PARAMETRIC ANALYSIS OF ETHYLENE OXIDE SYNTHESIS IN A CATALYTIC MICROCHANNEL REACTOR

by

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to my family

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ABSTRACT

PARAMETRIC ANALYSIS OF ETHYLENE OXIDE SYNTHESIS IN A CATALYTIC MICROCHANNEL REACTOR

In this study, ethylene oxide synthesis over $Ag/\alpha\text{-}Al_2O_3$ is investigated in a catalytic microchannel reactor by COMSOL software. Microreactors are ideal devices to investigate highly exothermic reactions like ethylene oxide synthesis. These units can be run without risk of explosion with explosive reagents and with minimized transport resistances. Therefore, microchannel reactor geometry is used for simulation studies with the aim of investigating the effect of different feed temperatures and feedstock compositions on ethylene oxide synthesis. The two dimensional (2D) catalyst coated channel geometry is simulated by COMSOL Multiphysics™ using finite element method under isothermal conditions. Before the 2D simulation tests, the kinetic model obtained from the literature is validated by the experimental data adapted from the already published studies. When the higher feed temperatures are used in the simulations, ethylene conversion increases and the selectivity of ethylene oxide decreases. The maximum conversion value of 13.8% is obtained at 565 K and for Set 1 in 2D simulations. This conversion value is smaller than 1D simulation result (61%) which is obtained for the same operation conditions. The feed ratio, C_2H_4/O_2 should be small for higher selectivity and conversion values. Small C_2H_4/O_2 ratios and lower temperature values (483 K, 513 K) enhances the selectivity of EO. With the increase in temperature total oxidation of ethylene become dominant and the selectivity of ethylene oxide decreases.

ÖZET

KATALİTİK MİKROKANAL REAKTÖR ÜZERİNDE ETİLEN OKSİT SENTEZİNİN PARAMETRİK ANALİZİ

Bu çalışmada, katalitik bir mikrokanal reaktöründe $Ag/\alpha\text{-}Al_2O_3$ katalizörü kullanılarak etilen oksit sentezi COMSOL yazılımı ile araştırılmıştır. Mikroreaktörler, etilen oksit sentezi gibi yüksek ekzotermik reaksiyonları araştırmak için ideal cihazlardır. Bu üniteler patlayıcı reaktiflerle patlama riski olmadan ve en aza indirgenmiş taşıma direnci ile çalıştırılabilirler. Bu nedenle, farklı akış sıcaklıklarının ve besleme stoğu bileşimlerinin etilen oksit sentezi üzerindeki etkisini araştırmak amacı ile simülasyon çalışmaları için mikrokanal reaktör geometrisi kullanılır. İki boyutlu (2D) katalizör kaplı kanal geometrisi, izotermal koşullar altında sonlu elemanlar metodu kullanılarak COMSOL Multiphysics^{TM} tarafından simüle edilmiştir. 2D simülasyon testlerinden önce, literatürden elde edilen kinetik model daha önce yayınlanmış çalışmalardan uyarlanmış deney verileri ile doğrulanmıştır. Simülasyonlarda daha yüksek besleme sıcaklıkları kullanıldığında, etilen dönüşümü artar ve etilen oksitin seçiciliği azalır. %13.8'lik maksimum dönüşüm değeri 565 K'de ve Set 1 için 2D simülasyonlarda elde edilmiştir. Bu dönüşüm değeri aynı çalışma koşulları için elde edilen 1D simülasyon sonucundan (% 61) daha küçüktür. Yüksek seçicilik ve dönüşüm değerleri için besleme oranı, C_2H_4/O_2 küçük olmalıdır. Küçük C_2H_4/O_2 oranları ve düşük sıcaklık değerleri (483 K, 513 K), etilen oksitin seçiciliğini arttırır. Sıcaklığın artmasıyla etilenin toplam oksidasyonu baskın hale gelir ve etilen oksidin seçiciliği azalır.

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LIST OF SYMBOLS

c_A	Concentration of species A
$\bar{c}_A$	Average concentration of species A
D_{AB}	Diffusion coefficient of A in B
$D_{AB,eff}$	Effective diffusion coefficient in catalyst layer
dS	Area increment
d_p	Catalyst particle diameter
F_A	Flow rate of species A
$F_{C2H4_{in}}$	Initial flow rate of species C_2H_4
$F_{C2H4_{out}}$	Outlet flow rate of species C_2H_4
K_E, K_O	Adsorption constant for ethylene and oxygen
L	Channel length
V_0	Volumetric flow rate
v	Linear velocity
P_i	Partial pressure of component i
r_1	Rate of partial oxidation of ethylene
r_2	Rate of total oxidation of ethylene
r_3	Rate of oxidation of ethylene oxide
S	Cross sectional area of the channel
T	Temperature
ΔH_{rxn}	Enthalpy of reaction at T

ε_p	Porosity of the washcoat layer
κ	Permeability of the washcoat layer
μ	Viscosity
ρ	Density
ρ_{bed}	Density of catalyst layer
τ	Tortuosity of washcoat layer

1. INTRODUCTION

Ethylene oxide (oxirane, ethene oxide) is the simplest cyclic ether. It is a colorless gas with sweet odor. Ethylene oxide is highly reactive because of its special molecular structure. When it participates in reactions, its highly strained ring can be opened easily. Thus, it is one of the most versatile chemical intermediates (Rebsdat and Mayer, 2001). It is used to produce glycol, polyglicols and ethanolamines. Also, ethylene oxide participates polymerization and isomerization reactions. It is widely used in chemical industry and the worldwide production capacity is almost 19 million metric tons (Hernández Carucci *et al.*, 2010).

Ethylene oxide has been used widely in industrial processes since its discovery. Ethylene oxide has been produced by two methods, namely the chlorohydrin process and direct oxidation process. In recent years, the direct oxidation route replaced the two-step chlorohydrin process. In direct oxidation route, ethylene oxide can be produced over a silver-based catalyst and either air or pure oxygen can be used as the oxidant for the process. In industrial process, maximum selectivity of ethylene oxide is solely 80 percent (Weissermel and Arpe, 1997).

Industrial plants operate ethylene oxide reaction in cooled tubular reactors (Westerterp and Ptasiński, 1984). The feed mixture enters to a series tubular reactors which are located parallel to each other. Because of the exothermic nature of the reaction, released heat is removed by kerosene, tetralin or water, which are passed around the tubes containing the catalyst particles (Weissermel and Arpe, 1997).

Currently, all industrial catalyst systems are focused on silver-based catalysts for ethylene epoxidation (Rebsdat and Mayer, 2001). Silver is a good catalyst for ethylene oxidation because it provides weak bond ethane and oxygen and generates ethylene oxide and alpha alumina is convenient support material (Schouten *et al*., 1996; Lee *et al*., 1988). However, some scientists have given attention for alternative catalysts and support

materials. In addition to catalysts and support materials, researchers have also worked on promoters such as NO_2, cesium and DCE.

Even though the ethylene oxide reaction seems to be straightforward, there are no common kinetic mechanisms of the reactions because scientists do not agree on how is oxygen and ethylene reacts on catalyst surface (Salmi *et al*., 2013). For instance, Rebsdat and Mayer (2001) explained that oxygen adsorption can be in the form of atomic oxygen, molecular oxygen or subsurface oxygen. Accordingly, Klugherz and Harriot (1971) claimed that oxygen reacts molecularly; Borman and Westerterp (1996) claimed that oxygen reacts dissociatively.

Modeling and computer simulations are very beneficial to understand complex processes such as ethylene epoxidation systems without spending money and time during the test. The dynamic simulation of ethylene oxidation reactor processes includes a lot of applications which are the foundation and close up researches, system identification, safety, control, optimization and feasibility studies (Rahimpour *et al*., 2011). In order to produce ethylene oxide with high selectivity is important for industry and a lot of researchers study on this subject by changing different parameters which are temperature, pressure and reactant concentrations (Peschel *et al*., 2011).

Microreaction technology has several advantages compared to the conventional reactors for ethylene oxide synthesis. Microchannels have very good heat and mass transfer characteristics and they provide that explosive reactants react safely in very small volumes. Also, microchannels allow a uniform temperature distribution along the catalyst bed. Owing to their improved heat and mass transfer rates, microreactors become ideal and interesting options for the synthesis ethylene oxide and measuring intrinsic reaction rates (Salmi *et al*., 2012; Peschel *et al*., 2011).

This work investigates ethylene oxide synthesis in a catalytic microchannel reactor via modeling and simulation studies with using suitable rate equations and kinetic data which are obtained from the literature. The effects of contact time, feed temperature and feed composition on conversion of ethylene, selectivity of ethylene oxide, and product

distribution over the ethylene oxide bed are studied. In these investigations, suitability of the kinetic data, i.e. its validation with the experimental data obtained from the literature is tested in COMSOL Reaction Engineering Lab that runs pseudo homogeneous, steady state reactor models in one dimension. After validation of the kinetic data, two-dimensional channel is designed in COMSOL Multiphysics. Mass and momentum equations forming a set of partial differential equations are solved together with the validated kinetic data using finite element method with COMSOL Multiphysics.

The literature survey about ethylene oxide synthesis, catalysts, promoters and support materials, microchannel technology is given Chapter 2. Mathematical modeling and simulation of the microchannel system are presented in Chapter 3. Results and discussion of simulations are given in Chapter 4. Finally, in Chapter 5 includes major outcomes and recommendations for possible future work.

2. LITERATURE SURVEY

2.1. Reaction of Ethylene Oxide Synthesis

Ethylene oxide has been produced commercially by two basic methods which are chlorohydrin process and direct oxidation process. The industrial production of ethylene oxide started with Wurtz's chlorohydrin process in 1914 (Rebsdat and Mayer, 2001). After the Wurtz's reconnaissance in 1931, Lefort discovered the direct oxidation of ethylene to ethylene oxide over silver catalysts and this method has been used widely in industrial processes (Kestenbaum *et al.*, 2000).

2.1.1. The Ethylene Chlorohydrin Process

In this method, firstly, ethylene reacts with hypochlorous acid to obtain ethylene chlorohydrin intermediate. This primary product reacts with lime to obtain ethylene oxide and calcium chloride is occurred as a by-product. The main reaction steps are the following (Weissermel and Arpe, 2003):

$$C_2H_4 + Cl_2H_2O \rightarrow HOCH_2CH_2Cl + HCl \quad (2.1)$$

$$2HOCH_2CH_2Cl + Ca(OH)_2 \rightarrow 2C_2H_4O + CaCl_2 + 2H_2O \quad (2.2)$$

Although the selectivity of chlorohydrin process was about 80%, this process had some crucial disadvantages. These are unsuitable economic conditions, corrosion which is the outcome of the using chlorine and unavoidable production of largely useless calcium chloride. Therefore, the direct oxidation method displaced the chlorohydrin process (Kursawe, 2009).

2.1.2. Direct Oxidation Process

In the direct oxidation of ethylene to ethylene oxide, the reaction is performed in the presence of air or oxygen over a silver based catalyst. Air-based process and oxygen-based process have different advantages and disadvantages.

In the air-based process, the system uses free air and ethylene oxide is obtained at low cost. However, feed contains low ethylene concentration; therefore, the system needs a few reactors to attain higher selectivity. On the contrary, oxygen based process needs just one reactor and feed contains high ethylene concentration, inert gas and limited oxygen concentration due to the risk of explosion (Kursawe, 2009). Under ambient conditions, the flammable limit for ethylene in air is 2.7-36%, whereas this limit is 3-100% for ethylene oxide (Lide, 2005). Also, ethylene oxide plants generally use oxygen-based process. The main reactions of oxidation process can be shown in Figure 2.1.

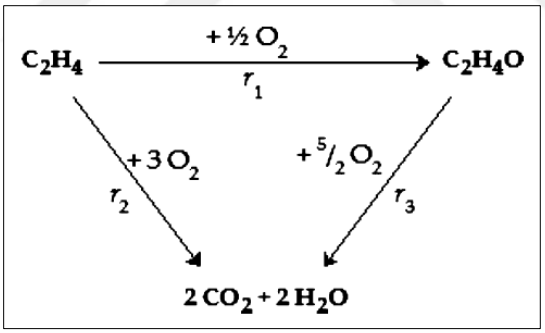

Figure 2.1. The general reaction schemes for oxidation of ethylene to ethylene oxide (Hernández Carucci *et al.*, 2010).

Ethylene oxide is obtained by partial oxidation of ethylene (r_1) over a silver catalyst, water and carbon dioxide are produced by total oxidation of ethylene (r_2) and oxidation of ethylene oxide (r_3). Reaction scheme is generally considered to be parallel because the oxidation rate of ethylene oxide is much smaller and negligible than other reactions. Also, all reactions are highly exothermic and reaction enthalpies are -105 kJ/mol, -1323 kJ/mol and -1218 kJ/mol for r_1, r_2 and r_3 respectively (Russo *et al.*, 2015).

The basic ethylene oxidation process is highly exothermic and removal of the heat released by the reaction is very crucial. Therefore, using fluidized-bed reactor seemed to be suitable for industrial production because fluidized-bed reactors are known to remove the heat easily due to the intense mixing of the reactive flow and catalyst bed, and improved heat transfer coefficients with the heat exchange surfaces. However, this type of reactor has some mechanical problems such as attrition and sintering. As a result, ethylene oxide plants currently use fixed-bed tubular reactors. When fixed-bed reactors are used, bed diameter must not be excessive for good heat transfer. Tube diameters vary between 25-40 mm (Zomerdijk and Hall, 1981).

Each of two possible reactors needs to provide isothermal conditions in the beds because maintaining the operating optimum temperature is very important for catalyst activity and selectivity. Therefore each of them needs circulation or evaporation of the coolant. A boiling system will have better heat transfer in the reactor and it provides to save liquid pump energy. Generally, organic coolant (e.g. isododecane) or water is used in the evaporative cooling. Both of organic coolant and water have some disadvantages compared to each other. Organic coolant can be flamed and water causes higher pressures on the coolant side (Rebsdat and Mayer, 2001).

2.2. Ethylene Oxide Synthesis Catalysis

Silver is the most suitable catalyst for the epoxidation of ethylene due to weak bond strength of oxygen and chemical nature of the adsorbed oxygen. Oxygen can adsorb on silver dissociatively and silver catalyst provides high oxygen coverages. The weak bond strength which is between oxygen and silver thermodynamically admits formation of ethylene epoxide (Van Santen and Kuipers, 1987).

Although silver is the only metal and α-alumina is the single commercial support material which performs ethylene epoxidation, Rojluechai *et al*. (2007) studied to find an alternative catalyst and different support materials. Therefore, they investigated reactions over Au and Au-Ag bimetallic catalyst which are on TiO_2 and CeO_2. Only Au catalyst on Al_2O_3 showed no activity for oxidation of ethylene. When a bimetallic catalyst was

created with a suitable amount of Au (0.63 wt.%) and Ag, new single silver sites which provided to increase the selectivity of ethylene oxide occurred. Besides, a good performance for the selectivity of ethylene oxide was showed by the Au/TiO_2 catalyst in contrast to conversion of ethylene. In addition, they presented that ceria is not an appropriate support for Au and it causes total combustion of ethylene.

Using more selective catalysts is important to obtain high selectivites and to prevent the formation of carbon dioxide. Therefore, Jankowiak and Barteau (2005) researched effects of the Cu-Ag bimetallic catalysts on the performance of the monolith reactor at varied reaction temperatures, feed compositions and reactant feed pressures. Activation energy measurements showed that bimetallic samples cause 1-2 kcal/mol decrease for ethylene consumption. In addition, their study indicates that the Ag and Ag-Cu bimetallic catalysts' results are similar because small amount of Cu does not influence the reaction mechanism and kinetics of the process dramatically. Also, copper-silver bi metallic catalysts provide an increase in ethylene oxide selectivity imperceptibly.

Nakatsuji *et al.* (1997) investigated the chemisorption and activation of oxygen molecule on Cu, Ag and Au surfaces. Also, they studied the reactivity and stability of oxygen species on the same Group 1B elements. Superoxide species have similar reactivities on Cu, Ag and Au surfaces for the formation of ethylene oxide. On the contrary, superoxide species show dissimilar catalytic activities due to the unlike stabilities. On the other hand, electron transfer which is an important determinant for chemisorption is very difficult for Au surface. Also, superoxide turns into peroxide quickly on Cu surface and superoxide cannot find enough time to form ethylene oxide. Finally, these negative factors for Cu and Au surfaces help to explain why silver is only catalyst for ethylene oxide synthesis.

Kursawe and Hönicke (2001) investigated Ag/Al and $Ag/\alpha\text{-}Al_2O_3$ microchannel systems' effect on selectivity and conversion. The maximum selectivities and conversion are different for each reactor. The selectivity is 61% and 51% for Ag/Al microchannel reactor and $Ag/\alpha\text{-}Al_2O_3$ microchannel reactor. Although silver coted α-alumina

microreactors are more active, it shows 62% conversion and almost 15% selectivity which is lower than Ag/Al reactor in the same reaction conditions.

Using suitable catalyst support is important to reach higher catalytic performance of reactions. Although α-Al_2O_3 has low surface area, it is the most suitable support material for commercial catalysts because it prevents isomerization of ethylene oxide to acetaldehyde with suitable surface acidity (Lee *et al.*, 1988). Researchers have studied on different support materials and their effects on ethylene epoxidation. Chongterdtoonskul *et al.* (2012) studied with different supports which are various aluminum oxides with different specific surface areas without Ag loading (α-Al_2O_3 (0.03), Al_2O_3 C (89.8), Al_2O_3, $_{Acid}$ (108.5)), SiO_2 90, TiO_2 and $SrTiO_3$ at the same temperature range. They found that 17.16 wt % Ag/$SrTiO_3$ provides the best results for ethylene oxide yield and selectivity at 548 K. Also, total oxidation of ethylene does not occur using the Ag/$SrTiO_3$ catalyst at the low reaction temperature from 548 K.

Moss and Thomas (1967) studied different Pd-Ag compositions and they observed an increase for the activation energy of CO_2 formation between 40% and 60% palladium and with a lower heat of oxygen chemisorption. Dellamorte *et al*. (2011) obtained 70% selectivity of ethylene oxide and 3% conversion of ethylene with Pd-Ag catalyst. However, both studies found out that Pd promoted Ag catalysts have some structural complications. According to Dellamorte *et al*. (2011) Pd-Ag catalysts need much more time to reach steady state and this situation causes complexity.

2.2.1. Effects of Promoters

Using promoted silver catalyst is important to increase selectivity to ethylene oxide and catalyst activity. Selectivity can be enhanced almost 20-30% with gaseous (DCE, CO_2 and NO_x) or solid promoters (Cs, Rb, Re, P, B,S or Sn). Therefore, Kursawe and Hönicke (2001) studied the effect of promoters NO_2 and Cs on selectivity using Ag/Al microchannel reactor. They obtained that the presence of NO_2 provides an increase of selectivity at any temperature. Cs promoted Ag/Al catalyst shows 70% selectivity which

is a few points low from NO_2 promoted catalyst. When Cs and NO_2 are applied together, the selectivity does not change greatly so, using two promoters together does not need.

Jun *et al*. (1992) added rhenium in the range 1.9-6.5 ppm as a promoter to electronic silver catalyst and they investigated the effect of rhenium on the adsorption of oxygen which is sign for selectivity of ethylene oxide. Their experiments show different adsorption states, much lower activation energy for desorption of molecular oxygen and dissimilar distance for adsorption of oxygen on catalyst surface from only silver samples. These results indicate that adding rhenium causes a decrease on electron density and weaker bond between silver and oxygen. All of these provide increase both of selectivity and conversion.

Chlorine promoters have an important role to improve selectivity for ethylene epoxide production and many scientists have studied about this subject. C. T. Campbell (1986) investigated results of chlorine addition on silver atoms. Chlorine adotoms blocks vacant Ag sites which are necessary for further oxidation process that produces CO_2 and H_2O. Thus, chlorine atom provides an increase in selectivity. In addition to chlorine atoms, some people researched the effect of different levels (0-3.3 ppm) 1, 2-dichloroethane (DCE) in the inlet. They observed that 3.3 ppm DCE provides 80% selectivity to ethylene oxide for very low ethylene conversion. Therefore, 1-2 ppm DCE provides optimal results for selectivity and conversion (Lafarga and Varma, 2000).

2.3. Kinetic Studies of Ethylene Oxide Synthesis

Many researchers have studied to elucidate the kinetics of ethylene epoxidation and combustion with using different reactors, operation conditions, feed concentrations and promoters by experimentally and theoretically. Nevertheless, they have not established general mechanisms for partial oxidation and total oxidation due to the reaction mechanisms' discrepancies (Hernández Carucci *et al*., 2010). First discussion is related to the fact that oxygen reacts atomically or molecularly for the epoxidation and combustion. The other controversy is about whether ethylene reacts in the gas phase or adsorbed form (Salmi *et al*., 2013).

Klugherz and Harriot (1971) studied to define a kinetic model using supported silver catalyst, wide range of ethylene and oxygen pressures at 493 K. They used Langmuir-Hinshelwood mechanism and suggested two rate equations for atomic and molecular adsorption of oxygen. However, the experimental results are more compatible with the rate equation involving molecular adsorption of oxygen.

A different kinetic model which includes inhibition of reaction products and dichloroethylene was studied by Metcalf and Harriot (1972). They used Langmuir-Hinshelwood theory to define rate expression. The experimental results show that molecular oxygen is responsible for both ethylene oxide formation and the formation of carbon dioxide. Also, partial pressures of ethylene oxide and dichloroethylene show small changes in the reaction rate and they do not be in the model.

Kinetics of ethylene oxidation over a supported silver catalyst with air were studied in the temperature range 490-620 K by a group. They investigated the effects of different partial pressures of ethylene and oxygen on reaction rates. According to the kinetic measurements, they suggested reaction rates for partial and total oxidation of ethylene and oxidation of ethylene oxide. Partial and total oxidation of ethylene show the same partial pressure dependence and the apparent activation energies are not very different each other. Also, the ethylene oxide oxidation rate is affected only partial pressure of ethylene oxide (Dettwiller *et al*., 1979).

Ghazali *et al*. (1983) and Park and Gau (1986) defined a similar kinetic model with using semi-differential fixed bed reactor at low temperature. Both studies showed that deposits which are the intermediates of the combustion reaction are important on the reactivity of the catalyst. In addition, they used a dual-site Langmuir-Hinshelwood mechanism to explain the data.

Petrov *et al*. (1985) used fixed-bed reactor and $Ag/\alpha\text{-}Al_2O_3$ promoted by Ca additive in the temperature interval 483-565 K to investigate rate equations for partial and total oxidation of ethylene. Experimental results show that ethylene reacts with adsorbed

molecular oxygen in the gas phase and rate equations are defined by a single site Eley-Rideal mechanism.

Stoukides and Pavlou (1986) studied to describe rate expressions and to observe the effects of excess ethylene oxide in the feed and external transfer limitations. CSTR was used with silver catalyst at temperatures 553-673 K for experiments. They assumed that partial and total oxidations occur on the same site. They determined rate expressions for three reactions and rate constants which were fit the test results. Besides, they found that external heat and mass transfer limitations cause to decrease the selectivity to ethylene oxide.

A different group used again CSTR which contains commercial $Ag/\alpha\text{-}Al_2O_3$ to find rate expressions for ethylene oxidation reactions at temperature range 553-593 K. They used a gas feed containing ethylene (3% - 6.5%), oxygen (18% - 19.5%) and nitrogen as a balance to measure reaction rates of ethylene oxidation reactions. Their experimental data shows that activation energies of the epoxidation and combustion are higher than other studies and carbon dioxide was the only compound which inhibits both reactions (Al-Saleh *et al*., 1988).

Borman and Westerterp (1995) investigated to define a kinetic expression for epoxidation reaction and combustion like many researchers. They studied with an industrial Ag/α-alumina catalyst in an internal recycle reactor and tested three sets of rate expressions. One of the sets described their experimental data and reaction rates for this set are affected all reactants and reaction products. Also, the rate-limiting step was assumed to be a bimolecular surface reaction between adsorbed ethylene and dissociatively adsorbed oxygen. Epoxidation and total oxidation are assumed to occur on different catalytic sites.

Lafarga *et al*. (2000) studied to determine the rate expressions for the oxidation of ethylene experimentally and they used a differential reactor which includes cesium-dopped silver catalyst supported on α-alumina pellets at the range of temperatures 483-543 K. According to the data obtained for 3-12% ethylene and oxygen, they presented

rate expressions for both epoxidation and total combustion reactions based on a dual-site Langmuir-Hinselwood mechanism. These reaction rates show that both ethylene and oxygen affect the reaction rates; however, small pressures of reaction products do not influence the reaction rates.

Some scientist studied with microchannels to determine the kinetic expression of partial and total oxidation of ethylene. Hernández Carucci *et al*. (2010) used $Ag/\alpha\text{-}Al_2O_3$ wash-coated and pure silver microchannels for experiments and they suggested two models for partial oxidation of ethylene. The first model assumed that ethylene and dissociatively oxygen compete for adsorption on the catalytic surface. The second model assumed competitive adsorption of ethylene and molecular oxygen on the surface and the surface reactions are rate-limiting steps for both models. Models were fitted with experimental results in a very high percentage; however, the second model was more excellent.

Salmi *et al*. (2012) aimed to propose a kinetic expression for epoxidation reaction using a microreactor system which contains non-supported silver catalyst plates. They considered three models for partial oxidation of ethylene. The first two models are based on Langmuir-Hinselwood mechanisms. The first model explains that oxygen adsorbs on the silver surface dissociatively, the second model represents an equation for atomic and molecular oxygen co-exist on catalyst surface, and the third one is based on Eley-Rideal mechanism in which adsorbed ethylene reacts with molecular oxygen in the gas phase. Experiments were made after the pretreatment which is used to get more stable and active catalyst at 4 bar and 523 K. Although the experimental results were not compatible with the first model, second model and especially third model gave the suitable results with the experimental data.

$E+{}^*=E^*$	2^*
$O_2+2^*=2O^*$	1
$E^*+O^*=EO+2^*$	2

$2E+O_2=2EO$

$$R_1=\frac{k'c_Ec_{O2}{}^{1/2}}{(1+K_Ec_E+K_{O2}{}^{1/2}c_{O2}{}^{1/2}+K_{H2O}H_{H2O})^2} \quad (a)^{**}$$

$E+{}^*=E^*$	2
$O_2+{}^*=O_2{}^*$	1
$E^*+O_2{}^*=EO+O^*+{}^*$	2
$2O^*=O_2{}^*+{}^*$	1

$2E+O_2=2EO$

$$R_1=\frac{k'c_Ec_{O2}}{(1+K_Ec_E+K_{O2}c_{O2}+K_{O2}{}^{1/2}K_O{}^{1/2}c_{O2}{}^{1/2}+K_{H2O}H_{H2O})^2} \quad (b)^{**}$$

$E+{}^*=E^*$	2
$O_2+E^*=EO+O^*$	2
$2O^*=O_2+2^*$	1

$2E+O_2=2EO$

$$R_1=\frac{k'c_Ec_{O2}}{(1+K_Ec_E+K_{O2}{}^{1/2}c_{O2}{}^{1/2}+K_{H2O}H_{H2O})} \quad (c)^{**}$$

* The integers represent the stoichiometric numbers of the steps in the mechanism, ** Water adsorption included since water is formed in the total oxidation.

Component vector ($\mathbf{a}^T$): [E O_2 EO CO_2 H_2O].

$$\text{Stoichiometricmatrix}(\boldsymbol{\nu}^T): \begin{matrix} -1 & -1/2 & 1 & 0 & 0 \\ -1 & -3 & 0 & 2 & 2 \end{matrix}.$$

Reaction stoichiometry: $\boldsymbol{\nu}^T\mathbf{a}=\mathbf{0}$.

Figure 2.2. Reaction mechanisms and rate equations of ethylene oxide synthesis (Salmi *et al.*, 2012; Salmi *et al.*, 2013).

The same group who did the study in the previous paragraph wants to develop the kinetic results found from the previous work. They considered the same three alternatives again. Experiments were made for different ethylene and oxygen concentrations under the similar operation conditions in the same microreactor. Experimental results show that the adsorption term of oxygen and water is very small when compared with adsorption term of ethylene. Therefore, they neglected these terms from rate equation. Also, selectivity

analysis showed that dissociatively adsorbed oxygen is responsible for total oxidation of ethylene (Salmi *et al*., 2013).

Russo *et al*. (2015) studied to explain the effects of the change of concentration and temperature on reaction rates of ethylene oxide synthesis. Therefore, they defined two models, one for a washcoated microreactor and the other one for a non-supported silver plate microreactor, for partial and total oxidation of ethylene. They collected experimental data from previous studies. The experimental data were collected for washcoated microreactor by Hernández Carucci *et al*. (2010) and for pure silver by Salmi *et al*. (2013). According to the data, atomic adsorption of oxygen is responsible for total oxidation and its effect on denominator was ignored. Besides, kinetic and adsorption parameters were obtained for each reactor.

Table 2.1. Kinetic expressions for oxidation of ethylene.

References	**Reaction Rate Expressions**
Klugherz and Harriot (1971)	$r_1 = \frac{k_1.P_E.P_O^2}{(1+K_E.P_E+K_O.P_O+K_P.P_P)^2.(1+\sqrt{K_S.P_O})^2}$
Metcalf and Harriot (1972)	$r_{1,2} = \frac{k_i.P_E.P_O^{3/2}}{(den)^2}$ $den = 1+K_1.P_O^{0.5}+K_2.P_O+K_3.P_E+K_4.P_E.P_O^{0.5}+K_5.P_c.P_O^{0.5}$ $+K_6.P_W.P_O^{0.5}$
Dettwiller *et al*. (1979)	$r_1 = \frac{k_1.P_E.K_E}{1+P_E.K_E}$ $r_2 = \frac{k_2.P_E.K_E}{1+P_E.K_E}$ $r_3 = k_3.P_E$

Table 2.1. Kinetic expressions for oxidation of ethylene (cont.).

References	**Reaction Rate Expressions**
Ghazali *et al*. (1983) and Park and Gau (1986)	$r_1 = \frac{k.K_E.K_O.P_E.P_O}{(1+K_E.P_E+K_O.P_O+K_{EO}.P_{EO})^2}$
Petrov *et al*. (1985)	$r_1 = \frac{K1.P_O.P_E}{1+K3.P_O+K4.P_E}$ $r_2 = \frac{K2.P_O.P_E}{1+K3.P_O+K4.P_E}$
Stoukides and Pavlou (1986)	$r_1 = \frac{k_1.K_E.P_E}{1+K_E.P_E+K_{EO}.P_{EO}^2}$ $r_2 = \frac{k_2.K_E.P_E}{1+K_E.P_E+K_{EO}.P_{EO}^2}$ $r_3 = \frac{k_3.K_{EO}.P_{EO}^2}{1+K_E.P_E+K_{EO}.P_{EO}^2}$
Al-Saleh *et al*. (1988)	$r_1 = \frac{k_1.P_O^{0.5}.P_E^{0.6}}{1+K_C.P_C}$ $r_2 = \frac{k_2.P_O^{0.5}.P_E^{0.5}}{1+K_C.P_C}$
Borman and Westerterp (1995)	$r_{1,2} = \frac{k_i.K_E.P_E.K_O^{1/2}.P_O^{1/2}}{(1+K_E.P_E+K_O^{1/2}.P_O^{1/2}+K_C.P_C+K_W.P_W+K_{EO}.P_{EO})^2}$
Lafarga *et al*. (2000)	$r_1 = \frac{k_1.P_E.P_O^{0.58}}{(1+K_{E,1}.P_E)}$ $r_2 = \frac{k_2.P_E.P_O^{0.30}}{(1+K_{E,2}.P_E)}$

Table 2.1. Kinetic expressions for oxidation of ethylene (cont.).

References	Reaction Rate Expressions
Hernández Carucci *et al*. (2010)	$r_1 = \frac{k.K_E.K_O.C_E.\sqrt{C_O}}{(1+K_E.C_E+\sqrt{K_O.C_O})^2}$ $r_1 = \frac{k.K_E.K_O.C_E.C_O}{(1+K_E.C_E+K_O.C_O)^2}$
Salmi *et al*. (2012)	$r_1 = \frac{k.K_E.K_O.C_E.C_O}{(1+K_E.C_E+K_O.C_O+\sqrt{K_O.C_O}+K_W.C_W)^2}$ $r_1 = \frac{k.K_E.K_O.C_E.C_O}{(1+K_E.C_E+\sqrt{K_O.C_O}+K_W.C_W)}$
Salmi *et al*. (2013)	$r_1 = \frac{k.K_E.K_O.C_E.C_O}{(1+K_E.C_E)^2}, r_1 = \frac{k.K_E.K_O.C_E.C_O}{(1+K_E.C_E)}$ $r_2 = \frac{k.K_E.K_O.C_E.\sqrt{C_O}}{(1+K_E.C_E)^2}$
Russo *et al*. (2015)	$r_1 = \frac{k.K_E.K_O.C_E.C_O}{(1+K_E.C_E+K_O.C_O)^2}$ $r_2 = \frac{k.K_E.K_O.C_E.\sqrt{C_O}}{(1+K_E.C_E+K_O.C_O)^2}$

2.4. Modeling and Simulation Studies

Modeling and simulation studies are very essential for chemical reaction engineering because they help to understand process very well. Thanks to the well-defined process, different variables and parameters are used further simulation studies to optimize and control the process. Also, using modeling and simulation studies provides great convenience to perform dangerous reactions and to prevent loss of money in order to a lot of experiments.

Optimization of ethylene oxide reaction is not straightforward and a lot of factors should be considered in a successful reactor model. Zhou and Yuan (2005) studied about optimization of the fixed-bed reactor for ethylene epoxidation. In their study, ethylene oxide optimization problems were investigated, and steady-state and dynamic optimization approaches were introduced with a selected kinetics for the catalyst according to their attention. They changed some operating variables which are temperature, feed concentration, feeding rate, operating pressure and inlet ethylene dichloride concentration and coolant temperature for a maximum benefit. The productivity was enhanced significantly by increasing the operating pressure and inlet ethylene (from 24 to 32%) or oxygen (from 6 to 8%) concentrations. However, in practice oxygen and ethylene concentrations are constrained by explosive limits. Also the optimal ethylene dichloride concentration level was identified by the sintering to temperature and it was independent of productivity.

It is very important to ensure safe operation while increasing productivity and Galan *et al.* (2009) aimed to maximize ethylene oxide selectivity with optimal coolant temperature which prevents hot spots in the presence of 1, 2-dichloroetan for a fixed-bed multi-tubular reactor. They used the kinetics of ethylene epoxidation from studies of Petrov *et al.* (1986) and Eliyas *et al*. (1990), and they studied for low oxygen (7% mol) and ethylene (16% mol) concentrations in the range of 473-523 K and 18-20 bar. Also, using optimum and constant inhibitor concentration (5 ppm) is very important point for the reactor safety because it blocks total oxidation of ethylene oxide and an increase in oxygen concentration is observed along the reactor. Besides, the use of circulating oil as coolant with high flow rate provides a slight increase (7°C) in outflow coolant.

Rahimpour *et al.* (2011) studied to define the level of optimum ethylene dichloride using 1D heterogeneous model for an industrial fixed-bed reactor. Also, they observed the effect of inlet gas velocity on ethylene oxide mole fraction of gas and solid phases. For modeling study, they obtained data which are reactor and catalyst properties, feed compositions and feed flow rate from operating data sheets of ethylene oxide plant. According to the simulation results, maximum selectivity of ethylene oxide is obtained the presence of 0.37-0.42 ppm ethylene dichloride. Besides, higher gas velocities provide

similar ethylene oxide mole fraction profiles for gas and solid phases because higher linear velocity prevents the mass transfer resistance of gas film around the catalyst particle.

Bayat *et al*. (2013) investigated the behavior of a novel dual-type industrial ethylene oxide reactor instead of conventional single type reactor. They used the same industrial data with Rahimpour *et al.* (2011) for 1D heterogeneous dynamic model. They aimed to observe positive effect on catalyst life time and rate of ethylene oxide production. Simulation results showed that thanks to the two catalyst bed, catalyst poisons do not reach the second reactor and the reaction temperature is kept at low values along the reaction pathway. As a result, higher catalyst activity, longer catalyst lifetime and an increase in ethylene oxide production rate are obtained.

The same group who did the study in the previous paragraph studied about the dynamic optimization of an industrial fixed-bed ethylene oxide reactor. They investigated two cases. In the first one, they studied optimal conditions of four variables, namely feed gas temperature (T_f = 499.3 K), inlet pressure (22 bar) and molar flow rate in the reaction side (0.9 mole/s) and cooling water temperature (T_{shell}=503.52 K). In the second case, cooling water and feed gas optimal temperatures were obtained. Optimization studies were found to provide up to ca.4.2% yield enhancement in ethylene oxide production (Bayat *et al*., 2013).

Nawaz (2016) studied to define optimum feed flow, oxygen concentration and feed pressure to boost ethylene oxide productivity and selectivity. They used a heterogeneous one-dimensional model which is developed in ACM (Aspen Custom Modeler). After the base simulation, they obtained almost 11.8 wt % conversion and 84 % selectivity of ethylene oxide. Also, they observed that oxygen injection enhanced the reactor productivity by 10-20 % and a pressure value of about 22 MPa is an ideal value for ethylene conversion and selectivity of ethylene oxide.

2.4. Microstructured Systems

Microfabrication techniques have been developed significantly in recent years (Pan *et al*., 2014). Thermal and chemical process engineering has obtained benefits from developments of the microstructure devices such as micro heat exchangers, micromixers and microstructure reactors (Schubert *et al*., 2001; Pattison and Baldea, 2015). Microreactors' benefits include better heat and mass transfer, easier scale-up, improved process control, lower cost and safety. Therefore, lots of literature studies have taken interest in microchannel reactors (Ehrfeld *et al*., 2000).

Microchannel reactors have a lot of advantages and they have better results than conventional reactors. Generally, microreactors contain multiple parallel channels with diameters between 0.1 - 0.3 mm. This construction provides high surface area-to-volume ratios in the range of 10000 - 50000 m^2/m^3 and provides effective heat and mass transfer compared to the conventional reactors (Kiwi Minsker and Renken, 2009). Thanks to the very high heat transfer rates, highly exothermic reactions, even those in the explosive range can run safely in microchannel reactors (Stankiewicz and Moulijn, 2000).

High heat exchanging efficiency provides isothermal conditions and restrains hot spots and undesirable side reactions (Jahnisch *et al*., 2004). In addition to heat transfer, microchannel reactors provide high mass transfer under laminar flow conditions (Tonkovich *et al*., 2004). Also, thin catalyst layer eliminates internal mass transfer resistance in the catalyst pores. Therefore, operation continues within the intrinsic kinetic regime (Russo *et al*., 2015).

Thanks to these advantages, microreactors find both experimental and industrial application areas. Especially, microreactors are very useful tools for experimental works such as screening of new catalyst and carrying out kinetic experiments (Salmi *et al*., 2012). Microreactors are also used effectively in simulation studies because they provide to integrate control, sensor and reactor functionality. Also, reaction engineering analysis is necessary to understand and analyze the operating characteristic of microreactors (Jensen *et al*., 1998; Jensen, 2001).

2.4.1. Ethylene Oxide Synthesis in Microchannel Reactors

Microchannel reactors are widely used in the field of heterogeneous catalysis and explosive reactants can be carried out in these reactors safely because of dimensions which are below the quench distance (Janicke *et al*., 2000). Due to this characteristic, microreactors are very secure devices for ethylene oxidation process. In addition to security, their improved heat and mass transfer specifications make these reactors ideal for kinetic studies which are presented in Section 2.3. (Salmi *et al.*, 2012).

Kestenbaum *et al*. (2000) investigated the potential of a microreactor for the synthesis of ethylene oxide. For this reason, they designed a microreactor with silver foils for catalytic activity. The microreactor had 126 channels and each of them had 9 mm long, 50 μm high and 500 μm wide. Most of the experiments were worked at specific range temperatures (500-570 K) and pressures (5-15 bar) and reactant gas composition was changed to obtain the best selectivity and conversion.

Kestenbaum and coworkers (2002) compared performances of an industrial process and a microreaction system. Experiments are made for different temperature between at 513 K and 563 K. The ethylene concentration changes between 1 and 15 vol % and the oxygen concentration changes from 5 to 85 vol %. Experimental results show that microreactor reaches the same conversion value with industrial oxygen based reactor but it has lower selectivity because microreactor does not contain any promoters.

3. MODELING AND SIMULATION OF THE MICROCHANNEL REACTOR

This chapter describes a single washcoated microchannel reactor because a single channel represents the behavior of the entire microreactor and the methods used to simulate the reactions and transport phenomena occurring in the system. Simulations are made by COMSOL Multiphysics software which contains finite element method based calculations. In this study, ethylene oxide synthesis over Ag/α-Al_2O_3 catalyst is selected due to its suitability for the synthesis reaction and availability of kinetic data in the literature. Physical properties required for calculations were also obtained from the literature. Simulations were performed for four different temperatures and feed compositions under isothermal conditions.

3.1. Modeling

The microchannel reactor involves parallel, rectangular-shaped channels. Schematic presentation of the reactor is illustrated Figure 3.1. and a single channel is presented in Figure 3.2. Top and bottom surfaces of rectangular channel are coated with a porous, alpha alumina supported Ag catalyst layer. Channel dimensions, given in Table 3.1, are defined according to necessary of the process and general microchannel properties.

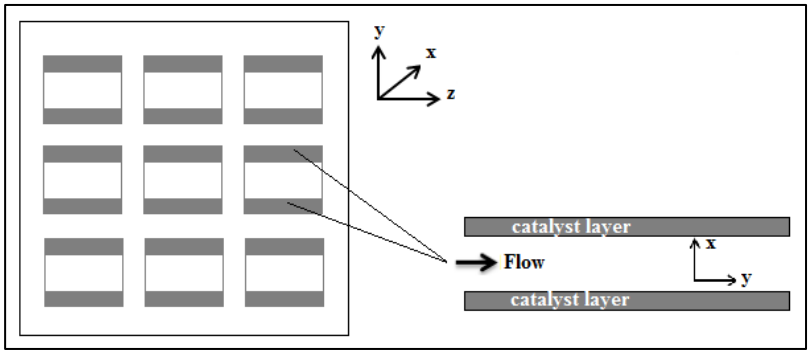

Figure 3.1. Schematic presentation of the microchannel reactor.

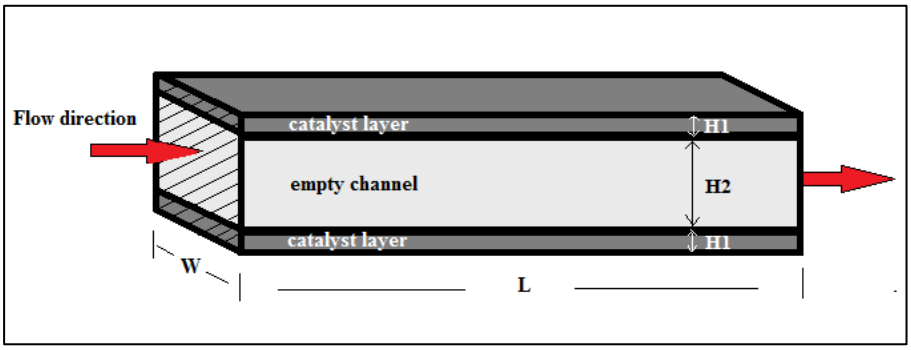

Figure 3.2. One single channel configuration.

Modeling studies are carried out in Cartesian coordinates and the effect of z direction (i.e. the third spatial dimension) is assumed to be negligible. Thus, two-dimensional channel is used for simulations. Dimensions of the microchannel are provided in Table 3.1. Also detailed description of channel is given Figure 3.3 which is used to define boundary conditions and the solution domain. Due to the symmetry, modeling of the half channel is sufficient to capture the changes in the complete channel. Moreover, it is assumed that the feed to the multichannel reactor (Figure 3.1) is distributed equally into each channel, and, as a result, one channel can describe the behavior of the multichannel device.

Table 3.1. Dimensions of microchannel

Width (W)	0.001 m
Length (L)	0.1 m
Catalyst layer height (H1)	50 μm
Empty channel height (H2)	400 μm
Flow area	$5*10^{-7}$ m^2
Volume of the channel	$5*10^{-8}$ m^3

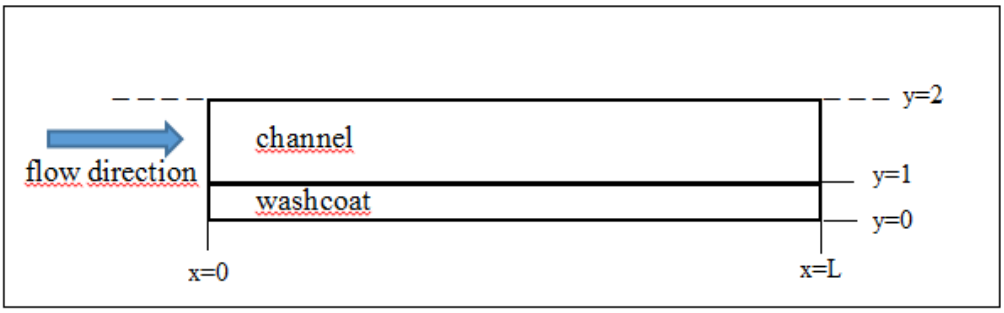

Figure 3.3. Half part of the single channel.

Reactant stream flows inside the channel and reaction takes place only in washcoated porous catalyst layer and there is no reaction occurs in fluid phase. The assumptions are that flowing gases are incompressible Newtonian fluids and behave ideally. Conservation of momentum is valid for washcoat layer and empty channel. The two dimensional Navier-Stokes equations in Cartesian coordinates for Newtonian fluid is used to solve conservation of momentum for fluid phase. The equation is given as follows (Bird *et al*., 2007):

$$\rho\left(v_x\frac{\partial v_x}{\partial x}+v_y\frac{\partial v_x}{\partial y}\right)=-\frac{\partial p}{\partial x}+\mu\left(\frac{\partial^2 v_x}{\partial x^2}+\frac{\partial^2 v_x}{\partial y^2}\right) \tag{3.1}$$

Conservation of momentum in the washcoat catalyst layer is solved by Brinkman equation which is a modified form of momentum conservation equation (Bird *et al*., 2007):

$$\left(\frac{\mu}{\kappa}\right)v_x=-\frac{\partial p}{\partial x}+\left(\frac{1}{\varepsilon_p}\right)\mu\left(\frac{\partial^2 v_x}{\partial x^2}+\frac{\partial^2 v_x}{\partial y^2}\right) \tag{3.2}$$

$$\left(\frac{\mu}{\kappa}\right)v_y=-\frac{\partial p}{\partial x}+\left(\frac{1}{\varepsilon_p}\right)\mu\left(\frac{\partial^2 v_y}{\partial x^2}+\frac{\partial^2 v_y}{\partial y^2}\right) \tag{3.3}$$

In Equations (3.2) and (3.3), ε_p is the porosity and κ is the permeability related to with the catalyst. The porosity is taken as 0.4 (Russo *et al*., 2015) and permeability is estimated by Equation (3.4) (Sen and Avcı, 2014):

$$\kappa = \frac{d_p^2}{150}\frac{\varepsilon_p^3}{\left(1-\varepsilon_p\right)^2} \tag{3.4}$$

In Equation (3.4), d_p is the catalyst particle diameter, but it is taken as the catalyst layer thickness. Boundary conditions related to Equations (3.1) to (3.3) are given in Table 3.2.

Table 3.2. Boundary conditions used for the momentum conservation equations.

$x = 0$	$y_1 < y < y_2$	$v_1 = v_1^0$
$x = L$	$y_1 < y < y_2$	$p_1 = p_{1out}$
$y = y_1$	$\forall x$	$n.v_1 = 0$
$y = y_2$	$\forall x$	$n.v_1 = 0$
$y = 0$	$\forall x$	$v_1 = 0$

In the reaction channel, mass transport of the species should be calculated, because concentrations of the reactants and products change along the channel and catalyst layer as a result of the ethylene oxidation. Considering the fact that reactions occur only catalyst layer, the Equations (3.5) and (3.6) are used to calculate mass transfer in the reaction channel and washcoat layer (Bird *et al*., 2007):

$$v_x\frac{\partial c_A}{\partial x} + v_y\frac{\partial c_A}{\partial y} = D_{AB}\left(\frac{\partial^2 c_A}{\partial x^2} + \frac{\partial^2 c_A}{\partial y^2}\right) \tag{3.5}$$

$$v_x \frac{\partial c_A}{\partial x} + v_y \frac{\partial c_A}{\partial y} = D_{AB,eff} \left(\frac{\partial^2 c_A}{\partial x^2} + \frac{\partial^2 c_A}{\partial y^2} \right) + r_A \tag{3.6}$$

The subscript A is used to specify the species C_2H_4, O_2, C_2H_4O, CO_2 and H_2O. Boundary conditions related to Equations (3.5) and (3.6) are given in Table 3.3.

Table 3.3. Boundary conditions used in mass transport equations.

$x = 0$	$y_1 < y < y_2$	$c_A = c_A^0$
$x = L$	$y_1 < y < y_2$	$n.(-D_{AB} \nabla c_A) = 0$
$y = y_2$	$\forall x$	$n.(-D_{AB} \nabla c_A + c_A v_1) = 0$
$y = 0$	$\forall x$	$n.(-D_{AB} \nabla c_A + c_A v_1) = 0$

Effective diffusivity appearing in Equation (3.6) is calculated from binary diffusivity. Binary diffusivity is calculated with using tortuosity which is taken as 2 (Nawaz, 2016) and porosity of 0.4:

$$D_{AB,eff} = \frac{\varepsilon_A}{\tau} D_{AB} \tag{3.7}$$

Nitrogen constitutes a very large proportion of the gas mixture. Therefore, we assume that all species show the same diffusivity value with nitrogen. Binary diffusivity value is calculated for diffusion of nitrogen of interest in air by Equation (3.8):

$$D_{AB} = \frac{10^{-3} T^{1.75} \left[\frac{1}{M_A} + \frac{1}{M_B} \right]^2}{P \left[(\sum \vartheta)_A^{1/3} + (\vartheta)_B^{1/3} \right]} \tag{3.8}$$

Finally, the continuity equation used fluid channel and catalyst layer can be given as Equation (3.9) (Bird *et al*., 2007):

$$\frac{\partial v_x}{\partial x} + \frac{\partial v_x}{\partial y} = 0 \tag{3.9}$$

Reaction stoichiometries and enthalpies of partial and total oxidation of ethylene are given in Table 3.4. Rate equations for ethylene oxide synthesis and kinetic constants are taken from Petrov and cowerkers' (1985) study. Equation (3.10) represents partial oxidation of ethylene while Equation (3.11) represents total oxidation of ethylene. Kinetic constants are listed in Table 3.5.

Table 3.4. Reaction stoichiometries and enthalpies of ethylene oxidation.

Reaction	**Stoichiometry**	**ΔH_{rxn} (kJ/mol)**
Partial oxidation	$C_2H_4 + 0.5O_2 \rightarrow C_2H_4O$	-105
Total oxidation	$C_2H_4 + 3O_2 \rightarrow 2CO_2 + 2H_2O$	-1323

$$r_1 = \frac{K1.P_O.P_E}{1 + K3.P_O + K4.P_E} \tag{3.10}$$

$$r_2 = \frac{K2.P_O.P_E}{1 + K3.P_O + K4.P_E} \tag{3.11}$$

Table 3.5. Rate expression parameters (Petrov *et al.*, 1985)

Parameter	**Dimension**	**Value**			
		483 K	**513 K**	**537 K**	**565 K**
K1	mole h^{-1} g-cat^{-1} atm^{-2}	0.00297	0.00486	0.00693	0.0101
K2	mole h^{-1} g-cat^{-1} atm^{-2}	0.00166	0.00378	0.00685	0.0128
K3	atm^{-1}	0.980	0.625	0.453	0.321
K4	atm^{-1}	19.2	11.8	8.38	5.81

In order to test the validity of the rate expressions and kinetic constants, they are implemented into 1-D pseudo homogeneous plug flow reactor model which works under COMSOL Reaction Engineering Lab. In Reaction Engineering Lab, concentration gradient is allowed only to develop in the axial direction. The species mass balances are given by the following equation (Fogler, 2006):

$$\frac{\partial F_i}{\partial V} = R_i \tag{3.12}$$

Also, reactant flow rates are entered in COMSOL Reaction Engineering Lab. Reactants flow rates are defined using catalyst mass and the same contact time values which are represented in Petrov *et al*. (1985). For calculations of feed flow rates, Equations (3.13) and (3.14) are used and bed density is taken as 1800 kg/m^3 (Nawaz, 2016). Calculations are made for four different sets of feed compositions and five contact time values which are selected from the given range (from 119 to 1905 g_{cat} h mol^{-1}) and four different feed compositions.

$$\text{Contact time} = \frac{W}{F_e} \tag{3.13}$$

$$V = \frac{W}{\rho_{bed}} \tag{3.14}$$

The volumetric flow rates of species (oxygen and nitrogen) are calculated by using the ethylene flow rates under normal temperature and pressure.

$$V_A = \frac{F_A RT}{P} \tag{3.15}$$

After the calculating the volumetric flow rate of oxygen and nitrogen, flow rates of this species can be calculated with Equation (3.15).

Solution of the model equation is performed using the COMSOL Multiphysics package. COMSOL uses finite element method (FEM) to solve the partial differential equations. Stationary solver type is used because the solution is proposed to be achieved when the system approaches steady state. Whether to use a linear or non-linear solver is automatically decided by COMSOL with an analysis of the residual and the constraint Jacobian matrices.

In order to execute the solution, initial temperature and total pressure of the system, inlet linear velocity to the channel and, for reaction channel only, initial compositions of species are entered in COMSOL. Calculations for composition values should be made to find corresponding values at the specified operational conditions of the system. While pressure and temperature of the feed is constant and the molar fractions of the species are known the concentrations (mol/m^3) in feed stream are calculated by Equation (3.16):

$$c_{A_0} = \frac{P_{A_0}}{RT_0} = \frac{y_{A_0} P_0}{RT_0} \tag{3.16}$$

As inlet linear velocity and the geometry of the channel are known, the volumetric flow of feed, and the inlet molar flow of species can be calculated:

$$F_{A_0} = c_{A_0} V_0 \tag{3.17}$$

The outlet concentration and molar flows are given at their average values via integration over the boundaries as follows:

$$\bar{v}_1 = \frac{\int v_1 dS}{\int dS} \tag{3.18}$$

$$\bar{c}_A = \frac{\int c_A v_1 dS}{\int dS} \tag{3.19}$$

$$\bar{F}_A = \bar{c}_A \bar{v}_1 S \tag{3.20}$$

Partial pressures of species are required for calculating the rate of reactions. At any point within the reaction channel, partial pressures are calculated by ideal gas assumption:

$$P_A = c_A RT \tag{3.21}$$

3.2. Parameters Analyzed During the Simulations

In this study, effects of bed temperatures, different feed compositions, feed ratio of C_2H_4/O_2 and contact time on ethylene conversion, selectivity of ethylene oxide and product distribution are investigated. Parametric analysis is carried out four different temperatures, namely 483 K, 513 K, 537 K and 565K. Also, four different sets and feed compositions of these set are given Table 3.6. Inlet flow rates for ethylene oxygen and nitrogen at different contact times are listed in Table 3.7., Table 3.8. and Table 3.9.

Table 3.6. Feed compositions of four series.

Set	Feed Composition
1.set	50% O_2, 25% C_2H_4 , 25% N_2
2.set	33.3% O_2, 33.3% C_2H_4, 33.3% N_2
3.set	25% O_2, 50% C_2H_4, 25% N_2
4.set	20% O_2, 60% C_2H_4, 20% N_2

Table 3.7. Contact times and inlet flow rates of ethylene.

Contact time	F_C_2H_4_in (mol/s)
1 (120 g_{cat} h mol^{-1})	2.083E-07
2 (500 g_{cat} h mol^{-1})	5.000E-08
3 (1000 g_{cat} h mol^{-1})	2.500E-08
4 (1500 g_{cat} h mol^{-1})	1.666E-08
5 (1900 g_{cat} h mol^{-1})	1.315E-08

Table 3.8. Inlet flow rates of oxygen.

	Contact time 1	Contact time 2	Contact time 3	Contact time 4	Contact time 5
Set 1	4.16E-07	1.00E-07	5.00E-08	3.33E-08	2.63E-08
Set 2	2.08E-07	5.00E-08	2.50E-08	1.66E-08	1.31E-08
Set 3	1.04E-07	2.50E-08	1.25E-08	8.33E-09	6.57E-09
Set 4	6.94E-08	1.66E-08	8.33E-09	5.55E-09	4.38E-09

Table 3.9. Inlet flow rates of nitrogen.

	Contact time 1	**Contact time 2**	**Contact time 3**	**Contact time 4**	**Contact time 5**
Set 1	2.08E-07	5.00E-08	2.50E-08	1.66E-08	1.31E-08
Set 2	2.08E-07	5.00E-08	2.50E-08	1.66E-08	1.31E-08
Set 3	1.04E-07	2.50E-08	1.25E-08	8.33E-09	6.57E-09
Set 4	6.94E-08	1.66E-08	8.33E-09	5.55E-09	4.38E-09

In all cases selectivity, conversion and yield are calculated according to the definitions provided in the literature (Petrov *et al.*, 1985):

$$\text{Conversion} = \frac{F_{C2H4_{in}} - F_{C2H4_{out}}}{F_{C2H4_{in}}} \tag{3.22}$$

$$\text{Selectivity} = \frac{r_1}{(r_1 + r_2)} \tag{3.23}$$

$$\text{Yield} = \text{Conversion} \times \text{Selectivity} \tag{3.24}$$

4. RESULTS AND DISCUSSION

The reaction mechanism of ethylene oxidation reactions is first tested in a 1D pseudo-homogeneous model by using COMSOL Reaction Engineering Lab and the parametric analysis of system defined in the previous chapter is carried out using COMSOL Multiphysics package. Simulations are done with four different temperatures and feedstock compositions.

4.1. Results of COMSOL Reaction Engineering Lab

It is important to understand nature of the ethylene oxide synthesis reactions and observe the compatibility of the kinetic values and inlet molar flow rates used before starting any further calculations on these reactions. The values adapted from the study Petrov *et al*. (1985) are used for this test and simulation results are consistent with the ones provided in the literature. For example; contact time versus molar concentration results for our simulation and the study of Petrov *et al*. (1985) are similar for Set 2 and at the same temperature. When the outlet concentrations of ethylene are examined for contact time 3, a value of about 25% is observed in both studies. Also, figures of temperature versus selectivity give similar results for Set 3 in both studies. EO selectivity of 44% at 483 K and 27% at 565 K values are obtained from the simulation and literature. When figures of the feed ratio versus selectivity are examined, ethylene oxide selectivity of almost 65% at ratio 0.5 and 20% at ratio 3 are obtained for both studies.

4.1.1. The Effect of Contact Time

Contact time is an important factor which affects the concentrations of all the reactants and products. For this reason, the change in molar concentration values of all products and reactants against the different contact time values was also obtained at 483 K, 513 K, 537 K and 565 K. Molar concentration profiles were obtained for Set 2 (C_2H_4: O_2: N_2= 1:1:1). It can be observed that the product molar concentrations increase with the increase of the contact time for all temperature values. On the contrary, reactant

concentrations decrease with the contact time. Also, decrease in oxygen concentration is occurred faster than decrease in ethylene concentration because of the reaction stoichiometry.

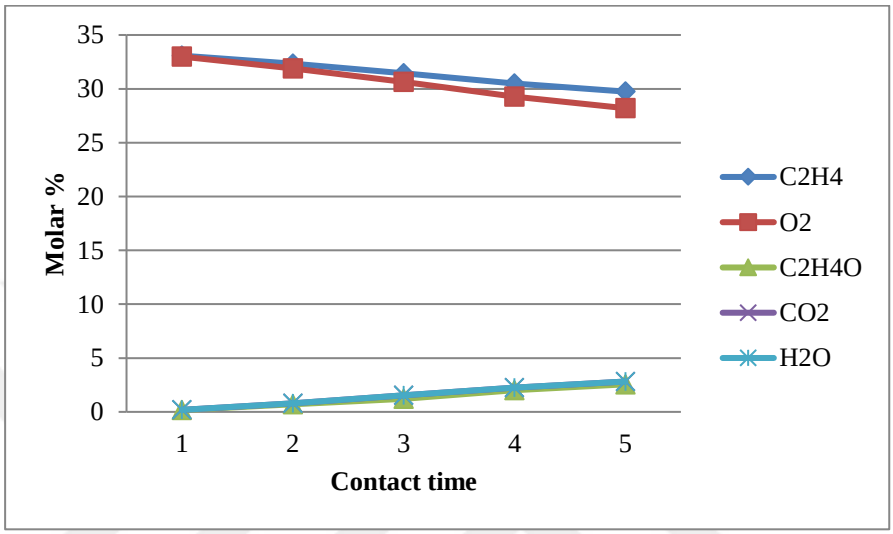

Figure 4.1. Concentrations of the reactants and products versus contact time at 483 K for Set 2.

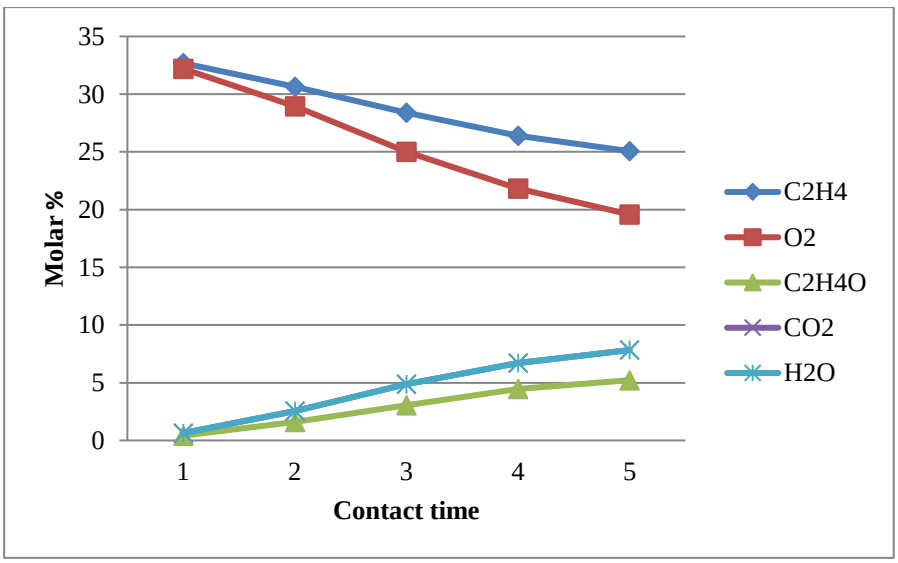

Figure 4.2. Concentrations of the reactants and products versus contact time at 513 K for Set 2.

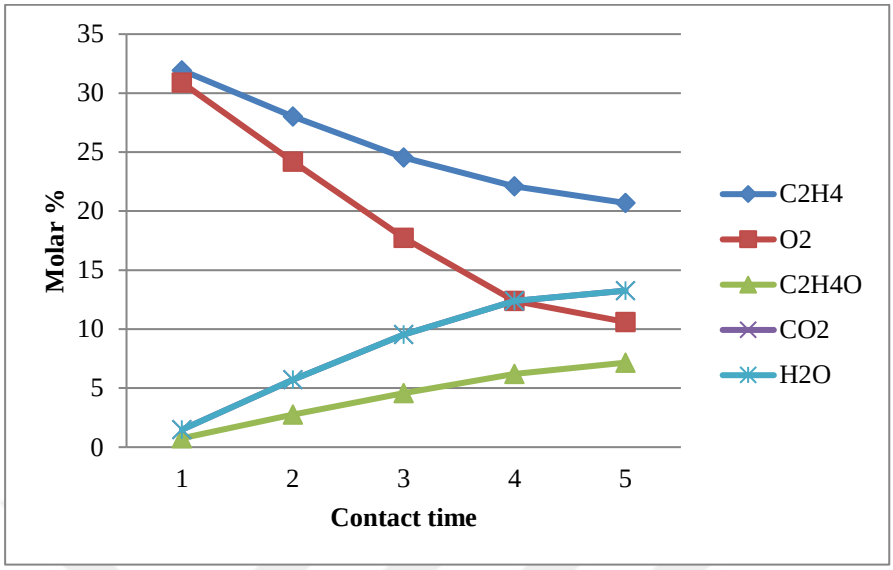

Figure 4.3. Concentrations of the reactants and products versus contact time at 537 K for Set 2.

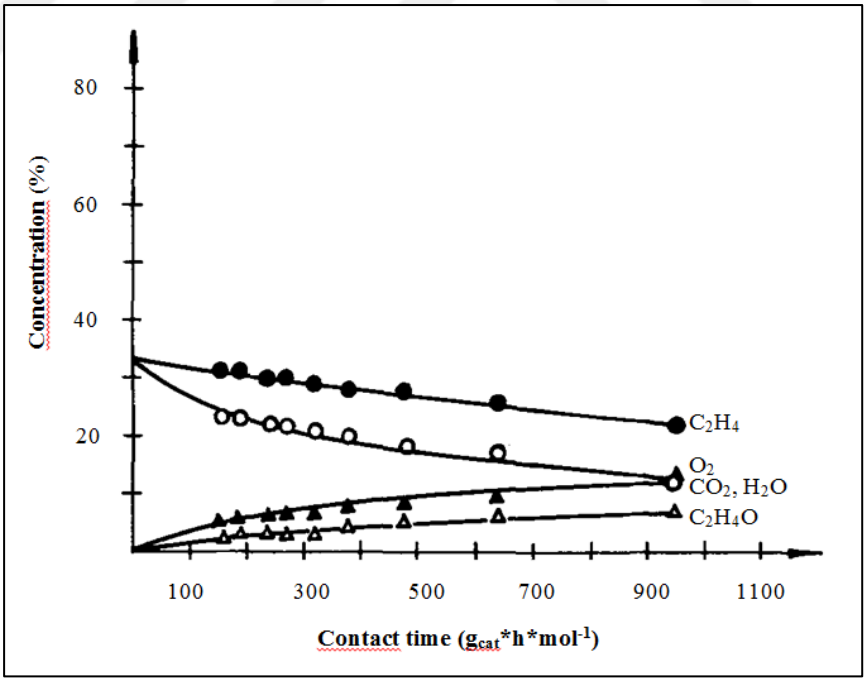

Figure 4.4. Concentrations of the reactants and products versus contact time at 537 K for Set 2 (Petrov *et al.*, 1985).

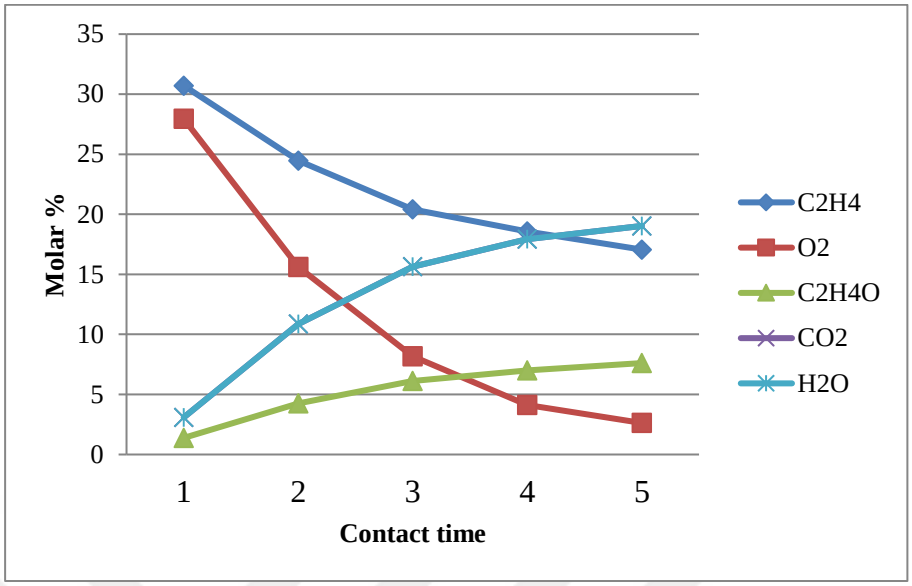

Figure 4.5. Concentrations of the reactants and products versus contact time at 565 K for Set 2.

In addition to reactant concentration, it is observed that when product concentrations (ethylene oxide, carbon dioxide and water) are compared, they show different profiles with increasing temperature. H_2O and CO_2 concentrations increase more rapidly than C_2H_4O concentration because the rate of total combustion of ethylene is higher than the rate of partial oxidation of ethylene. This is evident when the reaction rates for different temperatures are examined and Figure 4.5. and Figure 4.6 shows reaction rates at different temperatures. Petrov and colleagues (1985) explain that this difference between ratios is due to the fact that the complete combustion reaction has higher activation energy.

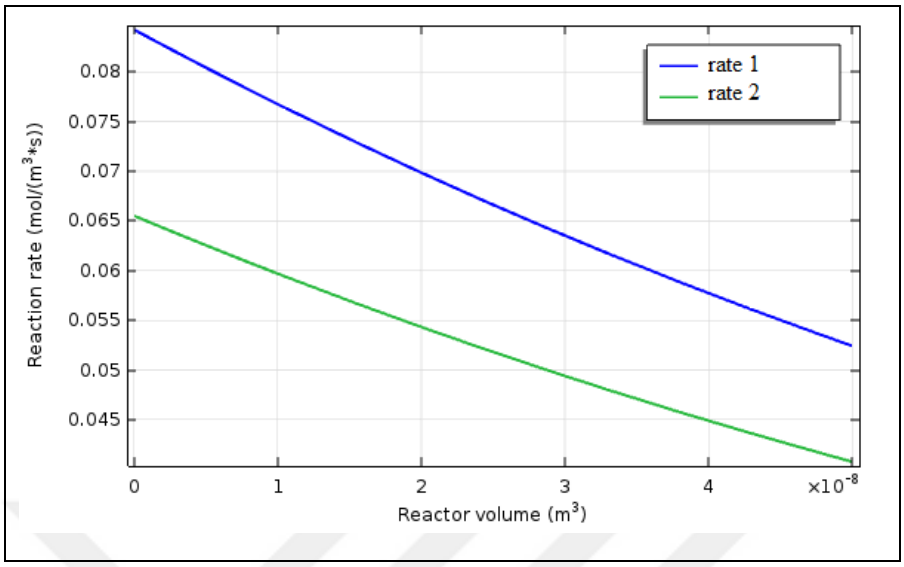

Figure 4.6. Reaction rates for partial oxidation of ethylene (rate 1) and total oxidation of ethylene (rate 2) for Set 2 at 513 K.

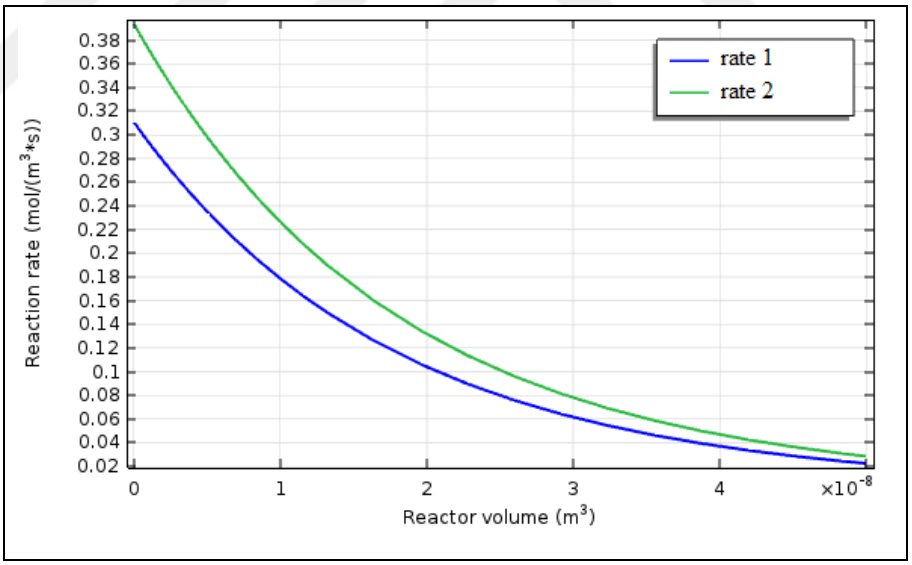

Figure 4.7. Reaction rates for partial oxidation of ethylene (rate 1) and total oxidation of ethylene (rate 2) for Set 2 at 565 K.

Contact time is also an important factor for conversion. Longer contact times provide an increase on conversion. Figure 4.8. shows that maximum conversion value is obtained for the longest contact time and the highest temperature.

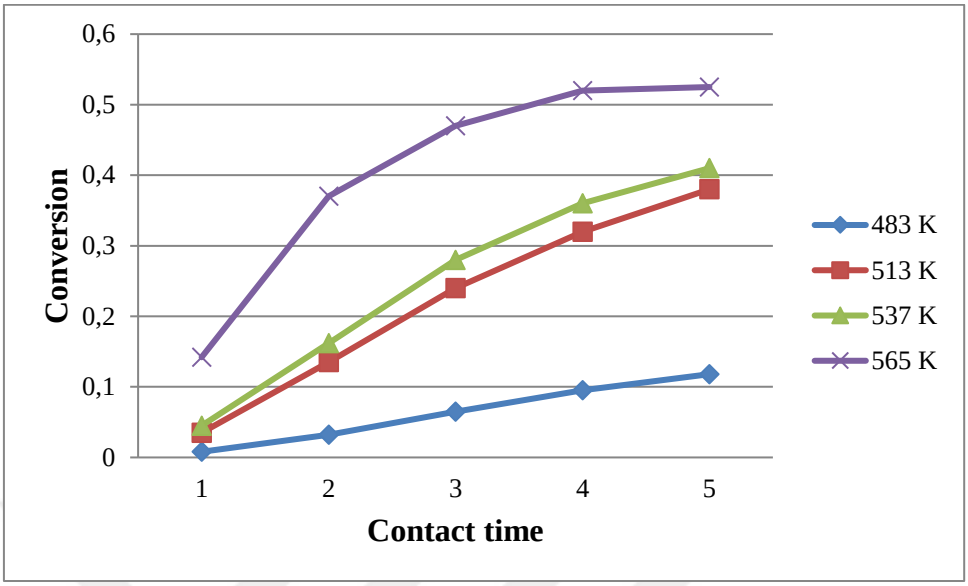

Figure 4.8. Influences of contact time on conversion at all temperatures for Set 2.

4.1.2. The Effect of Temperature

The effect of temperature on conversion and selectivity for Set 3 is shown in Figure 4.9. The conversion of ethylene increases from 5 to 24.5%, while the temperature increases from 483 K to 565 K for Set 3. On the contrary, the selectivity decreases from 44 to 27.5% at the same temperature values because the total combustion reaction is more dominant at high temperatures. Similar results are found by different researchers for example, Hernández Carucci *et al*., 2010 and Kestenbaum *et al*., 2002.

Figure 4.10. shows influence of temperature for all sets and it can be seen that the conversion increases with temperature rising for all sets and the maximum conversion is obtained for Set 1 at 565 K. On the contrary to the trend shown by the conversion, the selectivity of ethylene oxide decreases with temperature rising for all sets and Figure 4.11. shows that the maximum selectivity value is obtained at 483 K for Set 1.

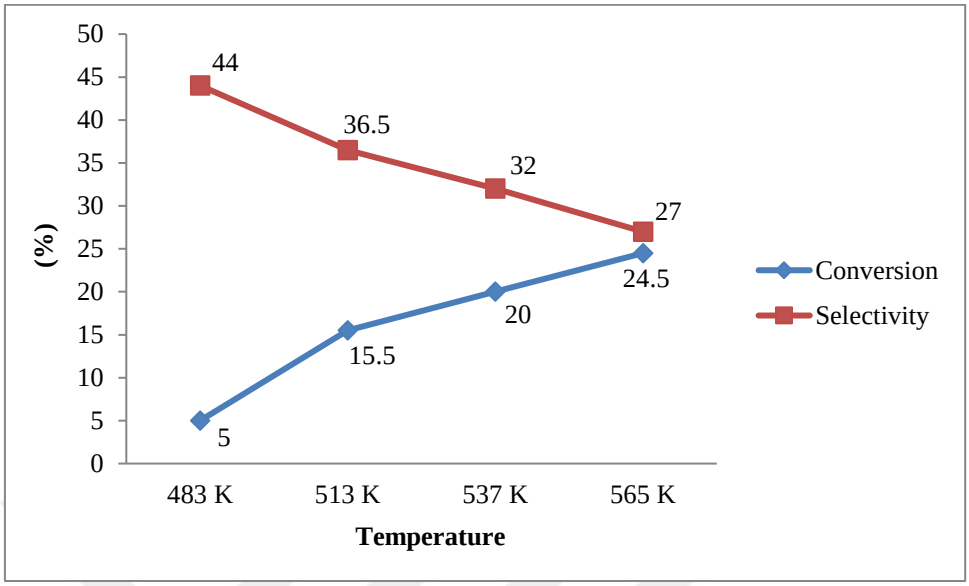

Figure 4.9. Influence of temperature on conversion and selectivity for Set 3.

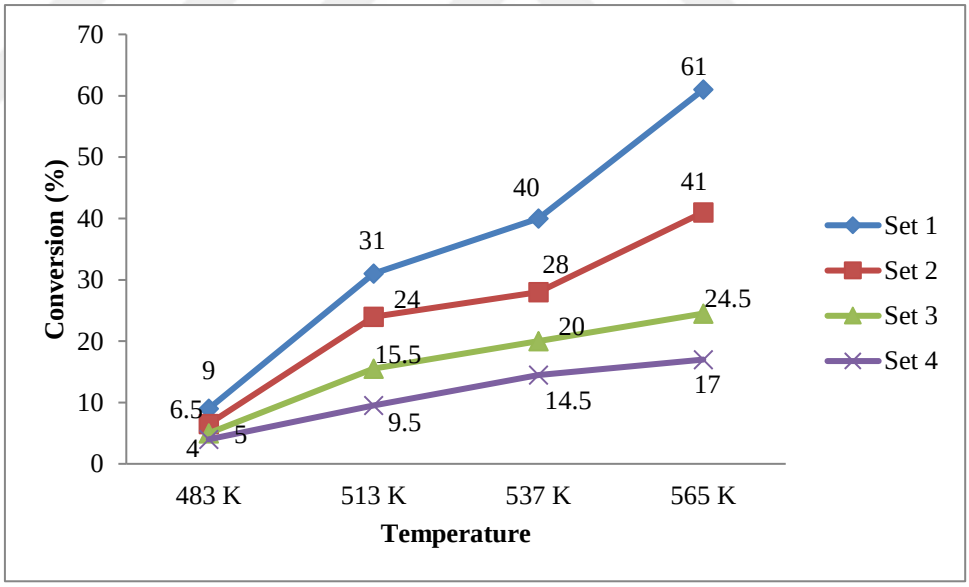

Figure 4.10. Influence of temperature on conversion for all sets and contact time 3.

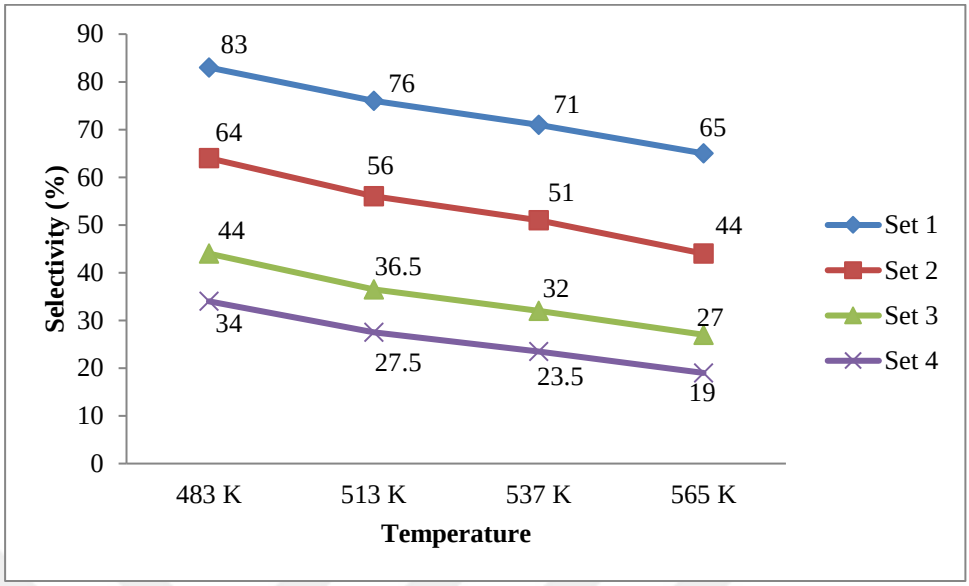

Figure 4.11. Influence of temperature on selectivity for all sets.

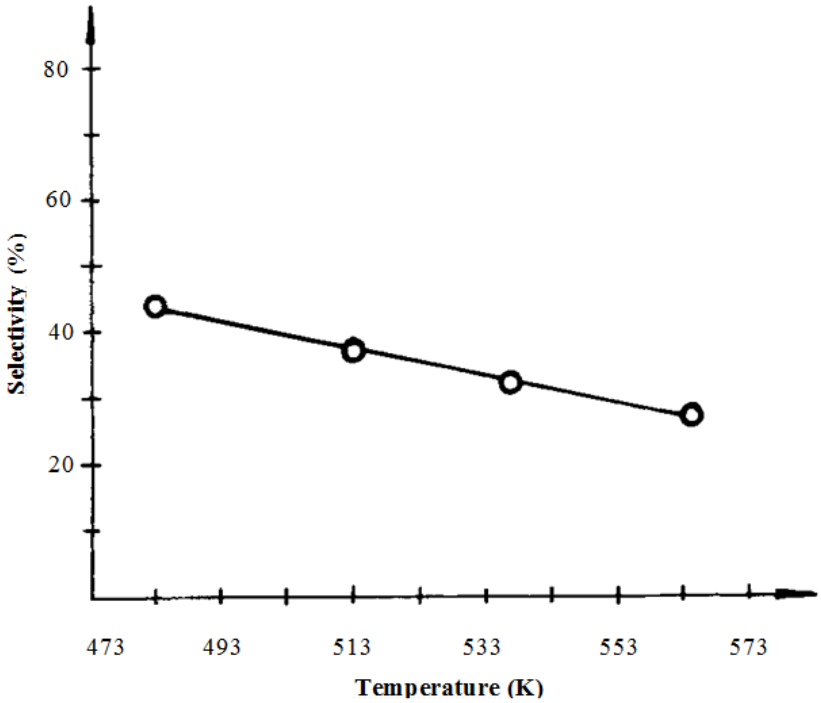

Figure 4.12. Influence of temperature on selectivity for Set 3 (Petrov *et al.*, 1985).

4.1.3. The Effect of Feed Ratio

Different feedstock compositions affect conversion of ethylene and selectivity of ethylene oxide directly and four different C_2H_4/O_2 ratios were used to observe this change. Feed compositions, ethylene and oxygen ratios are given Table 4.1.

Table 4.1. Ethylene and oxygen ratios of feedstock sets.

Set	C_2H_4/O_2
Set 1 (50% O_2, 25% C_2H_4, 25% N_2)	0.5
Set 2 (33.3% O_2, 33.3% C_2H_4, 33.3% N_2)	1
Set 3 (25% O_2, 50% C_2H_4, 25% N_2)	2
Set 4 (20% O_2, 60% C_2H_4, 20% N_2)	3

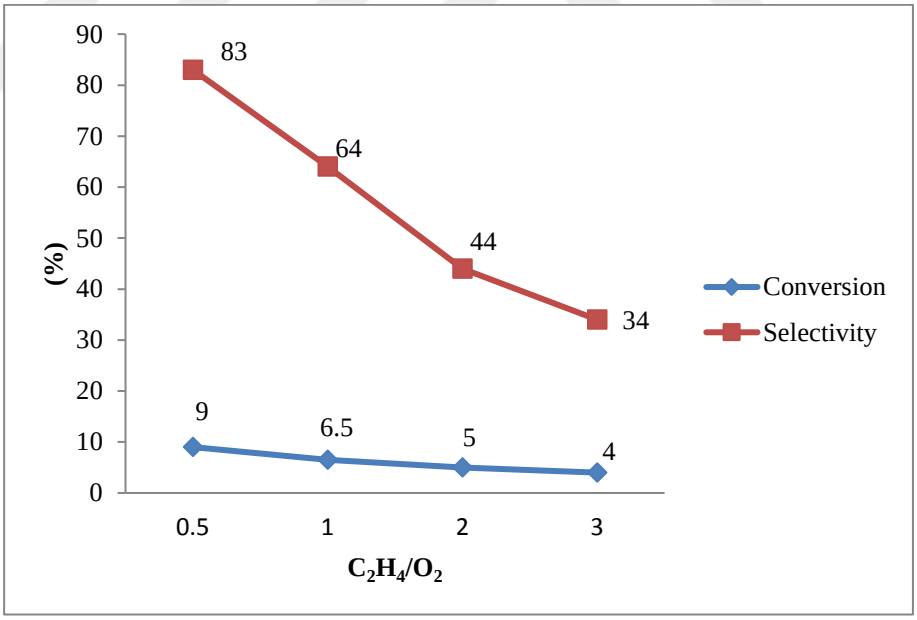

Figure 4.13. Influence of feed ratio on conversion and selectivity at 483 K.

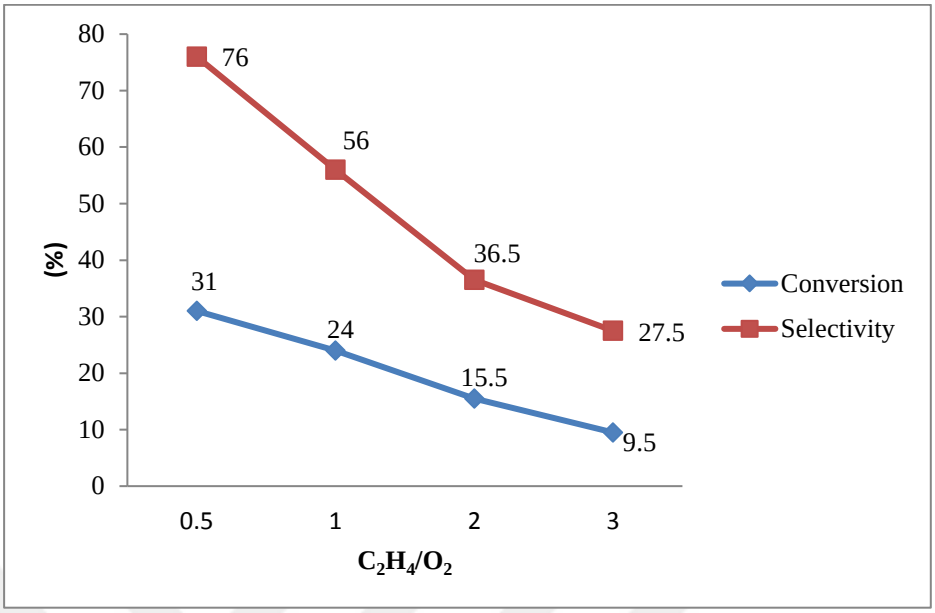

Figure 4.14. Influence of feed ratio on conversion and selectivity at 513 K.

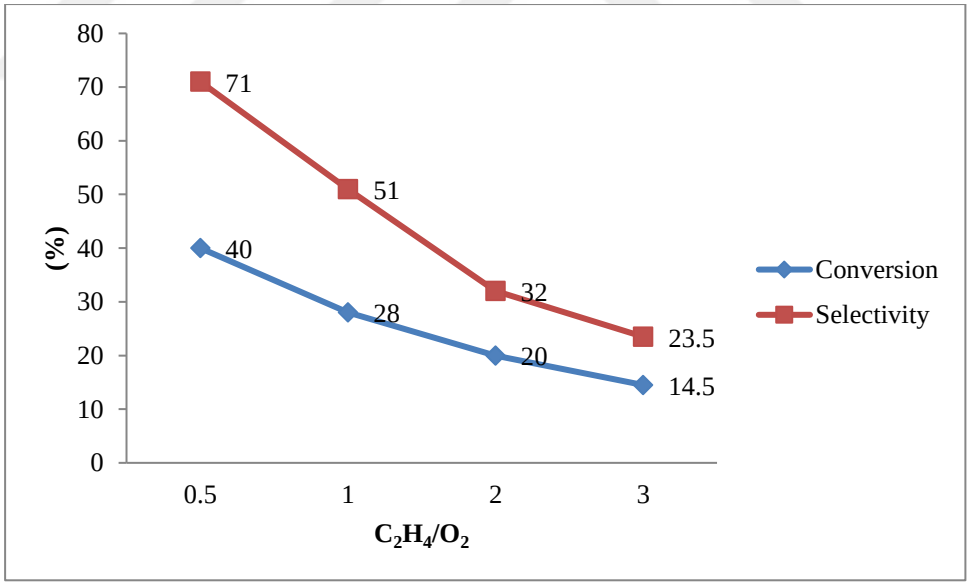

Figure 4.15. Influence of feed ratio on conversion and selectivity at 537 K.

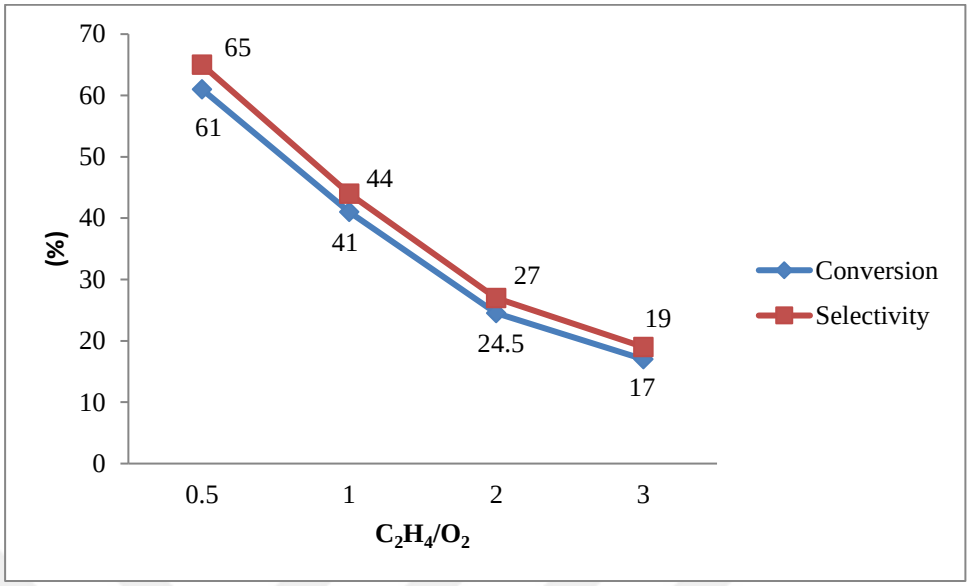

Figure 4.16. Influence of feed ratio on conversion and selectivity at 565 K.

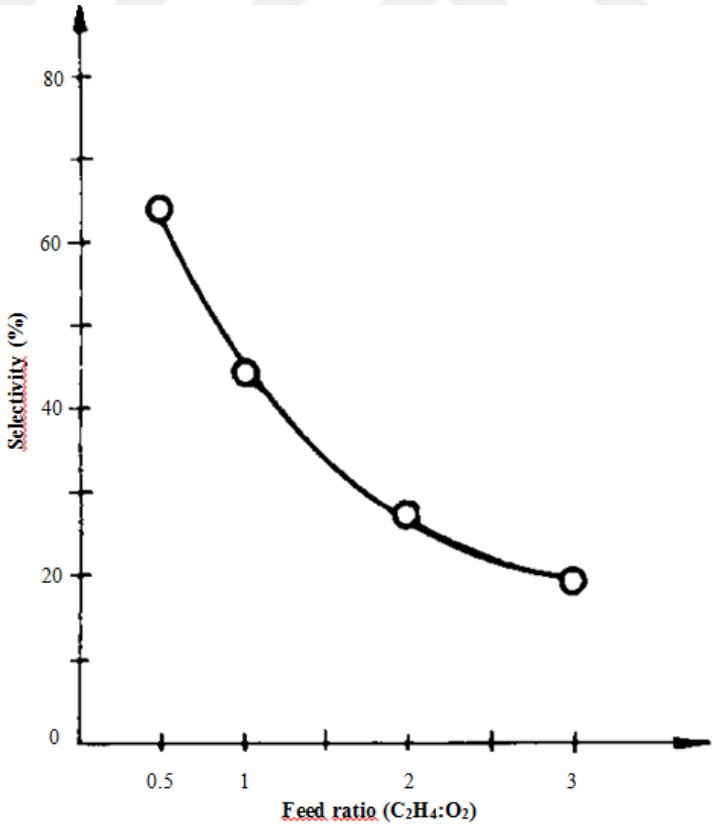

Figure 4.17. Influence of feed ratio on selectivity at 565 K (Petrov *et al.*, 1985).

Figure 4.13., 4.14., 4.15. and 4.16. show that increasing the C_2H_4/O_2 ratio causes the ethylene conversion and the ethylene oxide selectivity to decrease because oxygen concentrations in the feed decreases. When the oxygen concentration has the minimum value selectivity and conversion have the smallest value at all temperatures.

Positive effect of higher oxygen concentration on conversion and selectivity is observed and when the oxygen concentration is 50% which is not use in conventional reactor due to the safety, 61% conversion is obtained at 565 K. This positive influence of oxygen concentration was reported in previous studies by Kestenbauem *et al*. (2000) and (2002).

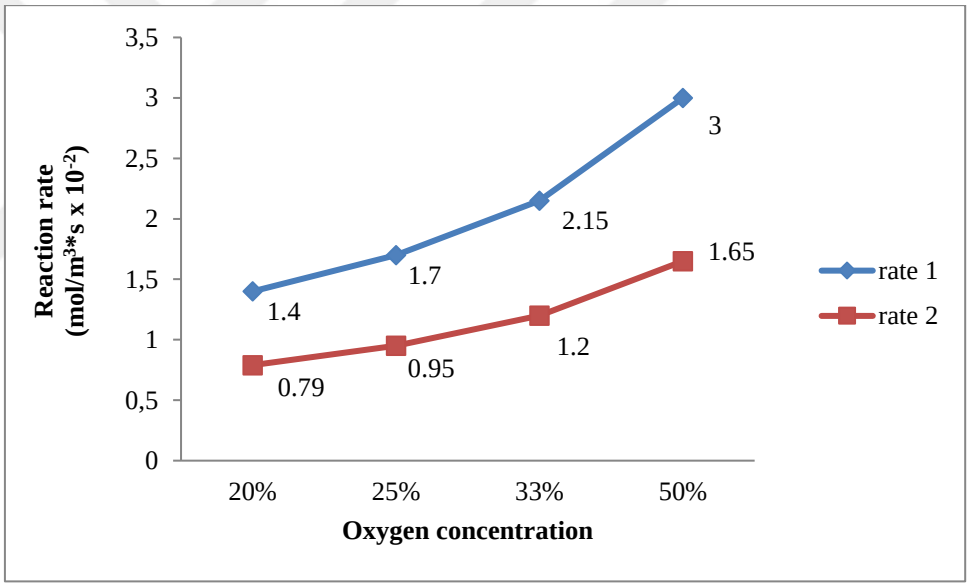

Figure 4.18. Influence of oxygen concentration in the feed on reaction rate at 483 K.

In addition to the conversion, Figure 4.18. shows that reaction rate of ethylene epoxidation (rate 1) increases with higher oxygen concentrations and reaches $3.0*10^{-2}$ (mol/m^3*s) and reaction rate of total oxidation of ethylene reaches $1.65*10^{-2}$ (mol/m^3*s) at 483 K.

4.2. Results of COMSOL Multiphysics Simulations

After Reaction Engineering Lab results are obtained similar with the results of Petrov et al. (1985), COMSOL Multiphysics simulations were carried out. For COMSOL Multiphysics simulations, an average contact time is selected because long contact time values are not suitable for real experiments due to the deactivation of catalyst. Tests are carried out for all sets and temperatures.

4.2.1. The Effect of Temperature and Feed Ratio

Increasing temperature has a positive effect on conversion. COMSOL Multiphysics part's results show that increasing temperature provides improved conversions, but the changes are not as high as Reaction Engineering Lab results. The maximum conversion value which is almost 14% is obtained with Set 1 at 565 K. Table 4.2. and Figure 4.19 give all conversion values for different temperatures and sets.

Table 4.2. Conversion values for different temperatures and feedstock compositions.

	483 K	**513 K**	**537 K**	**565 K**
Set 1	6.30	8.37	9.55	13.80
Set 2	5.90	7.68	8.34	11.60
Set 3	7.00	7.76	8.99	11.80
Set 4	6.01	6.60	7.63	10.02

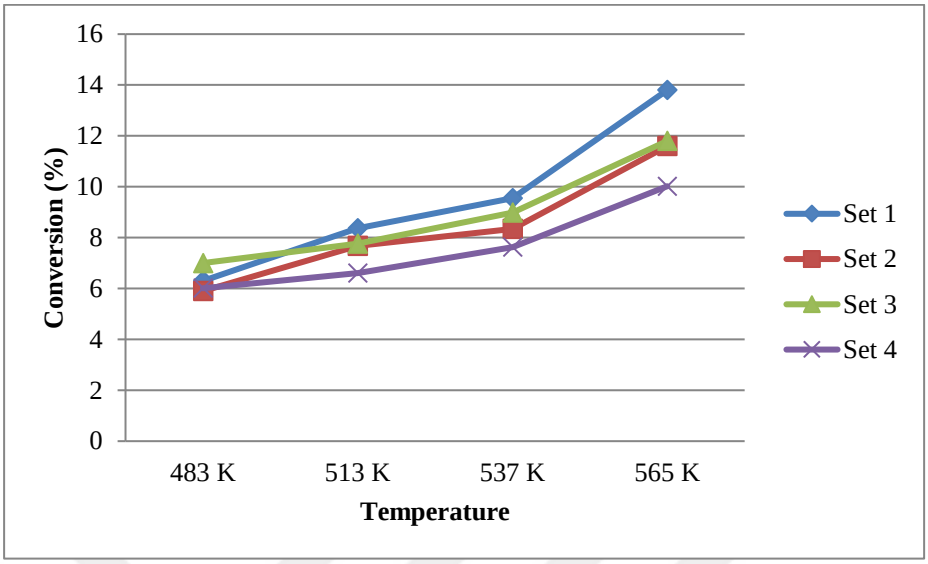

Figure 4.19. Influence of temperature on conversion for all sets.

The results of microreactor studies in the literature are parallel to the 2D microchannel reactor model results. For example, when the feedstock concentration ratio (C_2H_4/O_2) was 2, conversion was obtained almost 18 % at 553 K by Carucci *et al.* (2010) and this result is not far from our result. In addition to Carucci *et al.* (2010), Kestenbaum *et al*. (2000) reached almost 10 % conversion at 555 K with 33% oxygen concentration in the feed.

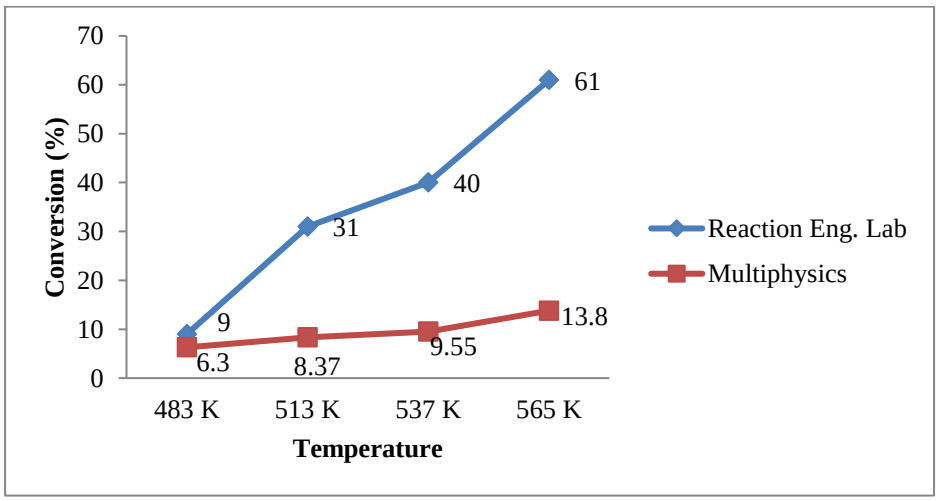

Figure 4.20. Comparison of conversion results of Reaction Engineering Lab part and Multiphysics part for Set 1.

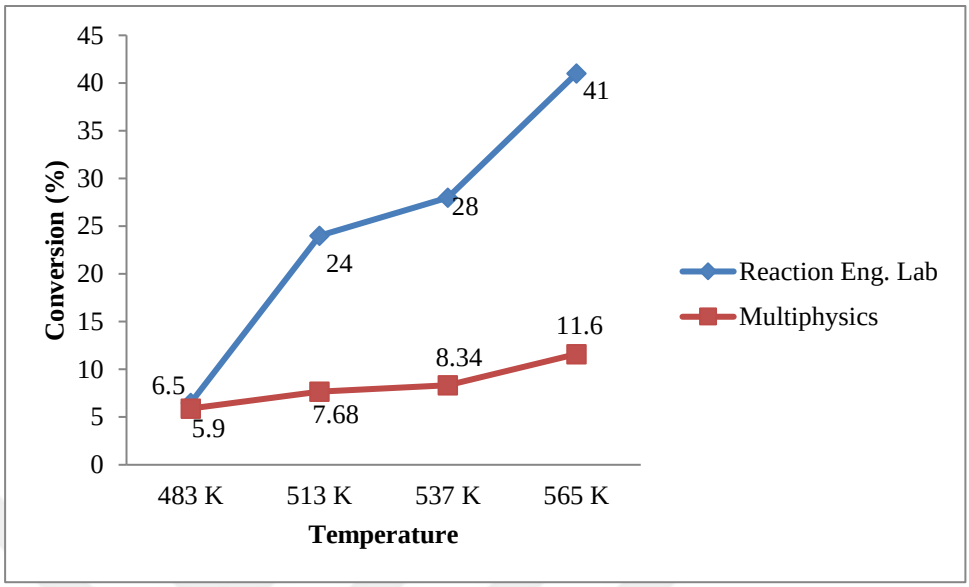

Figure 4.21. Comparison of conversion results of Reaction Engineering Lab part and Multiphysics part for Set 2.

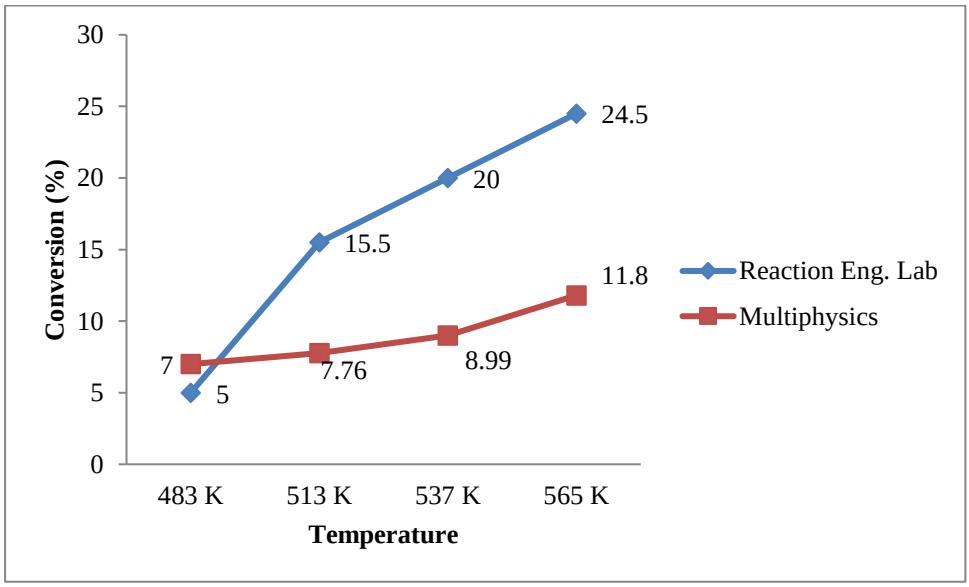

Figure 4.22. Comparison of conversion results of Reaction Engineering Lab part and Multiphysics part for Set 3.

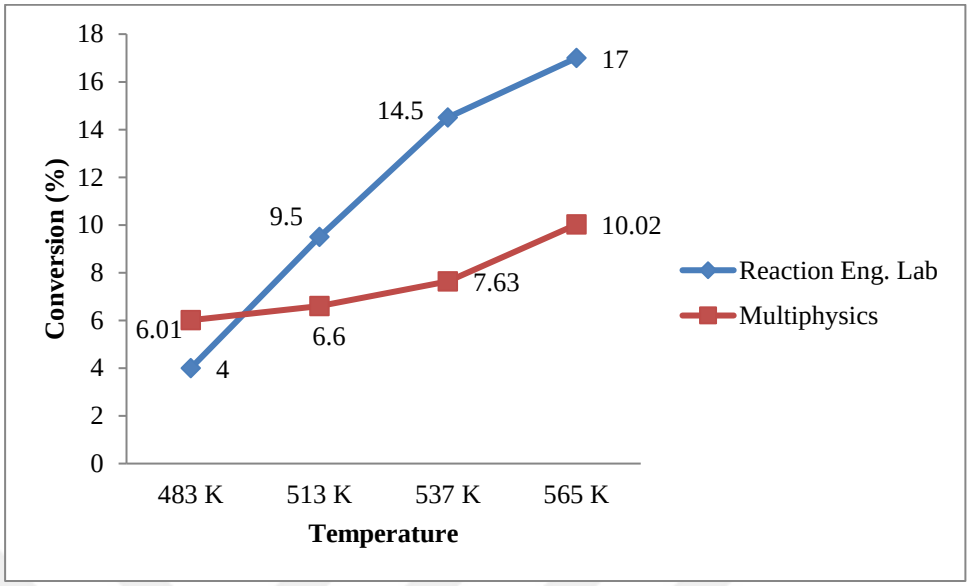

Figure 4.23. Comparison of conversion results of Reaction Engineering Lab part and Multiphysics part for Set 4.

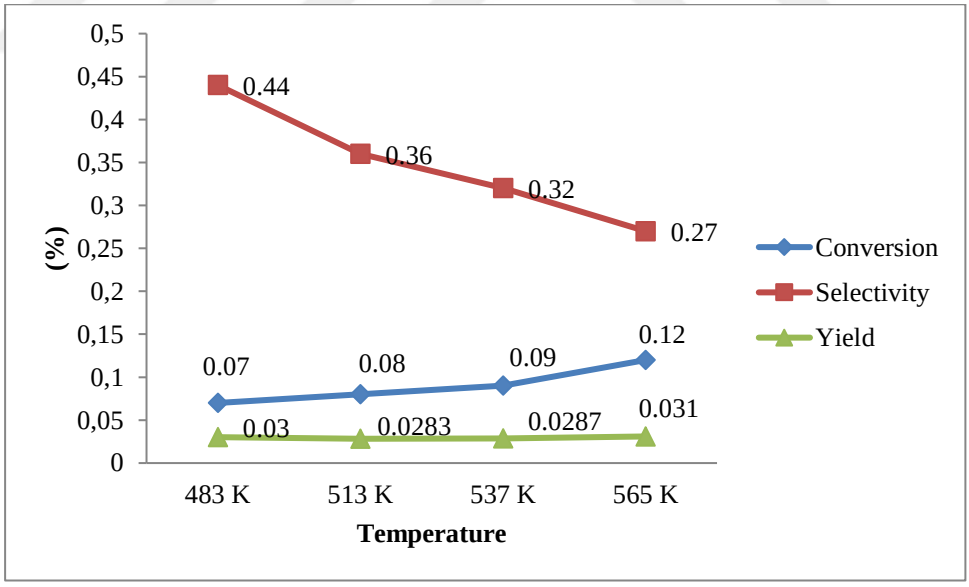

Figure 4.24. Influence of temperature on conversion, selectivity and yield for Set 3.

Figure 4.24. shows that selectivity is affected by temperature negatively and selectivity decreases linearly from 44 to 27%. Also, a slight increase can be seen by temperature on yield. Figure 4.25. clearly shows that when the oxygen concentration in

the feed is increased, conversion of ethylene enhances. For 50% oxygen concentration, 13.8 % conversion is reached at 565 K.

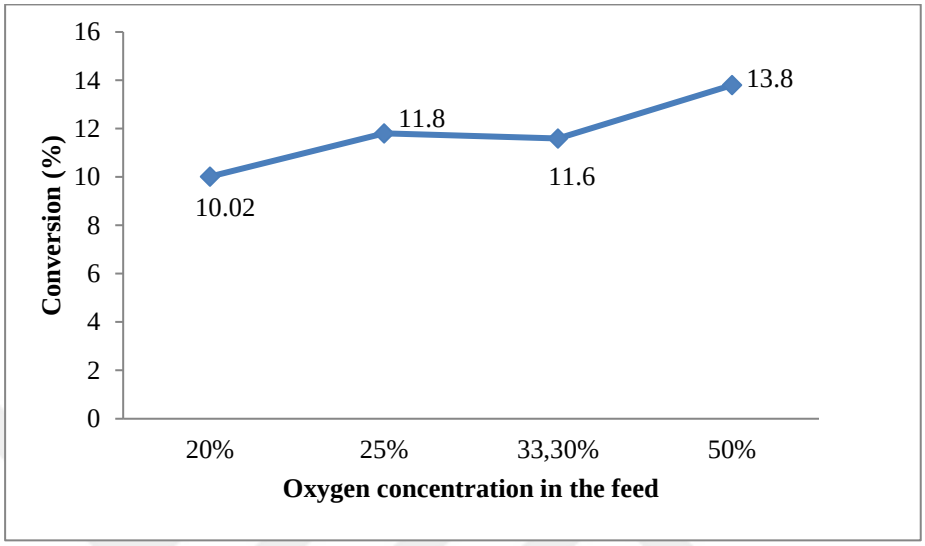

Figure 4.25. Influence of oxygen concentration in the feed on conversion at 565 K.

5. CONCLUSION

5.1. Conclusions

Ethylene oxide synthesis was performed in a 1D and 2D microchannel reactor via COMSOL software. For both of simulation tests, four different temperatures and feedstock compositions are used. In addition, different contact times were used for 1D simulation tests. The major conclusions obtained from this study are listed below:

- Increase in contact time provides an increase in concentration of the products. The maximum molar concentrations of the products are obtained for the longest contact time value.
- Molar concentrations of reactants decrease with increasing residence time and molar concentration of oxygen decreases faster than molar concentration of ethylene because of the reaction stoichiometry.
- Increase in contact time contributes the development of conversion and conversion of 52.5 % is obtained with the longest residence time for Set 2.
- Both of the rates of ethylene oxidation increase with temperature but the rate of combustion of ethylene shows a faster increase than the rate of partial oxidation of ethylene and the rate of total oxidation of ethylene becomes higher.
- CO_2 and H_2O concentrations increase more rapidly than C_2H_4O concentration due to the higher reaction rate of total oxidation than the rate of partial oxidation at higher temperatures.
- Increase in temperature has a positive influence on conversion, but this increase is not the same for 1D and 2D simulations. While the ethylene conversion of 61% is reached for 1D simulation, the ethylene conversion of almost 14% is reached in 2D simulation at the same temperature.
- Selectivity is affected by temperature negatively and the lowest selectivity values are obtained at 565 K.

- When the ratio of C_2H_4/O_2 in the feed is increased, conversion and selectivity values diminish. Therefore the highest results are obtained for when the ratio of C_2H_4/O_2 is 0.5.
- When the oxygen concentration in the feed is increased, the reaction rates of ethylene oxidation increases.
- Increase in oxygen concentration in the feed enhances the ethylene conversion. This increase is again lower for 2D simulation.

5.2. Recommendations

According to the results of this study, the recommendations can contribute for the future works:

- Non-isothermal reactor simulations can be carried out and the catalytic microchannel can be integrated to a cooling channel.
- Simulations can be made for different catalyst layer thickness.
- Different kinetic expression data can be used to control whether the results are consistent with the ones obtained in this study.

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