

Modelling, Sensitivity Analysis and Optimization of Acetylene Hydrogenation Reactor

Mehran Moazeni Targhi, * Mehdi Rafizadeh

Department of Chemical Engineering, Islamic Azad University- South Tehran Branch, Tehran, Iran
Corresponding Author: Mehdi Rafizadeh

Abstract: Acetylene is considered as an undesired component in polymerization reactors, which can afford unwanted properties in the final products and harmful effects on the related catalyst. The most efficient method to eliminate Acetylene and to decrease its purity to 2-3 part per million is the selective hydrogenation process. Even though widespread experimental efforts have been implemented on different aspects of acetylene hydrogenation reactors in many articles, they mostly represent a modelling which may be accurate for that special case study, and different parameters variations which are effective in the modelling, have not been investigated based on valid industrial process criteria as sensitivity analysis and optimization cases. In this article, Acetylene hydrogenation reactor modelling is being implemented on a pseudo homogenous one dimensional adiabatic steady state plug flow reactor in order to investigate temperature and concentration changes along the reactor length which is achieved by solving mass and energy balance equations simultaneously which shows less than 1% error for molar Acetylene conversion. Subsequently sensitivity analysis is implemented on the modelling based on two process limitations which are inlet temperature and Hydrogen to Acetylene molar ratio. Furthermore, optimization is performed on various objective functions such as selectivity and Yield to achieve the most optimum values for these reactors inlet conditions.

Keywords: Reactor modelling, Hydrogenation of Acetylene, Reactor optimization, Golden section search optimization method, Sensitivity analysis.

Date of Submission: 12-09-2017

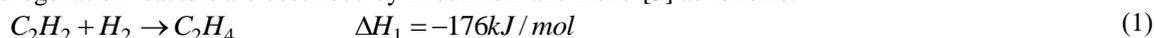
Date of acceptance: 07-10-2017

I. Introduction

One of the most important processes in petrochemical industries is naphtha cracking which produces different products such as Ethylene and other hydrocarbons (including Acetylene as impurity). These products are introduced as the main feed in polymerization and polyethylene production processes. Acetylene is known as the impurity of this process which inactivates the Ziegler-Natta catalysts in Ethylene polymerization reactor. Even small amounts of Acetylene remained in the outlet cracking streams can be harmful to these catalysts. Excess Acetylene in the stream will lead to increase impurity in the steam and affects ethylene grade and polymer properties in the polymerization process negatively [1].

For removing Acetylene, it is possible to apply one of the widely used industrial methods such as hydrogenation processes by selective catalysts which uses hydrogenation phenomena in order to convert Acetylene into other components. Selective catalysts shall conduct the reactions to maximum conversion of the desired reaction as well as minimizing the undesired reaction yields and also lead them to a minimal loss of the main component in the process which is Ethylene here [1]. Elements such as Fe, Co and Ni are being used in catalysts of the reactors applied in hydrogenation processes. Palladium is among the most widely used industrial catalysts in Acetylene Hydrogenation processes which is placed in multi-bed adiabatic reactors as Eggshell Catalyst pellets. Selectivity of the catalyst has a significant importance because several reactions take place simultaneously and the only desired reaction in this process is the hydrogenation of Acetylene. Therefore increasing the catalyst's selectivity can prevent the other undesired reactions [2].

Over the past few decades, extensive research has been implemented on the Acetylene hydrogenation process catalysts and one of the most successful one is the studies conducted by Bond et al (1950) that used palladium in this process for the first time. Several years later these results were represented as a commercial catalyst in acetylene hydrogenation process which contained 0.04 wt.% palladium deposited on Aluminum Oxide Pellets [2]. Catalyst optimizations led this catalyst to bimetallic eggshell catalysts especially Pd-Ag/Al₂O₃ to reduce the mass transfer resistance effect during the reaction. Reactions that occur in acetylene hydrogenation reactors are described by Brodzinski and Bond [3] as follows.





The desired reaction is the selective hydrogenation of Acetylene reaction (1) while in the undesired reaction (2) Ethylene is converted into Ethane by hydrogenation. Also in reaction (3) Acetylene is converted to Butene by hydro oligomerization reaction which is a desired reaction to convert Acetylene but its product is a heavier hydrocarbon. Acetylene hydrogenation takes place in two different process arrangements called front-end and tail-end processes. These are named according to the location of hydrogenation reactor versus the Coldbox. In the front-end process the reactors are located before the Coldbox while in the tail-end process it is located after it. Chemical reactors are designed based on the reliable and operational kinetics relations. The first step to obtain a kinetic equation is to investigate to achieve the perfect catalyst in the related reaction that has specifications such as selectivity and high production yield while multiple reactions occur simultaneously. After the catalytic studies, the experimental investigation on the reaction in the laboratory based on the catalyst will be implemented where a considerable number of experimental tests are carried out and the reactions kinetics can be formulated by different statistical methods. Extensive research is conducted on the selective Acetylene hydrogenation reaction kinetics which indicates the importance of this process to avoid damaging the downstream catalysts of the next reactors and increase the purity in the final product.

Table 1 indicates some of the most trusted and widely used kinetic equations. Each of the kinetic equations presented are based on a pre-defined mechanism according to its related assumptions and all of them have showed compatibility with the experimental data in numerous articles. Some of the mechanisms used for kinetic studies of this process are Langmuir-Hinshelwood, Rideal-Eley and power law mechanisms.

In Table 1 results of studies related to Kho Gva [4], Menshchikov et al [5], Schbib et al. [6] and Godinez et al [7], have led to the presentation of new kinetic models consistent with the experimental data. The Kinetic methods used in Brodzonski and Cybulski [8], Moustofi et al [9] and Zhvanetskii and Berenblyum [10] are based on the kinetic relations in other studies. Operating temperature range used in Vincent and Gonzales [11] is different from the known conditions of this process which indicates lack of detailed analysis of the related study.

Table 1- Different kinetics studies of acetylene hydrogenation reaction

Item	Acetylene Hydrogenation Kinetic Equations	Reference
1	$r_{C_2H_6} = \frac{k_2' \times P_{C_2H_4}^{0.5} \times P_{H_2} + k_1' \times P_{C_2H_2} \times P_{H_2}^{1.5}}{(\sqrt{P_{H_2}} + D_3 \times P_{C_2H_2} + D_2 \times P_{C_2H_2})^2}$ $r_{C_2H_2} = \frac{k_4' \times P_{C_2H_2}^{0.5} \times P_{H_2} + k_1' \times P_{C_2H_2} \times P_{H_2}^{1.5}}{(\sqrt{P_{H_2}} + D_3 \times P_{C_2H_2} + D_2 \times P_{C_2H_2})^2}$	Duisenbaev et al. [12]
2	$r_{C_2H_6} = \frac{k_2' \times P_{C_2H_4} \times P_{H_2}}{(1 + k_{C_2H_2}'' \times P_{C_2H_2} + k_{C_2H_4} \times P_{C_2H_4})^3}$ $r_{C_2H_2} = \frac{k_4' \times P_{C_2H_2} \times P_{H_2}}{(1 + k_{C_2H_2} \times P_{C_2H_2}) \times (1 + k_{H_2} \times P_{H_2})}$	Bos et al. [13]
3	$r_{C_2H_6} = \frac{k_2' \times P_{C_2H_4} \times P_{H_2}}{P_{H_2} + Z_2 \times P_{C_2H_2} + Z_3 \times P_{H_2} \times P_{C_2H_2} + Z_6 \times P_{C_2H_4}}$ $+ \frac{k_1' \times P_{H_2}^2 \times P_{C_2H_2}}{(P_{H_2} + Z_2 \times P_{C_2H_2} + Z_3 \times P_{H_2} \times P_{C_2H_2} + Z_6 \times P_{C_2H_4})^2}$ $r_{C_2H_2} = \frac{(k_1' + k_4') \times P_{H_2}^2 \times P_{C_2H_2} + k_4'' \times P_{H_2} \times P_{C_2H_2}}{P_{H_2} + Z_2 \times P_{C_2H_2} + Z_3 \times P_{H_2} \times P_{C_2H_2} + Z_6 \times P_{C_2H_4}}$	Zwanetski et al. [10]
4	$r_{C_2H_2} = k_4' \times P_{C_2H_2}^{m_1} \times P_{H_2}^{m_2} \quad r_{C_2H_6} = k_2' \times P_{C_2H_4}^{m_4} \times P_{H_2}^{m_5}$	Godinez et al. [7]
5	$r_{C_2H_6} = \frac{k_2' \times P_{C_2H_4} \times P_{H_2}}{(1 + k_{C_2H_2}^E \times P_{C_2H_2} + k_{C_2H_4}^E \times P_{C_2H_2})^2} + \frac{k_1' \times P_{C_2H_2} \times P_{H_2}^2}{(1 + k_{C_2H_2}^A \times P_{C_2H_2})^3}$	Borodzinski, Cybulski [8]

	$r_{C4} = \frac{k_5' \times p_{C2H2}^2 \times p_{H2}}{(1+k_{C2H2}^A \times p_{C2H2})^3}$ $r_{C2H2} = \frac{k_3' \times p_{C2H2}}{1+k_{C2H2}^A \times p_{C2H2}} + \frac{k_4' \times p_{C2H2} \times p_{H2}}{(1+k_{C2H2}^A \times p_{C2H2})^2} +$ $\frac{2k_5' \times p_{C2H2}^2 \times p_{H2} + k_1' \times p_{C2H2} \times p_{H2}^2}{(1+k_{C2H2}^A \times p_{C2H2})^3}$	
6	$r_{C2H2} = -\frac{k_1 \times C_A \times C_{H2}}{(1+\sqrt{k_{H2} C_{H2}} + k_{C2H2} C_{C2H2} + k_{Ey} C_{Ey} + k_{Ea} C_{Ea} + k_{CO} C_{CO})^3}$ $r_{Ey} = -\frac{k_2 \times C_{Ey} \times C_{H2}}{(1+\sqrt{k_{H2} C_{H2}} + k_{C2H2} C_{C2H2} + k_{Ey} C_{Ey} + k_{Ea} C_{Ea} + k_{CO} C_{CO})^3}$	Schbib et al. [6]
7	$r_{C2H2} = \frac{k_1 \times K_A \times K_{H2} \times p_{C2H2} \times p_{H2}}{(1+k_{C2H2} \times p_{C2H2} + k_{Ey} \times p_{Ey}) \times (1+k_{H2} \times p_{H2})}$ $r_{C2H2} = \frac{k_2 \times K_{Ey} \times K_{H2} \times p_{Ey} \times p_{H2}}{(1+k_{C2H2} \times p_{C2H2} + k_{Ey} \times p_{Ey}) \times (1+k_{H2} \times p_{H2})}$	Menshchikov [5]
8	$r_{C2H2} = -\frac{k_1 \cdot K_1 \cdot K_2 \cdot K_3 \cdot p_{C2H2} \cdot p_{H2}}{1+k_2 \cdot p_{C2H2} + k_5 \cdot p_{C2H4}}$ $r_{C2H6} = -\frac{k_2 \cdot K_1 \cdot K_5 \cdot K_6 \cdot p_{C2H4} \cdot p_{H2}}{1+k_2 \cdot p_{C2H2} + k_5 \cdot p_{C2H4}} - \frac{k_3 \cdot K_1 \cdot K_8 \cdot K_9 \cdot p_{C2H4} \cdot p_{H2}}{(1+k_8 \cdot p_{H2} + k_{11} \cdot p_{C2H2})^3}$ $r_{C2H2} = -\frac{k_1 \cdot K_1 \cdot K_2 \cdot K_3 \cdot p_{C2H2} \cdot p_{H2}}{1+k_2 \cdot p_{C2H2} + k_5 \cdot p_{C2H4}} - \frac{k_2 \cdot K_1 \cdot K_5 \cdot K_6 \cdot p_{C2H4} \cdot p_{H2}}{1+k_2 \cdot p_{C2H2} + k_5 \cdot p_{C2H4}}$ $-\frac{k_3 \cdot K_1 \cdot K_8 \cdot K_9 \cdot p_{C2H4} \cdot p_{H2}}{(1+k_8 \cdot p_{H2} + k_{11} \cdot p_{C2H2})^3}$	Gva and Kho [4]
9	$r_{C4} = \frac{k_3 \times p_{C2H2} \times p_{H2}^{0.5}}{(1+K_{A,13} \times p_{C2H2})^2}$ $r_{C2H2} = \frac{k_1 \times p_{C2H2} \times p_{H2}^{0.5}}{(1+K_{A,13} \times p_{C2H2})^2}$ $r_{C2H4} = \frac{k_2 \times p_{C2H4} \times p_{H2}^{0.5}}{(1+K_{A,2} \times p_{C2H2})^2}$	Pachulski [2]

In this paper, the kinetic equations which are being used in the reactor modeling are developed by Pachulski [2] in a comprehensive experimental work. The mentioned kinetics are selected for various reasons such as the reliability of the introduced equations based on the presented results, full compliance with the laboratory results, developed statistical method with reproducibility, applicability in industrial operations because of the industrial catalyst and using these kinetic equations to design a new TEMKIN reactor with the new structure that has been fully investigated in reference [14]. The general form of kinetic model used in reference [2] is based on Langmuir-Hinshelwood mechanism. This equation is written in terms of partial pressure in which p_i is the partial pressure of component i and includes the reaction degree $n_{i,j}$ and the number of active sites participating in the reaction is shown as γ as can be seen in equation (4).

$$r_j = \frac{k_j \cdot \prod_{i=1}^N K_i p_i^{n_{i,j}}}{\prod_{i=1}^N (1 + \sum_{i=1}^N K_{i,j} \cdot p_i)^\gamma} \tag{4}$$

Temperature dependency of kinetic equations can be observed in the rate constant k_j and absorption constant $K_{i,j}$ which are presented by Arrhenius and Van Hoff equations which are indicated in equation (5) and (6).

$$k_j = k_{j\infty} \cdot \exp\left(-\frac{E_j}{RT}\right) \tag{5}$$

$$K_{i,j} = K_{i,j\infty} \cdot \exp\left(-\frac{\Delta_{ads} H_{i,j}}{RT}\right) \tag{6}$$

II. Reactor Modeling

Acetylene hydrogenation reactor modeling is based on solving mass and energy balance equations simultaneously. Mass and energy balance equations are generally expressed by ordinary differential equations. The result of kinetic modeling of chemical reactors includes the concentration and Temperature gradients of different components. The intended reactor is a one-dimensional pseudo-homogeneous adiabatic reactor at steady-state. The geometry of the reactor is presented in Figure 1.

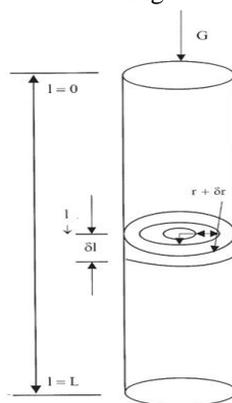


Figure 1- Acetylene hydrogenation reactor model

Acetylene hydrogenation reactor operating conditions which are experimentally examined in [2], are presented in Table 2.

Table 2- Experimental reactor operating conditions for acetylene hydrogenation reaction [2]

Operating Conditions	
Gas Flowrate (m ³ /h)	365
Pressure (bar)	19
Catalyst filling length (mm)	700
Reactor diameter (mm)	400
Allowable inlet temperature (K)	293-423
Allowable outlet temperature (K)	313-523
Allowable H ₂ /C ₂ H ₂ mole ratio	0.8-2

Also the gas compositions measured in ref. [2] is according to Table 3.

Table 3- Molar composition percentage of the gas [2]

Components	Inlet (mol%)	Outlet (mol%)
Acetylene	1.02270	0.45116
Hydrogen	0.81769	0.09353
Ethylene	78.6129	79.6627
Ethane	19.5465	19.7926
Butane	---	---

The Temperature gradient versus the length of reactor measured experimentally in reference [2] which is mentioned in Table 4:

Table 4- The temperature gradient

Reactor Length (mm)	Temperature (K)
0	308.15
175	320.15
325	332.15
475	333.15
625	335.15

Stream properties are mentioned in Table 5.

Table 5-Chemical parameters

Chemical properties		
\bar{c}_p	Kj/kmol.K	49.03
$\bar{\mu}_g$	Kg/(ms)	1.22
\bar{M}	Kg/kmol	28.29
$\bar{\rho}_g$	Kg/m ³	21.415

Reactor’s pressure drop is in the negligible range of less than 0.1 bar. One of the assumptions for this modeling includes ignoring the penetration and thermal conductivity in two radial and axial directions because they have negligible impacts. The gas and catalyst can be considered as pseudo-homogeneous and equation variables are only related to the axial direction. Thus the reactor can be modeled by one-dimensional pseudo-homogeneous adiabatic calculations at steady state.

There are various methods for fixed bed reactors modelling that vary according to initial assumptions considered for reactor modeling. The equations can be one-dimensional or two-dimensional for the intended reactor. Here modeling is considered as one-dimensional for simplicity thus the thermal and concentration gradient do not exist in radial direction and only the change in the parameters is considered in the longitudinal direction of the reactor. This simplification is correct in adiabatic reactors. If the reactor is considered as adiabatic, heat transfer does not occur in the walls of the reactor thus the flow velocity profile is plug and the lack of transmission mechanism in the radial direction can be seen. Of course, it should be noted that the thin layer fluid film will be on the wall and will cause a slight error. Hydrogenation reactor is considered as pseudo homogeneous. In the pseudo homogeneous the Temperature of the flow, catalyst and reactor walls are considered as equal. In case of modeling the pseudo homogeneous reactor, this modeling can be used in various industrial applications due to its high accuracy.

2.1 Acetylene hydrogenation mass balance

To model the pseudo homogeneous adiabatic plug flow reactor at steady state the population balance equations shall be written separately for each one of the components (with index j) and solved at the same time along with the energy balance equation. A control system including an increment of catalyst (ΔW) related to the volume $\Delta W/\rho_b$ as the reactor cross section is considered [15]:

$$\left[\begin{matrix} \text{Rate of } j \text{ flowing out} \\ \text{of the volume element} \end{matrix} \right] - \left[\begin{matrix} \text{Rate of } j \text{ flowing in to} \\ \text{the volume element} \end{matrix} \right] = \left[\begin{matrix} \text{Rate of production of } j \\ \text{in the volume element} \end{matrix} \right] - \left[\begin{matrix} \text{Rate of consumption of } j \\ \text{in the volume element} \end{matrix} \right] \quad (7)$$

So it can be written as follows:

$$\Delta F_j = \Delta W \sum_{n=1}^n v_{j,n} \hat{r}_n \quad j = 1, \dots, c \quad (8)$$

Now by tending ΔW to 0 the following equation is obtained:

$$\rho_b \frac{dF_j}{dW} = \rho_b F_A \frac{dn_{ja}}{dW} = \rho_b \frac{dn_{ja}}{d(W/F_A)} = \frac{G.Y_{A0}}{M_F} \frac{dn_{ja}}{dz} = \rho_b \sum_{n=1}^n v_{j,n} \hat{r}_n \quad j = 1, \dots, c \quad (9)$$

In the intended section the composition, temperature, catalyst and flow conditions are considered constant. The equation (9) considers mass velocity (G) and due to its association with the transport phenomena equations, this term is widely being used in technical discussions and design of chemical reactors [30]. For each of the components the following equations can be written [15]:

$$\frac{G.Y_{A0}}{M_F} \frac{dn_{ja}}{dz} = \rho_b \sum_{n=1}^n v_{j,n} \hat{r}_n \quad j = 1, \dots, c \quad (10)$$

$$\frac{dn_{ja}}{dz} = \frac{M_F \cdot \rho_b}{G.Y_{A0}} \sum_{n=1}^n v_{j,n} \hat{r}_n \quad j = 1, \dots, c \quad (11)$$

$$\frac{G.Y_{A0}}{\rho_b \cdot M_F} \frac{dn_{Aa}}{dz} = \frac{dn_{Aa}}{d(W/F_A)} = -\hat{r}_A \quad \Rightarrow \quad -\frac{dn_{Aa}}{d(W/F_A)} = \hat{r}_A \quad (12)$$

Since $-dn_{Aa} = dx_A$ then:

$$\frac{G Y_{A0}}{\rho_b \cdot M_F} \frac{dx_A}{dz} = - \frac{dx_A}{d(W / F_A)} = -\hat{r}_A \quad (13)$$

Where x_A indicates conversion (mole A converted per mole A feed) and $-r_A$ is the rate of consumption of A [15].

2.2 Acetylene hydrogenation reactor energy balance

To analyze energy balance it is possible to consider a control volume as Fig 2 the volume is equal to ΔV , the molar flow of the reactant A and enthalpy are presented as F_A and H respectively [16].

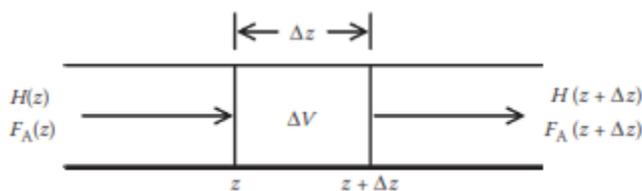


Figure 2- Modeling the control volume

Energy balance is studied to evaluate the enthalpy changes and these changes are due to the temperature and composition variations in the reaction. Here the kinetic and potential changes are ignored. Heat loss to the surrounding environment for an adiabatic reactor considers as zero. Energy balance can be written as follows [16]:

$$[Enthalpy In] - [Enthalpy Out] = 0 \quad (14)$$

$$-Q_V \rho C_p \Delta T = \Delta V \rho_b \eta (-R_A)_s \Delta H_R = 0 \quad (15)$$

Now by tending the term of ΔV to dV , it is possible to bring the length of the reactor into account:

$$dV = A_c dz \quad (16)$$

$$- \frac{Q_V}{A_c} \rho C_p \frac{dT}{dz} - \rho_b \eta (-R_A)_s \Delta H_R = 0 \quad (17)$$

Where A_c is the cross-sectional area of the reactor. The above equation can be written as follows based on the superficial mass velocity ($G = \rho v_s$) is constant which is considered constant here:

$$- v_s \rho C_p \frac{dT}{dz} - \rho_b \eta (-R_A)_s \Delta H_R = 0 \quad (18)$$

Since several reactions occur simultaneously, the energy balance can be written as follows:

$$- v_s \rho C_p \frac{dT}{dz} - \rho_b \sum_{i=1}^n \eta_i (-R_i)_s (\Delta H_R)_i = 0 \quad (19)$$

Specific heat capacity C_p is a function of temperature and composition. Solving mass and energy will represent the temperature and concentration profiles [16].

2.3 Acetylene hydrogenation reactor modelling

In order to produce concentration and Temperature profiles along the reactor, four ODE equations that include an energy balance equation (Eq. 13) and three population balance equations (Eq. 19) for each of the key components in the reactor shall be solved at the same time. Hence Four boundary conditions are considered to solve the above equations that are acetylene, ethane and butane conversions at the beginning of the reactor and the reactor input temperature as follows [2]:

$$x_{in} (Acetylene) = 0 \quad (20)$$

$$y_{in} (Ethane) = 0 \quad (21)$$

$$y_{in} (Butene) = 0 \quad (22)$$

$$T_{in} = 308.15 \quad (23)$$

MATLAB software is being used to model and optimize the discussed reactor. In order to solve differential equations of mass and energy balances, the ODE23S solver is applied which uses the modified second order Rosenbrock method. Rosenbrock method is formulated by Runge Kutta method which is also known as diagonally implicit Rung Kutta method. Modified Rosenbrock method uses the following approximation for the Jacobian matrix:

$$J = \frac{\partial f(y_0)}{\partial y}(t_0, y_0) + hB + O(h^2) \quad (24)$$

Modified Rosenbrock three-step algorithm is as follows [17]:

$$f_0 = f(t_0, y_0) \quad (25)$$

$$k_1 = W^{-1}(f_0 + hdT) \quad (26)$$

$$f_1 = f(t_0 + 0.5h, y_0 + 0.5hk_1) \quad (27)$$

$$k_2 = W^{-1}(f_1 - k_1) + k_1 \quad (28)$$

$$y_1 = y_0 + hk_2 \quad (29)$$

$$f_2 = f(t_1, y_1) \quad (30)$$

$$k_3 = W^{-1}[f_2 - e_{32}(k_2 - f_1) - 2(k_1 - f_0) + hdT] \quad (31)$$

$$error \approx \frac{h}{6}(k_1 - 2k_2 + k_3) \quad (32)$$

Where the following values are replaced in the above formulas:

$$W = I - hdJ \quad (33)$$

$$d = \frac{1}{(2 + \sqrt{2})} \quad (34)$$

$$J \approx \frac{\partial f}{\partial y}(t_0, y_0) \quad (35)$$

$$T \approx \frac{\partial f}{\partial t}(t_0, y_0) \quad (36)$$

$$e_{32} = 6 + \sqrt{2} \quad (37)$$

This method uses the value of y_1 to achieve the solution of each step. If the value is accepted, the corresponding f_2 value will be used as f_0 in the next step. Using this method calculates the Jacobian matrix at each step. One of the advantages of this method is to change the size of step at each step that accelerates convergence, prevents trapping in local minimum and leads to more accurate results. Since the reaction is not in the gas phase and pressure drop is very low, analyzing the pressure gradient in the reactor is ignored. It should be noted that in case of the need to analyze the pressure gradient in this system, Ergun equation can be considered [17].

2.4 Acetylene hydrogenation reactor optimization

As the process plants have become more advanced, the optimization of chemical reactors' parameters is considered as a necessity in process research and development. Therefore, using a reliable algorithm to optimize parameters correctly is inevitable. In order to achieve this purpose, the first step is to choose an appropriate algorithm. In this study, optimization is implemented by golden section search algorithm along with parabolic interpolation that has a relatively good convergence rate to find nonlinear functions' optimums. This function investigates the minimum value within the interval $x_1 < x < x_2$ [18].

The next step is to define the objective function for optimization. In systems with chemical reactions it is possible to use yield, selectivity, economic and energy functions as objective functions. The overall selectivity can be considered as the ratio of reaction rate equations. The intended optimization objective function which is used in this article is acetylene to ethane selectivity:

$$f(1) = \frac{r(1)}{r(2)} \quad (38)$$

The intended variables for optimization are based on table 6:

Table 6-Optimization variables

Optimization variables	Description
x(1)	Acetylene conversion
x(2)	Ethane Yield (%)
x(3)	Butene Yield (%)
x(4)	Reactor inlet temperature

Thus the vector containing the target variables is considered as below:

$$X = [x_1, x_2, x_3, x_4] \quad (39)$$

Different constraints can be used for optimization. In this study the inequality constraints are used to limit the scope of variables and avoid being trapped in local minimum as follows:

$$0.5 \leq x_1 \leq 0.6 \tag{40}$$

$$0.2 \leq x_2 \leq 0.25 \tag{41}$$

$$0.06 \leq x_3 \leq 0.1 \tag{42}$$

$$330 \leq x_4 \leq 340 \tag{43}$$

Choosing the values in constraints for optimization is based on two approaches. The first approach is the industrial and laboratory range of the values based on different reports in the papers [2]. The second approach is to choose a range based on the modeling results in this study because the first reactor modeling is conducted and then after extracting the results a limiting range is considered for the reported variables as the optimized variables.

III. Results

3.1 Acetylene hydrogenation reactor modelling results

In this section the results will be discussed and their reliability is evaluated by converging to the experimental data. In order to validate the modelling, the results of this article are compared with the data from reference [2] which results are from an extensive laboratory work along with developing new kinetics as they are mentioned in the table 7:

Table 7- Experimental data on gas molar percentage changes

Components	Inlet composition (mol%)	Outlet composition (mol%)	Composition variations
Acetylene	1.02270	0.45116	0.57154
Hydrogen	0.81769	0.09353	0.72416
Ethylene	78.6129	79.6627	1.0498
Ethane	19.5465	19.7926	0.2461
Butene	---	---	---

MATLAB software is applied for reactor modelling and the results and convergence in the different sections are shown in Table 8.

Table 8- Concentration and temperature gradients in terms of reactor's length

Length of catalytic bed (m)	Acetylene converted (mole fraction) or Conversion	Ethane produced (mole fraction) or Ethane yield	Butene produced (mole fraction) or Butene yield	Temperature (K)
0	0	0	0	308.15
0.07	0.0751	0.0375	0.0105	311.72
0.14	0.1603	0.0787	0.0223	315.73
0.21	0.2553	0.1226	0.0355	320.15
0.28	0.3563	0.1665	0.0496	324.76
0.35	0.4525	0.2039	0.0629	329.03
0.42	0.5268	0.2265	0.0733	332.15
0.49	0.5639	0.2328	0.0784	333.56
0.56	0.5666	0.233	0.0788	333.66
0.63	0.5667	0.233	0.0788	333.66
0.7	0.5667	0.233	0.0788	333.66

As it can be observed, the acetylene conversion is increased along the reactor and converged to 0.5667. Also based on the conducted modeling, the ethane and butane yields at the end of reactor are calculated as 0.233 and 0.0788. The reactor temperature is also increased along the reactor and has reached 333.66 K based on the modeling.

The Conversion and Temperature profiles (as reactor modeling results) are presented in figure 3 to 6 which indicate Acetylene Conversion, Ethane and butane yields and Temperature gradient along the reactor respectively. Figure 3 shows the conversion gradient of Acetylene in terms of the length of reactor. In the figure 3 the gradient of conversion indicates acetylene concentration changes which has its maximum inclination at the length of 0.38 m equals with 0.48 Acetylene conversion and the gradient is reduced until the length of 0.5 m and the conversion converged to the values of 0.5667 which has slight error of 0.85% in comparison with the experimental data.

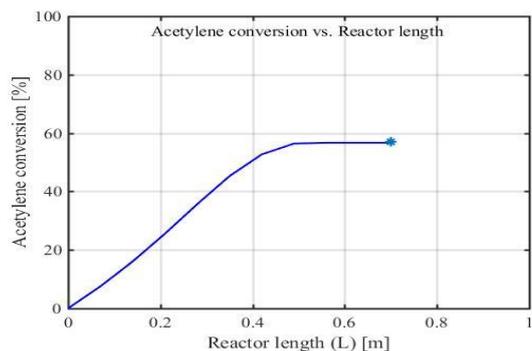


Figure 3- Acetylene conversion along the reactor

Figure 4 and 5 show Ethane and butane yields versus length of the reactor. Their analysis is similar to the analysis of Acetylene conversion which has converge into 0.233 and 0.0788 respectively.

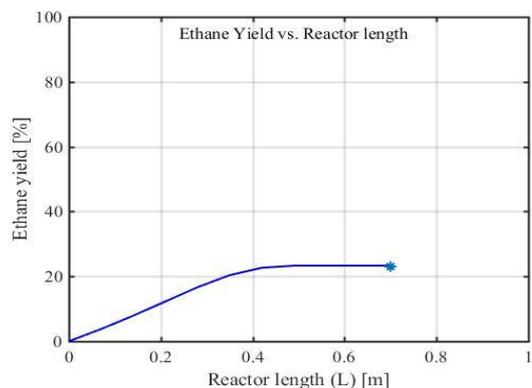


Figure 4- Ethane yield versus the reactor length

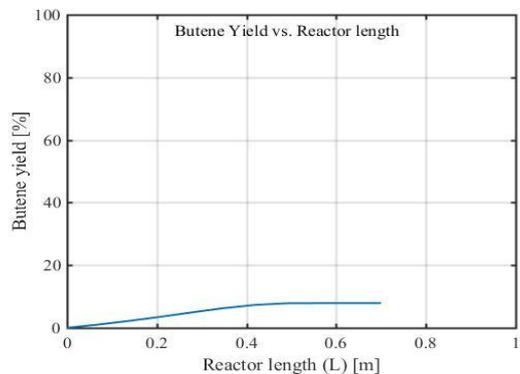


Figure 5- Butane yield versus the reactor length

Figure 6 represents the Temperature gradient which has nearly overlapped the experimental data and converged into the amount 333.66 °K at the end of the reactor.

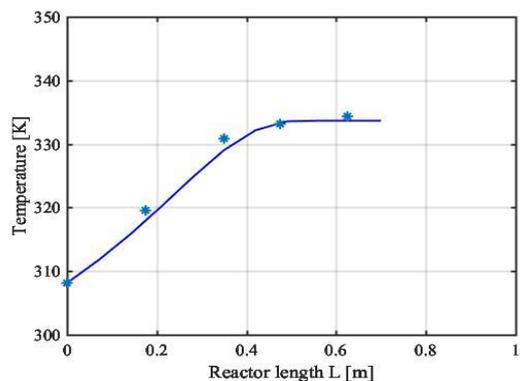


Figure 6- Temperature gradient along the reactor

In order to calculate the error between the modeling and experimental data the equation 43 is used. The numerical comparison between modeling and experimental data are mentioned in table 9.

$$\%Error = \left| \frac{Theory - Experiment}{Theory} \right| \tag{43}$$

Table 9- The results of modeling and experimental values [2]

Item	Acetylene converted (mol) or Conversion	Ethane produced (mol) or Ethane yield (%)	Butene produced (mol) or Butene yield (%)	Temperature (K)
Experimental	0.57154	0.2461	---	335.15
Modelling	0.5667	0.233	0.0788	333.6642
Error (%)	0.85	5.62	---	0.44

According to table 9 the insignificant errors of 0.85% and 0.44% are obtained for Acetylene conversion and the temperature at the end of reactor respectively which indicate correct modeling and acetylene hydrogenation reaction selectivity. Also the calculated error for Ethane yield is 5.62% which might be due to laboratory errors associated with Ethane production reaction. Due to the absence of experimental data for butane yield its error is neglected.

3.2 Acetylene hydrogenation reactor sensitivity analysis results

In this section Acetylene hydrogenation reactor behavior is investigated by considering different operating changes as sensitivity analysis. According to table 2 the typical industrial process condition criteria in C2 tail end process are the input temperature and H₂/C₂H₂ mole ratio. According to these criteria, the minimum input and output Temperatures of the reactor for this process are 293 and 313 K while the maximum values are 423 and 523 K respectively. H₂/C₂H₂ molar ratio is considered as a significant and applicable criterion as an inlet in order to control the products purities which is between 0.8 and 2, thus these values can be used for sensitivity analysis. To achieve this purpose both criteria are evaluated. For sensitivity analysis the inlet temperature and H₂/C₂H₂ molar ratio changes at the inlet of the reactor are studied and all other parameters such as operating conditions and reactor dimensions are used the same as the modeling values. The results are extracted to Microsoft Office Excel 2017 for plotting.

3.2.1 Sensitivity analysis case A: Changing inlet temperature to the reactor

The first case for sensitivity analysis was implemented by changing the inlet Temperature to the reactor temperature from 308.1 K to 355 K in 6 steps. Figures 7 to 10 indicate the system behavior for this case. In Figure 7, by increasing the inlet temperature the slope of the acetylene conversion gradient line increases along the reactor and converges into its maximum value of 0.617 at 355 K in 0.13 m of the reactor's length. Also by decreasing the temperature to 308.15 K, acetylene conversion is converged to 0.57 at 0.51 m of the reactor's length which shows a considerable decrease in slope of the gradients rather than higher temperatures. Thus the higher temperature leads to an increase both in the gradient slope and the final value of Acetylene conversion and a considerable decrease in reactor length. The interpretation of the Figure 9, which is related to butane yield in this sensitivity analysis case, is similar to Acetylene conversion analysis.

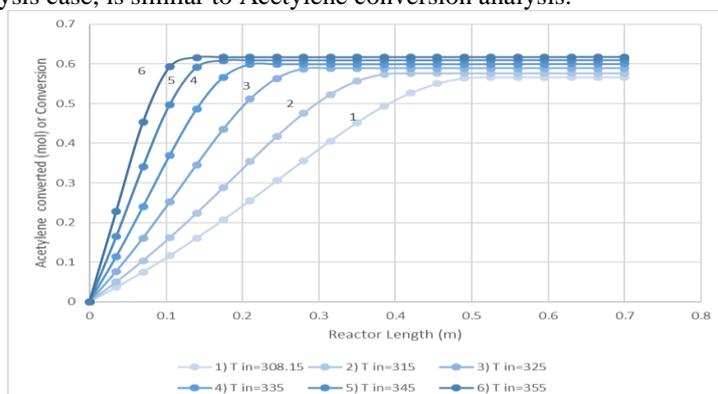


Figure 7- The effects of changing inlet Temperature on the acetylene conversion along the reactor

Figure 8 represents Ethane yield along the reactor. By increasing the input temperature to the reactor (from 308.1 K to 355 K) the amount of butane product converges into a lower value (from 0.23 to 0.18) but the reaction rate increases so that the gradient slope increases accordingly and the converging takes place in smaller

lengths of the reactor. In fact, this reaction is an unwanted reaction in our system and it should be prevented by increasing the input temperature but this will increase the energy consumption of the system.

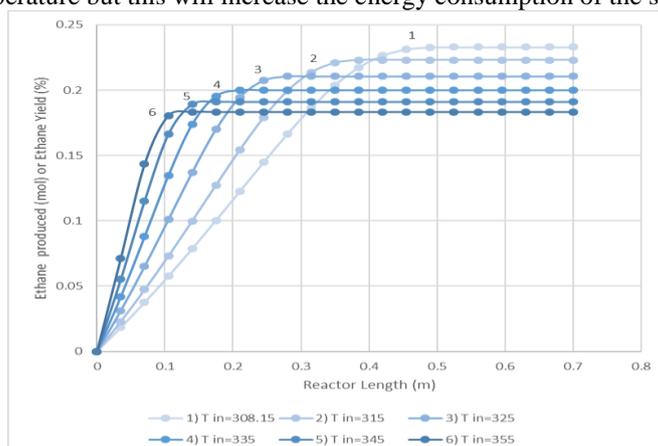


Figure 8- The effects of changing inlet Temperature on the Ethane yield along the reactor

According to Figure 10 increasing the input temperature shows direct effect on the temperature gradient itself as it soars to higher values. With changing the initial Temperature to 355 K, not only a substantial increase in the slope of the temperature gradient and final value is observed but also the effective reactor length is decreased from 0.48 m to 0.11m.

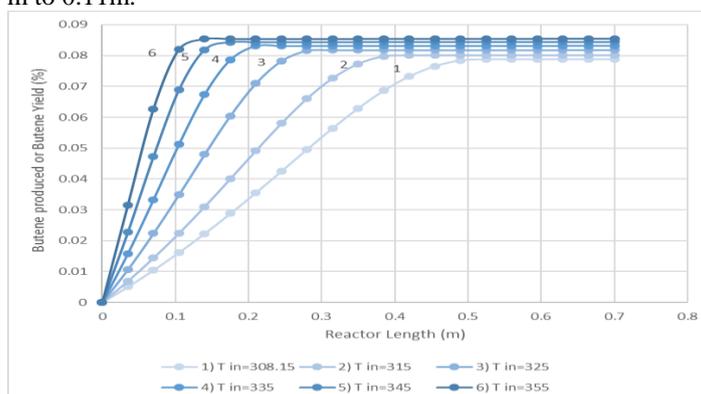


Figure 9- The effects of changing inlet Temperature on the Butane yield along the reactor

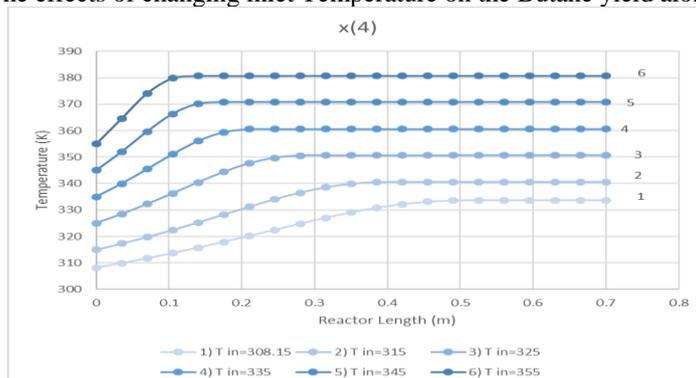


Figure 10- The effects of changing inlet Temperature on the Temperature gradient along the reactor

3.2.2 Sensitivity analysis case B: Changing inlet H_2/C_2H_2 mole ratio

For the second sensitivity analysis case, the mole ratio of H_2/C_2H_2 is changed from 0.8 to 2 in 6 steps in order to analyze the system behavior while the other inputs remained constant. As it is shown in figures 10 to 13 all figures have similar behaviors.

In Figure 11, increasing the inlet H_2/C_2H_2 mole ratio from 0.8 up to 2 will result a significant progress in all reactions specially in the desired Acetylene reaction, which converged to 0.93 of conversion in shorter length of the reactor in comparison with lower mole ratios.

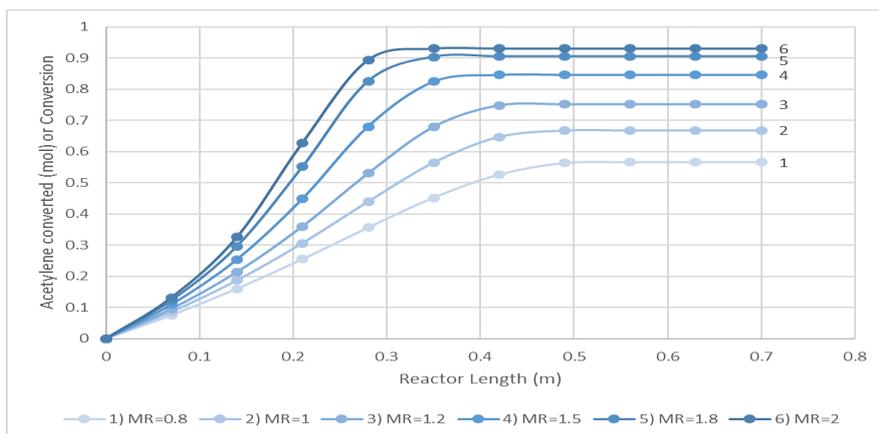


Figure 11- The effects of changing inlet H_2/C_2H_2 mole ratio on the Acetylene conversion along the reactor

Figure 12 indicates the impact of changing the inlet H_2/C_2H_2 mole ratio in Ethane production reaction which showed a similar behavior as the yield increased up to the final value of 0.97. Since this reaction is an unwanted reaction and causes the main component in the feed (Ethylene) to consume, it should be prevented by reducing the H_2/C_2H_2 molar ratio in order to prevent Ethylene loss.

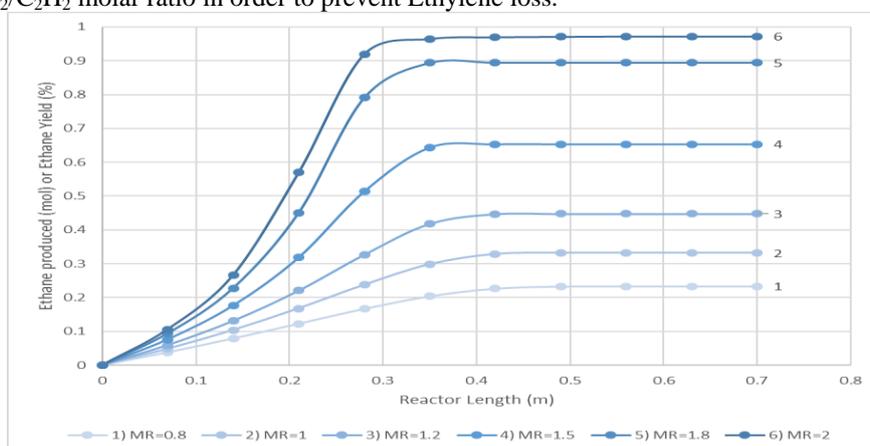


Figure 12- The effects of changing inlet H_2/C_2H_2 mole ratio on the Ethane yield along the reactor

Figure 13 illustrated equivalent behavior as the Butene yield changed from 0.078 to 0.129 which shows a considerable increase in Acetylene conversion.

Figure 14 represents Temperature gradient in the reactor. Increasing the inlet H_2/C_2H_2 mole ratio indicated an excess growth in outlet Temperature value and gradient's slope as the higher mole ratio will lead to more progress in all the reactions and will lead them to completely consume the related components. Also all reactions are exothermic and results a remarkable excess growth in the temperature of the stream along the reactor. By reducing this ratio to 0.8 the temperature will converge into 333 K while in the mole ratio of 2 the final value will converge into 370 K.

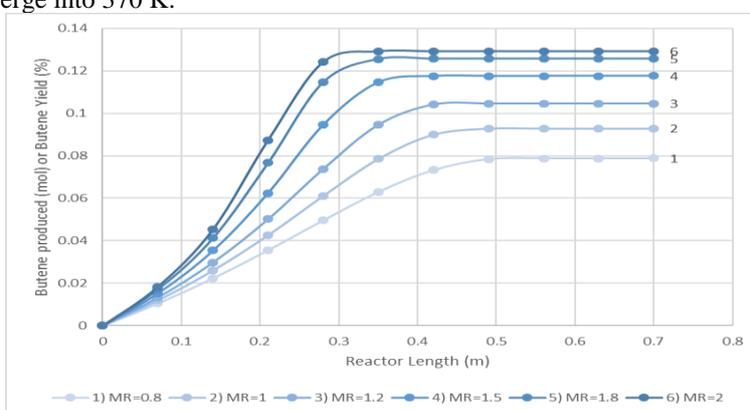


Figure 13- The effects of changing inlet H_2/C_2H_2 mole ratio on the Butene yield along the reactor

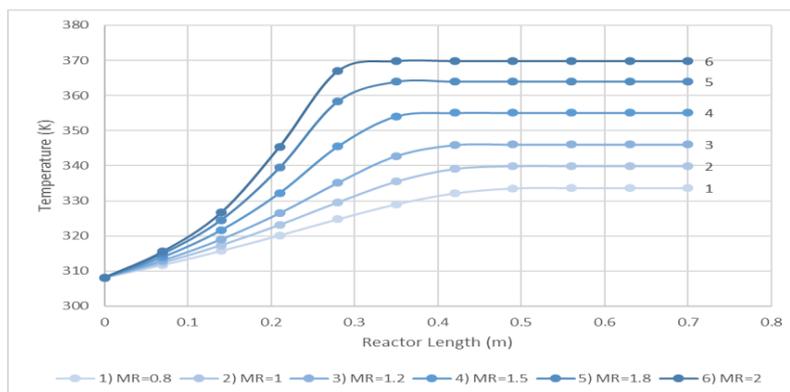


Figure 14- The effects of changing inlet H₂/C₂H₂ mole ratio on the Temperature gradient

3.3 Optimization results

The method which was used for optimization was golden section search algorithm along with parabolic interpolation. The considered objective function was the selectivity of Acetylene to Ethane and the purpose was to maximize this function which contained four parameters such as Acetylene conversion, Ethane and Butane yields and outlet Temperature. The reason for choosing the outlet values in order to optimize is that the unwanted reaction of the system is Ethane production reaction thus the outlet yield of the related reaction should be maintained at the optimized level. The obtained optimized values are provided in table 10:

Table 10– Acetylene Hydrogenation reactor optimization results

Item	Acetylene converted (mol) or Conversion	Ethane produced (mol) or Ethane yield (%)	Butene produced (mol) or Butene yield (%)	Temperature (K)
Experimental	0.57154	0.2461	---	335.15
Optimization with fminbnd algorithm	0.5382	0.2381	0.065	331.459

As it can be observed the reported outlet temperature in optimization is 3.69°C less than the experimental value which affords less Acetylene conversion and Ethane yield and keeps Ethylene loss (Ethane production) at minimum in these conditions.

IV. Conclusion

In this study, a mathematical model is discussed in order to implement the modelling of an experimental acetylene hydrogenation reactor which can be used to investigate conversion and yield gradients of different components as well as temperature gradient along the reactor. In this modeling, the acetylene conversion, Ethane and Butene yields and Temperature gradient are plotted against the length of reactor. In any scientific calculation, error is undeniable and the conducted modeling is not an exception, however it should be noted that the results of this modeling are converged to experimental data with a slight difference and the calculated error percentages of less than 1% for acetylene conversion and outlet temperature are observed.

Sensitivity analysis for two process restrictions of inlet temperature and H₂/C₂H₂ molar ratio are conducted. In both cases the conversion, yield and temperature gradients along the reactor are plotted and ultimately it is inferred that with increasing inlet temperature or H₂/C₂H₂ molar ratio, not only the Acetylene conversion gradient's inclination will be increased but also it leads to converging into higher values in lower length of the reactor. As the Acetylene hydrogenation reactions rates are increased, the unwanted Ethane production reaction which consumes the main component of the stream (Ethylene), is occurred more rapidly. Higher inlet H₂/C₂H₂ molar ratio leads to more Ethane production while increasing inlet Temperatures causes higher gradients' slopes but converge to lower values for the unwanted Ethane production reaction due to the selectivity of the catalyst in higher Temperatures.

Optimization is implemented by golden section search algorithm and parabolic interpolation with the Acetylene to Ethane selectivity function as the optimization objective function which is used in order to optimize the function for four outlet variables (Acetylene conversion, Ethane and Butane yields and Temperature). Based on the reported optimized values, the Ethane production reaction which is the undesired reaction, is remained at lower values in lower operating temperatures.

References

- [1] H. M. D. Salam Al-Dawery, "MODELING AND CONTROL OF ACETYLENE HYDROGENATION PROCESS," Emirates Journal for Engineering Research, vol. 17, no. 1, pp. 9-16, 2012.
- [2] R. S. P. C. Axel Pachulski, "Kinetics and reactor modeling of a Pd-Ag/Al₂O₃ catalyst during selective hydrogenation of ethyne," Applied Catalysis A: General, Vols. 445-446, no. 1, pp. 107-120, 2012.
- [3] G. C. B. Andrzej Borodziński, "Selective Hydrogenation of Ethyne in Ethene-Rich Streams on Palladium Catalysts, Part 2: Steady-State Kinetics and Effects of Palladium Particle Size, Carbon Monoxide, and Promoters," Catalysis Reviews, vol. 50, no. 1, pp. 379-469, 2008.
- [4] K. K. L. Gva, "Kinetics of acetylene hydrogenation on palladium deposited on alumina," Kinet. Catal. (Engl. Transl.), vol. 29, no. 1, pp. 381-386, 1988.
- [5] V. F. Y. a. A. M. Menshchikov, "Hydrogenation kinetics of acetylene on a palladium catalyst in the presence of Ethylene," Kinet. Catal., vol. 16, no. 1, pp. 1338-1355, 1975.
- [6] M. A. G. C. E. G. A. F. E. Schbib. N.S., "Kinetics of front-end acetylene hydrogenation in ethylene production," Ind. Eng. Chem. Res, vol. 35, no. 5, pp. 1496-1505, 1996.
- [7] A. L. C. . G. V. C. Godínez, "Experimental study of the tail end selective hydrogenation of steam cracking C₂-C₃ mixture," The Canadian Journal of Chemical Engineering, vol. 74, no. 1, pp. 84-93, 1996.
- [8] A. C. A. Borodzinski, "The kinetic model of hydrogenation of acetylene-ethylene mixtures over palladium surface covered by carbonaceous deposits," Applied Catalysis A-GENERAL, vol. 198, no. 1, pp. 51-66, 2000.
- [9] A. G. R. S.-G. N. Mostoufi, "Hydrogenation of acetylene: Kinetic studies and reactor modeling," International Journal of Chemical Reactor, vol. 3, no. 1, pp. 1-18, 2005.
- [10] A. B. I.M. Zhvanetskii, "Selective Acetylene Hydrogenation in Mixtures with Ethylene in the Presence of a Palladium Catalyst," Neftekhimiya, vol. 30, no. 4, pp. 453-457, 1990.
- [11] R. D. G. M. J. Vincent, "A Langmuir–Hinshelwood model for a hydrogen transfer mechanism in the selective hydrogenation of acetylene over a Pd/γ-Al₂O₃ catalyst prepared by the sol–gel method," Applied Catalysis A: General, vol. 217, no. 1, pp. 143-156, 2001.
- [12] M. A. K. Z. T. B. S. K. S. E. Duisenbaev, EuropaCat II Congress (Book of Abstracts), Maastricht, 3-8 September 1995.
- [13] A. B. K. W. A.N.R. Bos, "Mechanism and kinetics of the selective hydrogenation of ethyne and ethene," Chemical engineering and processing : process intensification, vol. 32, no. 32, pp. 1-7, 1993.
- [14] M. K. P. C. Dominik Götz, "Numerical modelling and performance studies of the original and advanced TEMKIN reactor in laboratory scale testing of industrial egg shell catalysts for the selective hydrogenation of acetylene," Chemical Engineering Research and Design, vol. 94, p. 594–604, 2014.
- [15] H. F. Rase, Fixed-bed reactor design and diagnostics, Austin, Texas: Butterworth, 1990, pp. 126-132.
- [16] P. M. R. E. Hayes, Introduction to chemical reactor analysis, Florida: Taylor & Francis Group, 2013.
- [17] M. W. R. Lawrence F. Shampine, "The MATLAB ODE Suite," SIAM Journal on Scientific Computing, vol. 18, no. 1, pp. 1-22, 1997.
- [18] S. A. T. W. T. V. B. P. F. William H. Press, Numerical recipes in C (2nd ed.): the art of scientific computing, New York: Cambridge University Press, 1992.

Mehran Moazeni Targhi. "Modelling, Sensitivity Analysis and Optimization of Acetylene Hydrogenation Reactor ." IOSR Journal of Applied Chemistry (IOSR-JAC) , vol. 10, no. 9, 2017, pp. 65–78.