, the most

Table 3: The operating conditions used in the process simulation [15].

Temperature (°C)	Pressure (psi)	EPA flow rate (mL/min)	Hydrogen flow rate (mL/min)
155	65	0.05	198

Table 4: Amount of error for different number of elements.

Number of elements	Height of elements (m)	RD(%)
20	0.0250	9.23
40	0.0125	6.99
60	0.0083	5.57
80	0.0063	4.89
100	0.0005	4.43
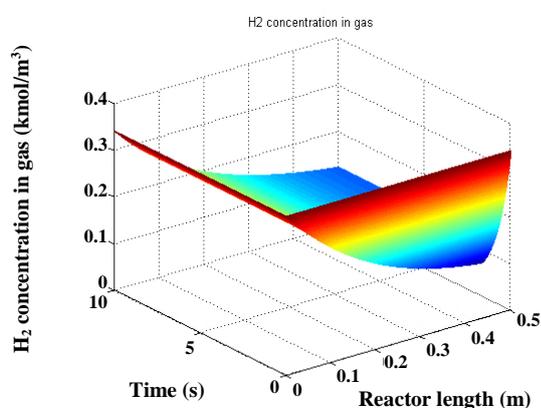
Fig. 4: Hydrogen concentration in gas phase with respect to time and reactor length, at temperature of 155 °C and pressure of 65 psi.

Fig. 5: 2-ethyl-hexenal concentration in liquid phase with respect to time and reactor length, at temperature of 155 °C and pressure of 65 psi.

appropriate number of elements is 80, Therefore the simulation has performed by 80 elements.

In the process model, equations are functions of time and reactor length, so the result of the equations set solution are components concentration profile with respect to time and reactor length. The variation of hydrogen n gas phase including 2-ethyl-hexenal, 2-ethyl-hexanol, and hydrogen in the liquid phase concentration with respect to time and reactor length are shown in sequence in Figs. 4 to 6. According to the plots at each specific length of the reactor after a short time the plots will be horizontal so, the reactor will operate in steady state condition.

The variation of hydrogen in the gas phase as a function of the reactor length is shown in Fig. 7. As it can be seen in Fig. 7, hydrogen concentration in gas phase is decreasing. The reaction takes place in the liquid phase
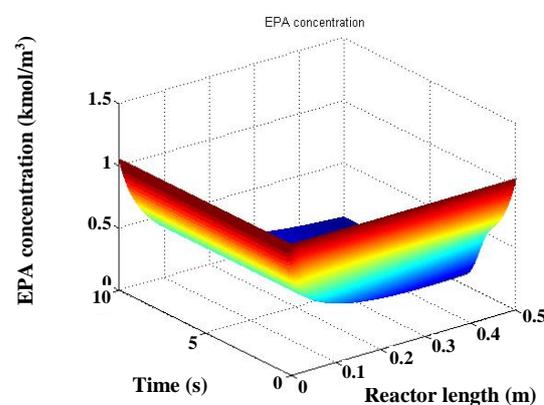
and there is no reaction in the gas phase. The hydrogen in gas phase transfers to the liquid phase so the amount of hydrogen in the gas phase decreases through the reactor length. Along the reactor height, the mass transfer driving force decreases so mass transfer rate decreases and rate of hydrogen amount reduction decreases. As it can be seen in Fig. 7, slope of the curve is decreasing.

The variation of 2-Ethyl-hexanol concentration in the liquid phase as a function of the reactor length is shown in Fig. 8. As it can be seen in Fig. 8, 2-Ethyl-hexenal decreases along the reactor because it consumes in the reaction. The slope of the curve is decreasing because the reaction rate decreases.

2EH produces through the reaction so as it can be seen in Fig. 9 its concentration will increase along the reactor length. Fig. 10 shows variation of hydrogen concentration
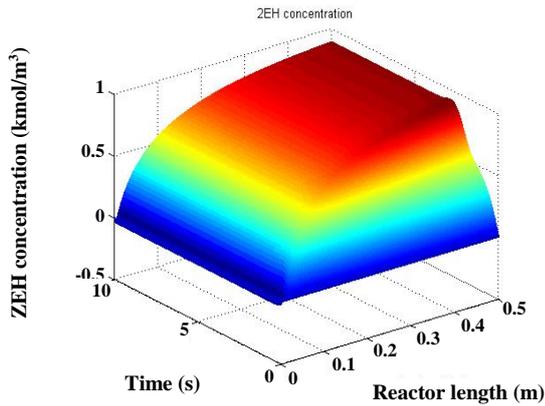
Fig. 6: 2-Ethyl-hexanol concentration in liquid phase with respect to time and reactor length, at temperature of 155 °C and pressure of 65 psi.
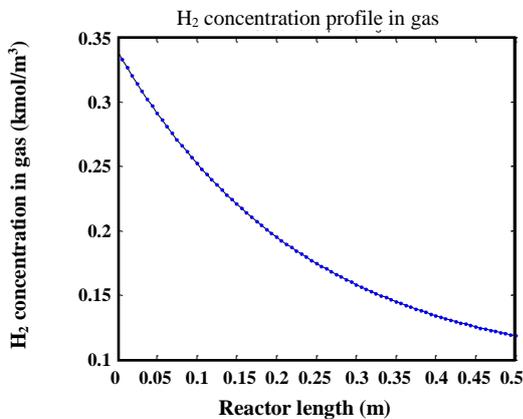
Fig. 7: Hydrogen concentration in gas phase along the reactor length, at temperature of 155 °C and pressure of 65 psi.
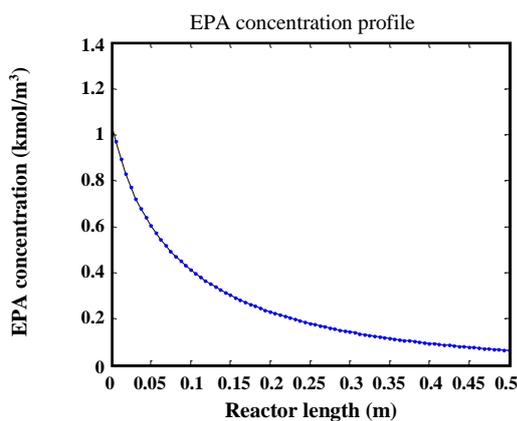
Fig. 8: 2-ethyl-hexenal concentration in liquid phase along the reactor length, at temperature of 155 °C and pressure of 65 psi.

in the liquid phase. The variation of hydrogen concentration in the liquid phase is affected by hydrogen mass transfer rate to the liquid phase and the consumption of the hydrogen through the reaction. Figs. 11 and 12 show the gas and liquid flow rate variation against the reactor length, respectively. The gas flow rate decreases in order to hydrogen mass transfer to the liquid phase and the liquid flow rate increases by the same reason.

2EH production is affected by some parameters such as: inlet gas pressure, hydrogen flow rate, temperature and 2-ethyl-hexenal flow rate. By increasing the inlet gas pressure, hydrogen concentration in the inlet of the reactor increases and in order to Henrry's law hydrogen saturation concentration in the liquid phase increases so it has a positive effect on reaction and 2EH production.

The process simulation results were evaluated with experimental data. Figures 13 to 16 show the effect of process operating conditions including pressure, hydrogen flowrate, temperature, and EPA flowrate on the process conversion. The evaluation results show that the simulations results have good agreement with the experimental data. In Fig. 13, the simulation result of inlet pressure effect on process conversion was compared with experimental data. It can be seen in Fig. 13, by increasing the inlet gas pressure the process conversion will increase.

At constant nitrogen flow rate, by increasing hydrogen flow rate, hydrogen concentration in the inlet of the reactor increases and it has a positive effect on the reaction and 2EH production. So, it can be seen in Fig. 14, by increasing the hydrogen flow rate conversion will increase.

By increasing the temperature, the reaction rate constant will increase, therefore conversion will be increased in order to Fig. 15. But increasing the temperature more than 145 ^{0}C, it doesn't have significant effect on the conversion however the process cost will be increased.

According to Fig. 16, the minimum amount of 2-Ethyl-hexenal flow rate used in the process is enough to reaction taking place. Therefore, increasing the 2-Ethyl-hexenal flow rate to a specific value doesn't have significant effect on the conversion and more than this value conversion will be decreased because the more amount of available 2-Ethyl-hexenal.

CONCLUSIONS

In this work, a dynamic pseudo-homogeneous model for modeling of the hydrogenation process in a laboratory
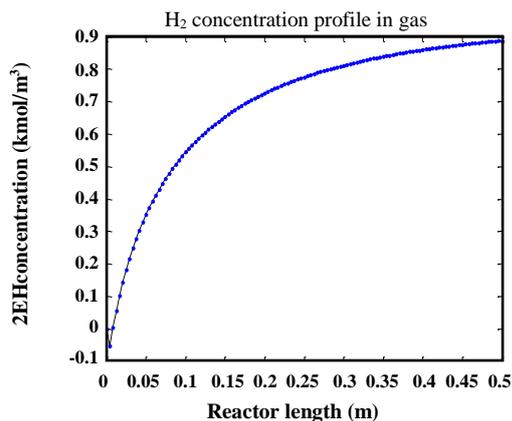
Fig. 9: 2EH concentration in liquid phase along the reactor length, at temperature of 155 ℃.
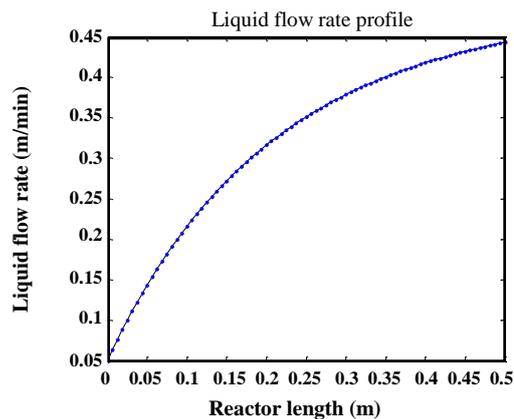
Fig. 10: Hydrogen concentration in liquid phase along the reactor length, at temperature of 155 ℃ and pressure of 65 psi.

Fig. 11: Gas flow rate variation against reactor length, at temperature of 155 ℃ and pressure of 65 psi.
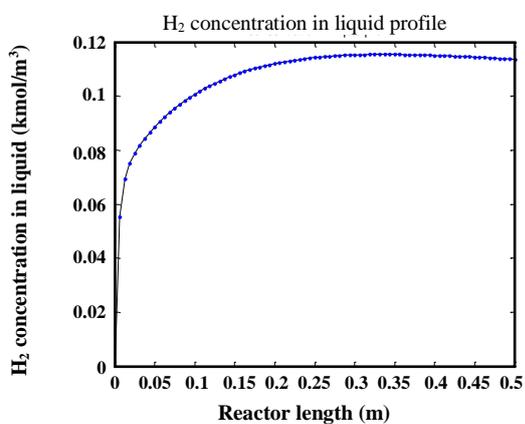
Fig. 12: Liquid flow rate variation against reactor length, at temperature of 155 ℃.
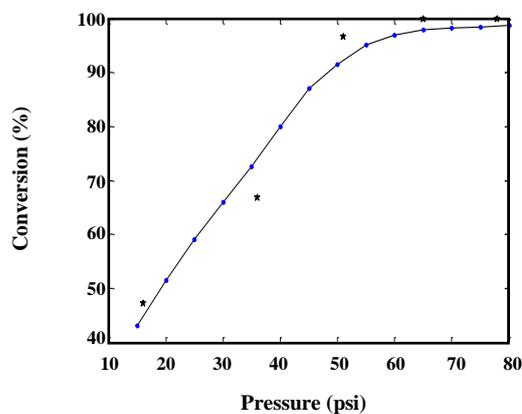
Fig. 13: Effect of inlet gas pressure on the conversion, at temperature of 155 ℃.
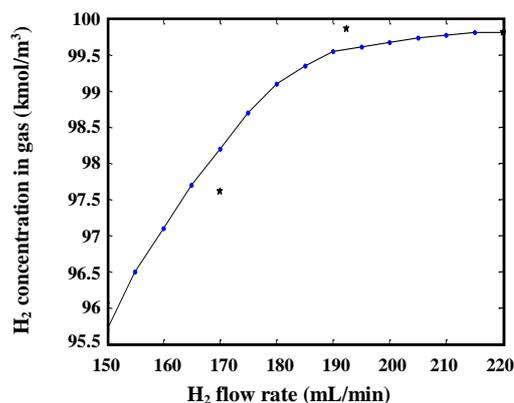
Fig. 14: Effect of hydrogen flow rate on the conversion, at temperature of 155 ℃.
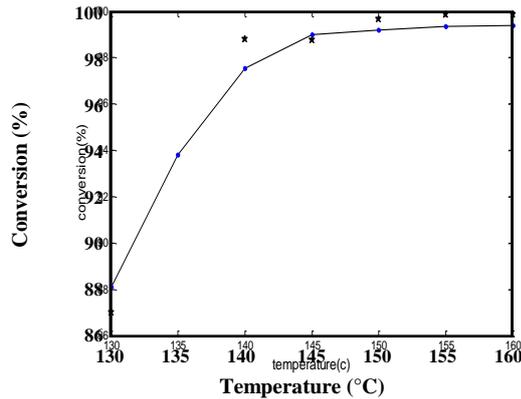
Fig. 15: Effect of temperature on the conversion.

Fig. 16: Effect of 2-Ethyl-hexenal flow rate on the process conversion, at temperature of 155 °C.

scale reactor was presented. In the modeling, the total and component mass balances in both gas and liquid phases were introduced. The model equations including a set of partial and ordinary differential equations were solved simultaneously using the combination of method of lines and finite difference technique. The results showed that the developed model can predict the reactor performance and process behavior. So the developed model can be used in the further studies to design optimization and develop control models for industrial reactors. The simulation results were evaluated with experimental data from the laboratory scale reactor. The simulation with 80 elements of reactor has 4.89 percent minimum deviation. The results also showed that with increasing of temperature, pressure and hydrogen flow rate the process conversion increases and increasing of 2-Ethyl-hexenal flow rate doesn't have significant effect on the process conversion.

Nomenclature

a	Specific surface area, m²/g
$C_{L,A}$	2-Ethyl-hexenal concentration in the liquid phase, mole/L
$C_{L,C}$	2-Ethyl-hexanal concentration in the liquid phase, mole/L
$C_{L,B}$	2-Ethyl-hexanol concentration in the liquid phase, mole/L
ε_G	Gas phase porosity
$C_{L,H}^*$	Equilibrium concentration of hydrogen in liquid phase, mole/L

C_{G,H_2}	Hydrogen concentration in the gas phase, mole/L
F_{G,H_2}	Hydrogen flow rate, mol/s
F_{Li}	Molar flow rate per unit surface area of component I, mol/s
H	Henery coefficient, (-)
N_{GL,H_2}	Mass transfer rate of hydrogen in the gas phase, mol/m² s
ρ_{bed}	Bed density, kg/m³
$K_{L,G}$	Mass transfer coefficient of the liquid phase, m/s
Q_G	Gas phase flow rate, mL/min
Q_L	Liquid phase flow rate, mL/min
v_L	Superficial liquid phase, m/s
v_G	Superficial gas phase, m/s
Re_L	Liquid phase Reynold number, (-)
ε_S	Solid volume fraction, (-)
ε_L	Liquid phase porosity, (-)

REFERENCES

[1] Dupont L.A., Gupta V.P., Degradative Transesterification of Terephthalate Polyesters to Obtain DOTP Plasticizer for Flexible PVC, *J. Vinyl Technol.*, **15**: 100-104 (1993).

[2] Yu L., Li S., Ma G., Sun J., Experimental Research on The Effect of 2-Ethylhexanol on Water Boiling Heat Transfer At Subatmospheric Pressure, *Heat Transfer-Asian Res.*, **45(2)**: 199-208 (2016).

Research Article

[3] Hreczuch W., Dąbrowska K., Chruściel A., Sznajdrowska A., Materna K., 2-Ethylhexanol Derivatives as Nonionic Surfactants: Synthesis and Properties, *J. Surf. Detergents*, **19(1)**: 155-164 (2016).

[4] Komoń T., Niewiadomski P., Oracz P., Jamróz M. E., Esterification of Acrylic Acid With 2-Ethylhexan-1-Ol: Thermodynamic And Kinetic Study, *Appl. Catalysis, A: General*, **451**: 127-136 (2013).

[5] Gunther K., Cornils B., Gick W., Ernst W., Hibbel J., Bach H., Zgorzelski W., Process for The Production of 2-Ethyl-Hexanol, *U.S. Patent* 4684750, (1987).

[6] Miller R., Bennett G., Producing 2-Ethylhexanol by the Guerbet Reaction, *Ind. Eng. Chem.,* **53 (1)**: 33-36 (1961).

[7] Poe R.L., Greater Selectivity in the Guerbet Reaction, *U.S. Patent 3328470*, (1967).

[8] Gunther K., Cornils B., Gick W., Ernst W., Hibbel J., Bach H., Zgorzelski W., Process for the Production of 2-Ethyl-Hexanol. *U.S. Patent, 4684750* (1987).

[9] Thurman L.R., Harris J.B., Process for the Production of 2-Ethylhexanol, *U.S. Patent 5227544*, (1993).

[10] Lueken H.G., Uwe T., Wilhelm D., Ludwig G., Gubisch D., Process For The Preparation of 2-Ethylhexanol by Liquid-Phase Catalytic Hydrogenation of 2-Ethylhexenal, and Catalyst, U.S. *Patent 4968849*, 6, (1990).

[11] Collins D.J., Grimes D.E., Davis B.H., Kinetics of the Catalytic Hydrogenation 2-Ethyl-Hexenal, *Can. J. Chem. Eng.*, **61**: 36-39 (2009).

[12] Smelder G., Kinetic Analysis of the Liquid Phase Hydrogenation of 2-Ethyl-Hexenal in the Presence of Supported Ni,Pd and Ni-S Catalyst, *Can. J. Chem. Eng.,* **67**: 51-61 (1989).

[13] Rajashekharam M. V., Jaganathan R., Chaudhari V., A Trickle Bed Reactor Model For Hydrogenation of 2,4 Dinitrotoluene: Experimental Verification, *Chem. Eng. Sci.*, **53**: 787-805 (1998).

[14] Both R., Cormos A. M., Agachi P.-S., Festila C., Dynamic Modeling And Validation of 2-Ethyl-Hexenal, *Comput. Chem. Eng.*, **52**: 100-111 (2013)

[15] Ghaemi A., Zerehsaz M. H., Experimental Study on Operating Conditions of 2-Ethylhexanol Manufacturing Process, *Mater. Manuf. Process.*, **33**: 829-834 (2018).

[16] Lange R., Schubert M., Dietrich W., Grunewald M., Unsteady State Operation of Trickle Bed Reactors, *Chem. Eng. Sci.*, **59**: 5355-5361 (2004).

[17] Authayanun S., Pothong W., Saebea D., Modeling of Industrial Fixed Bed Reactor Based on Lumped Kinetic Models for Hydrogenation of Pyrolysis Gasoline, *J. Ind. Eng. Chem.*, **14**: 771-778 (2008).

[18] Scott Fogler H., "Elements of Chemical Reaction Engineering", Fifth Edition, The University of Michigan, Ann Arbor, The United States of America (2006).

[19] Lange R., "Beitrang Zur Experimentellen Untersuchung Und Modellierung Von Teilprozessen fur Katalytische Dreiphasenreaktionen Im Rieselbettreaktor", Ph.D. Thesis, Technical University of Leuna Merseburg, Germany, (1978).

[20] Ghaemi A., Shahhosseini S. Ghannadi Maragheh M., Nonequilibrium Dynamic Modeling of Carbon Dioxide Absorption by Partially Carbonated Ammonia Solutions, *Chem. Eng. J.*, **149**: 110-117 (2009).