KINETIC MODELING OF CO OXIDATION
BY GENETIC PROGRAMMING

by

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to my husband

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ABSTRACT

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In this thesis, the kinetic modeling of CO oxidation was performed using genetic programming. A reaction rate equation was created from the experimental data, and then this equation was used to predict the mechanism of the reaction. Firstly; the generic reactions, of which both rate equation and mechanism were known, were studied in order to test the applicability of genetic programming in generating the rate expressions and to have a basic understanding about the method. The functions used in program were obtained from the functional terms commonly appears in catalytic rate equation. It was verified that the rate expressions derived using genetic programming were quite similar in terms of their structures and the groups that describes the main features of the rate equations in the literature.

Then, the catalytic CO oxidation reaction was modeled to derive the model equations using three different experimental data sets; one of them was generated in our laboratory and the remaining two were obtained from the literature over various catalytic systems. After generating possible model equations, they were statistically evaluated by comparing with the experimental results and the other models proposed in the literature. The plausible models were then used to understand the mechanism of the reaction by analyzing the form of the rate expressions and the value of the parameters. The results were generally satisfactory, and it was concluded that genetic programming can help to understand the mechanism and the kinetics of the similar catalytic reactions.

ÖZET

KARBON MONOKSİT OKSİDASYONUNUN GENETİK PROGRAMLAMA KULLANILARAK KİNETİK MODELLEMESİ

Bu tezde, karbon monoksit oksidasyonunun genetik programlama kullanılarak kinetik modellemesi çalışılmıştır. Deneysel veriler kullanılarak reaksiyon hız denklemi oluşturulmuş ve bu denklem reaksiyon mekanizmasını anlamak için kullanılmıştır. Genetik programlamanın hız denklemi eldesinde uygulanabilirliğinin test edilmesi ve metod hakkında temel bilgi edinilmesi açısından, ilk olarak hız denklemleri ve mekanizması bilinen genel reaksiyonların modellemesi yapılmıştır. Programlamada kullanılan fonksiyonlar, genel olarak katalitik hız denklemlerinde bulunan fonksiyonel birimlerden elde edilmiştir. Genetik programlama kullanılarak oluşturulan hız denklemlerinin yapıları ve içerdikleri fonksiyon grupları itibarıyla başka kaynaklardan elde edilen denklemlere büyük benzerlik gösterdiği doğrulanmıştır.

Daha sonra, katalitik karbon monoksit oksidasyonu reaksiyonunun modellemesi yapılmış ve bunun için bir tanesi laboratuarımızda üretilen, diğer ikisi ise farklı kaynaklardan elde edilen üç farklı katalitik sisteme ait deneysel veri seti kullanılmıştır. Uygun model denklemleri oluşturulduktan sonra, bu modeller deneysel sonuçlarla ve kaynaklarda önerilen diğer modellerle istatistiksel olarak karşılaştırılmıştır. Ayrıca; uygun modeller, hız denklemlerinin formunu ve parametrelerin değerlerini analiz ederek, reaksiyonun mekanizmasını anlamak için kullanılmıştır. Sonuçlar tatmin edici bulunmuş ve genetik programlamanın benzer katalitik reaksiyonların mekanizma ve kinetiğini anlamak için kullanılabileceği sonucu çıkarılmıştır.

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$F_{CO,in}$	CO flow rate in the feed
k_i	Rate constant of step i
k_i^b	Rate constant of backward reaction of step i
k_i^f	Rate constant of forward reaction of step i
K_i	Equilibrium constant of reaction step i
P_i	Partial pressure of component i
r_i	Reaction rate according to component i
R^2	Regression coefficient
T	Temperature
W_{CAT}	Weight of catalyst
X_{CO}	CO conversion
$\Delta H°$	Enthalpy of the reaction at the standart conditions
$\theta_{O\bullet}$	Coverage of adsorbed oxygen on ceria sites
EA	Evolutionary Algorithm
GA	Genetic Algorithm
GP	Genetic Programming
LHHW	Langmuir–Hinshelwood Hougen Watson
PEM	Polymer Electrolyte Membrane
PROX	Preferential Oxidation
WGS	Water-Gas Shift Reaction

1. INTRODUCTION

There has been a great attention for hydrogen production in recent years because the hydrogen is considered as one of the cleanest energy sources and has an increasing demand in the fuel cell application and the chemical industry (Cao *et al*., 2005). The great decrease in fossil fuel reserves and increase in the air pollution and green house gas emissions made the use of alternative energy sources necessary, and the fuel cells are believed to have the capability to provide a clean energy using the hydrogen as the fuel (Sahoo *et al*., 2007).

A fuel cell is an electrochemical device that combines hydrogen fuel with oxygen to produce electric power, heat, and water. A fuel cell consists of an anode, an electrolyte, and a cathode. On the anode, the fuel is oxidized electrochemically to positively charged ions. On the cathode, oxygen molecules are reduced to oxide or hydroxide ions (Perry *et al*., 1999). The positively charged ions move to cathode through the electrolyte while the electrons passes through an electrical circuit creating electricity, and they are combined with oxygen on cathode to form water as by product. Operational fuel cell systems are varying from 5 kW to 2 MW (Ferguson *et al*., 2004). The oxygen is taken mostly from the air and the natural gas, methanol, propane and diesel are used as a hydrogen source. Among the various types of fuel cells, Proton Exchange Membrane (PEM) fuel cells seem to be most promising energy conversion system.

PEM fuel cells have been investigated recently for widespread usage. They possess a polymer electrolyte in the form of a thin, permeable sheet. This membrane is small and light. It operates at low temperatures about 80ºC, uses hydrogen as a fuel and its efficiency is around 50% (Grujicic *et al*, 2004). In order to operate the proton-exchange membrane (PEM) fuel cells efficiently, very pure hydrogen is needed. However, hydrocarbon or alcohol reforming produces not only hydrogen but also carbon monoxide, carbon dioxide and steam. In order to avoid the poisoning of the electrodes in the fuel cell, the carbon monoxide level must be decreased to levels between 10 and 50 ppm. To achieve this level, various steps including the water–gas shift (WGS) reaction have to be used in the process.WGS reaction is used to convert CO into CO_2 by using water with a suitable

catalyst and has an advantage to supply additional hydrogen (Quiney and Schuurman, 2007). In this way, the effluent gas stream becomes richer in H_2 and CO concentration level reduces to 0.5-1 percent (Pozdnyakova *et al* 2006a). But this low level of CO should further be reduced to 10 ppm level since it can not be tolerated by PEMFCs.

There are several methods that can be used to purify the H_2 streams including pressure-swing adsorption, Pd membrane separation, catalytic methanation, and catalytic preferential oxidation (PROX) of CO. However, PROX is an advantageous solution among them by providing the lowest cost and ease of implementation (Matthew *et al*., 2008). This process was recognized as the most promising, straightforward and cost effective approach (Arias et al., 2005). In PROX reactions high activity and selectivity is needed and the reaction temperature should lie between the exit temperature of a low temperature water gas shift reactor (200–250°C) and operating temperature of a PEM fuel cell (80 $\circ$C). Therefore the catalysts should be chosen according to these operating conditions.

Kinetic modeling of CO oxidation plays an important role in determining the reaction rates taking place in the system. Therefore, researchers give great attention and spend a lot of time to design the processes and develop the kinetic models of the reactions like catalytic CO oxidation in hydrogen rich streams (Boozarjomehry and Masoori, 2007). Determining the kinetic models and obtaining rate expressions are important issues in optimization and control of commercial fuel reformers (Özyönüm,2005 ; Nibbelke,1997).

Chemical engineers perform kinetic analysis for the optimization of the chemical reaction processes. In addition to this, avoiding the secondary reactions and increasing the safety during the operations are important subjects that need to be considered. However, all these issues require a lot of time studying the detailed mechanism of the complex reactions. Therefore, producers and developers search for fast and effective methods instead of dealing with complex chemical reaction processes. Hence, fast, easier and successful ways are necessary to approximate kinetic models of the complex reaction systems, and these kinetic models can be used in order to establish the fundamentals for the chemical reaction process optimizations in further steps (Cao *et al*., 1999).

Lately, evolutionary algorithms (EAs) have been applied very well in a wide range of economic, engineering, chemistry and scientific computation due to their abilities of self-adaptation, self-organization, self-learning, intrinsic parallelism and generality, (Cao *et al*., 1999). Therefore, these algorithms can be successfully used for kinetic modeling of chemical reactions.

EA's originally consisted of three groups including genetic algorithms (GAs), evolutionary programming (EP) and evolution strategies (ES). In the 1990s, a new group was introduced by John Koza called genetic programming (GP) (Koza, 1994). GP is a method that creates a working computer program understanding the things to be done to solve the problem and automatically creates a computer program for the solution of the problem (Wootsch *et al*., 2006).

In GP, the created programs are represented in a tree structure. In this tree structure, the branch nodes include arithmetic operators and elementary functions coming from pre-defined function set and leaf nodes include variables, constants and functions of no arguments coming from terminal set. The evaluation of fitter programs is done by fitness cases. After selecting the fitter programs, they are recombinated to create the next generation by using crossover and mutation operators. This iteration is repeated for some number of generations until the termination criterion of the run has been satisfied. (Cao *et al*., 1999).

Representation of the solution is the main difference between GP and GA. GP creates computer programs as the solution whereas GA creates a stream of numbers that represent the solution. There are four steps in GP that leads to the solution of the problems. First step is the generation of an initial population of random compositions of the functions and terminals of the problem. Then it executes each program in the population and determines the fitness value of each individual according to how well it solves the problem. Thirdly it creates a new population of computer programs by copying the best existing programs or creating new computer programs by mutation or crossover. Lastly, the best computer program that was found in any generation is presented as the result of genetic programming.

GP can be a very useful method to analyze the kinetics of complex reaction systems such as catalytic CO oxidation in the hydrogen rich streams. It can be used to derive an appropriate model that describes the main features of the rate equation by determining the most significant functional groups, which consist of various combinations of rate and equilibrium constants, power of partial pressures in the rate equation (Gianoli *et al*., 2007). This model can be used not only to calculate the reaction rates, but also to understand the reaction mechanisms by analyzing the form of the reaction rate expression and the value of parameters.

In this thesis, kinetic modeling of CO oxidation was performed using genetic programming. The experimental results obtained by Özyönüm (2005) and Oran (2001) and other studies from the literature for CO oxidation over various catalytic systems was utilized. The possible functional groups in the rate expression were derived from the similar mechanisms and rate equations proposed in the literature. The rate expressions obtained by this model were statistically verified by comparing with the experimental results and other models suggested in the literature. The rate expression will be also used to understand the mechanism of the reaction.

Chapter two contains a literature survey on kinetic studies in selective CO oxidation followed by detailed information about genetic programming. Chapter 3 contains the computational work done while the results obtained are presented in Chapter 4. Lastly, the conclusions and recommendations are summarized in Chapter 5.

2. LITERATURE SURVEY

2.1. Fuel Cell

Fuel cells are important enabling technologies for the hydrogen economy and have the potential to a major change in powering with offering cleaner, more-efficient alternatives to the combustion of gasoline and other fossil fuels. Fuel cells have the potential to replace the internal combustion engine in vehicles and provide power in stationary and portable power applications because they are energy-efficient, clean, and fuel-flexible.

Fuel cells use hydrogen as a source and generate power when fuel is supplied. It is not important where the hydrogen is supplied from, because a fuel reformer can generate hydrogen from diverse, domestic resources including fossil fuels, such as natural gas and coal; alcohol fuels, such as methanol or ethanol; from hydrogen compounds containing no carbon, such as ammonia or borohydride; or from biomass, methane, landfill gas or anaerobic digester gas from wastewater treatment plants. Hydrogen can also be produced from electricity from conventional, nuclear or renewable sources such as solar or wind. Hydrogen or any hydrogen-rich fuel can be used by this emerging technology.

Fuel cell is an energy conversion device. It produces electricity from various external quantities of fuel and oxygen. They are classified according to the electrolyte type they employ which determines the chemical reactions occurring in the cell, the operating temperature range of the cell and the fuel used. There are several kinds of fuel cells with different advantages and applications.

Proton exchange membrane (PEM) type fuel cells have many advantages of low weight and volume compared to other fuel cells with delivering high power density. PEM fuel cells use a solid polymer as an electrolyte and porous carbon electrodes containing a platinum catalyst. They need only hydrogen, oxygen from the air, and water to operate and do not require corrosive fluids like some other fuel cells. They are typically fueled with pure hydrogen supplied from storage tanks or onboard reformers. PEM fuel cells operate at low temperatures around 80°C providing a quick start and better durability. It requires that

a noble-metal catalyst (typically platinum) be used to separate the hydrogen's electrons and protons.

Hydrogen is a fuel with difficulties for its distribution as well as for its storage; consequently the challenge is to generate it in on board or in a service station, from the reforming or partial oxidation of natural gas, hydrocarbons, methanol or ethanol. In all cases the formation of carbon oxides (CO and CO_2) is unavoidable. The carbon monoxide must be eliminated because in concentrations higher than 10 ppm it leads to the deactivation of the catalysts in the electrodes of the PEM fuel cells (Siri *et al*., 2007). In catalytic purification processes, part of the carbon monoxide can be eliminated via water gas shift reaction (WGSR), up to levels between 500 and 1000 ppm which is not low enough to prevent poisoning of the fuel cell (Siri *et al*., 2007). This makes it necessary to employ an additional part to reduce CO in the hydrogen feed derived from an alcohol or hydrocarbon fuel. Due to the high sensitivity of PEM fuel cells towards CO, the concentration of CO should be decreased until 10ppm level to avoid poisoning. (Wootsch *et al*., 2004). Therefore, a CO removal system should be accomplished during the hydrogen production system before the hydrogen feed enters the fuel cell stack and the target CO concentration should be 10 ppm or below.

2.2. CO Oxidation

There are various methods for the removal of small amounts of CO existing after hydrocarbon reforming and water gas shift reaction. In order to remove these small amounts of existing CO (less than 1%), catalytic oxidation is suggested as the most plausible mechanism (Choi and Stenger, 2004). Between the several methods of catalytic oxidation, due to the economical options, quick responses and lower hydrogen consumption, preferential oxidation of CO (PrOx) is suggested as the most economical and preferred solution (Ghenciu, 2002). The purpose of PrOx is to accept hydrogen rich stream and to reduce the CO concentration in the gas below 10 ppm at the outlet (Bissett *et al*., 2005). The working method of preferential oxidation is adding small concentrations of oxygen in to the feed in order to oxidize the CO until acceptable limits and minimizing the hydrogen consumption at the same time (Bissett *et al*., 2005). The following reactions take place in the preferential CO oxidation reaction systems (Choi and Stenger, 2004).

Desired reaction   : $CO + \frac{1}{2} O_2 \rightarrow CO_2$ ($\Delta H = -283 kj/mol$)   (2.1)

Undesired reaction   : $H_2 + \frac{1}{2} O_2 \rightarrow H_2O$ ($\Delta H = -242 \ kj/mol$)   (2.2)
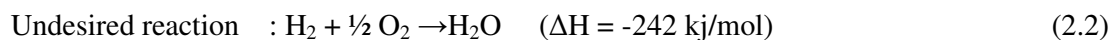
The need for pure hydrogen forces the research to investigate catalysts that are able to oxidize CO selectively and almost completely within the temperature limits (Şimşek *et al*., 2007). It is essential to choose the catalyst that minimizes the oxidation of hydrogen. There are numbers of studies done on selective CO oxidation and different catalytic systems have been used during studies.

These catalytic systems can be classified in three groups. First group is the catalysts based on supported Au. These catalysts have a very high activity at low temperatures. Preparation method is very important in these systems due to the deactivation and selectivity problems at temperatures higher than 80ºC. Also it is necessary to improve the resistance to poisoning and to sintering with the experiments for these systems (Siri *et al*., 2007).

The second group is the catalysts based on Cu support. These catalysts are also studied many times and they are found good for the activity. However, there are still problems with the stability of Cu and the control of its oxidation state.

The last group is the catalysts based on noble metals (Pt, Ru, Rh, Pd). These catalysts are highly active in CO oxidation even at low temperatures. In terms of efficiency; Pt based and transition metal oxide supported catalysts are the very promising catalysts. Number of studies was done with Pt/Al_2O_3 catalyst due to its high conversion levels and stability at moderate temperatures.

2.3. Kinetic Studies

Experiments in kinetic studies aims to characterize and confirm details of the mechanism involved in the chemical processes. In these experiments it is important to measure as many properties as possible of the reaction such as the concentration and temperature dependency of the reaction rate, the nature of all components used in the system and their concentrations and time dependences (Steinfeld, 1989). These measurements allow criteria to test the rate models of the reaction mechanism. With the

experimental data obtained, the consistency of the proposed mechanisms can be understood by transforming it into a mathematical model from which predictions can be made.

For catalytic oxidation of carbon monoxide reaction, kinetic studies are done in order to improve the conversions of pollutants like CO, hydro carbons and nitrogen oxides (Nibbelke *et al*., 1997). For this purpose, it is really necessary to fully understand the physical and the chemical aspects of the situation. In order to meet the level of future standards and to achieve further improvements in converting the pollutants, many researches and kinetic studies are done today. Especially, performing experiments and collecting reliable data in order to derive realistic kinetic models constitutes the most effective part of the studies. Therefore, kinetic studies are done in order to understand the changes of partial reaction orders of the components and to identify the reaction mechanisms depending on the experimental conditions by developing kinetic models based on elementary reaction steps. The reason of making the studies in the initial stages of a forward reaction is to observe the small changes in conversions of the reactants before the complications that can occur due to the reverse reactions or inhibitions by the products.

Kinetic studies based on experimental analysis provide more reliable and trustable results in terms of rate expressions. After completing the research related with the topic, the experimental conditions including pressure and temperature values are set. In addition to this, the catalyst that is going to be used is determined before performing the experiments. Then, many runs are made with different feed compositions at the same temperature to compare the experimental rates defined in terms of initial reactant concentrations with the equations proposed before. Uniform temperature of the differential bed is especially required due to the exponential influence of the temperature (Watson, 1961). After continuing the experiments, differential method is generally used to determine the kinetics of the reaction from the experimental data. This method is advantageous in terms of getting direct rate equations, fitting the data to the rate law easily and having high confidence on the final rates (Masel, 2001). Rate equations are best established from differential method in a differential reactor containing a bed of catalyst so small that relatively small changes of composition are obtained (Watson, 1961). In this method, the conversions of the components are calculated to obtain the reaction rates in the kinetic measurements. For CO

oxidation, the conversions of the components in the feed, CO and O_2, are calculated as follows:

$$CO_{convesion} \ (\%) = \frac{[CO]_{in} - [CO]_{out}}{[CO]_{in}} * 100 \tag{2.3}$$

$$O_{2 \ conversion} \ (\%) = \frac{[O_2]_{in} - [O_2]_{out}}{[O_2]_{in}} * 100 \tag{2.4}$$

After obtaining the results, reaction rates are calculated from the conversion versus residence time (W_{cat} / $F_{CO \ in}$) data from the following equation:

$$-r_{co} = \frac{(x_{co}) * (F_{co}, in)}{W_{cat}} \tag{2.5}$$

where, x_{CO} denoting the conversion, W_{cat} denoting the catalysts weight, $F_{CO,in}$ representing the CO flow rate in the feed and ($-rco$) stands for the rate of the reaction. When the rate of the reaction is obtained, it means that the reaction orders of the components CO and O_2 are determined. This provides to identify the plausible reaction mechanism and pathways.

2.3.1. Kinetic Studies in CO Oxidation

Numerous of kinetic studies have been extensively focused on catalytic oxidation of CO due to its importance in environmental issues of clean energy production (Salomons *et al*., 2007). CO oxidation is an ideal model system of a heterogeneous catalytic reaction due to relative simplicity of this reaction. The mechanical steps of this reaction has been investigated extensively with surface science techniques and the studies of the adsorption, desorption and surface reaction steps provided important knowledge about the interaction between the adsorbed O atoms and CO molecules and helped to

gather detailed information about the elementary process occurring in CO oxidation (Oran, 2001).

The catalytic reactions depend on the interaction between the active sites and the reactants, which manifest themselves as a series of chemisorption-desorption and surface reaction steps. In developing a rate expression, the elementary steps are in great importance of the reaction mechanism. However, there are global kinetic models that are used when the underlying mechanism is not known or it is not possible to determine the kinetic parameters in each individual steps. The classical approach for developing rate expressions in these situations is the Langmuir Hinshelwood Hougen Watson method (LHHW) due to the reported success of these models at predicting converter performance. (Salomons *et al*., 2006) In this model, the reaction on the surface occurs between adsorbed oxygen atoms and molecularly adsorbed CO. The mechanism can be summarized by the following steps:

$$CO + * \leftrightarrow CO* \qquad (2.6)$$

$$O_2 + 2* \rightarrow 2O* \qquad (2.7)$$

$$CO* + O* \rightarrow CO_2 + 2* \qquad (2.8)$$

$$O* + CO \rightarrow CO_2 + * \qquad (2.9)$$

Steps 1 to 3 represent LH mechanism and step 4 is an Eley Rideal step. Lynch *et al*. (1983) showed that this basic mechanism can account for many of the observed phenomena in CO oxidation when modeled as a series of elementary steps with some modification. However, many kinetic studies showed that this simple mechanism is insufficient to explain all of the complex behavior observed in CO oxidation like the oscillations. Also, surface science and modeling studies have suggested the Eley Rideal step is not plausible. The idea behind that was CO can not chemisorb on sites already covered by oxygen. However, Harold *et al*. (1991) showed that admission of CO to an oxygen covered surface causes a fast formation of CO_2 whereas oxygen introduced to CO covered surface does not. Also, Lynch *et al*. (1984) investigated the surface exclusion models to account for the adsorption of CO on an oxygen covered surface and found that CO is still able to adsorb on the unfilled sites although oxygen coverage was limited to less

than a monolayer. Therefore, Eley Rideal step is also suggested as an acceptable mechanism for the observed phenomena. Chatterjee *et al.* (2002) made a small modification in the LH model and considered all the steps as reversible. It was proposed that CO adsorption can take place on an oxygen covered surface by using the advantage of reversibility of oxygen atoms. However these models are just global models and generally best suited for steady state operations and less suited for extrapolation and engineering design due to the validity in limited range of conditions (Salomons *et al.*, 2007).

Recent research work has emphasized the use of transient reaction kinetics, and as a result some reaction mechanisms for the catalyzed reactions that occur in three way converters have been proposed. Nibbelke *et al.* (1998) was the one proposing reaction mechanism for CO oxidation in the absence of H_2O and CO_2 over a $Pt/Rh/CeO_2/Al_2O_3$ three-way catalyst. During the experiment, the feed stream was switched between 0.5 mol% CO containing and 0.5 mol% O_2 containing inlets at temperature range $393 - 433^oK$. According to the experimental results, detailed mechanism of the CO oxidation reaction was obtained which is given in Table 2.1. A transient kinetic model based on elementary reaction steps was developed containing both monofunctional and bifunctional contributions.

The reaction path A is a monofunctional path and active sites denoted as "*" are representing the Pt sites. In this path, competitive adsorption of CO and O_2 on the noble metal surface occurs and during the oxygen adsorption, the irreversible molecular chemisorption of O_2 proceed firstly and then the dissociation of O_2* follows. Lastly, the LH surface reaction takes place to form CO_2. The rate equation for path A in the case of adsorption equilibrium for CO is found as;

$$-r_{CO} = \frac{\left(2k_f^3 P_{O_2}\right)\left(K_1 k_4^f k_9^f P_{CO}[S]_0 - K_1 k_3^f k_9^f P_{CO} P_{O_2} - 2k_3^f k_4^f P_{O_2}\right)}{K_1 k_4^f k_9^f P_{CO}(K_1 P_{CO} + 1)} \qquad (2.10)$$

In monofunctional reaction path B, the adsorption of O_2 is followed by the irreversible reaction between adsorbed oxygen and gas phase CO. This is an Eley Rideal step that was mentioned above and this step forms the OCO* species on Pt that reacts to give CO_2 or desorbs giving CO in the gas phase (Nibbelke *et al.*, 1998). If molecular

chemisorbtion of oxygen is assumed to be the rate determining step, then the rate equation is found as:

$$\underline{\hspace{7cm}} \tag{2.11}$$

Table 2.1. Elementary step reaction path of CO oxidation by O_2 in the absence of H_2O and CO_2 over $Pt/Rh/CeO_2/Al_2O_3$ catalyst (Nibbelke *et al.*, 1998)

Elementary Step	Reaction Path			Step Number
	A	B	C	
	[a]σ_A	σ_B	σ_C	
$CO + * \underset{k_1^b}{\overset{k_1^f}{\Leftrightarrow}} CO*$	2	0	2	(1)
$O_2 + * \overset{k_2^f}{\rightarrow} O_2*$	1	1	0	(2)
$O_2* + * \overset{k_3^f}{\rightarrow} 2O*$	1	1	0	(3)
$CO* + O* \overset{k_4^f}{\rightarrow} CO_2 + 2*$	2	0	0	(4)
$CO + O* \underset{k_5^b}{\overset{k_5^f}{\Leftrightarrow}} OCO*$	0	2	0	(5)
$OCO* \overset{k_6^f}{\rightarrow} CO_2 + *$	0	2	0	(6)
$O_2 + s \overset{k_7^f}{\rightarrow} O_2s$	0	0	1	(7)
$O_2s + s \overset{k_8^f}{\rightarrow} 2Os$	0	0	1	(8)
$CO* + Os \overset{k_9^f}{\rightarrow} CO_2 + * + s$	0	0	2	(9)
$CO_2 + \gamma \underset{k_{10}^b}{\overset{k_{10}^f}{\Leftrightarrow}} CO_2\gamma$	0	0	0	(10)
$2CO + O_2 \rightarrow 2CO_2$				

The last reaction path C is a bifunctional path where "s" representing the ceria sites. In many three way catalysts, some amount of ceria is generally used because, it is observed that cerium oxide affects the reaction kinetics and acts as oxygen storage under oscillating conditions (Yao *et al*., 1984). It also improves the thermal stability of the supports (Harrison *et al*., 1988) and increases the noble metal dispersion (Summers and Ausen, 1979). This reaction path involves the adsorption of CO on the noble metal surface followed by O_2 adsorption on the ceria surface. Then the reaction between adsorbed CO and O_2 occurs at the noble metal-ceria interface. The rate expression is found as equation 2.12 by assuming that the noble metal surface is completely covered with CO and O_2 chemisorption is potentially slow as compared to its dissociation.

$$-r_{CO} = \frac{2k_5^f k_{10}^f P_{O_2}[S]_0[V]_0}{2k_5^f P_{O_2} + k_{10}^f[S]_0} \tag{2.12}$$

Akın *et al*. (2001) examined the low temperature CO oxidation over Pt-SnO_2/γ-Al_2O_3 in the absence of CO_2 and H_2O in the feed and two different mechanisms were considered. First mechanism was molecular adsorption of both CO and O_2 on Pt site followed by a surface reaction between adsorbed species to give CO_2 in the gas phase. However, the second mechanism was found to be the most plausible one, on the basis of kinetic analysis. In the second mechanism proposed, molecular adsorption of CO occurs on Pt site followed by the dissociative adsorption of O_2 on SnO_2 surface. Then the surface reaction takes place between adjacently adsorbed species and gaseous CO_2 forms. The mechanism is given below;

$$CO + * \leftrightarrow CO* \tag{2.13}$$

$$O_2 + 2\blacklozenge \leftrightarrow 2O\blacklozenge \tag{2.14}$$

$$CO* + O\blacklozenge \rightarrow CO_2 + \blacklozenge + * \tag{2.15}$$

where, "*" denoting the Pt sites and "♦" denoting the SnO_2 sites. The following rate expression is obtained by neglecting the surface concentration of oxygen in the ads (2.16) term from the principle of the most abundant reactive surface species.

$$-r_{CO} = \frac{kP_{O_2}}{(1 + K_1 P_{CO})^2}$$

Nibbelke *et al.* (1997) studied the oxidation of CO by O_2 over Pt/Rh/CeO$_2$/γ Al$_2$O$_3$ three-way catalyst in the presence of H_2O and CO_2 and developed a kinetic model based on elementary steps. Proposed mechanism and the pathways are given in Table 2.2. The reaction pathways involve adsorption of CO on Pt sites followed by adsorption of O_2 on ceria sites. These three reaction paths are different in terms of oxygen adsorption only. All pathways continue with the reaction between adsorbed CO and O_2 occurring at the noble metal-ceria interface.

Table 2.2. Elementary step reaction path of CO oxidation by O_2 in the presence of H_2O and CO_2 over Pt/Rh/CeO$_2$/Al$_2$O$_3$ catalyst (Nibbelke *et al.*, 1997)

	Reaction Path			
Elementary Step	A	B	C	Step Number
	[a]σ_A	σ_B	σ_C	
$CO + * \underset{k_1^b}{\overset{k_1^f}{\rightleftharpoons}} CO*$	2	2	2	(1)
$O_2 + 2s \xrightarrow{k_2^f} 2Os$	1	1	0	(2)
$2Os \xrightarrow{k_3^f} O_2 + 2s$	0	1	0	(3)
$O_2 + s \xrightarrow{k_4^f} O_2s$	0	0	1	(4)
$O_2s + s \xrightarrow{k_5^f} 2Os$	0	0	1	(5)
$CO* + Os \xrightarrow{k_6^f} CO_2 + * + s$	2	2	2	(6)
$2CO + O_2 \rightarrow 2CO_2$				

In reaction path A of Table 2.2., oxygen adsorption on ceria proceeds irreversibly and dissociatively in a single reaction step. By assuming θ_{CO} as 1, the rate of reaction is found as:

$$r_{CO_2} = k_6^f \, \frac{4k_2^f P_{O_2} + k_6^f - \sqrt{8k_2^f k_6^f P_{O_2} + (k_6^f)^2}}{4k_2^f P_{O_2}} \tag{2.17}$$

Reaction path B, oxygen adsorption on ceria is assumed to proceed reversibly and dissociatively in a single reaction step. Assuming that oxygen adsorption is in equilibrium then, rate of the bifunctional reaction path an be expressed as:

$$r_{CO_2} = \frac{k_6^f \sqrt{K_2 P_{O_2}}}{1 + \sqrt{K_2 P_{O_2}}} \tag{2.18}$$

In reaction path C, oxygen adsorption takes place in two consecutive steps. First, molecular adsorption of oxygen occurs on a single site then oxygen adsorption takes place dissociatively. By assuming oxygen adsorption is slower then its dissociation, rate expression is found as:

$$r_{CO_2} = \frac{2k_4^f k_6^f P_{O_2}}{2k_4^f P_{O_2} + k_6^f} \tag{2.19}$$

Oran and Uner (2004) studied CO oxidation in the absence of CO_2 and H_2O over Pt/CeO$_2$ catalyst and suggested the following mechanism for the reaction.

$$CO + {*} \leftrightarrow CO{*} \tag{2.20}$$

$$O_2 + 2s \rightarrow 2Os \tag{2.21}$$

$$Os + {*} \rightarrow O{*} + s \tag{2.22}$$

$$CO{*} + O{*} \rightarrow CO_2 + 2{*} \tag{2.23}$$

In this mechanism, CO adsorbs on Pt site denoted as "*" and oxygen dissociatively adsorbs on ceria site denoted as "s". Then, oxygen adatoms reverse spill over Pt surface and surface reaction take place between adsorbed CO and oxygen. If the reverse spill over oxygen adatoms to platinum surface is the rate determining step and CO is the most abundant surface species, then the rate expression is obtained as:

$$r_{CO_2} = \frac{k_2^f \theta_{O\cdot}}{(1 + K_1 P_{CO})} \tag{2.24}$$

Özyönüm (2005) studied the steady state kinetic model for the CO oxidation by O_2 in the presence of carbon dioxide and water vapor over Pt-Co-Ce/γ-Al$_2$O$_3$ catalyst. In this study, the elementary reactions constituting the CO oxidation mechanism were determined and experimental rate data were used to estimate the kinetic parameters of the model equations. By making regression analysis, it was found that two different reaction pathways satisfied the requirement of having positive rate and equilibrium parameters. First pathway is:

$$2CO + 2^* \leftrightarrow 2CO^* \tag{2.25}$$

$$O_2 + s \rightarrow O_2s \tag{2.26}$$

$$O_2s + s \rightarrow 2Os \tag{2.27}$$

$$2CO^* + 2Os \rightarrow 2CO_2 + 2^* + 2s \tag{2.28}$$
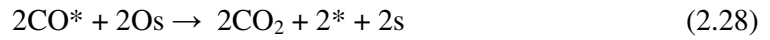
This is a bifunctional pathway with oxygen adsorption on cobalt-ceria surface denoted as "s" and a reaction at the interface, between CO adsorbed on the noble metal surface denoted as "*" and oxygen from cobalt-ceria. If the noble metal surface is assumed to be covered completely with CO and oxygen chemisorption is slower then the dissociation, the rate expression with the combine constants was suggested as:

$$-r_{CO} = \frac{K_1 P_{O_2}}{1 + K_2 P_{O_2}} = \frac{6.66 \times 10^{-6} P_{O_2}}{1 + 9.65 \times 10^{-4} P_{O_2}} \tag{2.29}$$

The second pathway found by Özyönüm (2005) is bifunctional path in which the gas-phase CO is adsorbed reversibly on both the noble metal denoted as "*" and cobalt-ceria sites denoted as "s". Then, oxygen adsorption on cobalt ceria sites takes place in two consecutive steps. It is followed by CO_2 formation via two Langmuir-Hinshelwood surface reaction. The proposed pathway is as follows:

$$CO + * \leftrightarrow CO* \qquad (2.30)$$

$$CO + s \leftrightarrow COs \qquad (2.31)$$

$$O_2 + s \rightarrow O_2s \qquad (2.32)$$

$$O_2s + s \rightarrow 2Os \qquad (2.33)$$

$$CO* + Os \rightarrow CO_2 + * + s \qquad (2.34)$$

$$COs + Os \rightarrow CO_2 + 2s \qquad (2.35)$$

If CO* is assumed to be the most abundant reaction intermediate, CO adsorption on cobalt-ceria sites is in equilibrium and chemisorption of oxygen is slower then the dissociation, the rate expression and the parameters were found as:

$$-r_{CO} = \frac{K_1 P_{O_2}}{1 + K_2 P_{CO}} = \frac{3.5 \times 10^{-6} P_{O_2}}{1 + 8.31 \times 10^{-4} P_{CO}} \qquad (2.36)$$

Also, a power law model was constructed by Özyönüm (2007) which was found to represent the experimental data very well. The empirical expression for the rate equation was found as in equation 2.37.

$$-r_{CO} = 0.001 \, P_{CO}^{-0.35} P_{O_2}^{0.53} \qquad (2.37)$$

The power law model shows that rate is proportional to oxygen partial pressure and inversely proportional to carbon monoxide partial pressure.

Oran (2001) studied the CO oxidation reaction over Pt catalyst to explain the reaction orders determined experimentally. It was found that the mechanism of the reaction depends on the type of the support. Over Pt/γ-Al$_2$O$_3$ catalyst, reaction proceeds through competitive adsorption of CO and O$_2$ on Pt surface and if dissociation of oxygen is considered to be rate determining step then the rate expression was found as:

$$-r_{CO} = \frac{k_3 K_2 P_{O_2}}{(K_1 P_{CO})^2} \tag{2.38}$$

Over Pt/CeO$_2$ catalyst it is also found possible for the reaction to proceed through non-competitive adsorption of CO and O$_2$ and in case of adsorption equilibrium for CO and O$_2$, if reverse spill over of the O adatoms to metal surface is the rate determining step then the rate equation was found as:

$$-r_{CO} = \frac{k_6}{K_1 P_{CO}} \tag{2.39}$$

2.4. Evolutionary Algorithms

The importance of the product quality, process performance and the environmental concerns in chemical industries increases the considerations on operational procedures (McKay *et al*., 1997). Chemical engineering production processes require high production knowledge leading to learn excellent mathematical modeling methods. Kinetic analysis for complex systems of chemical reactions requires a detailed study on complex stoichiometry and thermodynamics. In addition to this, kinetic analysis of heterogeneous reactions concern many factors affecting the reaction rate like mass diffusion, interfacial area, diffusion coefficient and many others which all requiring detailed knowledge of physics and chemistry (Cao *et al*., 1999). Due to these complexities of chemical reactions, studying a lot of time on detailed mechanism of complex reactions is not worthwhile for industrial applications. Therefore, fast and effective methods are needed in order to obtain approximate kinetic models and to optimize the processes for these complex reaction systems (Cao *et al*., 1999). This is why researchers have turned to the use of evolutionary algorithms (EA's) which are successfully applied in a wide range of engineering and

scientific computations (Goldberg, 1989). EA is a subset of evolutionary computation, a generic population-based optimization algorithm. They are adaptive methods for solving computational problems and applications in chemistry are also very wide.

There are originally three branches of EA's which differ in the implementation details and the nature of the particular applied problem. These three well known types of EA are genetic algorithms (GA's), evolutionary programming (EP) and evolution strategies (ES). A new technique was added to the group in 1990's by John Koza (Koza, 1992) called genetic programming. The main difference of this new branch is the representation of the solution which is created as a computer program.

2.4.1. Genetic Algorithms

Genetic Algorithms are first pioneered and developed by John Holland in 1960's and has been widely studied, experimented and applied in many fields of engineering world. Holland's book Adaptation in Natural and Artificial Systems (1975) provided a theoretical knowledge of genetic algorithms. The mechanisms under GA have been analyzed and explained later by Goldberg (Goldberg, 1989) and many others. GA's provide alternative methods in solving problems by developing ways to import the mechanisms of natural adaptation into computer systems. GAs were introduced as a computational analogy of adaptive systems and modeled on the principle of evolution.

The three main application of GA's are, optimization, machine learning and intelligent search and it has also been used by many researchers in engineering field for different problem domains; function optimization (Goldberg, 1989), the control of natural gas pipelines (Goldberg, 1989), the prediction of protein conformation (Schulze-Kremer, 1992), process control (Nordvik and Renders, 1991) and heat exchanger design (Androulakis and Venkatasubramanian, 1991).

In GA's, the terminology from the field of natural genetics is used to describe the algorithms. The structure that encodes how the solution is to be constructed is called the chromosome. In order to specify the solution completely, sometimes more than one chromosome may be needed. The complete set of chromosomes is called a genotype, and

the resulting candidate solution is called a phenotype. Each chromosome comprises a set of genes, each with a specific position or locus on the chromosome. GA's are implemented as a computer simulation and begins with a population of chromosomes of candidate solutions. Solutions are generally represented as strings of 0's and 1's. The evolution starts from a population of randomly generated individuals and happens in generations. In each generation, the fitness of every individual in the population is evaluated, and the best individuals based on their fitness are selected to form a new population. The important point is that, the survival of the best individuals depends mainly on selection process. After completing the selection process, genetic manipulation is carried out. It consists of crossover and mutation operations. Crossover manipulates a pair of individuals by exchanging corresponding segments from the individuals and produces two new individuals. On the other hand, mutation modifies one or more of the gene values of the individual and creates new individuals leading a variety in the population. This new population will be used in the next iteration of the algorithm until the termination criteria is met. This termination criterion may be the fitness value or the number of generations and when this termination criterion is reached, the generation process stops and the solution is found that satisfies the criteria.

2.4.2. Genetic Algorithms in Chemical Engineering

Being a fast and effective method for optimization and parameter estimation, application of genetic algorithms into chemical engineering problems is highly increasing in last years. The consistency of the results obtained, proved the success of evolutionary algorithm applications in chemical engineering. Many different studies have been done on kinetic modeling and parameter estimation by using genetic algorithms in recent years and there is an increasing demand in these applications by the researchers.

Moros *et al*. (1996) studied the use of genetic algorithm for generating initial parameter estimations for kinetic models of catalytic processes. It was aimed to provide suitable starting points for the applied combination of an integration process and a locally converging nonlinear parameter estimation algorithm. Also, the effect of control parameters of the GA which are the number of individuals, the mutation rates and the selection methods were investigated.

In the study of Moros *et al.* (1996), heterogeneous catalyzed oxidative dehydrodimerization of methane reaction to produce ethane and ethene was investigated. The mathematical modeling of this process on PbO/alumina catalyst, results in a nonlinear parameter estimation problem requiring a search for a suitable starting point for the optimization. GA's were used to create and implement an automatic search process for determining the starting points. The GA was implemented in the programming language Turbo-Pascal and the results were obtained. The results showed that, the application of GA leads to a decrease in computing time and increases the reliability of the model parameter solution. This is a very important decision especially for the models with higher complexity. Besides that, the mutation rate, the number of individuals and the selection method are highly effective in the solution reliability and the convergence rate of the algorithm. Therefore, many trials should be done for each experimental set to find the suitable values of these parameters. In this study, the number of individuals was selected as 300, the mutation rate was 80 and selection method was chosen as proportional and ranking.

Another study done using genetic algorithms in kinetic studies was done by Rein *et al.* (2006). In this study, GA's was used to determine the kinetics of polyurethane (PU) foam in smoldering combustion. The kinetic parameters which are needed in theoretical modeling of the foam's smoldering behavior are calculated and the results were found to have the best agreement between the lumped model and the experiment. Firstly, it was aimed to develop a methodology to obtain a global mechanism of thermo oxidative decomposition that is applicable to computer modeling of smoldering combustion. Then a global mechanism of PU kinetics with five reactions was proposed based on the previous experiments. Then, a lumped model was developed and used to numerically reproduce the experiments with the proposed mechanism. GA's was used as an optimization technique to find the set of kinetic parameters that provide the best match between the predictions and experiments. In this application, a set of values of kinetic parameters were selected as a candidate solution or an individual and mathematical formulations and the experimental results were creating the environment. The working principle of GA was randomly generating an initial population and selecting the best fitting of every generation to survive. The children for the next generation undergo reproduction or mutation operations to ensure

wide exploration and to avoid becoming trapped in a local extremum. The process continues until convergence is achieved. According to the numerical values obtained, it was found that calculated kinetic parameters and the five step mechanism worked well for the prediction of thermogravimetric data at different heating rates and using the kinetics developed, predicting the experimental observations of the species distributions in both directions was possible.

As it was mentioned before, the application of GA in scientific and engineering disciplines including chemistry has recently increased (Dawkins, 1999). The studies using GA's in kinetic modeling have been also increasing and good results have been obtained. However, as the articles mentioned above, most of them are based on implementation of GA in prediction of good initial estimates for further applications. Therefore, Boozarjomehry and Masoori (2007) studied the introduction of GA as a robust method for kinetic modeling of complex reaction mechanisms. Their work was found very similar and related with the study done in this thesis. In their work genetic algorithms are used whereas genetic programming is used in this work. Also, not the CO Oxidation but the Fischer-Tropsch synthesis (FTS) and Water Gas Shift (WGS) reactions were modeled in their work. However the studies are similar in methodology and systematic computational framework.

As mentioned above, Boozarjomehry and Masoori (2007) studied the kinetic modeling of FTS and WGS reactions since they have been recently used to obtain clean and environmentally safer fuel in gas to liquid processes. FTS is a set of complicated parallel and series reactions and the whole mechanism consist of seven steps including the WGS reaction. The experimental data was used for comparison of the models and taken from Van Der Laan *et al*. (2000). The rate equations that are used to for modeling are based on Langmuir-Hinshelwood-Hougen-Watson model and the optimum values of the unknown parameters in these models are obtained such the overall error in the prediction of the rate of reactions minimized using genetic algorithm. The GA parameters were selected as; population size is 50, crossover rate is 1, mutation rate is 0,15 and single point crossover was chosen. Calculated and experimental rates were compared by graphical method and the average percent relative errors of the models were tabulated. The value of these errors are changing from 22,8 to 86.8 which is a wide range. However, the majority

of the results are having errors below 27 proving the accuracy and the generality of the proposed kinetic models.

Furthermore, the performance of the Binary and Decimal encoded GA have been compared and Binary GA was found better in both convergence speed and possibility to get the closer point to the global optimum in am more general and less problem dependant manner. It was concluded that, GA is very useful technique to determine an optimum kinetic model for a set of complex reactions since it is flexible and general.

2.4.3. Genetic Programming

In chemical engineering, the optimization of chemical processes is the most important issue in kinetic analysis. Engineers, spend a lot of time in optimizations, safety issues, maximizing the yield and preventing the secondary reactions (Cao *et al*., 1999). At this point, significant emphasis is given on the kinetic studies of the complex reactions. These studies involve many complicated models and require a very detailed knowledge. Especially, heterogeneous reactions involve mass diffusion and speed of agitation, interfacial area, diffusion coefficients and many other factors are affecting the reaction rate (Cao *et al*., 1999). As it was mentioned before, dealing with all of these concerns requires a detailed study and a lot of time for the engineers. Therefore, a more effective and fast ways are preferred both by the engineers and the producers. Generally, the most well known methods are the approximation methods and the gray model method which is a method considers the mass and energy balances in order to reduce the complex reactions to simple kinetic equations and then estimates some kinetic parameter by using regression, integral method and differential method (Filippi *et al*., 1986). Besides that, approximation methods, uses many approximating functions like polynomials or trigonometric series without considering the structure of the reacting systems. Therefore, sometimes applying these models into real chemical processes cause complications and troubles for the engineers. In this situation, genetic programming provides simple and effective way to represent process system behavior by its capability of learning any continuous nonlinear input-output mapping.

Genetic programming is an evolutionary algorithm that automatically creates computer programs to solve the specified problems by means of natural selection. John R. Koza has the major responsibility for the popularization of GP within the field of computer science (Willis *et al.*, 1997). The GP algorithm written by Koza in LISP code has been applied to many kinds of problems concerning symbolic regression, control, robotics, games and classification (Willis *et al.*, 1997). His publications provide the foundational algorithms and structures and he is widely recognized for his ongoing work in the development of this technique.

The methodology of GP is based on the biological evolution and mainly differs from the GA's by the representation of the solution. GP creates computer programs in any computer languages as the solution while GA's create a string of numbers to represent the solution. GP utilizes tree structured, variable length chromosomes whereas GA's utilizes chromosomes of fixed length and structure. Also, GP codes the chromosomes in a problem specific fashion rather than binary strings.

GP is the application of biological principles to the automatic generation of computer programs. The environmental pressures placed upon the population results in the most fit individuals surviving, reproducing and continuing to adapt. Also, the individuals in the population adapt more easily into their environment by using genetic operations of reproduction, mutation and crossover. GP is the application of these and other concepts to the automatic writing of computer programs.

GP starts with a population of individuals which is a term coming from biological systems. The individuals of the population have different survivability coming from its own genetic information. The genetic information of the individuals provides the structural variety throughout the population. Genetic operations like reproduction, mutation and crossover ensure the changes in the population over time. An individual program is typically represented as a tree that provides significant representational flexibility and the framework in which a program is encoded. The survivability of an individual in a population is measured by fitness expresses. Fitness evaluation is the major concern in GP in order to determine the best program in each intermediate and final generation. It is generally based on the error between the actual and the predicted solutions (Mckay *et al.*,

1997). However, for symbolic regression problems, South *et al*. (1995) proposed the use of correlation coefficient between the actual and predicted outputs as an alternative to error based fitness functions.

In GP, it is also necessary to define a functional set which is a set of arithmetic operations and mathematical functions that the algorithm may use when constructing a potential solution to a given problem. Generally, the functional set includes operators like addition or multiplication and functions like square root, logarithm or exponential. The important point is that each function used in the set should accept or return a numerical value when presented with an input. GP algorithm, search the model which is constructed from the elements in the functional set and the terminal set which is the inputs of the computer program. Therefore each computer program created is a composition of functions taken from the function set and terminals taken from the terminal set.

In GP, initially a random population of the individuals is generated and then fitness of the each individual in the population is evaluated. Once the fitness of each individual has been determined, it is used as the basis for selecting members of the population for reproduction. There are different selection methods suggested in the literature and tournament selection is one of them. It is the random sampling of a fixed number of individuals from the parent population to form a subset and the fittest member of this subset is chosen to reproduce. The second method is fitness proportionate selection which is a sampling of an individual from parent population with a probability proportional to its fitness. The last method is elitist scheme in which the population is arranged in an order of decreasing fitness values and the fittest individuals undergo reproduction. After the selecting the fittest individuals, the genetic operators (reproduction, crossover and mutation) may be applied. The reproduction operator copies a member from the parent population to the next generation. Crossover operator takes two members of the population and combines them to create new offspring while mutation makes random alterations to the proposed model structure. These genetic and selection operators guide the evolution of the population and once they are performed on the current population, the population of the offspring replaces the old population. This process is repeated over and over again until the termination criteria are met. This criterion can be the number of generations as well as the fitness value and when it is met, the solution of the problem is created.

The variability of the programs created is an important issue in genetic programming. Specifying or restring the structure or the size of the program is against the random property of the programming. Because, it narrows the solution strategy of the program and can lead to elimination of the solution to the problem.

2.4.4. Genetic Programming in Chemical Engineering

Being a fast and effective method, GP have been successfully applied into many engineering and scientific computations (Mitchell, 1996). Especially, creating approximate models for complex reactions is a time consuming and good knowledge required study for chemical engineers. Therefore, GP provides more successful and effective method than the traditional methods for kinetic analysis. (Cao *et al.*, 1999) In addition to this, using GP in deriving kinetic models works better than GA and the reason is GP is the optimization of the structure of the model whereas GA is the optimization method for the model parameters. Therefore GP can provide a better understanding of both the structure and the parameter of the model.

Cao *et al.* (1999) studied the kinetic evolutionary modeling of complex systems of chemical reactions. A hybrid evolutionary modeling algorithm (HEMA) is used for modeling of ordinary differential equations of the chemical reactions. The main difference of this algorithm was utilizing both GA and GP during modeling. In other words, GA was inserted into GP where GA was used in order to optimize the model parameters and GP was used in order to optimize the structure of the model. The algorithms were used for two different chemical reaction systems. These two reactions studied are, the thermolysis reaction of chloro-cyclohexane and the reaction between formaldehyde and carbomide in aqueous solution to produce methylol urea respectively. During the modeling process, the fitness was calculated by modified Euler method with fixed stepsize 0.01 to do the integration and the selection strategy was chosen as tournament selection where elitism strategy was also adopted. The function set used for evolutionary modeling was including, $(+,-,*,/,x^y$ sin, cos, exp, ln) and the terminal set is composed of $(x_1...., x_n, t, c)$ where n is the number of equations in the system of ODE's and c is the set of random constants. The population size was chosen as 50, maximum tree dept of 3 and maximum generation

number of 50 was used in terms of parameter settings. According to the modeling results, it was found that the kinetic model built is capable of reflecting the kinetic characteristics of the thermolysis reaction. The interesting point with the results was the models containing an exponential function in the expression. It was commented as the success of the computer program since these kinds of functions are unimaginable by human minds. The average prediction error of the best models was given as 0.16 and average fitting error was calculated as 0.029 and these results proved the success of the program HEMA in model creations.

For the modeling of the reaction between formaldehyde and carbomide it was shown that the fitting curves of the best model and the simulated curves of the concentrations of the three components were coinciding and they were also having an exact match with predicted values calculated based on the literature values. According to the results obtained, it was concluded that the effectiveness of HEMA can be seen from the success of both the parameters and the structures of the created models.

The application of GP to develop empirical models of chemical process systems has been increasing recently. Willis *et al*. (1997) studied the systems modeling by GP and used GP to determine both the structure and the complexity of the model. First a steady state model was created and dynamic input output models were developed with the algorithm. Two different processes were studied and the first one is the vacuum distillation column. The main objective was to create a model that can be used to understand the bottom product composition. By using input-output data the model was developed and parameter settings were done as; population size of 25 and maximum generation number as 50. The results showed that GP algorithm has automatically discovered an accurate empirical model. Also, a model was developed for twin screw cooking extruder with 100 generations and a population size of 30. It was shown that, GP is advantageous in automatically eliminating the irrelevant model inputs and is an appropriate model offering method that can not be attainable by neural network.

GP is an optimization method which has many advantages in developing kinetic models. Firstly, it is not necessary to make priori assumptions and the structure and the complexity of the model evolve as the solution. Especially, neural networks do not provide

enough information about the structure of the model and it becomes more difficult to find the model that accurately represents the process characteristics (Willis *et al*., 1997).

The increasing trend of using data based modeling techniques to develop accurate models in industries affected the researchers to aim in evolutionary algorithms. McKay *et al*. (1997) studied steady state modeling of chemical process systems using GP. Continuous stirred tank reactor system, which consists of two CSTR in series, was chosen to be modeled. The function set was including; (+, -, /, *, x^y, $x^{1/2}$, x^2, log, exp). Fitness proportionate selection method was chosen and population size of 25, generation number of 60 was selected. Mutation, crossover probabilities were chosen as 0,2 and 0,8 respectively. After completing 50 runs, it was seen that 66-99% of the runs could be expected to be successful. The success was defined as the root mean square error which is a value obtained to estimate the probability of the success. The error was calculated as 0,06 indicating the achievement of successful models. It was commented that, GP has potential to discover significantly more information about the process characteristics than the neural network and the number of demonstrations in application of GP in process system engineering showed the effectiveness of the algorithm on reaction systems.

In addition to the studies given above, dynamic system modeling can also be done by GP. Developing process models from the plant data known as system identification is used to predict values of the process output accurately with a known process input values. Hinchliffe and Willis (2003) studied dynamic system modeling using genetic programming and used a multi-basis function GP algorithm in order to evolve discrete-time models of dynamic systems. The main difference of the algorithm used in this study was the ability to use past values of model terms although they are not specified explicitly in the function and terminal sets. It was shown that the models created by GP have a good prediction performance although more computational effort was required.

3. COMPUTATIONAL WORK

In this work, kinetic modeling of catalytic CO oxidation was performed using genetic programming. Some simple generic or specific reactions with known rate equations were used first to check the appropriateness of the method and to establish the procedure that should be followed. Then, by using the experimental data obtained in our laboratory as well as the data from the literature, the rate expressions for CO oxidation were derived by using GP Studio (Version 2.60) software package, and the results were analyzed in order to identify the most plausible reaction mechanism.

3.1. Reaction Rate Data Used

3.1.1. Data for Generic or Simple Real Reactions

In order to have a basic understanding of how genetic programming (GP) will work in modeling the reaction kinetics, generic or simple reactions with known rate equation were modelled using GP Studio software and the equations obtained were compared with the ones that reported in the literature.

First, the following unimolecular reaction was modelled using the rate data from Fogler (1992).

$$A \rightarrow B \tag{3.1}$$

For this reaction, proposed reaction rate in terms of the partial pressure of component A was given as follow:

$$-r_A = \frac{0.1\, P_A}{1 + 1.5 P_A} \tag{3.2}$$

By using the rate equation and the initial partial pressure of component A, the pressure vs rate data was generated and used for modeling with genetic programming.

The second reaction system used for modeling was dehydrogenation reaction of methylcyclohexane to produce toluene.

$$C_7H_{14} \rightarrow C_7H_8 + 3H_2 \tag{3.3}$$

The reaction was carried out over a 0.3% Pt/Al$_2$O$_3$ catalyst in a differential catalytic reactor in the presence of hydrogen to avoid coking. The experimental data was obtained by Sinfelt *et al* (1960),and reported by Fogler ,1992 with the form of reaction rate given below:

$$r_T = \frac{12.3 P_M}{1 + 9 P_M} \tag{3.4}$$

Then the rate equation for the bimolecular reaction of hydrogenation of ethylene to form ethane was determined. . The reaction is carried out over a cobalt molybdenum catalyst and the experimental data is obtained.

$$C_2H_4(E) + H_2(H) \rightarrow C_2H_6(EA) \tag{3.5}$$
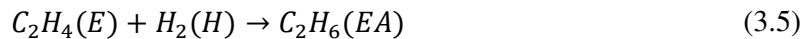
The following four different rate expressions were suggested in Fogler (1992), and the one that represent the experimental data best were asked as an exercise:

$$-r_E = \frac{3.19 \, P_H \, P_E}{1 + 2.1 P_E} \tag{3.6}$$

$$-r_E = \frac{3.35 \, P_E P_H}{1 + 0.043 P_{EA} + 2.2 P_E} \tag{3.7}$$

$$\tag{3.8}$$

$$-r_E = \frac{2P_E P_H}{(1 + 0.36P_E)^2}$$

The last rate expression proposed was a power law model as;

$$-r_E = 0.89\, P_E{}^{0.26} P_H{}^{1.06}$$

Between these four equations, equation 3.6 was suggested as the best model in describing the data.

Finally a more complex bimolecular reaction with two products was used for modelling. Pursley studied the formation of methane from carbon monoxide and hydrogen using a nickel catalyst (Fogler, 1992);

$$3H_2 + CO \rightarrow CH_4 + 2H_2O \tag{3.10}$$

The reaction was carried out at 500°F in a differential reactor. The partial pressures of H_2 and CO were determined at the entrance of the reactor. It was predicted that the rate limiting step in the overall reaction is the reaction between atomic hydrogen absorbed on the nickel surface and CO in the gas phase, then the rate law would be in the form;

$$r_{CH_4} = \frac{0.0183\, P_{H_2}{}^{\frac{1}{2}} P_{CO}}{1 + 1.5 P_{H_2}} \tag{3.11}$$

3.1.2. CO Oxidation Data

In order to determine a rate expression for CO oxidation, the experimental results obtained by Özyönüm (2005) in his M.S. Thesis in in Boğaziçi University were used. The results reported by Oran (2001) and Nibbelke *et al*. (1997) were also modelled.

Özyönüm (2005) studied the steady state kinetic model for the CO oxidation by O_2 in the presence of carbon dioxide and water vapor over Pt-Co-Ce/γ-Al$_2$O$_3$ catalyst. In his study, the elementary reactions constituting the CO oxidation mechanism were determined

and experimental rate data were used to estimate the kinetic parameters of the model equations (eqn 2.29, 2.36) or the mechanisms proposed in equations 2.25 through 2.28 and 2.30 through 2.35 (Özyönüm *et al.*, 2007).

The second experimental data were taken from the study done by Oran (2001). In this study, the effect of cerium oxide on carbon monoxide oxidation reaction mechanism over Pt / γ-Al_2O_3 catalyst was investigated. The isothermal CO oxidation reaction experiments were conducted for three different catalysts. Two of them were chosen to be modeled in this study. First experiment was performed with Pt/CeO_2 catalyst over a wide range of CO and O_2 partial pressures. Percentage of CO was changed from 2 to 6 % by volume while keeping the O_2 at 3 % by volume level and vice versa. Second experiment was performed with Pt / γ-Al_2O_3 catalyst. CO composition was changed from 3 to 6 % while O_2 was kept at 2.5% by volume and CO was kept at 5% while O_2 was changed from 2 to 3 % by volume. The rate equations proposed in his study were given in equations 2.38 and 2.39.

The last experimental data were taken from the literature. This study was done by Nibbelke *et al*. (1997). In this article, the oxidation of CO by O_2 was studied for a Pt/γ -Al_2O_3 catalyst and for a commercially available $Pt/Rh/CeO_2/\gamma$ -Al_2O_3 three-way catalyst. Kinetic experiments were carried out in an isothermal fixed-bed micro reactor under intrinsic conditions, i.e., in the absence of mass and heat transfer limitations, in the temperature range from 436 to 503^oK, with CO and O_2 inlet partial pressures between 0.12 and 8.3 kPa and H_2O and CO_2 inlet partial pressures between 0 and 10 kPa. The proposed mechanisms and the rate expressions were given in Table 2.2 and Equations 2.17 through 2.19 respectively.

3.2. Computational Details

Genetic programming utilizes principles from biological systems to enable the automatic creation of computer programs. In order to derive an appropriate model that describes the main features of the rate equation by genetic programming, GP Studio (Version 2.60) was used. This part, brings out a deep look into the concept of GP Studio

and what kind of arrangements were done for modeling of the reactions given in this work.

GP Studio is an integrated genetic programming model development environment which takes the data provided and generates a program that gives the best generated model. Therefore, to start with using GP Studio, the training data to be modeled should be imported. Once it has been imported, it becomes available for use within a project. However, the importing the training data is not the only step to generate good results. Modeling parameters plays an important role in the models. Especially, the functions are basic building blocks of the model. If the expected nature of the model is known, the evolutionary process can be made more efficient. Therefore, by looking at the proposed rate equations if exists, the functions used in given equations were selected to be used during the model creation.

After selecting the functions used, the numerical constants, which plays an important role in most models, should be determined. GP studio provides two kinds of constants which are integer and double. In this work, it was always selected the use of random double constants since it has a huge range of numbers including the decimal numbers. In addition to this, fitness functions were always selected as Raw Fitness which is a measure of absolute error of prediction versus a target value in the training data.

Program size reduction is an important issue in GP because the nature of genetic programming is generating a model without a guarantee to be the shortest possible solution. In fact, it can result in extremely large programs. However keeping the results as small as possible helps to have a better understanding of the mechanism of the reaction and avoids having very complex rate expressions. Therefore, multi objective option, which means that a model has multiple characteristics under consideration for fitness, is recommended to have smaller program size while still providing a solution to the data selected. A multi objective approach was selected for all the models in this work.

In genetic programming, size and operator setting are important issues which are used to create new programs that eventually create a solution to match the experimental data imported. However selecting the program size reduction option, which pressures to

find smaller program and to decrease the complexity of the equation, is destructive to a lot of information contained in a large population. It means, the small program fitness pressure, clears out a lot of options from the initial population by eliminating large and complex programs that may contain potentially useful structures. This result in the need to increase the reliance upon mutation and more generations are required. Therefore, while using the program size reduction to have a better model generalization, to have a faster simulation and to have a reduction in program size to reduce complexity of the model; profile setting should be done properly.

The profile settings played an important role in the models. Firstly the type was selected as regression in all reactions modeled in this work since kinetic models can only be created by regression type. After that, to create a random population, initialization should be done. In this work, in order to increase the variation in the structure, Ramped half-half method was used for creating population of all reactions. Once the initial random population has been created, the individuals need to be assessed for their fitness. Fitness functions were always selected as Raw Fitness which is a measure of the absolute error of the prediction value versus a target value in the training data. It means that, lower the raw fitness better the individual. Having applied the fitness test to all the individuals in the initial random population, the evolutionary process starts. Individuals in the new population are formed by three main methods which are reproduction and crossover and mutation.

These control parameters especially the operators need to be set by the user. The decisions are critically important as they have a limiting effect on the search space of possible programs. Probability of crossover decides the proportion of the population to undergo crossover before entering the new population. Koza, (1992) does not change this value from 0.90—90% of the population. In this work, probability of crossover was set to 45% which is the recommended value for using program size reduction. It is also the average value of Koza and sufficient to provide the source of new individuals. The probability of reproduction is the proportion of individuals in a population that will undergo reproduction. Throughout Koza's work this value stays constant, at 0.10—10% of the population and in this work it was kept at 5%. Lastly, the mutation rate was kept around 50% to introduce new options in the search.

The last profile setting is done when a modeling run is considered to be complete which is called the termination criteria. Since it is not always possible to discover a perfect model, the termination conditions should be entered. Maximum generation option is which specifies the maximum number of generations a modeling run should take in the case a perfect model is not found. It is important this option always utilized because most real world problems do not result in something that perfectly matches training data. In this work maximum generation was set generally between 25 – 100 generations which are average values to have enough generation a modeling should take and to keep running time shorter.

After these arrangements were made, the results were obtained in the form of a tree structure which was a diagrammatic view of the model. Then by inspecting the tree structure in a bottom up and left to right fashion, the correct equation was discovered. Figure 3.1. shows a representation of the tree structure.
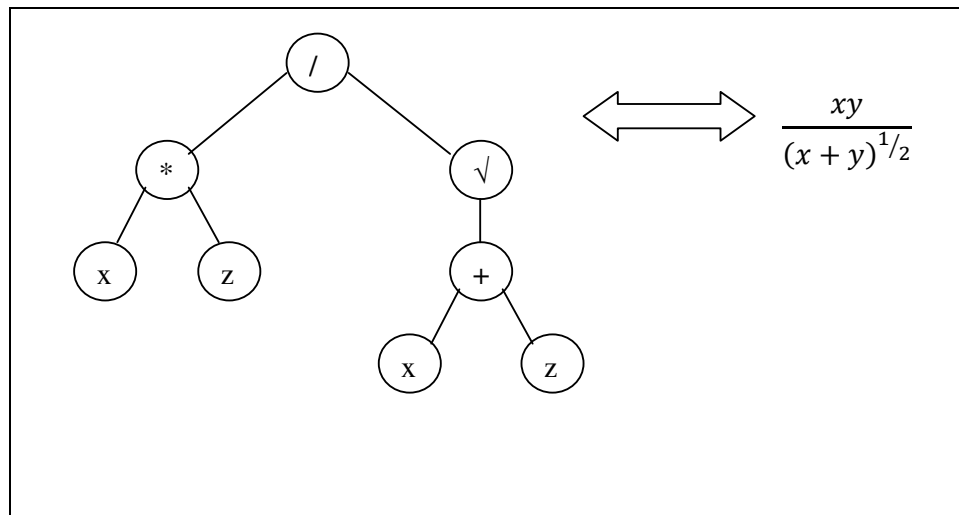

Figure 3.1. Graphical representation of a tree structure

However, understanding the tree structure depends on the complexity of the model. The important point is genetic programming technique makes no assumptions about the structure of a system to be modeled. Therefore, it can create highly complex models not possible with any other approach. Because no assumptions is made, no limitations is

placed on the model structure; it is possible to have a very complex (over-fitted) model that match the exact experimental data points. Although, the program size reduction option was selected for all models and all profile settings were done to reduce complexity of the model, there still might be models with very high complexities that have the risk of overfitting. The complexity of these models were so high that they were not understandable by human mind. Therefore, the results with very high complexities were not listed in this work. Generally, the equations with complexity level below 30 were elected to be discussed in this work. In order to have a better understanding of how the models change with their complexities, the models were listed with the values of their complexity in the results and discussion part.

To summarize, all the arrangements and selections made for the reactions modeled in this work are listed in Table 3.1. On the other hand, reaction specific selections like functions and number of generations are listed for each reaction in the results and discussion session.

Table 3.1. Summary of the profile settings

Profile Settings			
Type		Regression	
Structure		No structure was specified	
Constants		Double integer	
Fitness		Raw Fitness	
		Multi objective	
Population			
Parameters		*Operators*	
Initialization	Ramped half-half	*Reproduction*	5
Reproduction	Over selection	*Mutation*	50
Size	1000	*Crossover*	45

4. RESULTS AND DISCUSSION

In this work, the kinetic modeling of CO oxidation was performed using genetic programming. In order to have a basic understanding in deriving rate laws by GP, generic reactions were used firstly to generate kinetic models by GP Studio. Then, the experimental data for CO oxidation generated in our laboratory and obtained from literature were used to determine the CO oxidation kinetics and mechanism. In all cases, the reaction rate equation was derived first, and then it was used to predict the reaction mechanism.

In the generic reactions part, the pressure versus rate data obtained from the literature were imported to the GP studio and were used as the training data to derive the appropriate rate expressions representing the data points. During the model creation, the profile settings of the software were varied to obtain various models so that the one fits the data best could be identified. Then, the results obtained were compared with the rate laws proposed in the literature and the detailed mechanisms of the well matched reaction rates equations were proposed. The compatibility of the results obtained for generic reactions showed the success of the GP in deriving kinetic models.

In the CO oxidation part, firstly the experimental data obtained from the studies of Özyönüm (2005) and Oran (2001) were used to derive kinetic models for CO oxidation. Then the rate versus pressure data obtained from Nibbelke *et al.* (1997) were used for modeling and the results obtained are listed. The rate expressions generated for CO oxidation were verified by comparing with the experimental results and the models suggested in the literature. Then, the kinetic models were used to understand the mechanism of the reaction. In this part, a detailed discussion of the results derived for generic reactions and for CO oxidation and the detailed mechanisms of the reactions can be found.

4.1. Generic Reactions

GP can be used to derive an appropriate model that describes the main features of the rate equation by determining the most significant functional groups, which consist of the various combinations of rate and equilibrium constants and the power of partial pressures in the rate equation. In order to have a better understanding of GP in reaction kinetics, firstly, unimolecular reactions were used because of their simplicity in functional groups and rate expressions.

4.1.1. Unimolecular Isomerization Reaction

For a simple kind of a unimolecular isomerization reaction;

$$A \rightarrow B \qquad\qquad (4.1)$$

Rate law proposed in literature is given in equation 3.2 and the initial pressure of component A was given as 2 atm. By using this initial pressure and the rate equation given, the rate vs. pressure data were obtained and used as the training data to derive an appropriate model.

After creating and importing the rate data in GP studio, the functions were specified by looking at the proposed reaction rate in the literature. It can be seen that three basic functions (+, *, /) are used in the rate model. Selecting them for the model creation provided the model to be relevant with the expected nature. No more functions were selected since the more narrowly the search can be defined, the better opportunity to find the best model. Also, the number of generations was kept at 50 by experience. In general, most of the evolutionary benefit is seen within the first 10 to 20 generations, with incremental improvements continuing after that time. Therefore it is usually safe to suggest 50 generations which is usually more than enough for most of the problems. The major profile settings done for modeling were given in computational details part. But to summarize, the population size was increased around 1000 to contain more possibilities at the expense of greater computational work and memory resources, and the mutation rate was increased around 50% to introduce new options in the search. In addition to this, while

keeping the reproduction constant at 5%, the crossover rate was decreased around 45%. The model specific settings are summarized in Table 3.1.

After completing profile settings, the models were obtained in the form of a tree structure which is a diagrammatic view of the model. Then by reading the tree structures in a bottom up and left to right fashion, the correct equations were discovered.

The rate equations found were evaluated in terms of their complexity and structure. The models with very high complexities were eliminated since they are not understandable by human mind. Then, the models were evaluated according to their shape and structure, the most fitted models were suggested as the rate law. These results are listed in Table 4.1 with the functional groups selected, the number of maximum generations as the termination criteria and the complexity of the result equation which indicates the number of functions and terminals in the tree that formed the equation.

By looking at the results obtained in Table 4.1, it can be seen that both models are giving the same structure with the literature; as a matter of fact the second equation is exactly the same with the one given in the literature in terms of structure and reaction rate constants.

Table 4.1. List of models, functions used, number of generations selected and complexity of the models

Model No	Model	Functions	Generation	Complexity
1	$-r_A = \dfrac{0.092\, P_A}{1 + 1.29 P_A}$	+,/,*	50	7
2	$-r_A = \dfrac{0.1\, P_A}{1 + 1.5 P_A}$	+,/,*	50	9

Then the predicted reaction rates by these equations were compared with the one calculated from the literature and given in Figure 4.1. It is very clear that even model 1 has

a perfect match with the literature with the R^2 value of 0.999. No plot was prepared for Model 2 since it is exactly the same as the one that proposed in the literature
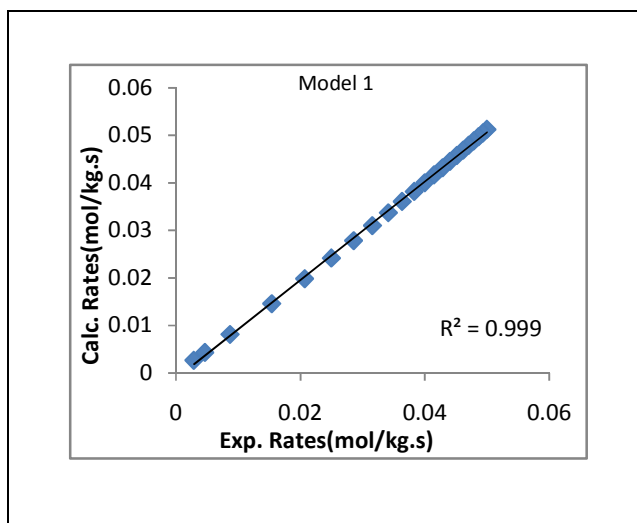

Figure 4.1. Calculated rates vs experimental rates for model 1

In terms of the mechanism of this unimolecular isomerization reaction, it can be concluded from the rate expression that, component A was adsorbed on the catalyst site while component B was not adsorbed since P_B does not exist in the denominator. Then the mechanism for this reaction equation (with the assumption that the adsorption of A is the rate determining step) can be proposed as:

$$A + * \leftrightarrow A* \quad step1 \tag{4.2}$$
$$A* \rightarrow B + * \quad step2 \tag{4.3}$$

where * denotes the active site.

This result showed that GP could be a good way to derive an appropriate model equation and hence the main features of the reaction mechanism. However, more test should be performed to be sure about the usefulness of GP in studying the kinetics of more complex reactions.

4.1.2. Dehydrogenation of Methylcyclohexane

In order to further examine the reliability of GP studio in deriving model equations, another unimolecular reaction, which is a real one this time, was chosen. Dehydrogenation of methylcyclohexane to produce toluene reaction was selected and the experimental data was obtained from Sinfelt *et al.*(1960) given in Fogler (1992) . The experimental data was given in Fogler (1992) for a question asking to find the best rate expression over four suggested rate expressions. This was a good test for the performance of GP in kinetics. Therefore, this question was used to find the best rate expression that describes the experimental data and the functions were chosen from a larger range covering all the functions used in four different rate expressions.

This reaction is carried out over a 0.3% Pt/Al_2O_3 catalyst in a differential catalytic reactor in the presence of hydrogen to avoid coking. For a given experimental data, the rate law of the reaction given in Equation 4.4 was determined.

$$C_7H_{14}\,(M) \rightarrow C_7H_8(T) + 3H_2 \tag{4.4}$$
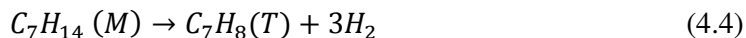
In order to find the rate law by GP, the generation of the rate expression was started with importing the experimental data to GP studio as the training data. The maximum number of generation was suggested as 50 based upon the successive experience in the previous model.

The results obtained for dehydrogenation reaction of methylcyclohexane are listed in Table 4.2 in terms of their complexities. The most important point that has to be emphasized is the structure of the equations. They all have the kinetic factors, the driving force groups and the adsorption group. This verifies that the results derived by using GP show an excellent rate expression structures and groups that describes the main features of the rate equation. In addition to this, as the complexity increases, the reaction orders are becoming more complicated and at highest complexity like in model 4, the partial pressure of hydrogen is introduced in the rate expression.

Table 4.2. List of models, functions used, number of generations selected and complexity of the models

Model No	Model	Function	Generation	Complexity
1	$r_T = \dfrac{2.36\, P_M^{\frac{3}{4}}}{\left(1 + 4.53 P_M{}^3\right)^{\frac{1}{4}}}$	$+,/,*,x^2,x^{1/2}$	50	15
2	$r_T = \dfrac{6.09\, P_M{}^{0.5}}{(1 + 3.23 P_M)^{0.5}}$	$+,/,*,x^2,x^{1/2}$	50	8
3	$r_T = \dfrac{13.53\, P_M}{1 + 10.19 P_M}$	$+,/,*,x^2$	50	9
4	$r_T = \dfrac{5.88\, P_{H_2}\, P_M{}^3}{1 + 1.47\, P_{H_2}\, P_M{}^3}$	$+,/,*,x^2$	50	19
5	$r_T = \dfrac{12.5 P_M}{1 + 9.15 P_M}$	$+,/,*,x^2$	50	16
6	$r_T = \dfrac{0.4 + 6.36\, P_M}{1 + 4.5 P_M}$	$+,/,*,x^2$	50	7

The plot of experimental versus calculated rates are presented in Figure 4.2 for all models. Although the R^2 values are quite reasonable, they do not provide conclusive evidence about the reaction mechanism. Model 5, seems to be more plausible considering that it has the same kinetic factors, the driving force groups and the adsorption group with the one suggested in the literature.

Indeed, the Model 5 model provided the detailed mechanism of the reaction by having an exact match with the literature. According to the equation in model 5, the mechanism of the reaction was found as below with star (*) denoting the catalyst side.

$$M +*\leftrightarrow M * \qquad step\ 1 \tag{4.5}$$
$$M *\rightarrow T + H_2 + * \quad step2 \tag{4.6}$$

From the mechanism of the reaction, it can be seen that methylcyclohexane was adsorbed first and decomposes to the products with the first step being the rate determining step.
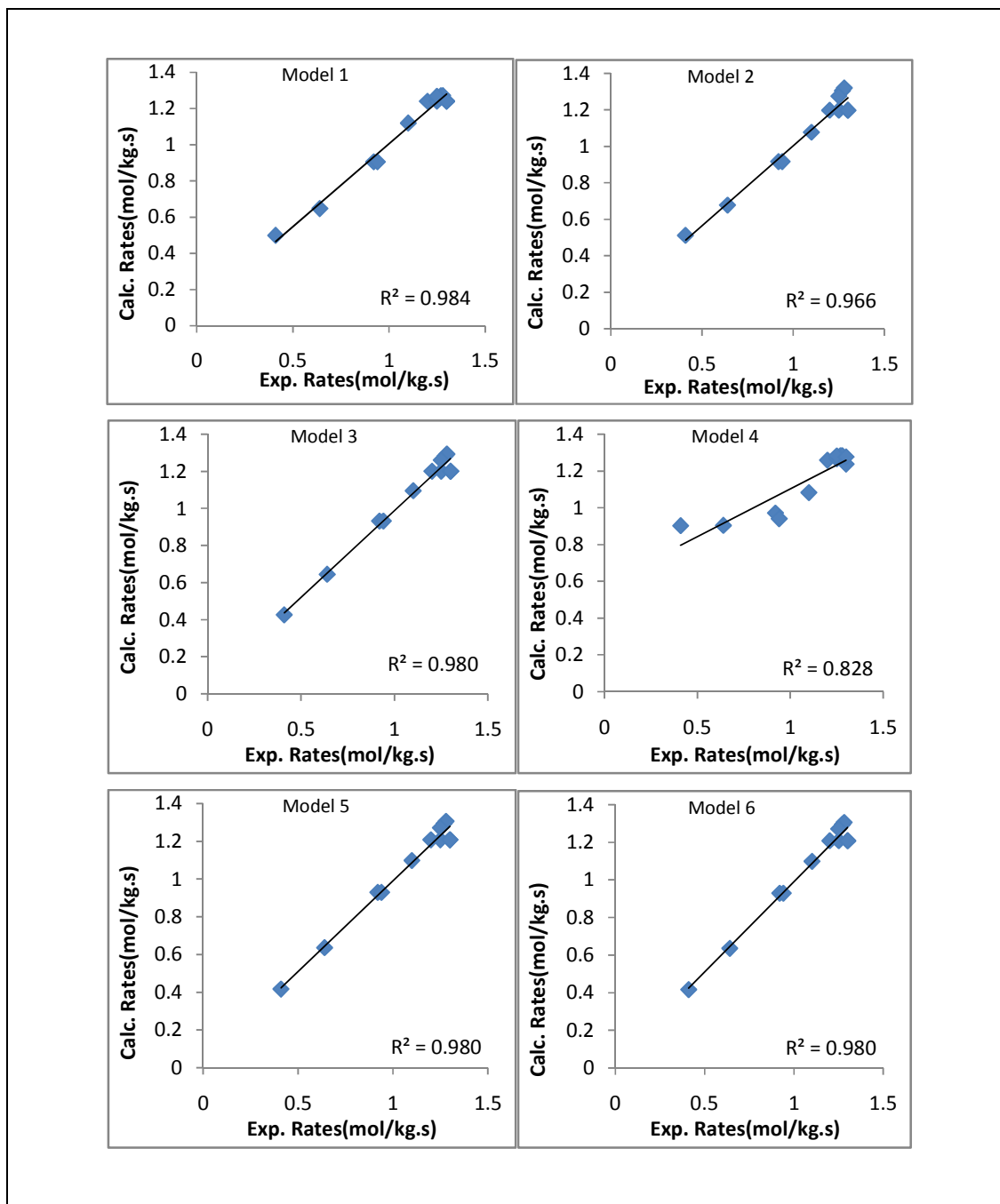

Figure 4.2. Calculated rates vs experimental rates for all models

4.1.3. Hydrogenation Reaction of Ethylene

After obtaining successful results on unimolecular reaction modeling, the bimolecular reaction types were also tested to examine the success of GP on more complicated reaction mechanisms. As the first trial of the bimolecular reaction type, the simple reaction style having same stochiometric coefficients was selected. The hydrogenation reaction of ethylene to form ethane was an ideal model for this form of reaction. Hence this reaction was modeled by using the experimental data described in Fogler (1992).

$$C_2H_4 \ (E) \ + H_2(H) \rightarrow C_2H_6(EA) \tag{4.7}$$

The reaction is carried out over a cobalt molybdenum catalyst, and the important point is four different rate equations given in equations 3.6 through 3.9 were suggested in Fogler (1992) to find the best rate equation describing the data. Therefore, this was an important task to test the genetic programming in determining the best model. In model creation, the function sets were taken from these possible four reaction rates given by Fogler (1992). The calculated results with different functions and 50 generations are given in Table 4.3. All three models are having the same structure and very close rate constants with the model equation proposed given in Equation 3.6. It can be seen that the equations with lower complexities are giving the power law model of the reaction whereas the results with higher complexity shows the exact rate law of the reaction.

Table 4.3. List of models, functions used, number of generations selected and complexity of the models

Model No	Model	Function	Generation	Complexity
1	$r_{EA} = 0.948 \, P_E{}^{1/4} P_H$	$+,/,*,x^2,x^{1/2}$	50	11
2	$r_{EA} = 0.946 \, P_E{}^{1/4} P_H$	$+,/,*,x^2,x^{1/2}$	50	9
3	$r_{EA} = \dfrac{3.16 \, P_H P_E}{1 + 2.11 P_E}$	$+,/,*$	50	17

The success of the model is also evident from the plot of experimental and calculated rate plots and their R^2 values given in Figure 4.3. Also model 3 has exactly the same structure and rate constants with the model proposed in the literature (equation 3.6). This is a very important result because between four different rate expressions suggested, the best model was found by using genetic programming. This result proves the applicability of GP in kinetic analysis by obtaining the most appropriate model between four different rate expressions.
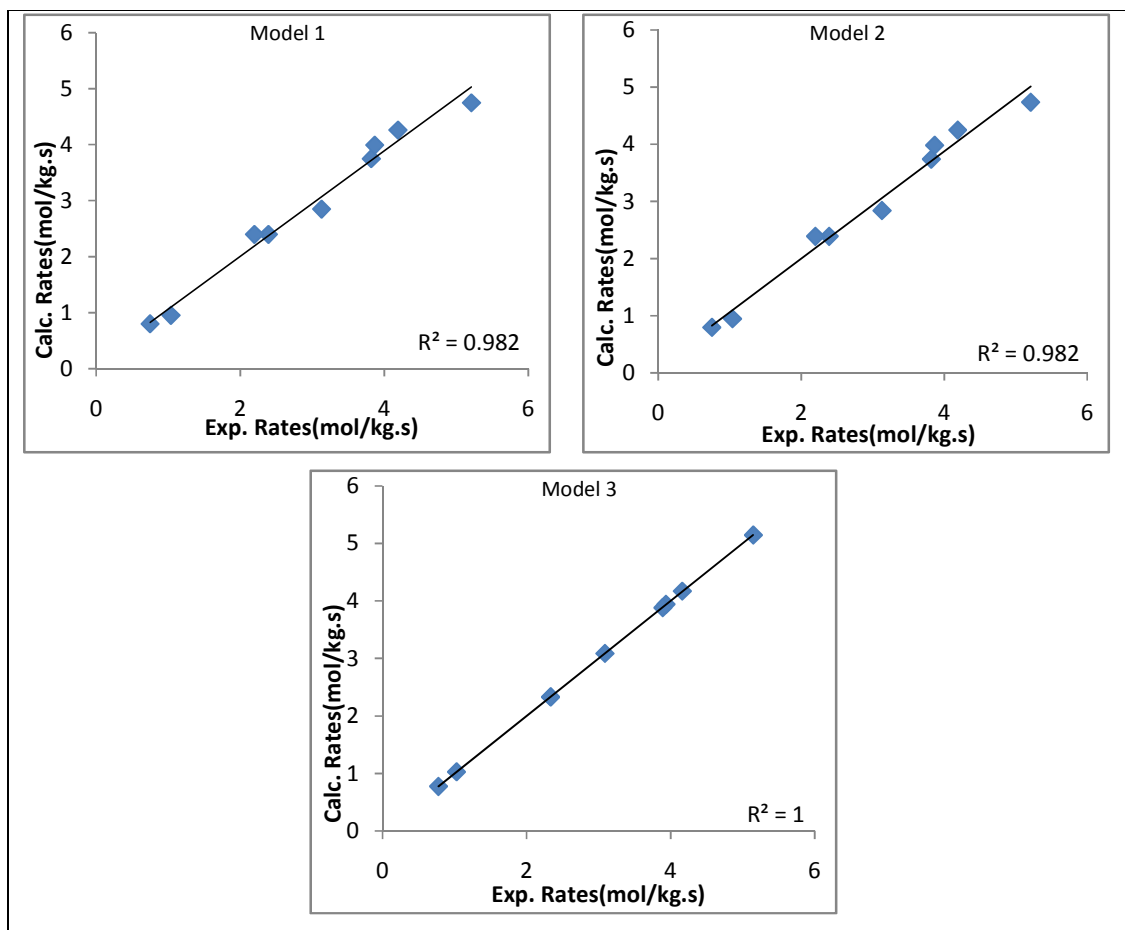

Figure 4.3. Calculated rates vs experimental rates for all models

For Model 3, which best fits the equation given in the literature, the detailed mechanism of the reaction is given below in which the star (*) denoting the catalyst side. In this mechanism, step 2 is found to be the rate limiting step giving Model 3 as the rate expression.

$$E + * \leftrightarrow E * \qquad (4.8)$$

$$E * + H_2 \rightarrow EA + * \qquad (4.9)$$

The results obtained in all previous reactions show a good match with the expected nature of the model. The exactness of the data and the simplicity of the expected equations can be a reason for this success. Therefore, the complexity of the equations was increased in every trial to evaluate the success of results with more complicated kinetics models. The next bimolecular reaction type selected was a little bit more complicated then the previous one due to different stochiometric numbers of the components.

4.1.4. Formation of Methane from Carbon Monoxide and Hydrogen

More complex bimolecular reactions with two products have more complex rate expressions. Pursley (1952) studied the formation of methane from carbon monoxide and hydrogen using a nickel catalyst.

$$3H_2 + CO \rightarrow CH_4 + 2H_2O \qquad (4.10)$$

The reaction was carried out at 500^oF in a differential reactor. The partial pressures of H_2 and CO were determined at the entrance of the reactor. It was predicted that the rate limiting step in the overall reaction is the reaction between atomic hydrogen absorbed on the nickel surface and CO in the gas phase, then the rate law would be in the form of equation 3.9. During modeling, not only experimental data were used but also extra data points were obtained by using the proposed rate law due to lack of sufficient experimental data.The models obtained for this reaction are summarized in Table 4.4. The models all have different structures and reactions orders. While keeping the generation number constant, the functions used during modeling was changed in some trials. This change was done especially to see if it is really necessary to select $x^{1/2}$ function during modeling. But it was found that, although $x^{1/2}$ function provides $P_{H_2}{}^{1/2}$ term in the numerator of the equations and a better match than the other trials, still does not lead to the exact match of the equation.

Table 4.4. List of models, functions used, number of generations selected and complexity of the models

Model No	Model	F*	G*	C*
1	$$r_{CH_4} = \frac{0.017\, P_{H_2}^{1/2}\, P_{CO}}{1 + 2.34 P_{H_2} + 2 P_{H_2}^{2}}$$	+,/,*,x$^{1/2}$	50	12
2	$$r_{CH_4} = \frac{0.0112\, P_{CO}^{7/4}}{\left(1 + 1.5 P_{H_2}\right)^{1/4}}$$	+,/,*,x$^{1/2}$	50	19
3	$$r_{CH_4} = \frac{0.0094\, P_{H_2}^{1/4}\, P_{CO}}{\left(1 + 2.7 P_{H_2}^{2}\right)^{1/4}}$$	+,/,*,x$^{1/2}$	50	15
4	$$r_{CH_4} = \frac{0.0182\, P_{H_2}\, P_{CO}}{1 + 4.6 P_{H_2}^{2}/(1 + P_{H_2})}$$	+,/,*	50	23
5	$$r_{CH_4} = \frac{0.018\, P_{H_2}^{5/6}\, P_{CO}^{9/8}}{\left(1 + 16.1 P_{H_2}^{7/2}\, P_{CO}\right)^{1/8}}$$	+,/,*,x$^{1/2}$	50	23
6	$$r_{CH_4} = 0.0017\, P_{CO} + \left(\frac{0.0094\, P_{H_2}^{1/2}\, P_{CO}}{0.6 P_{H_2}^{1/2} + \left(0.39 + P_{H_2}^{2}\right)^{1/2}}\right)$$	+,/,*,x$^{1/2}$	50	16
7	$$r_{CH_4} = 0.0048\left(P_{CO} + \frac{1.53\, P_{H_2}\, P_{CO}}{1 + 2.14 P_{H_2}^{2}}\right)$$	+,/,*	50	19
8	$$r_{CH_4} = \frac{0.012\, P_{H_2}^{1/2}\, P_{CO}}{P_{H_2}^{1/4}\left(1 + P_{H_2}^{3/2} + 0.66 P_{H_2}^{1/2}\right)^{1/2}}$$	+,/,*,x$^{1/2}$	50	17

F*: Function, G*: Generation, C*: Complexity

By looking at all models obtained, it can be concluded that they all have many similarities in terms of the rate constants, the partial pressures or both with the one obtained in the literature but none of them are giving the exact equation. For instance, the driving groups of the Model 1 and 8 are very successful in structure whereas the second model has a good match in terms of adsorption group and the fourth model has the same kinetic factor. It seems that, as the complexity of the expected nature of the model increases, the models derived is diverging from exact model. The experimental data may also have an important effect on the results. Since extra data points were used due to lack of sufficient experimental data, the results can have a poor match. The reason is that each point in the training data is tried to be exactly represented in the model by the program.

On the other hand, all models have a very good match with the experimental data since they all have R^2 values of nearly 1 (Figure 4.4) although they do not lead to any conclusive result for the reaction mechanism.
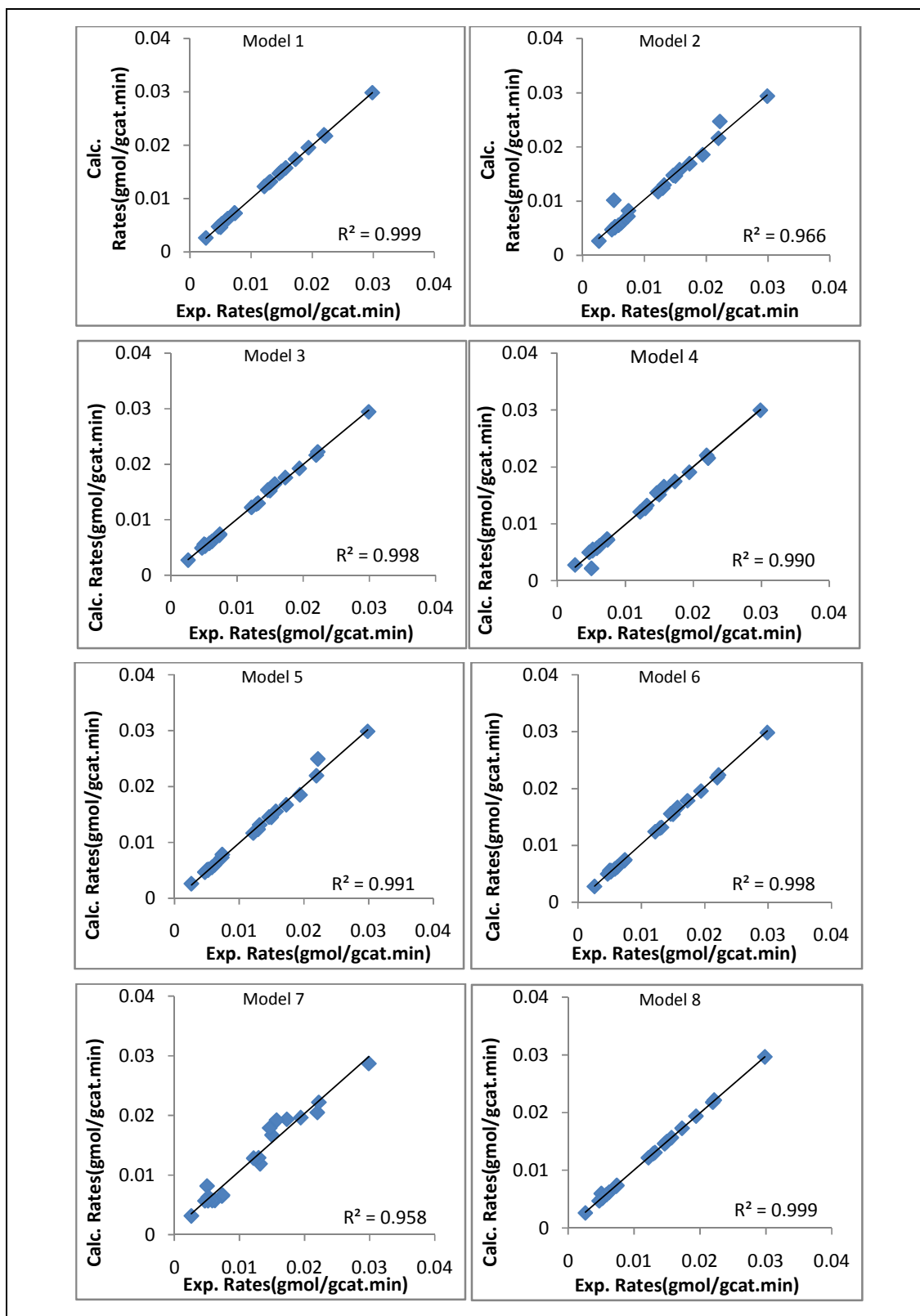
Figure 4.4. Calculated rates vs experimental rates for all models

4.2. Modeling of Experimental Data Taken from Özyönüm (2005)

Özyönüm (2005) studied the kinetics of selective CO oxidation in hydrogen rich streams over Pt-Co-Ce/Al_2O_3 catalyst. In his study, intrinsic kinetic data were obtained in the initial rate region in a micro flow reactor operating in a differential mode using eight different sets of CO and O_2 concentrations each at two space times at 110 ^{o}C in the presence of 25 percent CO_2 and 10 percent H_2O. (Özyönüm *et al*., 2007).

4.2.1. Generating Plausible Models

Firstly, three different function sets (+,*,/) were used since there are several expected forms of the rate law proposed (Özyönüm *et al*., 2007). Hence, * and / functions were kept in every run whereas -, +, $x^{1/2}$, x^2 functions were not used in every trial. At the beginning of the model creation, the functions that are unrelated with the model (exp, x^y, average) were also selected to try if the program uses them although they can not exist in a rate expression. However these unrelated functions do not appear in the model equation proving that the program works properly for a rate model creation. After obtaining six successful models, these unrelated functions were not selected anymore in the remaining runs.

Besides that, maximum generation number was changed between 25, 50 and 100 in various trials. The reason for this is 25 generation is mostly enough for evolutionary benefit but increasing the number can lead to visualize the incremental improvements continuing after that time. Hence, 100 generation was made in first runs and decreased properly to see the effect of generation number. The models showed that generally reducing the generation number provides to obtain more basic and simple equations as expected. The incremental improvements after that lead to very small terms and numbers to appear in the model, and they generally complicate the equation and makes it difficult to compare with the models in the literature. However it does not happen all the times and they can sometimes lead to derive exact models and very good matches as well. Therefore, the results obtained are created by different functions sets with different maximum generation criteria and the ones with better structure and lower complexities were tabulated in Table 4.5.

Table 4.5. List of models, functions used, number of generations selected and complexity of the models

Model No	Model	F*	G*	C*
1	$$r_{CO_2} = \frac{0.104\,{P_{O_2}}^{1/2}}{P_{CO}}$$	+,-,*,/,exp,x^y, $x^{1/2}$,average	100	6
2	$$r_{CO_2} = \frac{0.041\,{P_{O_2}}^{1/2}}{1 + 0.383\,P_{CO}}$$	+,-,*,/,exp,x^y, $x^{1/2}$,average	100	8
3	$$r_{CO_2} = \frac{0.01\left({P_{CO}}^{1/2} + P_{O_2}\right)^{1/2}}{P_{CO}}$$	+,-,*,/,exp,x^y, $x^{1/2}$,average	100	9
4	$$r_{CO_2} = \frac{0.00123\,P_{O_2}}{2.53P_{O_2} + P_{CO}}$$	+,-,*,/,exp,x^y, $x^{1/2}$,average	100	13
5	$$r_{CO_2} = \frac{{P_{O_2}}^{1/2}}{0.29\,P_{CO}\left(\left(P_{O_2} - P_{CO}\right)^{0.52} + P_{CO}\right)^{1/2}}$$	+,-,*,/,exp,x^y, $x^{1/2}$,average	100	14
6	$$r_{CO_2} = 0.0034\left(\frac{P_{O_2}}{P_{CO}}\right)$$	*,/	25	9
7	$$r_{CO_2} = 0.00367\left(\frac{P_{O_2}}{P_{CO}}\right)$$	*,/	25	7
8	$$r_{CO_2} = \frac{0.017\,P_{O_2}}{(1 + 4.7P_{CO})}$$	+,*,/	25	9
9	$$r_{CO_2} = 0.00166\left(1 + \frac{P_{O_2}}{P_{CO}}\right)$$	+,/,*	50	9
10	$$r_{CO_2} = 0.00287\left(1 + \frac{0.131\,P_{O_2}}{P_{CO}}\right)$$	+,/,*	50	19
11	$$r_{CO_2} = 0.002 + \frac{0.00146\,P_{O_2}}{P_{CO}}$$	+,/,*	50	19

Table 4.5. Continued

Model No	Model	F*	G*	C*
12	$r_{CO_2} = 0.00196 + \dfrac{1.28\, P_{O_2}}{P_{CO}{}^2}$	+,/,*	25	11
13	$r_{CO_2} = 0.0014 + \dfrac{0.0018\, P_{O_2}}{P_{CO}}$	+,/,*	25	13
14	$r_{CO_2} = \dfrac{1.7(P_{O_2}+P_{CO})}{(0.89 + P_{CO})(1.78 + P_{CO})}$	+,/,*	50	17
15	$r_{CO_2} = \dfrac{0.0055\, P_{O_2}}{(0.934\, P_{O_2}) + (0.627\, P_{CO})}$	+,/,*	50	9
16	$r_{CO_2} = \dfrac{0.00168\, P_{O_2}\,(P_{O_2} + P_{CO})}{(P_{O_2} + 0.841\,)P_{CO}}$	+,/,*	50	17
17	$r_{CO_2} = \dfrac{0.114\, P_{O_2}{}^{1/2}}{2.3 P_{O_2}{}^{1/2} + P_{CO}}$	+,-,*,/,exp,x^y, $x^{1/2}$,average	100	10
18	$r_{CO_2} = \dfrac{0.00698\, P_{O_2}}{(P_{O_2} + P_{CO})}$	+,/,*	50	13

F*: Function, G*: Generation, C*: Complexity

The results obtained were generally reasonable in terms of order of oxygen gas phase pressure and CO partial pressure. It can be seen that CO_2 production rate is found to be proportional to P_{O2} whereas it is inversely proportional to P_{CO} in most of the results. This is the expected nature of the reaction rate and was also proposed in the literature. (Nibbelke *et al.*, 1997).

In terms of the compatibility of the reaction rates, the model 8 shows very good match with the equation proposed in Özyönüm *et al.*(2007). The proposed equation that best describes his data is given in equation 2.36. Also, model 8 given in the table has the same structure and orders with the one stated. Although, the rate constants are not in very

good agreement with each other, the method is successful in deriving an appropriate model that describes the main features of the rate equation.

4.2.2. Evaluation of Plausible Models

In order to have a better idea of the models, the rate data obtained from the model equations were compared with the experimental data and R^2 values were calculated for each model. The R^2 values are given in Table 4.6. According to R^2 values of the models, it was seen that model 5, model 12 and model 14 showed very low match with R^2 values below 0,6 and they can be eliminated. Although having high R^2 values, models through 9 to 13 contain a summation term with a constant in the equations and that can not be a part of the rate equation. Therefore these equations fail to express a realistic rate expression for CO oxidation.

Table 4.6. R^2 values of the models

Model No	R^2	Model No	R^2
1	0.743	10	0.854
2	0.743	11	0.895
3	0.732	12	0.581
4	0.939	13	0.895
5	0.592	14	0.569
6	0.895	15	0.909
7	0.895	16	0.909
8	0.895	17	0.743
9	0.939	18	0.921

On the other hand, the models 1, 6 and 7 have a good fit in expressing the power law models of the reaction rate with acceptable R^2 values while model 1 is very consistent in terms of reaction orders. However, the Model 8 was found to be the best in describing the proposed models in terms of both structure and reaction orders. Consequently five models (1, 2, 6, 7 and 8) were found consistent with the literature. The experimental versus predicted rate plot for these models were presented in Figure 4.5.
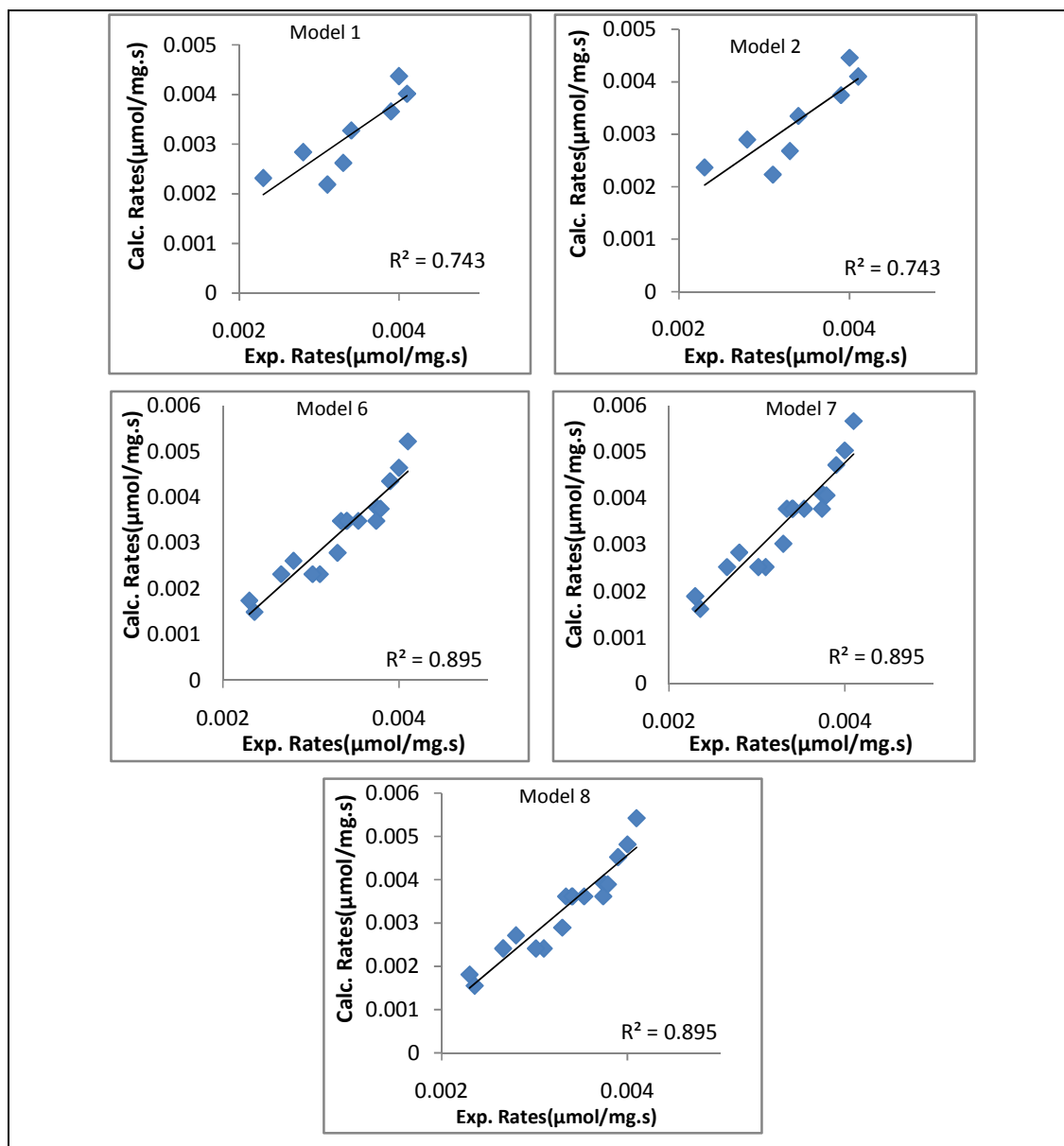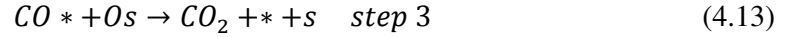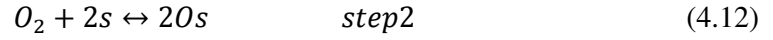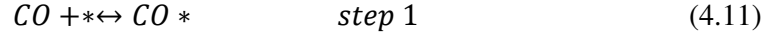
Figure 4.5. Calculated rates vs experimental rates for models 1,2,6,7 and 8

4.2.3. Pathway Analysis

In this part, pathway analysis of the models whose structure was found to be fitting with the literature was performed. The mechanistic steps of the reaction were discussed and related pathways were presented in order to understand the kinetic characteristic of CO oxidation reaction.

The best models derived by using the experimental data taken from the study of Özyönüm (2005) were model 1,2,6,7 and 8. The plausible pathways of the models created were given. For model 1, the pathway was found to be;

$$CO + * \leftrightarrow CO * \qquad step\ 1 \qquad (4.11)$$

$$O_2 + 2s \leftrightarrow 2Os \qquad step2 \qquad (4.12)$$

$$CO * + Os \rightarrow CO_2 + * + s \quad step\ 3 \qquad (4.13)$$

Özyönüm also stated the pathways of the models derived in his work. The power law model equation (Eqn 2.37) proposed in his study is similar to the one derived here. There is a consistency with the partial pressure of oxygen but partial pressure of CO has a difference. Therefore the reaction path of model 1 was derived by calculations and presented. In the reaction steps, "*" represents the platinum sites and "s" represents the cobalt-ceria surface. As CO_2 is comparatively weakly-bound to the surface, the desorption of this product molecule is relatively fast and the surface reaction between the two adsorbed species is the rate determining step. Then the rate expression is;

$$r_{CO_2} = k_3 \theta_{CO} \theta_O \qquad (4.14)$$

Assuming that the adsorption of CO is molecular, and the adsorption of O_2 is dissociative and the adsorbed species compete for the same adsorption sites then,

$$\theta_O = \frac{\sqrt{b_O P_{O_2}}}{(1 + \sqrt{b_O P_{O_2}} + b_{CO} P_{CO}} \qquad (4.15)$$

$$\theta_{CO} = \frac{b_{CO} P_{CO}}{(1 + \sqrt{b_O P_{O_2}} + b_{CO} P_{CO}} \qquad (4.16)$$

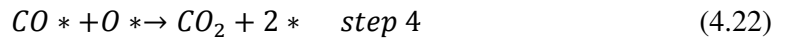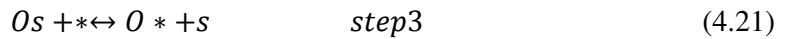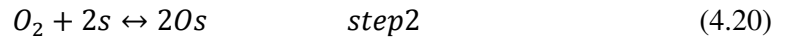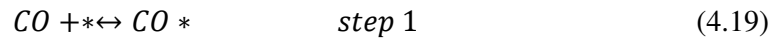Substituting these into the rate expression gives Equation 4.17.

$$r_{CO_2} = k\theta_{CO}\theta_O = \frac{k \, b_{CO}P_{CO}\sqrt{b_O \, P_{O_2}}}{\left(1 + \sqrt{b_O P_{O_2}} + b_{CO}P_{CO}\right)^2} \qquad (4.17)$$

If the CO is much more strongly bound to the surface such that $b_{CO}P_{CO} \gg (1 + \sqrt{b_O P_{O_2}})$ and hence that $(1 + \sqrt{b_O P_{O_2}} + b_{CO}P_{CO}) \approx b_{CO}P_{CO}$ then the rate equation simplifies to give:

$$r_{CO_2} \approx \frac{k \sqrt{b_O \, P_{O_2}}}{b_{CO}P_{CO}} = k' \frac{P_{O_2}^{1/2}}{P_{CO}} \qquad (4.18)$$

In this limit the kinetics are half-order with respect to the gas phase pressure of molecular oxygen, but negative order with respect to the CO partial pressure. The reason can be CO acts as a poison (despite being a reactant) and increasing its pressure slow down the reaction. This is because CO is so strongly bound to the surface that it blocks oxygen adsorbing, and without sufficient oxygen atoms on the surface the rate of reaction is reduced (Nix, 2008).

For model 2, the reaction steps for this model were taken from the study of Oran (2001) and found as;

$$CO + * \leftrightarrow CO * \qquad \qquad step \; 1 \qquad \qquad (4.19)$$
$$O_2 + 2s \leftrightarrow 2Os \qquad \qquad step 2 \qquad \qquad (4.20)$$
$$Os + * \leftrightarrow O * + s \qquad \qquad step 3 \qquad \qquad (4.21)$$
$$CO * + O * \rightarrow CO_2 + 2 * \qquad step \; 4 \qquad \qquad (4.22)$$

In this reaction mechanism, "*" denotes the platinum site and "s" denotes the cobalt-ceria site. In the case of adsorption equilibrium for CO and O_2, if the reaction between the adsorbed species is the rate determining step then the rate equation was proposed in the study of Oran (2001) as;

$$r_{CO_2} = \frac{(k_4 K_1 K_3 K_2^{1/2})P_{CO} \, P_{O_2}^{1/2}}{(1 + K_1 P_{CO})^2} \qquad (4.23)$$

If it is assumed that, $(1 + K_1 P_{CO}) \approx K_1 P_{CO}$ then the equation reduces to the form of Model 2. This is a reasonable assumption because partial pressure of CO is calculated in Pa and $K_1 P_{CO}$ term has a much higher value than 1.

For model 6.7 and 8, the detailed mechanism of these rate equations was taken from the study of Özyönüm (2007) and given in equations 2.30 through 2.35. This mechanism is a bifunctional path in which the gas phase CO is adsorbed reversibly on both the noble metal and cobalt-ceria sites. Then, the oxygen adsorption takes place in two consecutive steps. By making the necessary assumptions discussed in Chapter 2, equation 4.24 is obtained.

$$r_{CO_2} = \frac{k_2 P_{O2}}{1 + K_1 P_{CO}} \tag{4.24}$$

This rate equation satisfies the structure of model 8. This structure is also the same with equation 2.36, which is the model proposed in the study of Özyönüm (2007). Therefore, it can be concluded that Model 8 is a very successful equation with appropriate structure and orders. In addition to this, it proves the success of GP in kinetics by having exactly the same structure with the one proposed in the literature.

If the CO* is the most abundant reaction intermediate then the rate equation reduces to the form same as model 6 and 7;

$$r_{CO_2} = \frac{k_2 P_{O2}}{K_1 P_{CO}} \tag{4.25}$$

The other equations can be discussed in terms of their structure but can not be commented about the mechanism since no information or consistency was found in the literature. However, there are still some equations with well adjusted structure, compatible adsorption terms and driving forces. In addition to this, models from 15 to 18 have both CO and O_2 partial pressures in adsorption terms. This situation can take place when adsorbed oxygen

and gas phase CO comprise the formation of OCO* surface species. However, it is not for sure if this formation occurs in these models. Because the whole structure of the models are not exactly in the form of the expression for this formation.

4.3. Modeling of Experimental Data Taken from Oran (2001)

Oran studied the performances of $Pt/\gamma-Al_2O_3$ and Pt/CeO_2 powder catalysts on CO oxidation reaction. Isothermal CO oxidation reaction experiments were conducted for the catalysts and the rate data were given in terms of CO and O_2 partial pressures. First experiment was performed with Pt/CeO_2 catalyst and it was found that reaction rate showed zero order dependency with respect to O_2 partial pressure and negative first order dependency with respect to CO partial pressure. Second experiment was performed with $Pt/\gamma-Al_2O_3$ catalyst and reaction rate was found to be first order with respect to O_2 partial pressure and negative second order with respect to CO partial pressure. The rate data of experiments performed with $Pt/\gamma-Al_2O_3$, Pt/CeO_2 catalysts were used for developing rate equations and the results and evaluations were given below.

4.3.1. Generating Plausible Models for Pt/CeO$_2$ Catalyst

The experimental rate data of Oran's study was taken in order to develop rate expressions for CO oxidation reaction with Pt/CeO_2 catalyst. The rate data was imported to the program as the training data and the profile settings are done properly. Four different function sets were used during modeling. In these sets, two basic functions (*, /) were always selected to use and other functions were chosen based on success of the results obtained in the previous run. As it can be seen from the models created that, the first function set (+,*/) mainly produced models with zero order O_2 partial pressure. This was an expected result considering that the independency of the rate on oxygen was also stated in Oran's work. However, the function sets were changed for the further runs in order to provide variance in the models and to discover the small dependency of the rate on oxygen partial pressure. The results showed that, by adding the $x^{1/2}$ and x^2 functions into the set, the rate equations showed a tendency to include oxygen partial pressure in driving force groups. On the other hand, the generation number was changed between 30 and 50 and most plausible models were found at 30 generations. From all the results obtained, twenty

different models created were chosen to be the best in terms of structure and listed in Table 4.7.

Table 4.7. List of models, functions used, number of generations selected and complexity of the models

Model No	Model	F*	G*	C*
1	$$r_{CO_2} = \frac{3.12}{(1 + 2.6P_{CO})}$$	+,*,/	50	7
2	$$r_{CO_2} = \frac{P_{O_2}^{\;2}}{0.89P_{CO}^{\;2} + 1.19P_{CO}\,P_{O_2}^{\;2}}$$	+,*,/	50	13
3	$$r_{CO_2} = \frac{1}{(0.88\,P_{CO})}$$	+,*,/	30	5
4	$$r_{CO_2} = \frac{1}{(0.86\,P_{CO})}$$	+,*,/	30	5
5	$$r_{CO_2} = \frac{1.22}{P_{CO}}$$	+,*,/	30	7
6	$$r_{CO_2} = \frac{1.146}{P_{CO}}$$	+,*,/,x$^{1/2}$	30	3
7	$$r_{CO_2} = \frac{1.51\,P_{O_2}^{\;2}}{P_{CO}^{\;2} + P_{CO}\,P_{O_2}^{\;2}}$$	+,*,/	30	11
8	$$r_{CO_2} = \frac{P_{O_2}^{\;1/2} + 0.93\,P_{CO}}{P_{CO}^{\;2}}$$	+,*,/,x$^{1/2}$	30	10
9	$$r_{CO_2} = \frac{0.124\,P_{O_2} + P_{CO}}{P_{CO}(0.159 + P_{CO})}$$	+,*,/,x$^{1/2}$	30	11
10	$$r_{CO_2} = \frac{1.1\,P_{O_2}^{\;3/2}}{3.4 + P_{CO}\,P_{O_2}^{\;3/2}}$$	+,*,/,x$^{1/2}$	30	16
11	$$r_{CO_2} = \frac{0.75\,P_{O_2}^{\;1/8}}{P_{CO}}$$	*,/,x$^{1/2}$	30	10
12	$$r_{CO_2} = \frac{0.74\,P_{O_2}^{\;1/4}}{P_{CO}}$$	*,/,x$^{1/2}$	30	14

Table 4.7 Continued

Model No	Model	F*	G*	C*
13	$r_{CO_2} = \dfrac{P_{O_2}{}^{1/4}}{0.93\,P_{CO}{}^{1/4}\,P_{CO}}$	$+,*,/,x^{1/2},x^2$	30	9
14	$r_{CO_2} = \dfrac{P_{CO} + 0.11\,P_{O_2}}{P_{CO}{}^2}$	$+,*,/,x^{1/2},x^2$	30	10
15	$r_{CO_2} = \dfrac{0.397\,P_{O_2}}{1.36P_{CO} + 0.3P_{CO}\,P_{O_2}}$	$+,*,/,x^{1/2},x^2$	30	11
16	$r_{CO_2} = \dfrac{P_{CO} + 0.8\,P_{O_2}{}^{1/2}}{(0.36 + P_{CO})^2}$	$+,*,/,x^{1/2},x^2$	30	11
17	$r_{CO_2} = \dfrac{0.475\,P_{O_2}}{P_{CO}(1 + 0.41\,P_{O_2})}$	$+,*,/,x^{1/2},x^2$	30	13
18	$r_{CO_2} = \dfrac{0.9\,P_{CO} + P_{O_2}{}^{1/2}}{P_{CO}{}^2}$	$+,*,/,x^{1/2},x^2$	30	9
19	$r_{CO_2} = \dfrac{P_{O_2}{}^{1/2}}{0.95\,P_{CO}\,\left(P_{O_2} + 0.59\right)^{1/2}}$	$+,*,/,x^{1/2},x^2$	30	16
20	$r_{CO_2} = \dfrac{P_{CO} + P_{O_2}{}^{1/2}}{(0.847 + P_{CO})^2}$	$+,*,/,x^{1/2},x^2$	30	9

F*: Function, G*: Generation, C*: Complexity

If we consider the models individually, it can be seen that, model 1 and 3 to 6 do not include P_{O2} term in the equations. This situation can happen if some simplifications based on the assumptions are made on the reaction rate and was also stated in the study of Oran(2001).

4.3.2. Evaluation of Plausible Models for Pt/CeO$_2$ Catalyst

In order to evaluate the rate models with respect to experimental rate, R^2 values of the models were calculated. According to the results, all models have a good fit with the experimental rate with R^2 of about 0.7. It is interesting to obtain nearly the same consistency for all models created. Although, exact match with the experimental data is not

achieved in the results, the models do not seem to show a serious discord with the experimental results either.

Table 4.8. R^2 values of the models

Model No	R^2	Model No	R^2
1	0.699	11	0.718
2	0.704	12	0.718
3	0.695	13	0.691
4	0.695	14	0.698
5	0.695	15	0.714
6	0.695	16	0.688
7	0.704	17	0.703
8	0.676	18	0.676
9	0.699	19	0.698
10	0.702	20	0.703

In all models, smaller order of oxygen partial pressure exists. Moreover, for the models 3 to 6, the rate equation shows that rate is independent of oxygen partial pressure. Over Pt/CeO_2 catalyst, non competitive adsorption is favorable due to the availability of different sites for CO and O_2 (Oran, 2001). If the reaction occurs on the same surface between the adsorbed species, one of the adsorbed reactants must go to the other's site. For CO oxidation reaction, the expected transfer is the reverse spill over of the oxygen to the metal surface. If this is the rate determining step and CO adsorbed on platinum site and oxygen adsorbed on ceria site are the most abundant reaction intermediates, than the rate equation can reduce to a form having no dependency on oxygen partial pressure (Oran, 2001). Therefore, these equations can be regarded as the plausible models for CO oxidation in the presence of Pt/CeO_2 catalyst. The degree of the match of the model 3 and the experimental values can be seen in Figure 4.6.
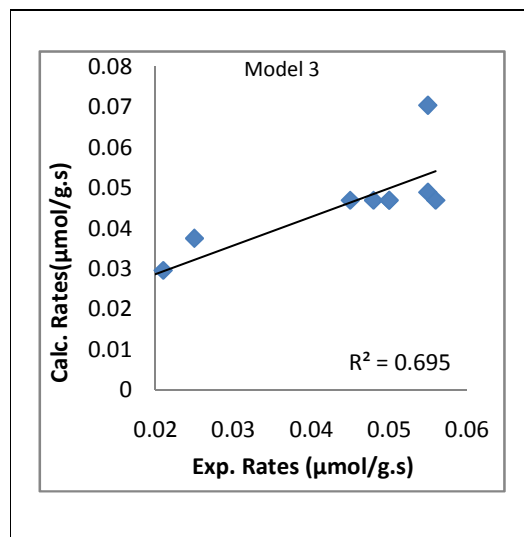
Figure 4.6 Calculated rates vs experimental rates of model 3

4.3.3. Pathway Analysis of the Models for Pt/CeO$_2$ Catalyst

Since models 3,4,5 and 6 have the same structure and nearly the same parameter, model 3 was chosen to show the pathway as representing the other models as well. In Oran's study the plausible pathway of this reaction was found as:

(4.26)

(4.27)

(4.28)

(4.29)

In the mechanism, "*" denotes the platinum site and "s" denotes the available adsorption sites on the ceria surface. Oran (2001) proposed that if the reaction occurs between the species adsorbed on the same site then, one of the adsorbed reactants must go to the other's site. For CO oxidation reaction, the expected transfer is the reverse spill over of the O atoms. In the case of adsorption equilibrium for CO and O$_2$ if this reverse spill over of the oxygen atoms (step 3), is the rate determining step then the rate equation becomes;

(4.30)

If the "CO*" and "Os" are the most abundant reaction intermediates, then the rate equation reduces to the form given in equation 4.31 which is the same with the model proposed by Oran (2001) in equation 2.39.

$$r_{CO_2} = \frac{K_3}{K_1 P_{CO}} \qquad (4.31)$$

4.3.4. Generating Plausible Models for Pt/γ- Al$_2$O$_3$ Catalyst

The experimental rate data of Oran's study was taken in order to develop rate expressions for CO oxidation reaction with Pt/ γ- Al$_2$O$_3$ catalyst. After importing the experimental rates into the program, the necessary setting of the profile were done accordingly. Although different sets of functions were used for modeling, the preferred models are derived from one function set only. It can be seen from the results that, the only function set used for the created models are (+,*, / ,x^2). Also, the generation number was kept at 30 based on the successful derivations done on the previous model. The models created showed good structure and partial pressure orders. The reason is; for the experiment performed with Pt/γ-Al$_2$O$_3$ catalyst, reaction rate was stated to be first order with respect to O$_2$ partial pressure and negative second order with respect to CO partial pressure in Oran's work. When compared with the results obtained, all models with no exception have the same order in terms of CO and O$_2$ partial pressures. Therefore, the kinetic models built are capable of reflecting the kinetic characteristic of CO oxidation reaction in the presence of Pt/ γ- Al$_2$O$_3$ catalyst. The effectiveness of genetic programming in developing rate expressions can be seen from the success of the structures of the created models.

Table 4.9. List of models, functions, number of generations and complexity of the model

Model No	Model	F*	G*	C*
1	$r_{CO_2} = \dfrac{0.79\,P_{O_2}{}^2}{P_{CO}{}^2(0.63 + P_{O_2})}$	$+,*,/\,,x^2$	30	13
2	$r_{CO_2} = \dfrac{0.77\,P_{O_2}}{P_{CO}{}^2}$	$+,*,/\,,x^2$	30	6
3	$r_{CO_2} = \dfrac{0.7(\,1.64 + P_{O_2})}{P_{CO}{}^2}$	$+,*,/\,,x^2$	30	10
4	$r_{CO_2} = 0.73\,P_{O_2}/P_{CO}{}^2$	$+,*,/\,,x^2$	30	13
5	$r_{CO_2} = \dfrac{0.78\,P_{O_2}}{P_{CO}(0.48 + P_{CO})}$	$+,*,/\,,x^2$	30	9
6	$r_{CO_2} = \dfrac{0.75\,P_{O_2}(0.53 + P_{O_2})}{P_{CO}{}^2(0.85 + 0.96P_{O_2})}$	$+,*,/\,,x^2$	30	17
7	$r_{CO_2} = \dfrac{0.78\,P_{O_2}}{P_{CO}(0.38 + P_{CO})}$	$+,*,/\,,x^2$	30	9
8	$r_{CO_2} = \dfrac{0.76\,P_{O_2}}{P_{CO}{}^2}$	$+,*,/$ $,x^2$	30	7
9	$r_{CO_2} = \dfrac{0.82\,P_{O_2}}{P_{CO}{}^2}$	$+,*,/\,,x^2$	30	9
10	$r_{CO_2} = \dfrac{P_{O_2}{}^2(0.37 + P_{O_2})}{P_{CO}{}^2(1.3 + P_{O_2})^2}$	$+,*,/\,,x^2$	30	16
11	$r_{CO_2} = \dfrac{0.75\,P_{O_2}}{P_{CO}{}^2}$	$+,*,/\,,x^2$	30	6
12	$r_{CO_2} = \dfrac{P_{O_2}}{0.79P_{CO}P_{O_2} + 0.79\,P_{CO}{}^2}$	$+,*,/\,,x^2$	30	9
13	$r_{CO_2} = \dfrac{0.76\,P_{O_2}}{P_{CO}{}^2}$	$+,*,/\,,x^2$	30	7
14	$r_{CO_2} = \dfrac{0.75\,(0.26 + P_{O_2})}{P_{CO}{}^2}$	$+,*,/\,,x^2$	30	10

F*: Function, G*: Generation, C*: Complexity

4.3.5. Evaluation of Plausible Models for Pt/γ- Al$_2$O$_3$ Catalyst

In order to examine the models in terms of fitting with the experimental rates, the rate comparison was made and the results showed nearly exact match of the models with the experimental values. All models have R^2 values above 0,9 and the values were coinciding.

Table 4.10. R^2 values of the models

Model No	R^2	Model No	R^2
1	0.991	8	0.991
2	0.991	9	0.991
3	0.991	10	0.991
4	0.991	11	0.991
5	0.991	12	0.990
6	0.991	13	0.991
7	0.991	14	0.991

If we look at the models individually, we can see that models 2, 4, 8, 9, 11 and 13 have exactly the same structure with each other which is proportional to P$_{O2}$ with an order of 1 and inversely proportional to P$_{CO}$ with an order of 2. This is a reasonable result and in the case of adsorption equilibrium for CO, if the O$_2$ chemisorption is considered to be the rate determining step and CO adsorbed on platinum site is the most abundant reaction intermediate. Then the rate equation takes the structure of the models discussed above. (Oran, 2001).

By considering the remaining models, it can be seen that the different structures were also created with the same partial pressure orders. In addition to the proper structure, they are also proved to have a very good fit with the experimental rates by achieving fitting with the R^2 above 0.9 . Figure 4.7 shows the degree of the match of the model 2 and the experimental values.
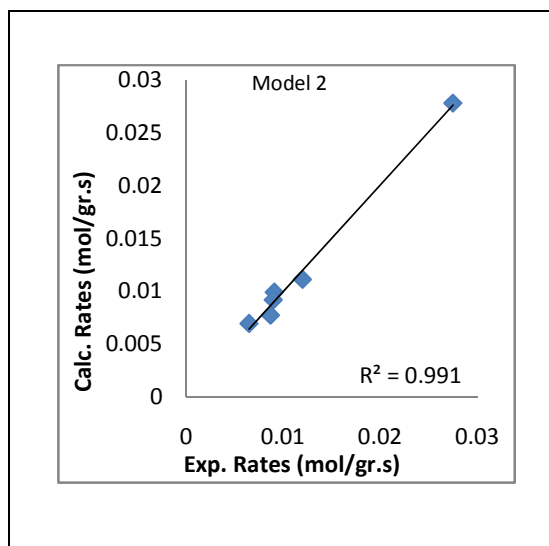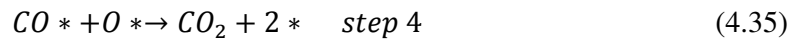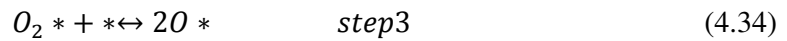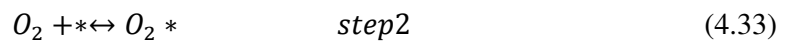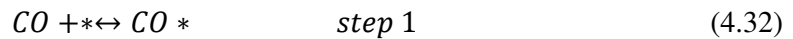
Figure 4.7. Calculated rates vs experimental rates of model 2

However, although good match of the models with the experimental rates was achieved, the exact match of the remaining models with the literature could not be found. Therefore, from the models created for CO oxidation with Pt/CeO_2 catalyst, only the models 2, 4, 8, 9, 11 and 13 whose structures are the power law models, have a plausible pathway. For the models created from Oran's study, the results are satisfying but, it would be better to develop rate expressions matching with the literature in the form of a Langmuir Hinshelwood model rather than the power law model. The Langmuir Hinshelwood models provide a better structure by means of adsorption groups or driving forces. However, this type of models could not be derived exactly. There are similar models of this type, but the constants and their proportionality does not exactly satisfy the needs of LH type models. The lack of enough data can be a reason for these derivations. Because, 5 different data points were taken for CO partial pressure with constant oxygen pressure and vice versa. Therefore only 10 data points were used during model creation with five constant oxygen and five constant CO partial pressures for Pt/CeO_2 catalyst. This comment is also valid for model creation of CO oxidation with $Pt/\gamma-Al_2O_3$ catalyst, only six data points with three constant oxygen and three constant CO partial pressures were used. This can be the reason for achieving results fitted only to the power law models.

4.3.6. Pathway Analysis of the Models for Pt/γ-Al₂O₃ Catalyst

From the models created for CO oxidation with Pt/CeO_2 catalyst, the models 2, 4, 8, 9, 11 and 13 whose structure is a power law model, have a plausible pathway. These six models have the same structure and nearly the same kinetic factors. Therefore only the pathway of model 2 was analyzed here.

$$CO + * \leftrightarrow CO* \qquad step\ 1 \qquad (4.32)$$
$$O_2 + * \leftrightarrow O_2* \qquad step2 \qquad (4.33)$$
$$O_2* + * \leftrightarrow 2O* \qquad step3 \qquad (4.34)$$
$$CO* + O* \rightarrow CO_2 + 2* \qquad step\ 4 \qquad (4.35)$$

In the case of adsorption equilibrium for CO and O_2, if the dissociation of O_2* (step3) is considered to be rate determining and under the condition CO poisons the surface, then the reaction rate can be found as;

$$r_{CO_2} = \frac{k_3\,K_2\,P_{O_2}}{(K_1\,P_{CO})^2} \qquad (4.36)$$

which is the same model with the one proposed by Oran (2001) in equation 2.39.

4.4. Modeling of Experimental Data Taken from Nibbelke *et al*. (1997) for Pt/Al₂O₃ catalyst

The last experimental data taken from the literature were the study of Nibbelke *et al* (1997). In their article, the oxidation of CO by O_2 over Pt/γ-Al₂O₃ catalyst is presented. The kinetic experiments were carried out in an isothermal fixed-bed micro reactor in the absence of mass and heat transfer limitations and in the temperature range from 436 to 503°K. CO and O_2 inlet partial pressures were between 0.12 and 8.3 kPa and H_2O and CO_2 inlet partial pressures were between 0 and 10 kPa. For the Pt/γ -Al₂O₃ catalyst, the CO_2 production rate was found to be directly proportional to the oxygen and inversely proportional to the carbon monoxide partial pressures. The rate expressions obtained by

Nibbelke *et al.*(1997) were given in equations 2.17 through 2.19. Also it was stated that, at large CO and small O_2 partial pressures, the deviations were occurred. The rate expression results obtained in this work by using genetic programming also showed similarities in terms of the proportionality and the powers of the oxygen and carbon monoxide partial pressures with the rate expressions presented by the authors mentioned above.

4.4.1. Generating Plausible Models

First of all, various combinations of functions were selected in every trial to obtain different model equations but 2 functions (*, /,) were always kept in the list to obtain the right structure of the rate expression. The generation number was also varied between 25 and 150. The reason is that, at 25 generations, the results were having nearly the same structure leading to similar results, and increasing the number of generation provided the change in the structure of the expressions. The reason of this similarity may be the excessive number of experimental data. Because, the experimental data obtained from Nibbelke *et al.* (1997) was nearly six times more than the other works and due to the nature of the program, each point in the training data is tried to be represented exactly in the model, the variety of the results were a few limited in order to generate an exact model of the data. However, increasing the generation number eliminated the similarity problem and the variance of the results was increased. It can be seen in the rate expressions obtained, the models from 5 to 10 have all similar structures indicating both CO and O_2 was adsorbed on the catalyst sites and the rate of the reaction was directly proportional with O_2 partial pressure existing in the driving force group. However, other models showed different structures and mechanisms by having different constitutions.

In spite of having similar structures, the proportionality of the equations was in good agreement with the equation proposed in the study of Nibbelke *et al.* (1997). As it was mentioned in their work, the kinetic models were generally found to be proportional with oxygen partial pressure and inversely proportional with CO partial pressure.

Table 4.11. List of models, functions used, number of generations selected and complexity of the models

Model No	Model	F*	G*	C*
1	$$r_{CO_2} = \frac{0.006\ P_{O_2}^{1/2}}{P_{CO}^{1/2}}$$	$+,-,*,/,x^2,x^{1/2}$	100	8
2	$$r_{CO_2} = \frac{0.04\ P_{O_2}}{1 + 3.2P_{O_2} + 3.2P_{CO}}$$	$+,*,/,x^2$	150	11
3	$$r_{CO_2} = \frac{0.007\ P_{O_2}}{0.00016P_{CO}^6 + P_{CO}}$$	$+,*,/,x^2,x^{1/2}$	150	14
4	$$r_{CO_2} = 0.0033\left(0.159 + P_{O_2} + \frac{0.328}{P_{CO}^{1/2} - 0.7}\right)^{1/2}$$	$+,-,*,/,x^2,x^{1/2}$	100	19
5	$$r_{CO_2} = \frac{0.01\ P_{O_2}}{\left(0.67P_{O_2} + P_{CO}\right)}$$	$+,*,/$	30	7
6	$$r_{CO_2} = \frac{0.0087\ P_{O_2}}{\left(0.46\ P_{O_2} + P_{CO}\right)}$$	$+,*,/$	25	9
7	$$r_{CO_2} = \frac{0.014\ P_{O_2}}{\left(P_{O_2} + 1.3P_{CO}\right)}$$	$+,*,/$	25	11
8	$$r_{CO_2} = \frac{0.00004\ P_{O_2}}{\left(1 + P_{O_2} + P_{CO}\right)}$$	$+,/,*$	150	11
9	$$r_{CO_2} = \frac{0.096\ P_{O_2}}{\left(0.58\ P_{O_2} + P_{CO}\right)}$$	$+,/,*$	25	7
10	$$r_{CO_2} = \frac{0.014\ P_{O_2}}{\left(0.8P_{O_2} + 1.48P_{CO}\right)}$$	$+,/,*$	25	15
11	$$r_{CO_2} = \frac{0.016\ P_{O_2}}{\left(0.74P_{O_2} + 2P_{CO}\right)}$$	$+,/,*$	25	9
12	$$r_{CO_2} = \frac{0.033\ P_{O_2}}{\left(1 + 1.6P_{O_2} + 3.3P_{CO}\right)}$$	$+,/,*$	25	11
13	$$r_{CO_2} = \frac{0.0069(P_{O_2} + 0.81)}{\left(1 + 1.18\ P_{CO}\right)}$$	$+,/,*$	25	11

Table 4.11 Continued

Model No	Model	F*	G*	C*
14	$$r_{CO_2} = \dfrac{0.14\, P_{O_2}\, P_{CO}}{\left(P_{O_2} + 3.8 P_{CO}\right)^2}$$	+,/,*	25	17
15	$$r_{CO_2} = \dfrac{4.3\, P_{O_2}}{\left(1 + 4P_{O_2} + P_{CO} + PO2^{1/2}\right)}$$	+,/,*x²,x^{1/2}	30	19
16	$$r_{CO_2} = \dfrac{0.02 P_{O_2}\, P_{CO}}{\left(1 + P_{O_2} P_{CO} + 2 P_{CO}{}^2\right)}$$	+,/,*	25	23
17	$$r_{CO_2} = \dfrac{0.01 P_{O_2}\, P_{CO}}{\left(P_{O_2} P_{CO}{}^{1/2} + P_{CO}{}^2\right)}$$	+,/,*x²,x^{1/2}	25	12
18	$$r_{CO_2} = \dfrac{0.033 P_{O_2}\, P_{CO}}{\left(0.64 P_{O_2}{}^2 + 4P_{CO}{}^2 + 0.36 P_{O_2}\right)}$$	+,/,*	30	23

F*: Function, G*: Generation, C*: Complexity

By considering the models, it can be seen that model 3 and 4 were failed to represent a rate model due to the structure. In model 3, the order of CO was found as 6 which is an inappropriate and unrealistic situation. Also, the structure of model 4 was disagreeable by having a summation term with a constant number. Therefore these models were both eliminated in finding the suitable mechanisms.

In this derivations, the majority of the results were found appropriate and in agreement with the literature in terms of structure and reaction orders. The adsorption terms of the models, especially models 12, 13, 15 and 16, have a good structure and shape. Also, the partial pressures of CO and O_2 were in proper places and orders. However, exact match of the models with the literature (Equation 2.17-2.19) could not be found.

4.4.2. Evaluation of Plausible Models

In order to have a better understanding of the models, the comparisons were made with the experimental results in terms of R^2 values.

Table 4.12. R^2 values of the models

Model No	R^2	Model No	R^2
1	0.824	10	0.797
2	0.718	11	0.827
3	0.886	12	0.753
4	0.325	13	0.811
5	0.798	14	0.753
6	0.813	15	0.562
7	0.775	16	0.613
8	0.709	17	0.699
9	0.798	18	0.739

All data points were read from rate versus partial pressure graphs stated in the study of Nibbelke *et al*. (1997) and rate data points at very low pressures were not taken into account during modeling and comparison since they cause significant error. It was seen that the rates of the models are in agreement with the experimental results. Only the model 4, showed lower agreement in terms of R^2 values which is an expected result. Model 4 can not be treated as a rate model due to the irrelevant structure and inaccurate representation. It was also obvious from the model but R^2 proved the irrelevancy. The remaining models have a good shape and structure with acceptable R^2 values.

4.4.3. Pathway Analysis of the Models

No definitive pathway could be determined for this data set.

5. CONCLUSIONS AND RECOMMENDATIONS

5.1. Conclusions

The kinetic modeling of CO oxidation was performed by using genetic programming. In order to have a basic understanding in deriving rate expressions by using GP, the generic reactions were used first and the successful models were obtained with appropriate functional groups consisting of different combinations of rate and equilibrium constants and the power of partial pressures. Secondly, CO oxidation reaction was modeled and appropriate model equations were proposed in this study. Three different experimental data, one of which obtained in our laboratory and the remaining two were obtained from the literature over various catalytic systems were used. After generating the plausible model equations, they were tested by comparing with the experimental results and the other models proposed in the literature. The appropriate models were also analyzed to understand the mechanism of the reaction. The major conclusions that can be drawn from this study are given as follows:

- The models derived using genetic programming verified that this technique can be very useful to identify the rate expression structures and the groups that describe the main features of the rate equation.
- The models created with the low complexity values were generally giving the power law model equations whereas the models with higher complexities were giving the LH type equations.
- The modeling parameters have an important role in the models. Therefore, if the expected nature of the model is known; the evolutionary process can be more efficient. Also reducing the program size provides simpler results and keeping the results as small as possible helps to have a better understanding of the mechanism of the reaction.
- The experimental data used have an important effect on the results. The increase in the errors of the experimental data or lack of sufficient data can cause poor match of the results.

5.2. Recommendations

By evaluating the results of the present work, the following recommendations for further studies can be done:

- In order to derive all models in the form of a rate equation with appropriate functional groups more easily, modular genetic programming software can be used. By this way, it would be much easier to create rate expressions with well defined structure and there would be no need to derive so many models in order to obtain the right structure.
- The kinetic modeling of different kind of reactions by genetic programming can be done with the excessive data. This can help to understand the method better.

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