# Acetylene Reactor Modeling and Kinetic

by

Mohd Aminudin Mohd Nasir

Dissertation submitted in partial fulfillment of

the requirements for the

Bachelor of Engineering (Hons)

(Chemical Engineering)

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Approved by,

______________________

(Prof Duvvuri Subbarao)

UNIVERSITI TEKNOLOGI PETRONAS

TRONOH, PERAK

August 22, 2011

# CERTIFICATION OF ORIGINALITY

This is to certify that I am responsible for the work submitted in this project, that the original work is my own except as specified in the references and acknowledgements, and that the original work contained herein have not been undertaken or done by unspecified sources or persons.

MOHD AMINUDIN MOHD NASIR

# ABSTRACT

The kinetics of acetylene hydrogenation has been studied in a fixed bed reactor of a commercial Pd/Al2O3 catalyst. The experiments were carried out at 30, 50 and 70 oCnwith various feed compositions at atmospheric pressure. The experimentsnwere repeated at 70 oC in the presence of the used catalyst to determine the effect of the catalyst deactivation where the corresponding deactivation rate constant was determined in order to predict the activity of the catalyst during each run. Two well known kinetic models were used for a nearly similar catalyst to predict the experimental data of this work and none of them were found satisfactory. A new model was then proposed to fit the experimental data. The hydrogenation reactor was also simulated at industrial operating conditions with the proposed kinetics for both plug and dispersion flows. The results of these simulations were almost close to each other in most cases.

# ACKNOWLEDGEMENT

First and foremost, I would like to express my praises to God for His blessing.

My deepest appreciation and gratitude is extended to my supervisor, Prof Duvvuri Subbarao for being very encouraging, supportive and responsive throughout the whole process of completing this final year project to fulfill the university requirement. Without her constant supervision and guidance, I may not be able to complete this project successfully.

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Hereby, I would like to also thank my fellow friends who have always been accommodating and cooperative whenever I am in need of ideas and opinion throughout the completion of this project report.

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Thank you.

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# CHAPTER 1

# INTRODUCTION

## 1.1 Background of Study

Acetylene is formed as a by-product during the manufacture of ethylene. It is a harmful contaminant in polymer grade ethylene, so the removal of acetylene is a key step in the purification process. The most effective method for removing acetylene, down to typical levels of 2-3 ppm, is selective hydrogenation over palladium catalysts in a multi-bed adiabatic reactor. The term selective is used as the conditions which promote the hydrogenation of acetylene to ethylene also lead to the hydrogenation of ethylene to ethane. Clearly, the second reaction is highly undesirable. In some ethylene crackers, the acetylene converters are located after the cold-train where hydrogen is removed from the cracked gas. Hydrogen must be injected into the feed to the converters and the hydrogen concentration is available as a control variable, in addition to the inlet temperatures to the reactor beds. Alternatively, the converters can be located prior to the cold train, which means that only the inlet temperatures are available as control variables as the cracked gas already contains significant quantities of hydrogen. This latter configuration was examined in this work.

There are two important control problems to be attacked. First, the net gain of ethylene should be maximized. If acetylene converters are operated correctly a net gain of ethylene is to be expected but poor operation can result in a major loss of ethylene. Second, the reactors must be protected against temperature runaways. Hydrogenation reactions are highly exothermic and excessive inlet temperatures can give rise to runaway conditions. These often lead to costly plant shutdowns. Fortunately, the two aims are not incompatible; both are realized by low feed temperatures. So the control problem seeks the minimum inlet temperatures to achieve the desired outlet acetylene concentration. The control problem has been addressed a number of times J~. Work tended to focus on the issue of reactor optimization, where feed conditions were selected to maximize the gain of ethylene while achieving the product specification, or on the rejection of disturbances by means of feed forward control. Very little effort has been spent in examining the feedback control of the reactors themselves.

## 1.2 Problem Statement

Poor operation in Ethylene cracker leads to increase the acetylene. So the production of acetylene will be more than ethylene. The reaction is highly exothermic and excessive inlet temperatures can give rise to runaway conditions. From this problem the selectivity of ethylene is decreasing and will result to the loss of ethylene product. Furthermore this process will facing the problem regarding the safety of the plant and will result to the plant shutdown.

Therefore, there are two important control problems to be attacked. First, the net gain of ethylene should be maximized. If acetylene converters are operated correctly a net gain of ethylene is to be expected but poor operation can result in a major loss of ethylene. Second, the reactors must be protected against temperature runaways. Hydrogenation reactions are highly exothermic and excessive inlet temperatures can give rise to runaway conditions. These often lead to costly plant shutdowns. Fortunately, the two aims are not incompatible both are realized by low feed temperatures. So the control problem seeks the minimum inlet temperatures to achieve the desired outlet acetylene concentration. The control problem has been addressed a number of times. Work tended to focus on the issue of reactor optimization, where feed conditions were selected to maximize the gain of ethylene while achieving the product specification, or on the rejection of disturbances by means of feed forward control. Very little effort has been spent in examining the feedback control of the reactors themselves.

Other than that, during the reactor runs, the ethylene selectivity decreases until reaching a limiting value when the catalyst bed is replaced or regenerated. The proposed solution was formulating a dynamic optimization problem, using a first principles mathematical model, to maximize the acetylene conversion, ethylene selectivity, and unit run time, subject to process constraints and catalyst deactivation, by controlling the inlet temperature of each reactor.

## 1.3 Objective

From the problem statement above, I come out with the objectives of this project.

1. To develop a model of acetylene converter
2. To study the behavior of acetylene converter reactor
3. To improve the process safety of the plant

## 1.4 Scope of study

This is the modeling, simulation and dynamic optimization of an industrial system for acetylene hydrogenation at Ethylene Polyethylene Malaysia Sdn Bhd (EPEMSB). In this project, the control problem has been addressed a number of times. So, my job is to focus on the issue of reactor optimization, where feed condition were selected to maximize the gain of ethylene while achieving the product specification, or on the rejection of disturbance by means of feed forward control. Despite the commercial importance of acetylene hydrogenation, few papers have been published on the kinetics of the reaction. Therefore, I start this project with detailed review from many journals that relate on this topic. From that, I use the basic idea and compare with the current data at EPEMSB.

Data from industry is used as basics to validate the simulation of the process behavior. Acetylene converter actual process data were obtained from Ethylene Polyethylene Malaysia Sdn Bhd (EPEMSB). All the data obtained will help us to understand the process behavior happening inside the industry

This latter problem has now been addressed. In the present study, a fundamental model of the process was developed and fitted to data from an industrial process. It was used to define the structure of a linear model, suitable for controller design. The parameters in the linear model were obtained by, again, fitting to plant data. Finally, the controllers derived from the linear model were tested against the fundamental model. Only the lead reactor is considered, as this was the more difficult reactor to control.

# CHAPTER 2

# LITERATURE REVIEW

## 2.1 Ethylene Process

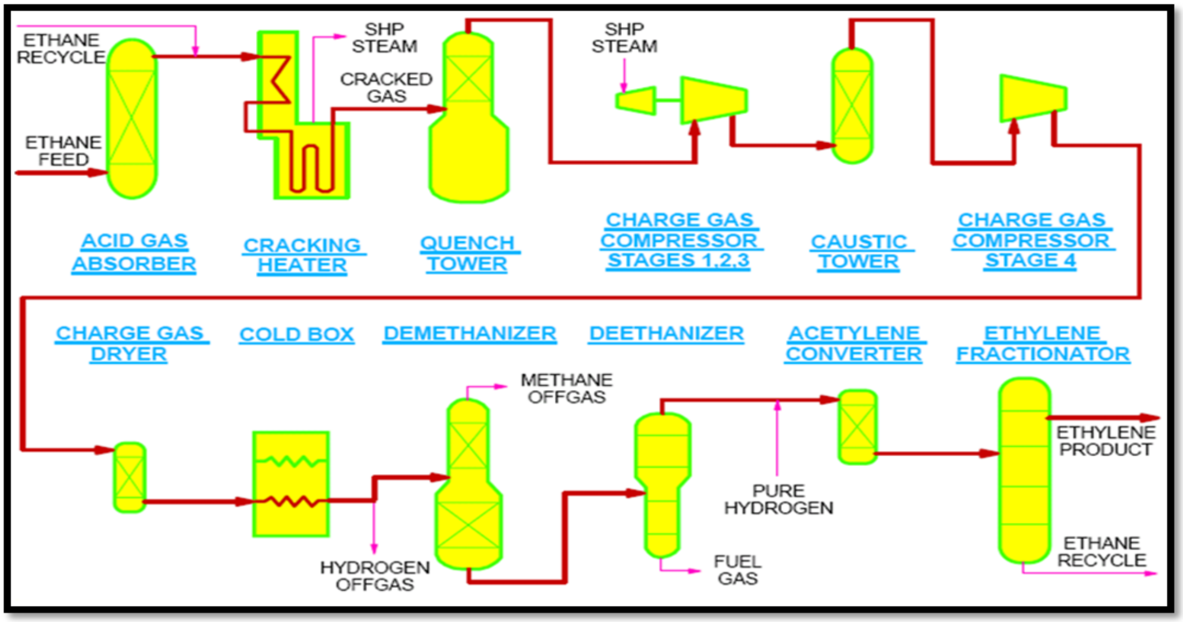


**Figure 1: Process Flow of Ethylene (EMSB, KERTEH)**

Figure 1 show the flow of the process of ethylene at Ethylene Malaysia Berhad, Kerteh Terengganu. Ethane enter the Acid Gas Absorber will react with the demetildesulfide (he gas will proceed to the Charge Gas Compressor and continue to charge gas dryer to remove the moisture before entering the cold box. The dry gas enter the cold box to at to reduce the temperature before enter the Demethanizer. At Demethanizer, the C3++ component will remove and the C1, and C2 will proceed to the Deethanizer. At deethanizer, the C1 will remove as a bottom product and C2 will react with pure hydrogen at acetylene converter to produce ethylene. Finally, the  ethylene as our product will go to the Ethylene Fractionator.

## 2.2 Dynamic analysis of acetylene convertor structure

The dynamic behavior of an industrial acetylene convertor is discussed in the present work. The reactor id used to remove unwanted unsaturated hydrocarbons by means of a hydrogenation. This exothermic reaction is carried out in an adiabatic fixed bed reactor train in series using a Pd/Al2O3 catalyst. Undesirable reactions accompany the main one. Therefore, the selectivity of the catalyst is very important. It is necessary to maintain stable operation while meeting product specification for extremely low acetylene concentration (<1 ppm).

The selective hydrogenation of acetylene in the presence of large amounts of ethylene is an important step in the ethylene process. Most commercial installations manage to reduce the acetylene impurity to the desired specification effectively. In practice, this unit may have control problems when the undesirable hydrogenation of ethylene becomes important, leading to a runway effect.

In industry the acetylene converter can be located at different point in the purification section of an ethylene plant. In one disposition the converter is placed after the conversion section. Another alternative involves the hydrogenation of the stream taken from the top of the de-ethanizer.

A great deal of research on acetylene hydrogenation has been undertaken. Most of it refers to kinetic studies under condition similar to those at the tail end and only a few paper study front-end condition. Only some work analyzes the steady state or dynamic behavior of a reactor with tail-end arrangement using Speedup software (Aspen Technology) for the dynamic simulation. Brown

## 2.3 Kinetics studies

The process of acetylene hydrogenation is consisted of adsorption of acetylene and hydrogen on the catalyst surface, chemical reaction between the adsorbed species, and desorption of the products from the surface (Vicent and Gonzalez, 2001). Bond (1962) proposed that since the enthalpy of adsorption of acetylene is higher than that of ethylene, the surface coverage ratio of acetylene to ethylene would be always high. Therefore, in this case it was expected that if a mixture of acetylene and ethylene is used, hydrogenation of ethylene would not start until all the acetylene in the mixture is consumed. However, the experiments conducted by Bos et al. (1993) and Brodzinski and Cybulski (2000) indicated that this assumption is not realistic and hydrogenation of ethylene cannot be completely prevented in any case. On the other hand, Al Ammar and Web (1978, 1979), Menshchikov et al. (1975) and Mc Gown et al. (1978) proposed that the catalyst surface contains at least two different types of active sites. Furthermore, Brodzinski and Cybulski (2000) proposed a model based on two active sites. They suggested that these sites are created on the palladium surface by carbonaceous deposits. Some of these sites can only take part in acetylene hydrogenation and others may be open to all the species in the gas phase. Figure 1 show a simplified representation of active sites on the catalyst surface which is proposed by Brodzinski and Cybulski (2000). As seen in this figure, different types of species are adsorbed and react on different types of sites. According to Brodzinski and Cybulski (2000), a type of site may exist which is too small for the species other than acetylene and hydrogen to be adsorbed on. As compared to ethylene, acetylene is selectively hydrogenated on these sites by hydrogen atoms which are also adsorbed on these sites.

## 2.4 Description of the process

Deethanizer net overhead stream is selectivity hydrogenated to convert acetylene to ethylene and ethane upstream of the Ethylene Fractionators in the Acetylene Converter. The converter feed is heated by heat exchange with converter effluent and LP steam as needed to the desired converter inlet temperature. This hydrogenation step is achieved in a single bed converter. The conversion occurs in the vapor phase. High purity (99.9mol %) hydrogen from the Hydrogen Purification Unit is added to the converter feed to achieve the desired acetylene conversion. A small amount of raw hydrogen containing CO is also added to moderate the activity of the catalyst. A small amount of polymer is formed in the catalyst bed and exits with the converter effluent. The effluent of the converter is cooled against cooling water and converter feed and sent to the C2 Green Oil Drum and Ethylene Dryer, before going on to the Ethylene Fractionators.

After certain period of time, regeneration of the Acetylene Converter will be required. Regeneration is performed using a mixture of steam and air as well as heated ethane recycles. SHP steam is used to heat the regeneration gas mixture while the ethane recycle is heated in the Acetylene Converter Regeneration Heater.

### 2.5 Acetylene Hydrogenation Chemistry

There are three major reactions considered in this project. From the reaction, I calculate the enthalpy value to use for calculation later. I divide the reaction into, Selective Hydrogenation, Non-selective Hydrogenation, Oligomerization and Non-Hydrogenation Reaction.

#### *2.5.1 Selective Hydrogenation:*

$$\underset{\text{Acetylene}}{CH \equiv CH} + \underset{\text{Hydrogen}}{H_2} \rightarrow \underset{\text{Ethylene}}{CH_2 = CH_2} \qquad \Delta H = -42.2 kcal / mol \quad (1)$$

Selective hydrogenation is the most commonly used process for the elimination of acetylene in the production of ethylene. This reaction is highly exothermic resulting in a temperature rise of 32 – 47°C per 1% Ac converted, depending on the feed composition and temperature. The rate of reaction is directly related to the temperature and the concentration of hydrogen. The reaction is suppressed by CO, sulfur, and other contaminates in the feed.

#### *2.5.2 Non-selective Hydrogenation*

$$\underset{\text{Ethylene}}{CH_2 = CH_2} + \underset{\text{Hydrogen}}{H_2} \rightarrow \underset{\text{Ethane}}{CH_3 - CH_3} \qquad \Delta H = -33.1 kcal / mol \quad (2)$$

Unfortunately, there are a number of side reactions which occur simultaneously to acetylene hydrogenation. The most common is ethylene hydrogenation. This olefin hydrogenation reaction is also exothermic resulting in a temperature rise of 25 – 30°C per 1% C2 = converted, depending on the feed composition and temperature. The rate of reaction is directly related to the temperature and the concentration of hydrogen. The reaction is suppressed by even low concentrations of acetylene and CO. Other contaminates, like sulfur, also suppress the reaction rate.

$$\underbrace{CH \equiv CH}_{\text{Acetylene}} + \underbrace{\tfrac{1}{2} H_2}_{\text{Hydrogen}} \rightarrow \underbrace{\tfrac{1}{2} CH_2 = CH - CH = CH_2}_{\text{1,3 Butadiene}} \quad \Delta H = -41.3 kcal / mol \quad (3)$$

The second common side reaction is the dimerization / partial hydrogenation of acetylene. This dimerization reaction is nearly as exothermic as the desired acetylene selective hydrogenation reaction, and occurs naturally on Pd catalysts. Therefore the reaction rate is a function of the catalyst formulation, and can be enhanced if the hydrogen concentration is low.

### *2.5.3 Oligomerization*

$$\underbrace{n CH \equiv CH}_{\text{Acetylene}} + \underbrace{m CH_2 = CH - CH = CH_2}_{\text{1,3 Butadiene}} \rightarrow \underbrace{C_{2n4m} H_{2n6m}}_{\text{Oligomer}} \quad (4)$$

The least desirable common reaction is oligomerization and polymerization of acetylene and 1,3butadiene. Green Oil, an oligomer with six or eight carbons, will exit the reactor in the gas phase, but will later condense forming a noxious liquid. Oligomers with 12 or more carbons will generally stick to the catalyst until regeneration. Oligomerization reaction rates have been lowered through catalyst reformulation, particularly with the introduction of promoters and modifications to the carrier. Green oil formation is greater with wet catalyst and at elevated operating temperatures.

### *2.5.4 Non-Hydrogenation Reactions*

$$\underset{\text{Ethylene}}{CH_2 = CH_2} \rightarrow \underset{\text{Coke}}{2C} + \underset{\text{Hydrogen}}{2H_2} \qquad \Delta H = -11 kcal/mol \quad (5)$$

$$\underset{\text{Ethylene}}{CH_2 = CH_2} \rightarrow \underset{\text{Coke}}{C} + \underset{\text{Methane}}{CH_4} \qquad \Delta H = -30 kcal/mol \quad (6)$$

$$\underset{\text{Ethylene}}{CH_2 = CH_2} \rightarrow \underset{\text{Polymer}}{-CH_2 - CH_2 -} \qquad \Delta H = -33 kcal/mol \quad (7)$$

If heated to 315°C or more, there are three different ways ethylene may react in the absence of hydrogen. These decomposition reactions may occur at lower temperatures in the presence of Pd catalysts, but have not been detected below 175°C. The coke and polymer generated by these reactions will deactivate the catalyst. Coke formed by ethylene decomposition cannot be completely removed by regeneration. In extreme cases, these "runaway" reactions can cause overheating of the catalyst and the reactor vessel

All the analysis of the process shows the reaction that involve in this process of hydrogenation. The analysis also considers the side reactions that occur during this process.

We also calculate the enthalpy value all the reaction. From the analysis above, we can conclude that:

1. This reaction is exothermic reaction because of the value of enthalpy is negative.
2. This reaction will produce a heat
3. From the calculation of lnK, we can conclude this reaction in the reactor is irreversible reaction

This exothermic reaction is carried out in an adiabatic fixed bed reactor train in series using a Pd/Al2O3 catalyst. This reaction is the irreversible reaction

Only two articles dealing with the kinetics of front-end systems were found in the literature. Using atmospheric pressure; a temperature range of 35-80 °C; and feed gas composed of methane, acetylene, ethylene, ethane, propadiene, methylacetylene, propylene, propane, hydrogen, and carbon monoxide, Godinez et al. (1995) proposed reaction rate equations, depending only on hydrogen partial pressure, for hydrogenation of acetylene, ethylene, methylacetylene, propadiene, and propylene. They assumed the first-order reaction for hydrogenation of acetylene and diolefins and the third-order for hydrogenation of olefins. Using pressures ranging from 0.1 to 3.2 MPa; a temperature range of 15-120 °C; and feed gas composed of methane, acetylene, ethylene, ethane, hydrogen, and carbon monoxide,

Schbib et al. (1996) proposed first-order reaction rate equations for hydrogenation of acetylene and ethylene for all reactant

## 2.6 Catalyst

The catalyst for this process is a commercial hydrogenation catalyst employing palladium metal on an alumina carrier Pd/Al2O3. The catalyst is operated as a selective catalyst and operating conditions are set to enhance the conversion of acetylene to ethylene. The conversion is exothermic and requires monitoring at all times. The characteristic of the catalyst achieve the following:

1. The high degree of selectivity attained.
2. Infrequent regeneration is required
3. The concentration of acetylene is reduced from several thousand vol.ppm to less than 1.0 vol.ppm.
4. The quantity of "green oil" formed during hydrogenation is insignificant so that fouling of downstream equipment following the hydrogenation unit is minimized.

## 2.7 Acetylene removal method

Another byproduct of ethylene production is acetylene. The yield of acetylene is 0.5 to 2.5 tons per 100 tons of ethylene, depending on the feedstock and cracking severity. The specification for Acetylene in the Ethylene Product is as low as 1.0 ppm for some Polyethylene processes to 50 ppm for VCM.

Acetylene cannot be separated from ethylene by conventional distillation. Early "front-end" designs using iron based catalysts had ethylene losses of 1 – 2%. In the early 1960's, the "tail-end" flow sheet was introduced. Using Pd based catalysts offered by Girdler (G-58) and CCI (C31-1A), theses systems were able to operate without ethylene losses averaged over the cycle. Presently, the four most common methods used for removing acetylene (SCI database, August, 2005) are: Tail-end Acetylene Selective Hydrogenation (C2 TE), Front-end Acetylene Selective Hydrogenation (C2 FE), Raw Gas Hydrogenation with NiS catalyst, and Extractive Distillation as summarized in Table 1.2.

| Method | Number of Plant | % of Plant |
|---|---|---|
| Tail end | 174 | 64% |
| Front-end-Palladium | 69 | 26% |

| | | |
|---|---|---|
| Front-end-Nickel | 9 | 3% |
| Extraction | 19 | 7% |
| **Total** | **269** | |

**Table 1: Method of Removal Acetylene**

The Table 1.2 shows, there are four method of removal acetylene in current industries. The most popular is tail end method which is 64%.

# CHAPTER 3

# METHODOLOGY / PROJECT WORK

## 3.1 Project Methodology

### 3.1.1 Process Information

By identifying background and problem statement of the project, conduct a research of the technical and pattern literature for the information on the project such as characteristic of the reactor at EMSB, reaction involve in this process, process consideration and criteria. The information obtained from the literature is gathered, analyze and applied for new conceptual design.

### 3.1.2 Critical Analysis

Based on the information obtained from the literature, critical analysis have to be done to analyze the information and relate to this project.

#### *3.1.2.1 Kinetic Models*

The process of acetylene hydrogenation is consisted of adsorption of acetylene and hydrogen on the catalyst surface, chemical reaction between the adsorbed species, and desorption of the products from the surface (Vicent and Gonzalez, 2001). Bond (1962) proposed that since the enthalpy of adsorption of acetylene is higher than that of ethylene, the surface coverage ratio of acetylene to ethylene would be always high. Therefore, in this case it was expected that if a mixture of acetylene and ethylene is used, hydrogenation of ethylene would not start until all the acetylene in the mixture is consumed. However, the experiments conducted by Bos et al. (1993) and Brodzinski and Cybulski (2000) indicated that this assumption is not realistic and hydrogenation o ethylene cannot be completely prevented in any case. On the other hand, Al- Ammar and Web (1978, 1979), Menshchikov et al. (1975) and Mc Gown et al. (1978) proposed that the catalyst surface contains at least two different types of active sites. Furthermore, Brodzinski and Cybulski (2000) proposed a model based on two active sites. They suggested that these sites are created on the palladium surface by carbonaceous deposits. Some of these sites can only take part in acetylene hydrogenation and others may be open to all the species in the gas phase. Figure 1 show a simplified representation of active sites on the catalyst surface which is proposed by Brodzinski and Cybulski (2000). As seen in this figure, different types of species are adsorbed and react on different types of sites. According to Brodzinski and Cybulski (2000), a type of site may exist which is too small for the species other than acetylene and hydrogen to be adsorbed on. As compared to ethylene, acetylene is selectively hydrogenated on these sites by hydrogen atoms which are also adsorbed on these sites.

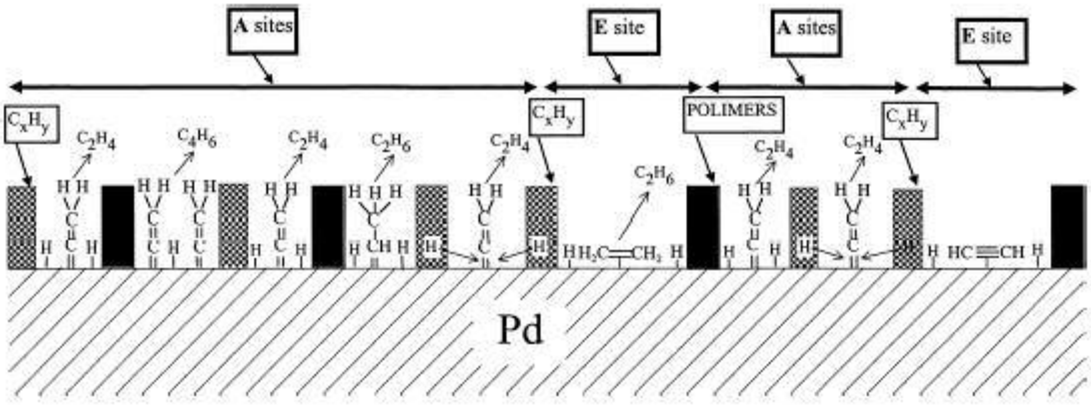


**Figure 2: Simplified representation of active sites on the catalyst surface (after Brodzineski and Cybulski, 2000)**

As mentioned above, researchers believe that different types of sites are formed on the surface of the catalyst pellet due to the presence of carbonaceous deposits in the process of acetylene hydrogenation. However, the exact source of these deposits is still in question. Based on the assumption that the origin of formation of C4 oligomers (which are the precursors to carbon deposits) is the acetylene adsorbed on the surface of catalyst, Al-Ammar and Webb (1978a, 1978b, 1979) suggested that these deposits are the source of deactivation and may contribute to acetylene hydrogenation. Recently, Fasi et al. (2000) found that there are several types of surface carbon and not all of them necessarily participate in the reaction. Larsson et al. (1998) showed that it is the type of carbon not its amount that results in an increase in the selectivity to ethylene. Therefore, carbon deposits can accept hydrogen at low temperatures and then release this hydrogen at higher temperatures to participate in the hydrogenation procedure by a hydrogen transfer mechanism (Vincent and Gonzalez, 2001). Based on this information, at least two possible mechanisms may be suggested for this reaction system:

*Mechanism 1*: This mechanism is based on the reaction of acetylene in the form of vinylidene with hydrogen molecules which are simultaneously adsorbed on the catalyst surface in a competitive way.

This is a Langmuir-Hinnshelwood mechanism and is the most common one which has been proposed by almost all the researchers for such reaction system.

*Mechanism 2*: This mechanism involves the hydrogen transfer from carbonaceous deposits at higher temperatures to the vinyl intermediate.

This mechanism is called Al-Ammar mechanism. These two proposed mechanisms are shown schematically in Figure 2. In addition to these two main mechanisms, i.e., Langmuir-Hinshelwood and Al-Ammar mechanisms, other mechanisms have been also considered for this system of reactions (Westerterp et al., 2002). Of course, the temperature in industrial reactors of acetylene hydrogenation is les than 100 ºC in which the only source of hydrogen comes from the dissociative adsorption of hydrogen followed by direct hydrogenation over Pd sites. However, there is an alternative mechanism which starts to happen at about 150 ºC which is much more selective towards ethylene formation than the low temperature mechanism. This mechanism involves hydride transfer from the growing carbonaceous layer. This alternative mechanism becomes dominant at temperatures in excess of 175 ºC. Vincent and Gonzalez (2002) have addressed this point in considerable detail.

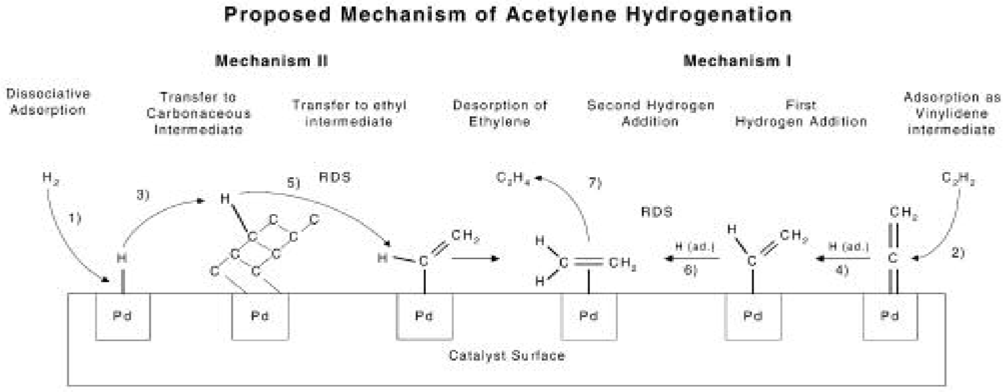


**Figure 3:Representation of the two proposed mechanisms on catalyst surface (after Vincent and Gonzalez, 2001)**

Different kinetic models have been proposed based on each of the above described mechanisms. Nevertheless, due to the complexity of the reactions in this system, none of the proposed kinetics can be considered as the best, yet. Among them, the kinetic expressions proposed by Boss et al. (1993), Brodzinski and Cybulski. (2000) and Menshchikov et al. (1975) seem to be more acceptable and have been used by other researchers (Westerterp et al., 2002; Vincent and Gonzalez, 2001). These kinetics expressions are given in Table 2.

| Kinetics Model | Reference |
|---|---|
| $r_{C_2H_2} = \frac{k_1 P_{C_2H_2} P_{H_2}}{(1+k_2 P_{C_2H_2})(1+k_3 P_{H_2})}$<br>$r_{C_2H_6} = \frac{k_4 P_{C_2H_4} P_{H_2}}{(1+k_5 P_{C_2H_2} + k_6 P_{C_2H_4})^3}$ | Bos et al. (1993) |
| $r_{C_2H_2} = \frac{k_1 P_{C_2H_2} P_{H_2}}{(1+k_2 P_{C_2H_4})(1+k_3 P_{H_2})}$<br>$r_{C_2H_6} = \frac{k_4 P_{C_2H_4} P_{H_2}}{(1+k_5 P_{C_2H_4})(1+k_6 P_{H_2})}$ | Menshchikov et al. (1975) |
| $r_{C_2H_2} = \frac{k_1 P_{C_2H_2} P_{H_2}}{(1+k_2 P_{C_2H_4})(1+k_3 P_{H_2})}$<br>$r_{C_2H_6} = \frac{k_4 P_{C_2H_4} P_{H_2}}{(1+k_5 P_{C_2H_4})^{1.25}(1+k_6 P_{H_2})}$ | This work |

**Table 2: Kinetic models studied in this work**

### 3.1.1 Conceptual Design

Making use of existing design model, do the screenings to examine all the parameter involve. Then, evaluate and do comparison of the plant data and. Based on that, we can clear about the problem statement of the project and will manipulate to get the optimum operating condition.

#### *3.1.1.1 Model of reactor*

The acetylene hydrogenation system considered in this work consists of only Reaction (1) and (2). All other side reactions are neglected. The industrial reactor of acetylene hydrogenation operates at non-isothermal conditions. Therefore, in order to model such a reactor, the mass balance equations have to be coupled with the energy balance equation and to be solved simultaneously. Up to now most of the simulation studies in this field have been based on the plug flow assumption for the reactor. Moreover, the few researchers, who have considered the dispersion model, did not report temperature and concentration profiles in a large scale reactor or make a comparison between these two models (Godinez et al., 1995; Szukiewicz et al., 1998). The acetylene hydrogenation reactor has modeled by both models in this study. The basic model are:

Assume:

$$-r_{Acetylene} = KC_{Acetylene}$$

$$FC_o = FC_1 + \Delta W K C_1 \text{ ---------------------------}(1)$$

$$(FCo - FC\_1)(-\Delta H_r) = F\rho C_p (T_1 - T_0)\text{-------------------------}(2)$$

$$C_o = C_1\left[1 + \frac{\Delta W}{F}K\right]$$

$$FC_1 = \frac{FCo}{\left[1+\frac{\Delta W}{F}K\right]}\text{---------------------}(3)$$

$$FCo\text{-}\frac{FCo}{\left[1+\frac{\Delta W}{F}K\right]}(-\Delta H_r) = F\rho C_p (T_1 - T_0)$$

$$(T_1 - T_0) = \frac{(-\Delta H_r)Co}{\rho C_p}\left[\frac{1 + \frac{\Delta W}{F}K - 1}{1 + \frac{\Delta W}{F}K}\right]$$

$$(T_1 - T_0) = \frac{\Delta W}{F}K\frac{(-\Delta H_r)Co}{\rho C_p}\left|\frac{1}{1 + \frac{\Delta W}{F}K}\right|$$

$$\frac{\Delta W}{F}K = \frac{1}{\frac{(-\Delta H_r)Co}{\rho C_p (T_1 - T_0)} - 1}$$

$$K = \frac{1}{\frac{\Delta W}{F}\left[\frac{(-\Delta H_r)Co}{\rho C_p (T_1 - T_0)} - 1\right]}$$

In the models that we are discussed we have neglected the presence of internal diffusion limitations. This simplifying assumption was based on the fact that the average pore diameter of the catalyst pellets was quite large, 1000 Å. However, due to the high hydrogenation rate and the homogeneous distribution of Pd in the pellet, internal concentration gradients may be present. In order to check for the absence of intrapellet diffusion limitations, we selected the criterion of Weisz and Prater (Froment and Bischoff, 1990) which in turn requires a measured value of the rate of reaction. Consequently application of this criterion was performed after adequate kinetic equations were available to calculate the rates of C2H2 and C2H4 hydrogenation at different conversion level

| | Detail/ Week | 1 | 2 | 3 | 4 | 5 | 6 | 7 | | 8 | 9 | 10 | 11 | 12 | 13 | 14 |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|

## 3.2 Project Gant Chart

| | | | | | | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| 1 | Identify Problem Statement | ■ | | | | | | | | | | | | | | |
| 2 | Gather Information | ■ | | | | | | | | | | | | | | |
| 3 | Perform Critical Analysis | ■ | | | | | | | | | | | | | | |
| 4 | Conceptual Process Design | ■ | | | | | | | | | | | | | | |
| 5 | Screening and Scoping Process Alternative | ■ | | | | | | | | | | | | | | |
| 6 | Develop Reactor Modeling | | ■ | | | | | | | | | | | | | |
| 7 | Application with the plant sample data | | | ■ | | | | | | | | | | | | |
| 8 | Result Analysis | | | ■ | ■ | ■ | ■ | ■ | | ■ | ■ | | | | | |
| 9 | Identify Possible Optimum Operating Condition | | | ■ | ■ | ■ | ■ | ■ | | ■ | ■ | | | | | |
| 10 | Evaluate The Result | | | | | | | | | | ■ | ■ | ■ | | | |

Suggested milestone

■ Process

# CHAPTER 4

# RESULT AND DISCUSSION

## 4.1 EPEMSB Reactor Model

The acetylene hydrogenation system consists of two converters. One converter is in service, while the second converter is in a standby condition or going through a regeneration cycle. Each of converters consists of one bed built into one vertical vessel. The heating and cooling is accomplished in a series of six heat exchanger units. The instruments associated with the converter include a safety interlock system designed to stop runway reaction.

### 4.1.1 Reactor Characteristic

From the reactor drawing, we can obtain the characteristic of the reactor as shown in the Table 3.

| **Parameter** | **Value** |
|---|---|
| Length | 3.3m |
| Diameter | 3.2m |
| Volume | 26.55m$^3$ |
| Weight of Catalyst | 25280kg |
| Residence Time | 3.6/hr |

**Table 3: Reactor Characteristic**

### 4.1.2 Design Data

For normal operating condition at EPEMSB is:

| **Acetylene Converter** | **Pressure. BarG** | |
|---|---|---|
| Top | 18.30 | |
| Bottom | 18.01 | |
| **Acetylene Converter** | **Temperature, °C** | |
| | **Start of run** | **End of run** |
| In bed | 35.0 | 72.5 |
| Out bed | 57.6 | 101.4 |
| | | |

| **Acetylene Converter** | **Flow, kg/hr** |
|---|---|
| In bed | 90, 932 |
| Out bed | 90, 932 |
| Deethanizer Overhead | 90, 864 |
| High Purity Hydrogen | 55 |
| Low Purity Hydrogen | 13 |

**Table 4: Design Data**

### 5.1.3 Plant Data

To continue this project, we use the data from EMSB to apply in this project. This data we take on 22 February 2011. From the calculation, we got the data as shown in the Table 4.

| **Parameter** | **Value** | **Unit** |
|---|---|---|
| Feed gas | 82.42 | Ton/hr |
| Total $H_2$ Flow | 40.30 | Kg/hr |
| CO Rich $H_2$ Flow | 8.59 | Kg/hr |
| CO in CO Rich $H_2$ | 0.10 | Mol% |
| $CH_4$ in CO Rich $H_2$ | 0.00 | Mol% |
| Inlet $C_2H_2$ | 0.43 | Mol% |
| Outlet $C_2H_2$ | *** | Mol% |
| MW of CO Rich $H_2$ | 2.57 | Kg/Kmol |
| Feed Gas | 2840.00 | Kmol |
| Inlet Acetylene | 12.20 | Kmol |
| Outlet Acetylene | 0.00 | Kmol |
| Treated Acetylene | 12.20 | Kmol |
| Total $H_2$ | 18.58 | Kmol |

|  |  |  |
|---|---|---|
| $H_2$/ $C_2H_2$ Ratio | 1.52 |  |

**Table 5: Actual Plant Data**

### 4.2 The Kinetic Equations.

Using the data of these industries, the reaction rates of acetylene consumption and ethane formation in each case were found to be as follows:

$$r_{C_2H_2} = \frac{F_{C_2H_2(in)} - F_{C_2H_2(out)}}{m}$$

$$r_{C_2H_6} = \frac{F_{C_2H_6(out)} - F_{C_2H_6(in)}}{m}$$

Initially, the two well known kinetic models of Bos et al. (1993) and Menshchikov et al. (1975) were considered as the base models and fitted the experimental data of this work to these models to obtain new kinetic parameters for the catalyst employed in this study. It is worth mentioning that in both models of Bos et al. (1993) and Menshchikov et al. (1975), the parameters have been provided for a different type of catalysts than that studied in this work and as the different types of catalysts may have different metal content and different porosities which certainly affect the kinetic studies. Therefore, new kinetic parameters have to be obtained to fit the new catalyst behavior. New reaction rate constants, evaluated from fitting the experimental data of this work to the above mentioned kinetic models, are given in Table 2. An Arrhenius type of temperature dependency is considered for the reaction rate constants as follows:

$$k_i = k_{i,0} \exp\left( \frac{-E_{a,i}}{RT} \right)$$

The parity plot of the calculated reaction rates based on the kinetic model of Bos et al. (1993) against the experimental reaction rates of this work are shown in Figures 4a and 4b for acetylene consumption rate and ethane formation rate, respectively. The constants of the Bos et al. (1993) model used in this figure are those reported in Table 2. It can be seen in Figure 4a that the model of Bos et al. (1993) over-predicts the acetylene consumption rates obtained in this work.

According to this figure, the higher the temperature, the higher is the deviation of the model from the reality. Figure 4b is the same comparison for ethane formation rate. It is evident in this figure that data scattering is less than what was observed for acetylene consumption rate (Figure 4a). Nevertheless, at lower temperatures the model of Bos et al. (1993) underestimates while at high temperatures the model overestimates the reaction rate and the difference between calculated and observed data is quit high. The same comparison for the kinetic model of Menshchikov et al. (1975) is shown in Figures 5a and 5b. The constants of the Menshchikov et al. (1975) model used in this figure are those reported in Table 2. Figure 5a compares the calculated and observed rates of acetylene consumption. Although the data points in this figure are scattered, these points are also evenly distributed around the unity line. This fact indicates that the kinetic model of Menshchikov et al. the data points to be scattered. This point could be more clearly understood if one compares Figure 5a with Figure 4a (corresponding to the same reaction rate with a different equation). In fact, in Figure 4a the data points are scattered as well as biased toward higher values. Thus, even if scattering of the data is contributed to the experimental error in Figure 4a, the kinetic model of Bos et al. (1993) is inadequate to estimate the acetylene consumption rate properly. Therefore, it can be concluded that the kinetic model of Menshchikov et al. (1975) with the newly calculated parameters is an appropriate model for evaluating the acetylene consumption rate for the catalyst employed in this work. Figure 5b is the same comparison for ethane formation rate. Although the agreement between this model and the experimental ethane formation rates is considerably better than that of the model of Bos et al. (1993) (compare Figure 4b with Figure 5b), however, still there are some points where the agreement is not satisfactory. It should be noted that the agreement between both Bos et al. (1993) model and Menshchikov et al. (1975) model is considerably better for the points with lower acetylene content in terms of acetylene consumption rate than those obtained with high acetylene content in the feed. Therefore, acetylene concentration of more than 20% in the feed, in both models would result in an unacceptable difference between calculated and observed rates.

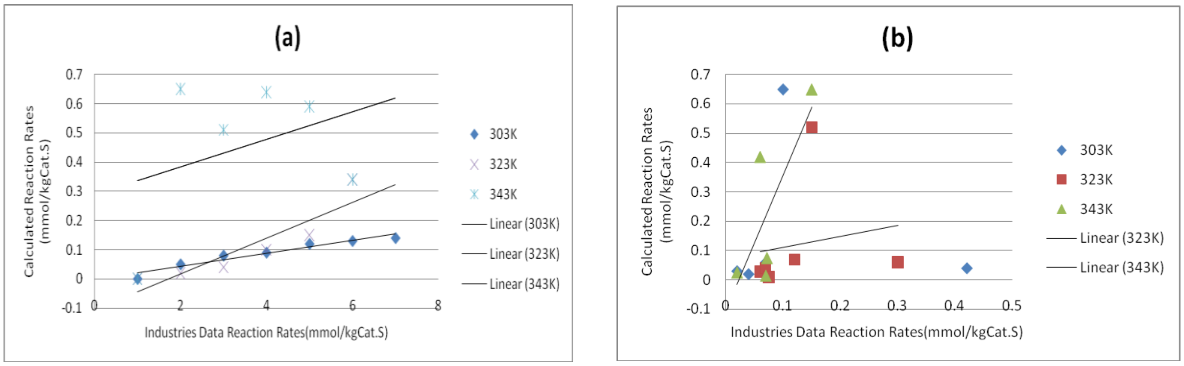


**Figure 4: Parity plot of experimental reaction rates vs those calculated by the model of Bos et al.(1993) (a) acetylene consumption rate (b) ethane formation rate**

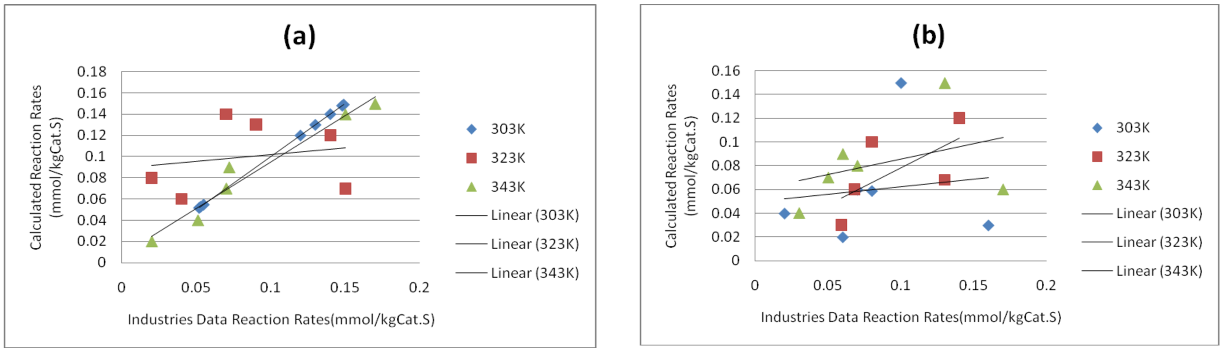


**Figure 5: Parity plot of experimental reaction rates vs those calculated by the model of Menshchikov et al. (1975) (a) acetylene consumption rate (b) ethane formation rate**

By considering all the above mentioned parity plots presented in Figures 4a, 4b, 5a and 5b, it can be concluded that the model of Bos et al. (1993) cannot predict the reaction rates of the catalyst employed in this study in the range and operating conditions of this study for either acetylene consumption rate or ethane formation rate. However, the model of Menshchikov et al. (1975) is able to predict the rate of acetylene consumption satisfactorily for the catalyst and conditions of this study while its rate of ethane formation still needs to be improved. Therefore, a new kinetic model is proposed here which consists of the acetylene consumption rate of the model of Menshchikov et al. (1975), for with new parameters which have been obtained in this study, and a new rate expression for ethane formation which better fits the experimental data.

After simplifying, this new model is given as follows:

$$r_{C_2H_2}=\frac{48.01\exp\left(-\frac{146.8}{T}\right)P_{C_2H_2}P_{H_2}}{\left[1+584.59\exp\left(\frac{668.6}{T}\right)P_{C_2H_4}\right]\left[1+2.855\exp\left(\frac{404.3}{T}\right)P_{H_2}\right]}$$

$$r_{C_2H_6}=\frac{202.67\exp\left(-\frac{4784}{T}\right)P_{C_2H_4}P_{H_2}}{\left[1+0.0742\exp\left(\frac{1502.7}{T}\right)P_{C_2H_4}\right]^{1.25}\left[1+2.89\exp\left(\frac{400}{T}\right)P_{H_2}\right]}$$

This model is presented in its general from in Table 1 and its parameters are also given in Table 2. It is worth noting that the power 1.25 in the denominator of Equation (13) is only a fitting parameter and does not correspond to mechanism of the reaction. A comparison between the calculated ethane formation rate and the experimental results of this work is shown in Figure 6. It can be seen in this figure that there is a good agreement between the model prediction and real reaction rates. The performance of the new rate equation, presented in Equation (13), is considerably improved as compared to those proposed by Bos et al. (1993) and Menshchikov et al. (1975). It seems that the reason that the new kinetic expressions [Equations (12) and (13)] fit the experimental data of this work better than the previous data in the literature is that the catalyst employed in this work (which is an industrial catalyst) slightly differs from those employed by other researchers.

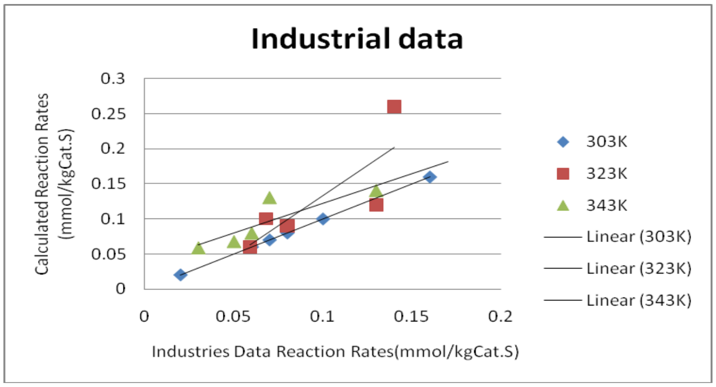


**Figure 6: Parity plot of experimental ethane formation rates vs those calculated by the model of this work.**

### 4.3 Reactor Modeling

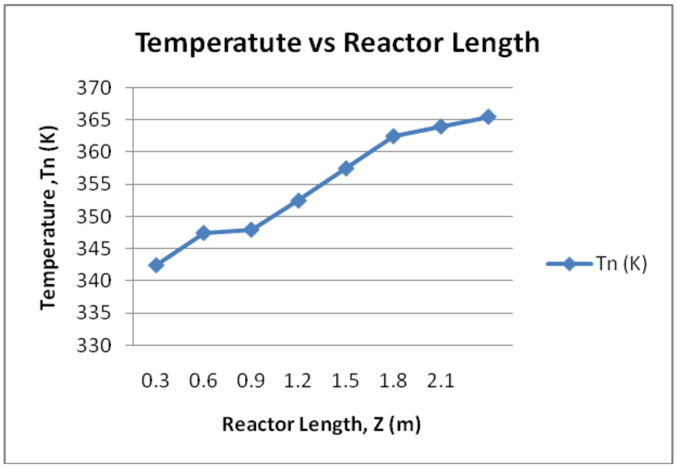
In order to check the validity of our kinetic equations to predict conversion and temperature profiles, an attempt was made to simulate the operation of an industrial acetylene hydrogenation reactor. The process scheme consists of an ethane cracker followed by three adiabatic reactors in series in a typical front-end hydrogenation configuration. The simulation was restricted to the first unit. The two flow models coupled with each of the three kinetic models described in the Theory section were solved for an industrial-scale reactor.

The operating conditions considered for the simulation are listed in Table 5. It is worth mentioning that in the industrial acetylene hydrogenation units, two reactors in series are employed for complete conversion of acetylene in the feed (Weiss, 1996). The values given in Table 3 are typical for the first hydrogenation reactor. Results of this simulation are shown in Figures 7a-d in terms of profiles of temperature, acetylene conversion, ethylene formation, and ethane formation along the reactor, respectively. In these figures, the results of simulation of the reactor by the two flow models, i.e., plug flow and dispersion flow, which are coupled with the three kinetic models and the proposed model in this study, are shown.

| Tn (K) | F (Kg/s) | dW ( kg) | dHr (KJ/mol) | Cn | ρ (Kg/m3) | Cp (kJ/KgK) | K | Z (m) |
|---|---|---|---|---|---|---|---|---|

| | | | | | | | | |
|---|---|---|---|---|---|---|---|---|
| 342.5 | 16.1 | 715 | 176.64 | 0.161315 | 1.73 | 1.674 | 0.01867 | 0.3 |
| 347.5 | 16.1 | 715 | 176.64 | 0.088192 | 1.73 | 1.674 | 0.02534 | 0.6 |
| 348 | 16.1 | 715 | 176.64 | 0.041495 | 1.73 | 1.674 | 0.02561 | 0.9 |
| 352.5 | 16.1 | 715 | 176.64 | 0.019415 | 1.73 | 1.674 | 0.02598 | 1.2 |
| 357.5 | 16.1 | 715 | 176.64 | 0.009014 | 1.73 | 1.674 | 0.03378 | 1.5 |
| 362.5 | 16.1 | 715 | 176.64 | 0.003605 | 1.73 | 1.674 | 0.034 | 1.8 |
| 364 | 16.1 | 715 | 176.64 | 0.001436 | 1.73 | 1.674 | 0.0397 | 2.1 |
| 365.5 | | | | | | | | |

**Table 6: Result of Data from Modeling Calculation**



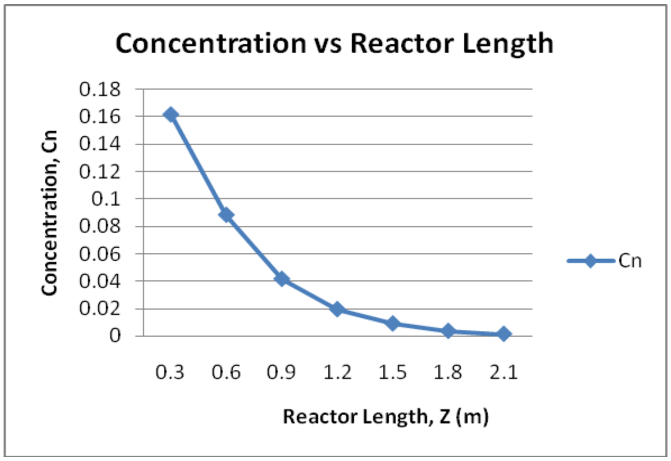


**Figure 7: Si**

**actor Length**

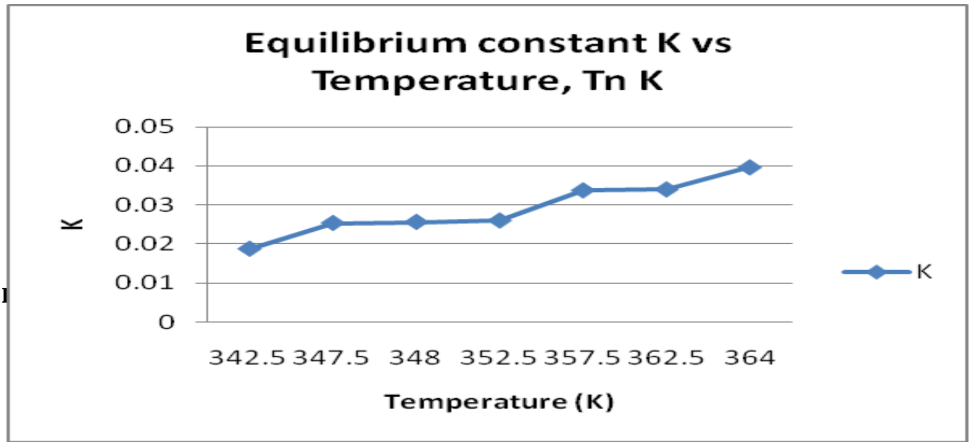
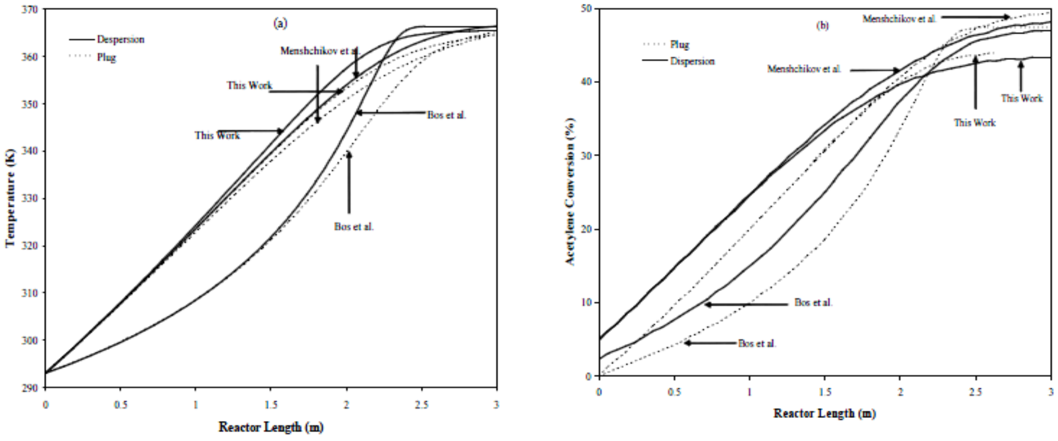


**Figure 9: Equilibrium constant K vs Temperature, Tn K**

Figure 7, 8, 9 Show the simulation results for different parameter using kinetic models investigated in this work (Figure 7) temperature profiles (Figure 8) acetylene conversion profiles (Figure 9) The Equilibrium Constant.

The corresponding acetylene conversion profiles are shown in Figure 7b. This conversion is calculated from the following formula:

$$X_{C_2H_2} = \frac{F_{C_2H_2(in)} - F_{C_2H_2}}{F_{C_2H_2(in)}}$$



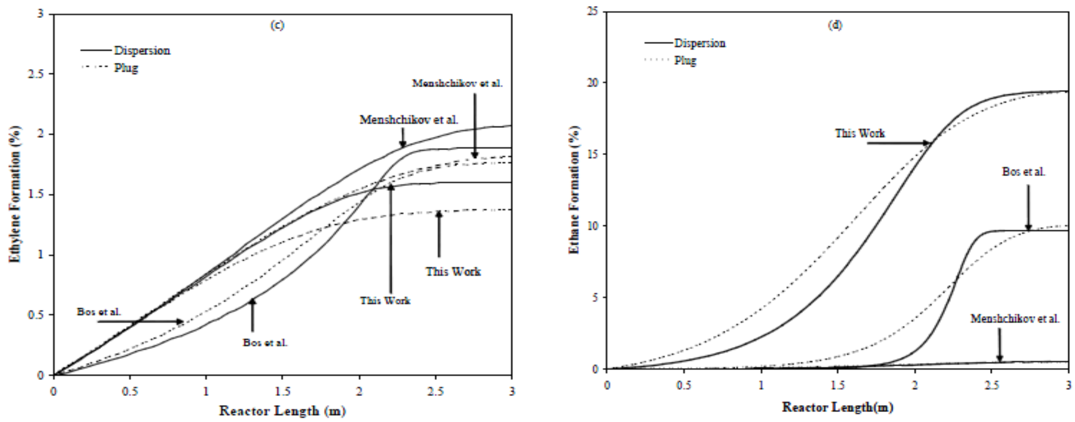


**Figure 9: Simulation results for different flow patterns combined with kinetic models investigated in this work (a) temperature profiles (b) acetylene conversion profiles (c) ethylene formation profiles (d) ethane formation profiles.**

It is also seen in Figure 9b that the profiles are close to each other and so do the exit conversions. This is an expected trend since all three kinetic models considered in this study provide quite the Mostoufi et al.: Hydrogenation of Acetylene: Kinetic Studies and Reactor Modeling 11 Published by The Berkeley Electronic Press, 2005 same acetylene hydrogenation rates (see Table 5). This figure illustrates that only about half of the acetylene is eliminated in the first hydrogenation reactor and the rest of this task remains to be accomplished in the second reactor. The reason for not completing the conversion of acetylene in a single reactor is controlling the temperature, as discussed in the introduction section and shown in Figure 9a.

Ethylene formation can be calculated from:

$$X_{C_2H_4} = \frac{F_{C_2H_4} - F_{C_2H_4(in)}}{F_{C_2H_4(in)}}$$

The profiles of ethylene formation along the reactor are shown in Figure 7c. It can be seen in this figure that the kinetic model of Menshchikov et al. (1975) predicts the highest ethylene formation among the three models and the model developed in this work predicts the lowest. The difference between the predictions of the three models observed in Figure 7c is due to the fact that in the process of ethylene formation, two reaction rates (i.e., acetylene conversion and ethane formation) are involved. Although all three kinetic models considered in this study provide almost the same acetylene conversion rates, they are dissimilar in the rate of ethane formation.

Therefore, different profiles are obtained from each kinetic model for ethylene formation. This figure also reveals that regardless of the kinetic model used in the simulation, the plug model provides lower ethylene formations compared to the dispersion flow model. This is something that can be expected because in dispersion flow the back mixing phenomena helps the conversion of acetylene to be higher than that of plug flow. Consequently, the ethylene formation would be also higher in this case. Ethane formation is calculated from:

$$X_{C_2H_6} = \frac{F_{C_2H_6} - F_{C_2H_6(in)}}{F_{C_2H_6(in)}}$$

Figure 9d shows the profiles of ethane formation along the reactor length for the models considered in this work. It is clear in this figure that each kinetic model predicts a different ethane formation rate as compared to another one. The discussions made for Figure 9c regarding the difference of the three kinetic models in terms of ethane formation rate are also valid here. In fact, the difference between these models, which is mainly originated from the difference in ethane formation rate, shows up noticeably in this figure. Since the reaction rates proposed in this work fits the experimental data better than the other two models (see Figures 4b, 5b and 6), the results of simulation with the new model can be more trusted for the employed catalyst and operating conditions of this simulation.

This increase in the temperature can raise the activity of the catalyst to some extent. Figure 7 demonstrates the effect of increasing the feed temperature on exit acetylene concentration with catalysts of different activities for the simulation parameters

# CHAPTER 6

# CONCLUSION

The kinetic and modeling reactor of an industrial reaction system for acetylene hydrogenation were carried out in this work. Using the experimental data of this work and existing kinetic models from the literature, a new kinetic expression for hydrogenation of acetylene was developed. The acetylene hydrogenation reactor was simulated with different flow models (i.e., plug flow and dispersion flow models) coupled with three different kinetic models (i.e., Bos et al., 1993; Menshchikov et al., 1975) and the new model developed in this study) The model is able to satisfactorily predict the outlet temperature and concentrations of ethane, acetylene, in each reactor (the available measured variables). The model developed also describes the optimum operating condition to make sure we get the high production of ethylene. The results were able to represent the conditions in an industrial plant with a front-end configuration.

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