KNOWLEDGE EXTRACTION FOR THE STEAM REFORMING OF METHANE FROM THE PUBLISHED PAPERS IN THE LITERATURE USING DATA MINING TECHNIQUES

by

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ABSTRACT

KNOWLEDGE EXTRACTION FOR THE STEAM REFORMING OF METHANE FROM THE PUBLISHED PAPERS IN THE LITERATURE USING DATA MINING TECHNIQUES

The aim of this thesis is to extract a general knowledge about the steam reforming of methane and to create models representing the data accumulated in the literature. The experimental data were collected from published articles in the literature. The conversion of methane was modeled as a function of various catalyst preparation and operational variables using decision tree classification and artificial neural networks, which were created by writing computer codes in MATLAB environment. Decision tree analyses for methane conversion were performed for the entire data, for Ni, Ru and Rh based catalysts, incipient to wetness impregnation method data and packed bed reactor data, separately. Analysis of total data resulted in 20.83% training error and 22.91% testing error. 21.41% training error and 24.52% testing error were obtained for Ni metal based data. 6.68% and 8.93% errors were found for training and testing of Rh metal based data. 8.03% training error and 14.77% testing error were calculated for Ru metal based data. Training error and testing error of incipient to wetness impregnation method data were 11.47% and 14.50%. For packed bed reactor data, training error and testing error were 20.01% and 21.78. The neural network analysis was also performed and the optimal neural network topology was found as 59-16-16-1 (59 input neurons, 16 neurons each in the first and second hidden layers and 1 output; with the activation function of hyperbolic tangent sigmoid function for all the layers), where “trainlm“ and “trainbr” functions were used for training and testing respectively. R^2 and RMSE values of training were found to be 0.97 and 6.03, whereas they were 0.93 and 8.78 for testing. Then, an input significance analysis was performed and it was found that base metal type within the input variables had the most significant effect on the methane conversion while catalyst preparation method was the least important parameter. Finally, the optimal neural network was forced to predict the results of experiments by using the data of the other experiments in the database. RMSE and R^2 were 69.6% and 9.03% for experiments and 44.07% and 18.64% for articles, respectively.

ÖZET

LİTERATÜRDE YAYINLANMIŞ MAKALELERDEN VERİ MADENCİLİĞİ TEKNİKLERİ KULLANARAK METAN BUHAR REFORMU İLE İLGİLİ BİLGİ ÇIKARIMI

Bu tezin amacı metan buhar reformu ile ilgili bilgi çıkarımı yapmak ve literatürden elde edilmiş verileri temsilen modeller oluşturmaktır. Deneysel veriler literatürde yayınlanmış makalelerden toplanmıştır. Metan dönüşümü, MATLAB'de yazılan bilgisayar kodlarınca oluşturulmuş karar ağacı sınıflandırması ve yapay sinir ağları kullanılarak çeşitli katalizör hazırlama ve operasyonel değişkenlerine bağlı bir fonksiyon gibi modellenmiştir. Metan dönüşümü için karar ağacı analizleri tüm verilere, Ni, Ru ve Rh metali tabanlı katalizörlere, emdirme yöntemli ve dolgulu reaktörlü verilere ayrı ayrı uygulanmıştır. Tüm verilerin analizi %20.83 eğitici hata yüzdesi ve %22.91 test hata yüzdesi ile sonuçlanmıştır. Ni metal tabanlı veriler için %21.41 eğitici hata yüzdesi ve %24.52 test hata yüzdesi elde edilmiştir. Rh metal tabanlı veriler için eğitici hata yüzdesi ve test hata yüzdesi %6.68 ve %8.93 bulunmuştur. Ru metal tabanlı veriler için %8.03 eğitici hata yüzdesi ve %14.77 test hata yüzdesi hesaplanmıştır. Emdirme yöntemli verilerin eğitici hata yüzdesi ve test hata yüzdesi %11.47 ve %14.5'tir. Dolgulu reaktör verilerinin eğitici hata yüzdesi ve test hata yüzdesi %20.01 ve %21.78'dir. Sinir ağı analizi de gerçekleştirilmiştir ve en uygun sinir ağı topolojisi, eğitici analizde "trainlm" ve test analizinde "trainbr" fonksiyonunun kullanıldığı, 59-16-16-1 (59 giren nöron, ilk ve ikinci saklı katmanın her birinde 16 nöron ve 1 sonuç; her katman için aktivasyon fonksiyonu hiperbolik tanjant sigmoid fonksiyonu) olarak bulunmuştur. Eğitici sinir ağı modelinin R^2 ve RMSE değerleri 0.97 ve 6.03 bulunurken test sinir ağı modelininki 0.93 ve 8.78 çıkmıştır. Girenlerin önem analizi sonucunda, giriş değişkenleri arasında metal türü metan dönüşümü üzerinde en önemli etkiyi göstermiştir. Katalizör hazırlama metodu ise en az önemli değişken olarak bulunmuştur. Son olarak, en uygun model, deneylerin sonuçlarını veritabanındaki diğer deneyler kullanılarak tahmin etmeye zorlanmıştır. RMSE ve R^2 %69.6 ve %9.03 çıkmıştır. Makaleler için de yapıldığında bu oranlar sırasıyla %44.07 ve %18.64 olarak bulunmuştur.

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LIST OF SYMBOLS

R^2	Coefficient of determination
Σ	Combination function
Φ	Measure of "goodness"
δ	Responsibility for a particular error
η	Learning rate
$\int$	Activation function

LIST OF ACRONYMS/ABBREVIATIONS

Calh	Calcination time
CalT	Calcination temperature
CART	Classification and regression tree
FBR	Fixed bed reactor
PBR	Packed bed reactor
pro	Promoter
Red	Reduction
Redh	Reduction time
RedT	Reduction temperature
RMSE	Root mean square error
SMR	Steam methane reforming
SSE	Sum of squared errors
T	Temperature
TOS	Time on stream
WGS	Water gas shift reaction
W/F	Catalyst weight / feed flow rate

1. INTRODUCTION

In parallel with increasing living standard in developing and developed nations, energy demands began to rise. Today most of the demand is fulfilled by the combustion of fossil fuels, which is a process resulting the emission of large volumes of greenhouse gases such as carbon dioxide. Thus, the people have realized that production of the energy must bring on significantly lower greenhouse gas emissions. By searching alternative technologies and renewable energy sources, the most proper process has been aimed in order to overcome these types of problems.

Hydrogen is known as a principal feedstock for major petrochemical, chemical, foods, and refining industries. After many researches, it is also considered as a pollution free energy career alternative for future applications. Both refineries and chemical companies use H_2 for the production of commodity, fine and specialty chemicals, such as pharmaceuticals and applications for synthesis gas (Armor, 1999; Rostrup-Nielsen, 2000).

Steam reforming of hydrocarbons is one of the processes which have been utilized to produce hydrogen in industrial ammonia synthesis and other applications. The fuel cells, which are considered as important technical developments to produce pollution free electricity, also mostly use hydrogen. In the current situation, 96% of the world's hydrogen demand is supplied by catalytic steam reforming (SR) of hydrocarbons and about half of this correspond to steam reforming (SR) of natural gas (Armor, 1999; Rostrup-Nielsen, 2000).

Steam reforming is the most vital route to convert CH_4 (methane) and H_2O (steam) into H_2 (hydrogen) as a green energy carrier and CO (carbon monoxide) as a by-product. There are two steps in steam reforming of methane. Steam methane reforming (SMR) reaction and water gas shift reaction (WGS) are carried out respectively. The steam methane reforming reaction step is endothermic, so the process is usually maintained at approximately 850°C to obtain desirable conversion levels. In order to increase amount of hydrogen, more steam is added and the water gas shift reaction is performed exothermically as the second step. Conventionally, multi-tubular fixed-bed reactors in the

presence of a metal catalyst are preferred for these reactions. Since overall steam reforming reaction is highly endothermic, the system is maintained at high temperature (700-900 °C) to reach a successful reaction with high conversion levels (Gallucci *et al.*, 2004; Gallucci *et al.*, 2006).

High level of the temperature yields some negative results because of expensive tubular reformers made of high alloy nickel chromium steel with fire burners, irreversible carbon formation in the reactor, and large energy consumption. If the reaction temperature is decreased to a lower level, although this seems like energetically and economically desirable, the conversion level reached at the end of the process becomes insufficient for the industrial process (Tong and Matsumura, 2005).

The most common catalysts are nickel-based, which encounter severe deactivation by coke deposition; during the reaction, coke is formed at high temperatures on both nickel and on the metal-support interface, causing the loss of small metallic particles from the support. Although rhodium and ruthenium are more active, the nickel-based catalysts are always preferred due to their lower cost in comparison with noble metals (100–150 times less expensive than noble metals). Thus, from an industrial point of view, the development of nickel catalysts with greater resistance to coking is an attractive research goal nowadays. In commercial catalyst, Ni can also be supported on metal oxides such as Al_2O_3, MgO, $MgAl_2O_4$ or their mixtures. As a result, the selection of the catalyst support as well the dispersion of the active metal have a crucial role in the chemical reactions involved in steam reforming of methane (Gallucci *et al.*, 2004; Gallucci *et al.*, 2006; Neto *et al*., 2007).

In the literature, a huge amount of experimental studies about steam reforming of methane have been reported. As a result of different studies from literature, it was realized that there are many parameters which affect the results of the chemical reactions involved in steam reforming of methane. These parameters are simply the types of base metals, catalyst preparation methods, calcination and reduction properties, the type of supports or promoters, feed compositions, time on stream, W/F ratio (catalyst weight/feed flow rate), temperature, pressure, and reactor types. By benefiting from data mining tools, some valuable knowledge can be extracted from this huge amount of experimental studies and can be used to improve the catalyst further.

Data mining can be explained as the science and technology of exploring data in order to discover previously unknown patterns in databases. It provides the discovery of useful information such as correlations, trends and patterns by using statistical and mathematical methods (Rokach and Maimon, 2008). Some of the common data mining tools are clustering, classification, prediction, multiple linear regression, decision trees, k-nearest neighbor algorithm, and artificial neural networks. Decision tree classification involves the construction of a tree composed of a collection of decision nodes, connected by branches, extending downward from the root node until terminating in leaf nodes. The terminal nodes of a tree are often called the "leaves" and these leaves include the main information that is conveyed by a tree model analysis. Artificial neural networks represent an attempt at a very basic level to simulate the type of nonlinear learning in the networks of neurons found in nature (Larose, 2005; Romero and Ventura, 2007).

According to studies of Günay and Yıldırım, an artificial neural network modeling for their experimental studies on selective CO oxidation over "Pt-Co-Ce/Al_2O_3" catalysts investigated the effects of all design parameters (such as Pt wt. %, Co wt. %, Ce wt. %, calcination temperature and time) on the process. As a result, the most significant input parameter was found as Pt wt. % and the model predictions for the effects of these parameters were also in a good agreement with the experimental results (Günay and Yıldırım, 2008).

In studies of Odabaşı *et al.*, decision trees, support vector machines (SVM) and artificial neural networks (ANN) techniques were performed for a database containing water gas shift reaction over noble metal catalysts (Pt and Au). Decision trees determined the empirical rules and conditions that lead to high catalytic performance (high CO conversion); artificial neural networks (ANNs) decided the relative importance of various catalyst preparation and operational variables and their effects on CO conversion; the support vector machines (SVMs) predicted the outcome of unstudied experimental conditions. As a result, the combination of these three models showed that knowledge extraction from the past published works can be successfully performed (Odabaşı *et al.*, 2014).

This thesis is composed of four main chapters starting from "Thesis Background" (Chapter 2) in which detailed information about reaction are given in "Steam Reforming of

Methane (Section 2.1 and 2.2); data mining fundamentals, decision trees, classification algorithm, neural network algorithm and their characteristics are summarized in “Data Mining Methods for Knowledge Extraction” (Section 2.3). The rule deduction is briefly explained in “Knowledge Extraction by Using Data Mining Methods” (Section 2.4). In Chapter 3, the details related to the collection of the data and construction of the database is given together with the computational details for the decision tree and artificial neural networks. In Results and Discussion (Chapter 4), results of decision tree and neural network analysis are presented and discussed in details. Finally in Conclusion and Recommendation (Chapter 5), the outcomes are summarized and some recommendations are given for future studies.

2. THESIS BACKGROUND

2.1. Steam Reforming of Methane

Steam reforming is the most vital route to convert methane (CH_4) and steam (H_2O) into hydrogen (H_2) as a green energy carrier product. The chemical reactions involved in steam reforming of methane are indicated as follows:

Steam methane reforming (SMR) reaction:

$$CH_4 + H_2O \leftrightarrow CO + 3H_2 \qquad \Delta H_{298} = 206 \text{ kJ/mol} \quad (2.1)$$

Water gas shift reaction (WGS):

$$CO + H_2O \leftrightarrow CO_2 + H_2 \qquad \Delta H_{298} = -41 \text{ kJ/mol} \quad (2.2)$$

Overall Steam Reforming Reaction:

$$CH_4 + 2H_2O \leftrightarrow CO_2 + 4H_2 \qquad \Delta H_{298} = 165 \text{ kJ/mol} \quad (2.3)$$

The steam methane reforming reaction is the main reaction and it has a positive heat of reaction value (endothermic). In addition to steam methane reforming reaction, water gas shift reaction is performed by addition of steam in order to produce more hydrogen and to reduce carbon formation has a negative heat of reaction value (exothermic). In total, overall methane steam reforming reaction is a highly endothermic process. Thus, the process is usually maintained at high temperatures (700-900 °C) to achieve desirable and high conversion levels (Gallucci *et al*., 2006).

2.2. Influencing Factors on Methane Steam Reforming

2.2.1. Base Metal

During steam reforming of methane, one of the most important parameters is base metal type used in the catalyst structure. Several types of base metals have been used and experienced in this process. The influence of metal loading percentages has been compared to determine the best base metal type with the best amount.

According to Kusakabe *et al.*, Pt, Ru and Rh catalysts were examined as the metal loading in subsequent experiments was fixed at 3 wt.% on the $Ce_{0.15}Zr_{0.85}O_2$ support. The supported Rh catalysts had the highest activity in the temperature range of 500–800°C in terms of CH_4 conversion. CH_4 conversion on 10 wt% $Ni/Ce_{0.15}Zr_{0.85}O_2$ was lower than those of noble metal catalysts in spite of its higher metal loading (Kusakabe *et al.*, 2004).

The activity of nickel supported on zirconium oxide was found to be high and stable in the study of Matsumura and Nakamori. Even the catalyst containing 5 wt.% of nickel (5 wt.% Ni/ZrO_2) produced a higher activity than that with 20 wt.% Ni/Al_2O_3. An increase in the content of nickel affected the activity of the catalyst positively (Matsumura and Nakamori, 2004).

In a set of experiments, $10\%Ni/ZrO_2$, $15\%Ni/ZrO_2$, $20\%Ni/ZrO_2$, $25\%Ni/ZrO_2$, and $30\%Ni/ZrO_2$ were compared. The sample $15\%Ni/ZrO_2$ is the best catalyst among the catalysts tested in this study in terms of activity and stability for MSR at 600°C (Nguyen *et al*., 2008).

2.2.2. Catalyst Preparation Method

Catalysts are obtained according to some common or some special preparation methods. In this project, catalyst preparation methods were collected under the nine titles as commercial, incipient to wetness impregnation, wet impregnation, co-impregnation, seq-impregnation, co-precipitation, sol gel precipitation, deposition precipitation and others. In some articles, catalysts are taken commercially without defining preparation method, which are categorized as “commercial” in the database and “others” are unique methods improved by some people, remaining methods are commonly used methods in the literature to create a catalyst.

In the study of Matsumura and Nakamori, nickel catalysts were prepared by an impregnation technique. Metal oxide supports such as γ-alumina, silica and zirconia were impregnated with nickel nitrate by evaporation of the aqueous solution at 80°C. They were dried in air at 110°C overnight and then they were heated at 700°C for 3 h. The samples (Ni/Al_2O_3, Ni/SiO_2, and Ni/ZrO_2, respectively) contained 5–20 wt.% of nickel (Matsumura and Nakamori, 2004).

Wang *et al*. examined a series of Rh/MgO–Al_2O_3 catalysts with varying Rh loadings (1, 5, and 10 wt%) and 6 wt% MgO. The catalysts were prepared by an incipient wetness method. Following the calcinations, an aqueous solution of magnesium nitrate hexahydrate was impregnated onto the calcined alumina then dried under vacuum at 110°C for 8 h and calcined at 900°C for 2 h. The resulting MgO–Al_2O_3 was further impregnated with Rh nitrate solution, then dried at 110°C and calcined at 500 8C for 3 h (Wang *et al*., 2004).

Some perovskite-type oxides including $LaAlO_3$ and $LaFeO_3$ were prepared by the sol–gel method. The metal nitrates were dissolved into water; then excess amounts of citric acid and ethylene glycol were added to the solutions. The molar ratio of total metal ion:citric acid:ethylene glycol was 1:3:3. The obtained solutions were evaporated until gel like materials were formed (Urasaki *et al.*, 2005).

The co-precipitated 2(Ni_xMg_v)/Al, 2($Ni_{0.05}M_{0.05}Mg_{0.9}$)/Al and impregnated Ni/MgO, Ni-M/MgO (M=Fe or Cu) catalysts were tested in the steam reforming of methane at 600-800°C and CH_4/H_2O=1:1 and 1:3. Co-precipitated catalysts resulted in higher CH_4 conversion than the impregnated catalyst (Djaidja *et al.*, 2006).

2.2.3. Calcination and Reduction

After preparation of catalyst, they are calcined in order to drive off water or to drive off carbon dioxide or other volatile constituents or to oxidize a part or the whole of the substance and they are also reduced. Calcination is heating the catalyst to high temperatures in the presence of air or oxygen for a certain time. Reduction is carried out in H_2 at a certain temperature for a certain time via a reducing agent (Ar, He or N_2).

In the study of Matsumura and Nakamori, no catalytic activity was found with 20 wt.% Ni/Al_2O_3 pretreated with hydrogen at 500°C for 1 h, but the catalyst reduced at 700°C was quite active (Matsumura and Nakamori, 2004).

In the study of Wang *et al*., catalysts were reduced in situ under pure H_2 at 350°C for 2 h (Wang *et al*., 2004). Urasaki *et al*. calcined the catalysts at 673 K for 2 h and reduced them in a hydrogen stream at 1073 K for 1 h (Urasaki *et al.*, 2005).

2.2.4. Support and Promoter

In the structure of a catalyst, supports and promoters are also used to increase the activity of the catalyst. Supports enhance the effectiveness and minimize the cost by dispersing on a second material. Supports decrease agglomeration and sintering of the small catalyst particles, exposing more surface area. The catalyst may be spread to increase the surface area on the surface of the support. The role of promoters is to prevent production of a mat of coke, or such material by covering up surface. They can aid the dispersion of the catalytic material as well bind to reagents.

Ceria–zirconia mixed oxide-supported metal catalysts are of interest because of their oxygen storage properties. In addition, ceria enhances a better catalytic activity at lower temperature by stabilizing metal dispersion. When Ni-loaded Ce–ZrO_2 was applied to the steam reforming of methane reaction, a higher catalytic activity and a higher stability than conventional catalysts were obtained (Kusakabe *et al.*, 2004).

Ru was used as promoter in Ni catalysts supported on Al_2O_3 or $MgAl_2O_4$. The Ni catalysts promoted with a small amount of Ru (≤1 wt%) showed a moderate reforming activity without a pre-reduction treatment using H_2; whereas the Ni catalysts unpromoted with Ru were active only after reducing the catalysts with H_2. The catalyst prepared by sequentially impregnating Ru showed higher reforming activity than the catalyst prepared by the co-impregnation. Between the two support materials, $MgAl_2O_4$-supported catalysts were more active than Al_2O_3-supported catalysts (Jeong *et al.*, 2006).

CeO_2 has been used either as a support or as a promoter due to its positive effects on the reactivities of Ni-based catalysts in methane reforming. Ni/SBA-15 catalysts, in which Ni contents ranged from 5wt% to 20wt%, as well as 10wt%Ni/10wt%$Ce_xZr_{1-x}O_2$/SBA-15 (x=0, 0.5, 1) catalysts were compared in terms of the catalytic performances for steam reforming of methane. Here, SBA-15 was a support material. As a result, both Ni/SBA-15 and Ni/$Ce_xZr_{1-x}O_2$/SBA-15 catalysts indicated higher CH_4 conversions under the given reaction conditions (Wan *et al.*, 2007).

A series of 15 wt% Ni/γ -Al_2O_3 catalysts with promoter B (boron) loadings of 0, 0.5 and 1.0 wt% were tested in a fixed-bed micro-reactor. During the 10 h reaction test, the unpromoted catalyst lost 21% of its initial activity, promotion with 0.5 wt% boron reduced

it from 21 to 14% and promotion with 1.0 wt% B further reduced the activity loss to 6%. The methane conversion for the promoted catalyst was higher than methane conversion for the unpromoted catalyst. As a result of the experiments, it was realized that promotion with 1.0 wt% B improves the stability and the residual activity of a Ni catalyst, though it does not completely prevent deactivation (Xu *et al.*, 2009).

The effects of promoters of sulfur, phosphorus, potassium, sodium, calcium and magnesium on rhodium catalysts were studied using steam methane reforming over a fixed bed of Rh/α-Al_2O_3 catalysts at 700°C. Among these promoters, sulfur decreased the methane conversion the most. While phosphorus, potassium and sodium decreased the methane conversion, calcium and magnesium caused negligible changes in methane conversion. Phosphorus resulted in formation of carbon filaments with rhodium particles at the tip which are formed by diffusion of surface carbon across the rhodium particle. Calcium and magnesium indicated negligible change on the catalytic activity of rhodium. In other components such as potassium and phosphorus, strong deactivation was observed (Chakrabarti *et al.*, 2011).

2.2.5. Feed Compositions

Feed compositions at the beginning of the reactions have also a significant effect on the results. Different carbon to steam ratios have been used in the studies, and their effects on the conversion of methane have been observed.

A stoichiometric carbon to steam ratio of 1 is the most economical condition and results in catalysts deactivatation rapidly due to deposition of graphitic carbon on catalyst surfaces. Typical steam/carbon ratio for the methane steam reforming is at least 2.5 to minimize coke formation. However, such a ratio requires higher reactor volume and steam recycling associated with the use of extra steam. The high steam/carbon ratio results also in syngas with a higher H_2/CO ratio that is not desirable for next processes such as methanol and Fischer–Tropsch synthesis in which H_2 is used as the main reactant (Wang *et al.*, 2004).

2.2.6. Time on Stream

Time on stream represent the the time period in which the reaction stream passed over the catalyst before the sample is taken, and it is the indicator of stability of catalyst.

Also, some catalysts may have high methane conversion just after starting the reaction or any other catalyst can be active after a certain time. However, the initial activity decay of the catalyst within the first 5 h can be attributed to surface restructuring and possible carbon formation (Halabi *et al.*, 2010). In another example, the methane conversion versus residence time of methane was observed in the different experimental conditions. The CH_4 conversion increases at increasing residence time and after a certain residence time, the CH_4 conversion no longer increases but reaches a quite stable value (Zeppieri *et al*., 2010).

2.2.7. W/F Ratio

W/F ratio is the catalyst weight over feed flow rate. The relation between feed amount and catalyst amount may change the results. The catalyst weight should satisfy the feed in order to reach higher conversion levels.

In a study, a Ni catalyst and a Ru doped Ni catalyst were compared. When the W/F was decreased by three times, the methane conversion over Ni catalyst declined from 97% to 61% during 90 h, whilst only a 7% (from 97% to90%) decline of methane conversion was shown over Ru doped Ni catalyst during 150 h (Zhou *et al.*, 2009).

2.2.8. Temperature

Temperature is known to be the most important variable to affect kinetic rate and composition of the product gas. Since the reaction process is endothermic, temperature level is important during reactions. Lower temperature levels are more likely to convert less CH_4.

The effect of reaction temperature on CH_4 conversion was studied. Ni/Al_2O_3 and $Ni/Ce_{0.5}Zr_{0.5}O_2$ catalysts showed no catalytic activities in the temperature ranges of 500–600°C, whereas they showed higher activities than Ni/ZrO_2, $Ni/Ce_{0.15}Zr_{0.85}O_2$ and $Ni/Ce_{0.25}Zr_{0.75}O_2$ at 800°C (Kusakabe *et al.*, 2004).

Jeon *et al.* ended up their study with the proof of the increase of CH_4 conversion as temperature increases. CH_4 conversion got changed from 70% to 98% as temperature increased from 873 to 1023K (Jeon *et al*., 2008).

2.2.9. Pressure

Steam reforming of methane process is mostly operated at atmospheric pressure. Sometimes, higher pressures are applied in some studies.

According to study of Jeon *et al*., the effect of reactor pressure on the composition of the product gas was also observed. While pressure was altering from 1.7 to 12.8 bar, the production of H_2 became lower. From these results, it could be realized that low pressure may be favored for the steam reforming of methane reactions. However, mostly reactors are operated under high pressure (15-30 bar) in order to avoid coking (Jeon *et al*., 2008).

2.2.10. Reactor Types

In general, packed bed, fluidized bed, membrane and micro reactors have been used in steam reforming of methane process.

Membrane reactors were comprised of a packed bed of catalyst and a hydrogen-selective membrane in the studies of Kusakabe *et al*.. When steam reforming of methane is operated in this membrane reactor, the hydrogen produced in the catalytic packed bed permeates through a hydrogen-selective membrane, which can reduce the reaction temperature through the influence of an increase in CH_4 conversion beyond equilibrium conditions. However, the dilution of hydrogen caused by selective hydrogen permeation from the catalytic packed bed favors coke formation. Therefore, catalysts used in membrane reactors should have high activities at low temperature and a high stability without coking (Kusakabe *et al.*, 2004).

In the study of Matsumura and Nakamori, a fixed (packed) bed continuous flow reactor in which a catalyst was placed and which is made of quartz glass was operated at atmospheric pressure (Matsumura and Nakamori, 2004).

Microchannel reactors are consisting of a large number of closely spaced channels with a gap of less than 1 mm. Heat transfer coefficients in microchannel reactors are higher compared to conventional reactors. Thus, it enhances the overall efficiency by reducing heat and mass transport distance. Microchannel reactors permit the operation of highly endothermic methane steam reforming at near isothermal conditions and provide the potential to significantly improve the efficiency of methane steam reforming process.

Methane steam reforming activity was tested in a 4 mm ID quartz microcatalytic reactor (Wang *et al*., 2004).

A fluidized bed reactor was operated with calcined natural dolomite as CO_2 sorbent and Ni/NiAl2O4 as catalyst. A steam to methane ratio was 4, temperature was 575°C and and the pressure was ambient pressure. Each run lasted 8 h. As a result of comparison fluidized bed with fixed bed reactor, kinetic data indicated that conversion levels of methane were significantly lower in our fluidized bed reactor (Arstad *et al*., 2012).

2.3. Data Mining Methods for Knowledge Extraction

Data mining can be considered as a combination of selection, exploration and modeling of large databases. As a result of data mining, previously unknown correlations, patterns and trends can be found by using statistical and mathematical methods. Therefore, data mining methods are used in order to extract knowledge from any data. Here, the most important point is that general knowledge obtained from collected database can be benefited for future studies as guidance or for new data to predict (Giudici, 2003).

According to Tufféry, data mining can be defined as the set of methods and techniques for exploring and analyzing data sets, in an automatic or semi-automatic way, to discover certain unknown or hidden rules, associations or tendencies. Data mining can be thought as the art of extracting information from data or knowledge extraction in other words. Data mining is divided into two groups as descriptive and predictive: the descriptive techniques are designed to bring out information that is present but buried in a mass of data, while the predictive techniques are designed to extrapolate new information based on the present information. Here, this new information may be qualitative as in classification or scoring or quantitative as in regression (Tufféry, 2011).

When huge amount of data have to be analyzed or a rapid determination about an issue have to be done, data mining should be used in order to reach the most accurate results. As a result of the effect of the growing power of computers on the data mining, it has become possible limit human subjectivity in decision-making processes and handle large number of files rapidly. This opportunity is widely used in different areas such as financial data analysis, telecommunication industry, biological data analysis and other scientific applications from the most general to the most specialized, from the most open to

the most secret, from the most practical to the most theoretical. Thus, various data mining techniques are developed in order to provide solutions to such an extensive demand (Tufféry, 2011).

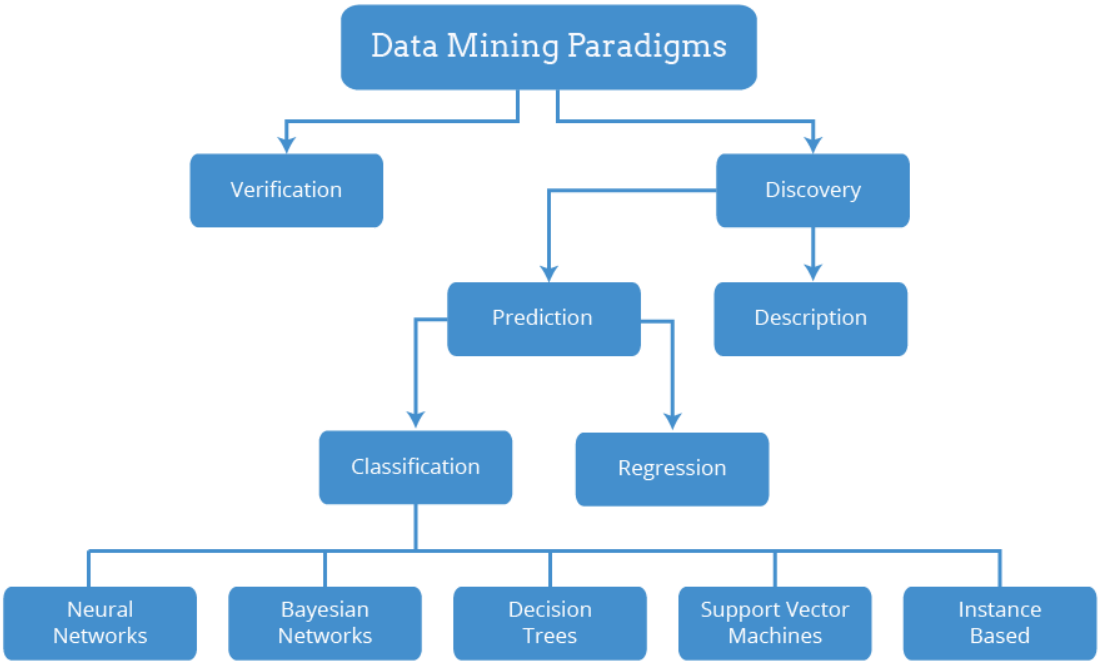

Figure 2.1. Taxonomy of data mining methods (Rokach, L. and O. Maimon, 2008).

As shown in Figure 2.1, data mining can be performed with different methods. In verification methods, the goodness-of-fit test, the t-test of means, and analysis of variance are included, but these are less related with data mining since in data mining, selecting a hypothesis is preferred rather than testing a known one. Most of the discovery-oriented methods are based on inductive learning. In inductive learning method, available training examples are categorized according to a model either explicitly or implicitly by generalization technique. As a result, the model is assumed valid for future (Rokach, L. and O. Maimon, 2008).

In my thesis, I used classification techniques in which relationship between input attributes as independent variables and a target attribute as dependent variable can be discovered by a model. The model can describe phenomena hidden in the dataset as well as it can be used for predicting the value of the target attribute when the values of the input attributes are known (Rokach, L. and O. Maimon, 2008).

2.3.1. Classification / Decision Trees

Tree models are divided into two groups as regression tress and classification trees. In regression trees, the response variable is continuous, whereas the response variable is quantitative discrete or categorical in classification trees. All tree models are created after a recursive procedure through which a set of statistical units are progressively divided into groups according to a division rule. This division rule is used to maximize a homogeneity or purity measure of the response variable in each of the obtained groups. So, at each step of the procedure, a division rule is specified by the choice of an explanatory variable to split and the choice of a splitting rule for such variable. As a result of partition of the observations, the main tree model is obtained (Giudici, 2003).

Decision tree as a classification tree involves the construction of a decision tree, a collection of decision nodes, connected by branches, extending downward from the root node until terminating in leaf nodes. Beginning at the root node, at the top of the decision tree diagram, attributes are tested at the decision nodes and then their each possible outcomes result in a branch. Each branch leads either to another decision node or to a terminating leaf node. Since terminal nodes are not further divisible, the tree stops at these nodes (Figure 2.2).The terminal nodes of a tree are often called the “leaves” and these leaves include the main information that is conveyed by a tree model analysis (Larose, 2005).

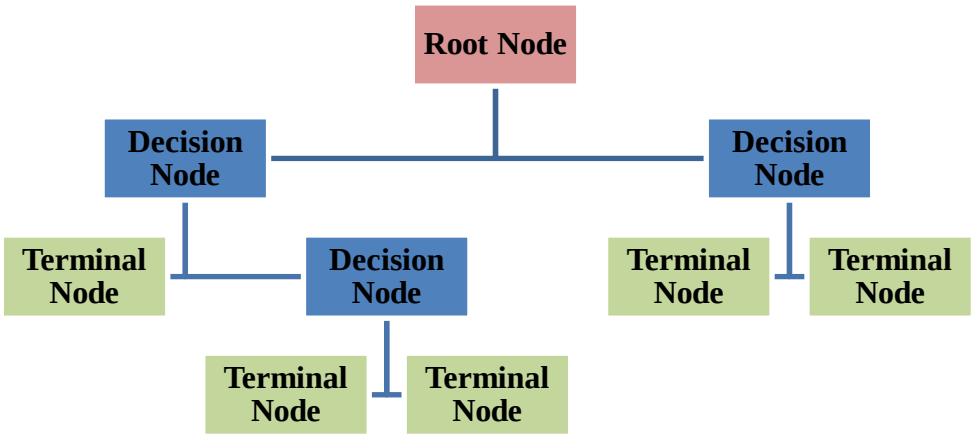

Figure 2.2. Decision tree terminology.

To apply decision tree algorithms, first of all, a training data set must be supplied in order to provide the algorithm with the values of the target variable. If the training data set is varied, the algorithm creates a reliable cross section of the types of records, which makes classification useful in the future. Otherwise, classification and prediction will be problematic or impossible. The last requirement is related with the target attribute classes. They must be discrete, not continuous to have only two choices as belonging to a particular class or not belonging (Larose, 2005).

Creating a set of leaf nodes that are as pure as possible is a key point to provide classification assignments with the highest measure of confidence available. For constructing decision trees, leaf node purity is measured by some algorithms such as classification and regression trees (CART) algorithm and C4.5 algorithm. Each instance attribute is considered such statistical algorithms to determine the best point at which the attribute can classify the training data. Then, the selected attribute is applied as the test at the root node of the tree. A descendant of the root node is formed for each possible value of this attribute and the training data are sorted to the convenient descendant node. The whole process is then repeated using the training data associated with each descendant node to choose the best attribute to test at that point in the tree. As a result of such an elaborative search, an acceptable decision tree can be obtained by using these types of algorithms which never backtracks to reconsider earlier selections (Larose, 2005; Mitchell, 1997).

When decision trees are created by CART algorithm, their models are strictly binary, containing exactly two branches for each decision node. In CART algorithm, training data set is divided into subsets with similar values for the target attribute and then tree is generated by conducting for each decision node, an exhaustive search of all available variables and all possible splitting values, selecting the optimal split according to the criteria (Larose, 2005).

$$\Phi(s|t) = 2\ P_L\ P_R \sum_{j=1}^{\#\ classes} |P\ (j|t_L) - P(j|t_R)| \tag{2.4}$$

$\Phi(s|t)$ is measure of the "goodness" of a candidate split s at node t. t_L refers left child node of node t, whereas t_R is right child node of node t.

$$P_L = \frac{number\ of\ records\ at\ t_L}{number\ of\ records\ in\ training\ set} \tag{2.5}$$

$$P_R = \frac{number\ of\ records\ at\ t_R}{number\ of\ records\ in\ training\ set} \quad (2.6)$$

$$P(j|t_L) = \frac{number\ of\ class\ j\ records\ at\ t_L}{number\ of\ records\ at\ t} \quad (2.7)$$

$$P(j|t_R) = \frac{number\ of\ class\ j\ records\ at\ t_R}{number\ of\ records\ at\ t} \quad (2.8)$$

Then the optimal split is determined when split maximizes measure of the "goodness" of a candidate split s at node t ($\Phi(s|t)$) over all possible splits at node t (Larose, 2005).

The CART algorithm should begin pruning nodes and branches, since if it memorizes the training set, the generalizability of the classification results decreases. Although obtained tree model has the lowest error rate on the training set, it may be too complex which causes overfitting. While each decision node is grown, the subset of records becomes smaller and less representative of the overall population. If tree is pruned, the generalizability of the results will increase. The data can be randomly divided into two equal sets: one set to be used for training and constructing the decision tree model while the other to be used for testing the generalization ability of the model (Larose, 2005).

The C4.5 algorithm uses the concept of information gain or entropy reduction to select the optimal split. First several candidate splits are created. A variable X having k possible values have probabilities of $p_1, p_2, \ldots, p_k$ and the entropy of X is defined as:

$$H(X) = -\sum_j p_j \log_2(p_j) \quad (2.9)$$

The candidate split S, which divides the training set into T subsets (T1, T2,…,Tk) has a total entropy calculated as:

$$H_S(T) = \sum_{i=1}^{k} P_i H_S(T_i) \quad (2.10)$$

Where, P_i represents the proportion of the records in subset i. Here gain is measured as

$$S = H(T) - H_S(T) \quad (2.11)$$

Information gain refers the increase in information produced by partitioning the training data according to this candidate split S. At each decision node, the optimal split with the greatest information gain is selected by C4.5 algorithm (Larose, 2005).

As in the CART, the C4.5 algorithm recursively visits each decision node, selecting the optimal split, until no further splits are possible. CART always produces a binary tree, whereas C4.5 produces a tree of more variable shape (Larose, 2005).

The error rate for each leaf node, that is the ratio of wrong classification results to the actual results of total data in that node, is minimized by choosing the best split. However, a large and complex tree with small error rate is not useful due to the lack of extraction ability. Therefore, the tree size should be optimized to have a sufficiently low training error and the highest generalization and extraction ability.

2.3.2. Classification / Neural Networks

Neural networks or artificial neural networks are used as a simple way in order to imitate the type of nonlinear learning which comes from the networks of neurons in nature. The main aim of training a neural network with data is creation of a model to be generalized or to obtain effective classifications and predictions when a new data are fed, so an exact representation of the training data is not expected (Giudici, 2003).

As an advantage, neural networks are quite robust with respect to noisy data. The network consists of many nodes or artificial neurons with their assigned weights for each connection, so the network can learn to work around these uninformative examples in the data set. As a disadvantage, all attribute values must be encoded in a standardized manner in neural networks by taking values between “0” and “1”, even for categorical variables and with respect to output, neural network output nodes always return a continuous value between “0” and “1”. Categorical variables with *k* classes may be translated into *k-1* indicator variables to define the definition of these indicators clearly (Larose, 2005).

In a real neuron, dendrites exist to gather inputs from other neurons and the input information is obtained by generating a nonlinear response when some threshold is reached. Then, the real neuron sends this information to other neurons via axon (Figure 2.3). In an artificial neuron, the inputs (x_i) are collected from upstream neurons (data set) and combined through a combination function “$\sum$”. After combination function, an

activation function "∫" is carried out to obtain an output response (y), which is then channeled downstream to other neurons (Larose, 2005).

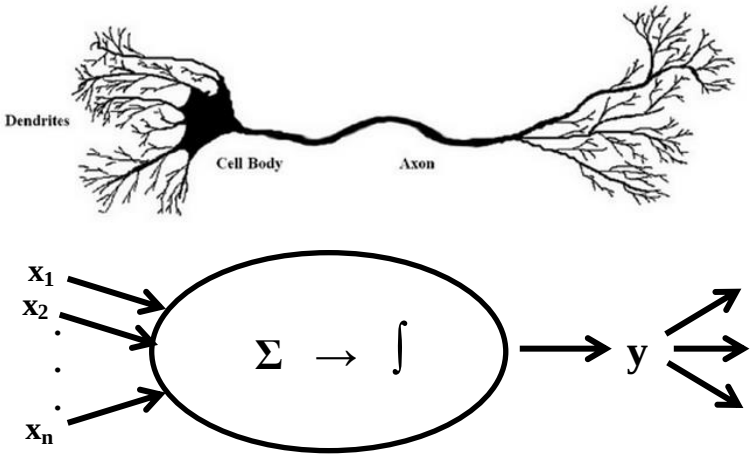

Figure 2.3. Real neuron and artificial neuron model (Larose, 2005).

A feedforward neural network consists of layers composed of completely connected network of artificial neurons or nodes. The nodes of neural networks are organized in layers. Mostly, three layers as input layer, hidden layer and output layer are used, as indicated in Figure 2.4.

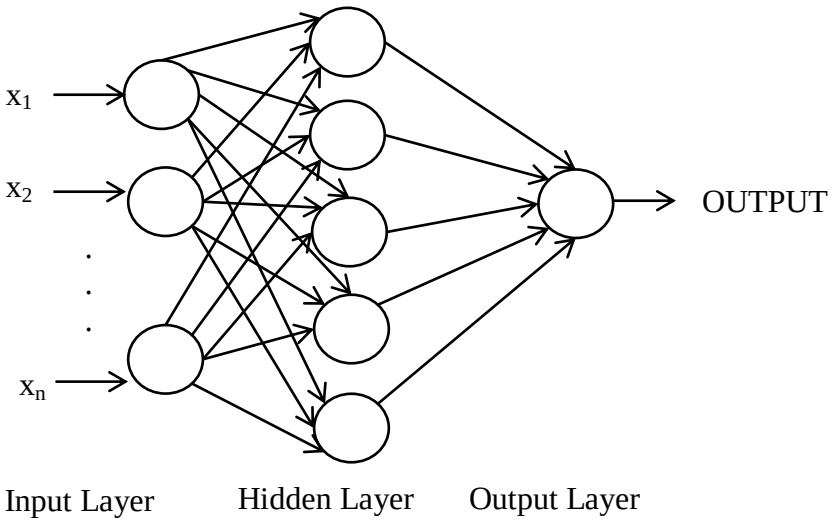

Figure 2.4. Neural network diagram.

The input layer receives information only from the external environment and transmits this information to the next level without performing any calculation. The output layer produces the final results to the outside of the system. As a result, each node corresponds to a response variable. Between the input and the output layers, one or more

hidden layers as intermediate layer exit without any contact with the external environment. Their function is to take the relationship between input and output variables and adapt it more closely to the data (Giudici, 2003).

The number of hidden layer may change, but one hidden layer is enough for most purposes. “Feedforward network” lets the network become a single direction of flow by preventing any looping or cycling. “completely connected network” makes every node in a given layer be connected to every node in the next layer. On a simple neural network, the nature of the network can be understood easily. As shown in Figure 2.5, each node is connected together through weighted connections, represented as “w”. At initialization, values between 0 and 1 are randomly assigned to these weights. Weight values are determined by the iterative flow of training data through the network (i.e. established during a training phase in which the network learns how to identify particular classes by their typical input data characteristics). After receiving inputs as a series of signals that dictate its activation, every node produces an output signal. These input signals reach the neuron simultaneously, therefore more than one input signal are received. However, only one output signal is obtained. At this point, the weighted connections have an effect on determining the relative importance the input can have in producing the final impulse transmitted by the node (Larose, 2005).

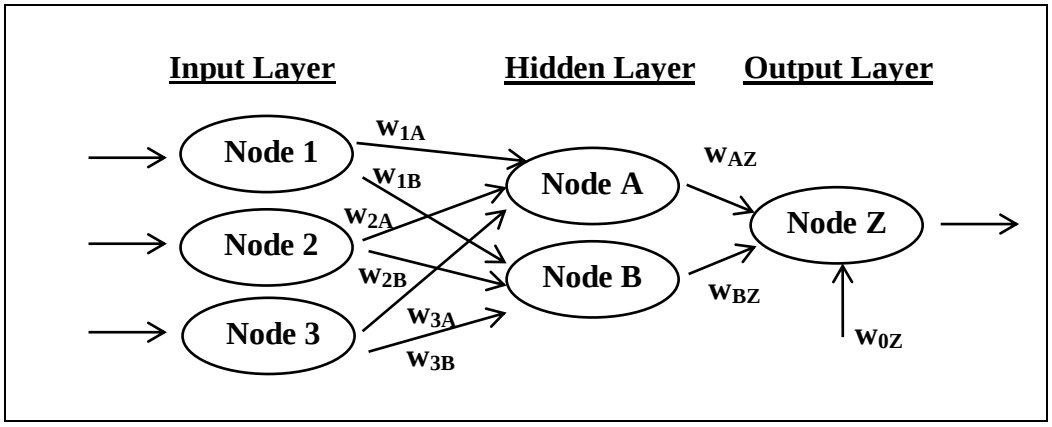

Figure 2.5. A simple neural network (Larose, 2005).

According to data set, number of input nodes may change in terms of number and type of attributes. The number of hidden layers and the number of nodes in each hidden layer are adjustable by the user. Because more nodes in hidden layer mean more power and more flexibility in the network, number of nodes may be increased in order to identify

complex patterns. However, so many nodes may lead to overfitting, memorizing the training set at the expense of generalizability to the validation set. By taking these two concerns into consideration, an optimum number of nodes in the hidden layer should be determined. Output layer depends on the particular classification task at hand, and therefore it may have more than one node. Since the input layer takes inputs from the data set without further processing, its nodes do not share the detailed node structure that the hidden layer nodes and the output layer nodes share (Larose, 2005).

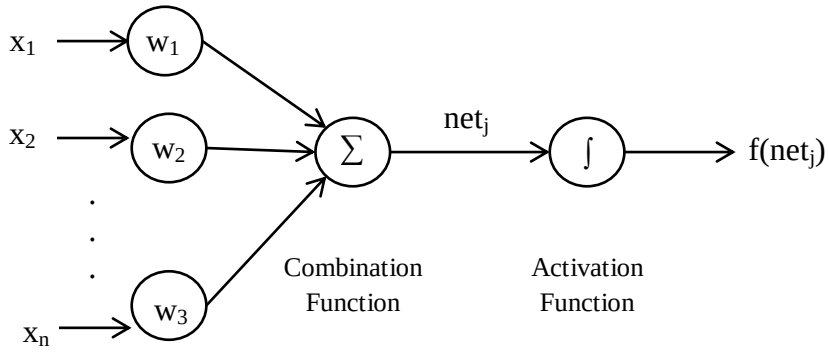

Figure 2.6. The structure of neural network.

While creating hidden layer nodes and output layer nodes, a combination function "∑" and an activation function are performed (Figure 2.6). First, the combination function "∑" is applied to produce a linear combination of the node inputs and the connection weights into a single scalar value. As a result, "net" term is obtained as the following equation (Larose, 2005).

$$\text{net}_j = \sum_i w_{ij}\, x_{ij} \tag{2.12}$$

Where x_{ij} is the i^{th} input to node j, w_{ij} is the weight associated with the i^{th} input to node j, and there are i+1 inputs to node j. Here, x_0 represents a constant input, analogous to the constant factor in regression models, which by convention uniquely takes the value $x_{0j}=1$ (Larose, 2005).

In biological neurons, signals are sent between neurons when the combination of inputs to a particular neuron crosses a certain threshold, and the neuron "fires", which is a nonlinear behavior. Artificial neural networks model this behavior through a nonlinear activation function as the following (Larose, 2005).

$$f(net_j) = f(\sum_i w_{ij}\, x_{ij}) \tag{2.13}$$

Where the activation function takes net_j as input and produces an output value.

Three types of activation function are commonly employed as linear, stepwise and sigmoidal. The linear activation function is

$$f(net_j) = \alpha + \beta\, net_j \tag{2.14}$$

where net_j is defined on the set of real numbers, and α and β are rel constants (when α is 0 and β is 1, it is a particular case for models requiring the output of a node to be exactly equal to its level of activation.) (Giudici, 2003).

The stepwise activation function is

$$f(net_j) = \begin{cases} \alpha & net_j \geq Q_j \\ \beta & net_j \leq Q_j \end{cases} \tag{2.15}$$

The activation function depends on whether the activation exceeds the threshold Q_j or not. For α=1, β=0 and Q_j=0 the so-called sign activation function can be obtained. As a result, value is taken as 0 if the potential is negative and it is taken as +1 if the potential is positive (Giudici, 2003).

The sigmoidal function is

$$f(net_j) = \frac{1}{1+e^{-net_j}} \tag{2.16}$$

This one is the most common activation function. The reason of being the most common activation function is that it combines nearly linear behavior, curvilinear behavior, and nearly constant behavior, which depend on the value of the input. Through much of the center of the domain of the input x, the behavior of function is nearly linear. While the input moves away from the center, function becomes curvilinear. By increasing the input value more and more, function becomes nearly constant (Figure 2.7). The sigmoid function takes any real-valued input and returns an output bounded between “0” and “1” (Larose, 2005).

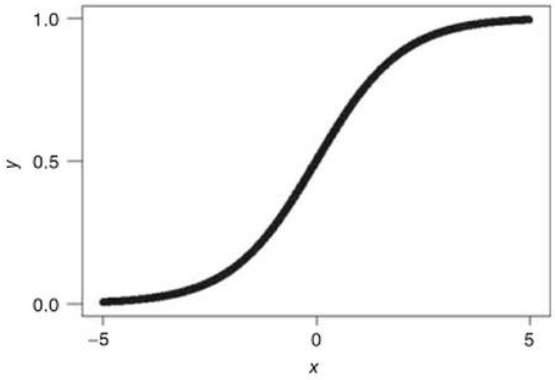

Figure 2.7. Graph of the sigmoid function [y = f(x) = 1 / (1+e^{-x})] (Larose, 2005).

Then, this output value is passed along the connection to the output node Z which combines all outputs from each node, through net_{output} using the weights associated with the connections between these nodes. The inputs x_i to node Z are not data attribute values but the outputs from the activation function from upstream nodes:

$$net_{output} = \sum_i w_{ioutput} f(net_j) \tag{2.17}$$

Here, $f(net_j)$ for i=0 represents a constant value and is taken as 1 as in x_{0j}=1 (Larose, 2005).

Finally, net_{output} is input into the activation function in output node.

$$f(net_{output}) = \frac{1}{1+e^{-net_{output}}} \tag{2.18}$$

This result gives the output from the neural network and represents the value predicted for the target variable for the first observation (Larose, 2005).

A supervised learning method comes from the neural network obtained from a large training set of complete records including the target variable. As each observation from training set is processed by the network, an output values are obtained from the output nodes. After comparing these output values to the actual value of the target variable for the training set observation, error is calculated by using the sum of squared errors:

$$SSE = \sum_{records} \sum_{output\ nodes} (actual - output)^2 \tag{2.19}$$

where the squared prediction errors are summed over all the output nodes and over all the records in the training set. While constructing a set of model weights, the SSE

should be minimized by estimating the true weight values in the data set. However, nonlinear nature of the sigmoid function, there exist no closed-form solution for minimizing SSE as exists for least-squares regression (Larose, 2005).

The back-propagation algorithm is applied in the prediction error (actual - output) for a certain data set. This algorithm has the following rules:

$$w_{i\,j,\,new} = w_{i\,j,\,current} + \Delta w_{i\,j} \tag{2.20}$$

$$\Delta w_{i\,j} = \eta\, \delta_j\, x_{i\,j} \tag{2.21}$$

where η is the learning rate ($0 < \eta < 1$), δ_j is the responsibility for a particular error belonging to node j, and $x_{i\,j}$ is the i^{th} input to node j.

It should be considered that the learning rate is not determined as neither very small nor very large value. If possible, it should change as the training moves forward. At the start of training, the training rate should be initialized to a relatively large value to approach the network to the general neighborhood of the optimal solution quickly. When the network is beginning to approach convergence, the learning date should gradually be reduced, thereby avoiding overshooting the minimum.

The responsibility for a particular error belonging to node j can be found by calculating the partial derivative of the sigmoid function with respect to net_j (Larose, 2005).

$$\delta_j = \begin{cases} output_j(1 - output_j)(actual_j - output_j) & for\ output\ layer\ nodes \\ output_j(1 - output_j)\sum_{downstream} w_{jk}\delta_j & for\ hidden\ layer\ nodes \end{cases} \tag{2.22}$$

$\sum_{downstream} w_{jk}\, \delta_j$ is the weighted sum of the error responsibilities for the nodes downstream from the particular hidden layer node (Larose, 2005).

The back-propagation algorithm steps are indicated in Figure 2.8 clearly.

These rules and equations are adjusted to proceed the neural network algorithm by working through the training set in order to minimize the prediction error. At this point, the algorithm requires some termination criteria in order to assess when the SSE on the training data reaches to some low threshold level. Most of the time, the following cross-validation termination procedure is applied (Larose, 2005).

(i) Retain part of the original data set as a holdout validation set.
(ii) Proceed to train the neural network as above on the remaining training data.
(iii) Apply the weights learned from the training data on the validation data.
(iv) Monitor two sets of weights as "current" and "best" set of weights. The former one comes from the training data, whereas the latter one is calculated by the lowest SSE so far on the validation data.
(v) When the current set of weights has significantly greater SSE than the best set of weights, then terminate the algorithm.

Not only termination criteria, but also stopping criteria is needed in order to arrive at the optimal solution (global minimum). Some applicable ways are (Larose, 2005):

(i) Multiple networks may be trained using different initialized weights until the best-performing model is selected as the final model.
(ii) A momentum term may be added to the back-propagation algorithm.

High complexity of a network and a large number of iterations in training make the data in the training set easily predictable. Although it seems like a desirable result, it is counterproductive in real applications. The reason is related with reduced predictive capacities on a new data set, which is known as overfitting. To overcome this overfitting problem, the complexity of the model should be controlled according to stopping criteria in the iterative procedure of learning by regularization. Regularization is provided by addition of a penalty term to the error function

$$\tilde{E}(w) = E(w) + \nu\Omega \tag{2.23}$$

Where E is an error function, Ω is the complexity of the network and ν is a parameter to penalize complexity. A complex network with good fit to the training data has a minimum value of E, while a very simple function has low value of Ω. Therefore, an optimization procedure between a simple model and a good fit to the data should be applied. A useful regularization function is based on weight decay as the following:

$$\Omega = \frac{1}{2}\sum_i w_i^2 \tag{2.24}$$

Here, the error function indicates an initial reduction followed by an increase which is related with overfitting. So, training can be stopped with the lowest prediction error (Giudici, 2003).

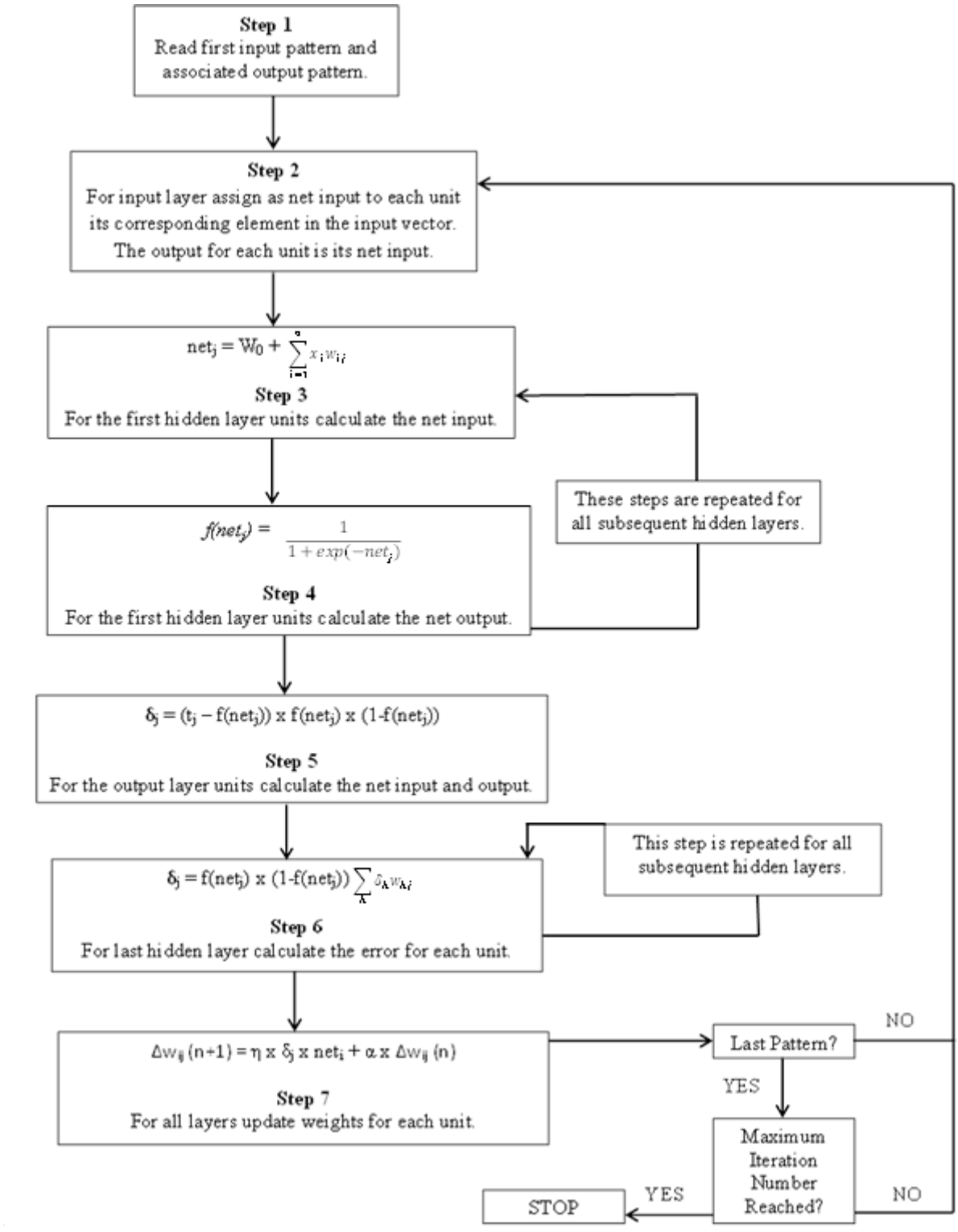

Figure 2.8. The back-propagation algorithm (Günay, 2012).

2.4. Knowledge Extraction by Using Data Mining Methods (Rule Deduction)

One of the most attractive aspects of decision trees is their interpretability, so the construction of decision rules can be done easily. Decision rules can be constructed from a decision tree simply by traversing any given path from the root node to any node. Therefore, the complete set of decision rules generated by a decision tree is equivalent to the decision tree itself.

After applying data mining techniques to collected and categorized data in detail, effect of input variables and effect of parameters related with these techniques are considered. While determining the best data mining method with the best results, optimization of these parameters is very important. Working on different approaches as well as observing decision tree results and error percentages, the best decision tree can be obtained. Although more complex tree means lower error percentage, rule deduction from such trees is more difficult. Thus, the best decision should be parallel with simplicity of decision tree and nominal error percentage.

According to selected decision tree, rule deduction is applied and a general rule is obtained at the end of the analysis. Beginning from the root node and following the decision nodes and terminal leaf nodes, a rule can be deducted easily just by visual examination. Since the aim is to use valuable knowledge extracted from the past data in the future works more effectively, the rule have a great importance on guidance.

3. DATABASE

3.1. Experimental Data Collection

The aim of this thesis was to contruct a large database on steam reforming of methane to extract the general knowledge hidden within the data. First of all, the time period for data collection was determined as 11 years from 2004 to 2014, which seem to represent the stream reforming literature well. Then the database was constructed by collecting the experimental data on steam reforming of methane in the publications in the the online sources such as Science Direct, Wiley, ACS (American Chemical Society), and Springer. In Figure 3.1, the number of articles published through years is presented.

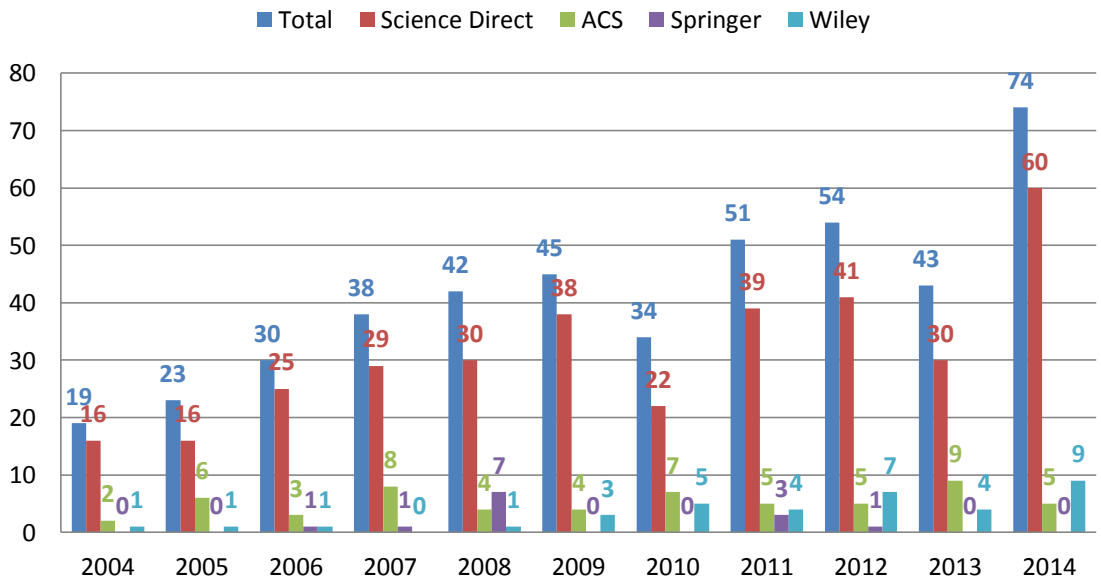

Figure 3.1. Article numbers in publications by years.

While gathering the experimental data from many various studies, it was realized that there are numerous parameters, which affect the results of the chemical reactions involved in steam reforming of methane. These parameters are simply the types of base metals (such as Ni, Pt and Pd), catalyst preparation methods (such as incipient to wetness impregnation, wet impregnation, co-impregnation, co-precipitation, etc.), calcination and reduction properties (as temperature and time), the type of supports or promoters, feed compositions,

time on stream, W/F ratio (catalyst weight/feed flow rate), temperature, pressure, and reactor types.

453 articles were reviewed during database construction, but 139 articles were selected as relevant, and 82 out of those were found to be suitable the project, so their data were recorded one by one by categorizing each parameter. However, some articles had to be excluded because inappropriate conditions associated with parameters and some missing values that might cause unreliable outcomes. Therefore, the final database consists of 5552 experimental data with 59 input variables and 3 output variables extracted form 59 articles in the literature. These variables are presented through Table 3.1 to 3.9 below.

Table 3.1. Properties of base metals in input variables.

PARAMETER	INPUT VARIABLE	DATA NUMBER	RANGE (wt%)
Base Metal	Ni	4143	0-60.9
	Pt	572	0-27.5
	Pd	87	0-5.0
	Ru	633	0-5.0
	Rh	725	0-20.0
	Ir	3	0-5.0
	Ag	64	0-0.6

The database contained seven base metals as Nickel (Ni), Platinum (Pt), Palladium (Pd), Ruthenium (Ru), Rhodium (Rh), Iridium (Ir), and Silver (Ag); Nickel is the most preferred base metal in publications. The number of data points over these netals and their loading ranges are presented in Table 3.1.

Catalyst preparation methods are also influential on the efficiency of methane steam reforming. As a result of literature search, the data over the catalyst prepared using nine catalyst preparation methods were extracted. Incipient to wetness impregnation is the most common catalyst preparation method in methane steam reforming as it can be seen in Table 3.2. The “others” category contains dissolution (for $NiAl_2O_4$), multibubble sonoluminescence under MBSL conditions, solution combustion technique or GNP, flame spray pyrolysis reactor, citcic acid method, EDTA-citrate method, Pechini method. These methods are not the common ones, but some researchers study on such different

approaches to improve the methane steam reforming process. Instead of analyzing such relatively less common processes one by one, collecting them in category was preferred to prevent unusual variables negatively affect the knowledge extraction for more comman variables. For each data points, the preparation used was labeled as “1” while “0” label was used for the remainings techniques.

Table 3.2. Catalyst preparation methods in input variables.

PARAMETER	METHOD	INPUT VARIABLE	DATA NUMBER
Catalyst Preparation Method	**Method 1**	Commercial	377
	Method 2	Incipient to Wetness Impregnation	2025
	Method 3	Wet Impregnation	466
	Method 4	Co-Impregnation	505
	Method 5	Seq-Impregnation	590
	Method 6	Co-Precipitation	627
	Method 7	Sol Gel Precipitation	171
	Method 8	Deposition Precipitation	242
	Method 9	Others	587

Table 3.3. Calcination in input variables.

PARAMETER	INPUT VARIABLE	RANGE
Calcination	Calcination Temperature	0-1673 K
	Calcination Time	0-12 h

After preparation, the catalysts were calcined at a certain temperature for a certain time. In Table 3.3, the calcination temperature and the calcination time ranges are indicated. The highest temperature reaches 1673 K, while the longest calcination period is 12 hours. In some cases, catalyst was not calcined; the calcination temperature and time for these cases are set as 0 K and 0 hour.

Table 3.4. Reduction in input variables.

PARAMETER	INPUT VARIABLE	RANGE
Reduction	Reduction Temperature	0-1173 K
	Reduction Time	0-6.5 h
	H_2 Reduction	0-100 %
	Ar - Reduction Medium	0-95 %
	He - Reduction Medium	0-95 %
	N_2 - Reduction Medium	0-95 %

In Table 3.4, the ranges of reduction temperature and time range are available. The highest temperature reaches 1173 K and the longest reduction period is 6.5 hours. Similar to the calcination, the reduction temperature and time was set as 0 K and 0 hour if the catalyst was not reduced. The most commonly, the reduction is performed in the hydrogen environment. However the other gasses are also used sometimes, and alter the performance of the catalyst, the reduction atmosphere (like Ar, He and N_2) are also taken as input variable.

Table 3.5. Support types in input variables.

PARAMETER	INPUT VARIABLE	DATA NUMBER
Support	α-Al_2O_3	936
	γ-Al_2O_3	1791
	δ-Al_2O_3	324
	$MgAl_2O_4$	192
	MgO	391
	CeO_2	1358
	ZrO_2	1094
	Gd_2O_3	165
	Commercial Ni-Based Catalyst	147
	SiO_2	372
	SBA-15	273

Table 3.6. Promoter types in input variables.

PARAMETER	INPUT VARIABLE	DATA NUMBER	RANGE (wt%)
Promoter	S	29	0-0.5
	P	29	0-0.5
	K	28	0-0.5
	Na	28	0-0.5
	Mo	185	0-2.0
	B	81	0-1.0
	CeO_2	138	0-10
	ZrO_2	118	0-10
	Ca	16	0-3.8
	Mg	41	0-53
	Ru	19	0-0.5

Table 3.5 contains the types of supports used in the in catalysts and their frequency and the ranges appered in the final database. These supports are Aluminium Oxide (Al_2O_3), Magnesium Aluminate ($MgAl_2O_4$), Magnesium Oxide (MgO), Cerium Oxide/Ceria (CeO_2), Zirconium Dioxide/Zirconia (ZrO_2), Gadolinium Oxide/Gadolinia (Gd_2O_3), Silicon Dioxide/Silica (SiO_2), and Mesoporous Silica (SBA-15). In data set, the pure supports were labeled as "1" (corresponding to 100% while the mixed supports were identified with their molar ratios).

As listed in Table 3.6, eleven promoters used in the structure of the catalysts are Sulfur (S), Phosphorus (P), Potassium (K), Sodium (Na), Molybdenum (Mo), Boron (B), Ceria (CeO_2), Zirconia (ZrO_2), Calcium (Ca), Magnesium (Mg), and Ruthenium (Ru).

Feed compositions, product compositions, time on stream, catalyst weight over feed flow rate, reaction temperature and pressure were also used as input variables (can be considered as operational variables while the other variables discussed abconsidered as catalyst design variables) as given in Table 3.7.

Table 3.7. Operational input variables.

PARAMETER	INPUT VARIABLE	RANGE
Other Parameters	CH_4 Composition	0.1-66.7 %
	H_2O Composition	0.4-84.6 %
	CO_2 Composition	0-0 %
	CO Composition	0.0-9.9 %
	H_2 Composition	0-23.8 %
	Time on Stream (TOS)	0-68012 min
	W/F (gcat.min/m^3)	2.41-449434
	Temperature	411-1173 K
	Pressure	1-20 atm

Table 3.8. Reactor types in input variables.

PARAMETER	INPUT VARIABLE	DATA NUMBER
Reactor Types	Packed Bed Reactor	4752
	Fluidized Bed Reactor	44
	Membrane Reactor	294
	Micro-Reactor	462

Table 3.9. Output variables.

OUTPUT VARIABLE	DATA NUMBER	RANGE
CH_4 Conversion	5552	0-100 %
CO Selectivity	1368	0-100 %
H_2 Selectivity	841	0 - ≥100 %

Lastly, the reactor types were also included to the database as aonother input variables. According to Table 3.8, packed bed reactors are frequently considered in methane steam reforming. In membrane reactor, Pd membrane reactor and silica-alumina membrane reactor were written. Micro-reactor consisted of wall-coated micro-channel reactor, wash-coated fecralloy®, micro-channel reactor, packed micro-channel reactor and micro-structured reactor.

Finally products of methane steam reforming are CO and H_2. Hence the output variables were taken from the publications as CH_4 Conversion, CO Selectivity and H_2 Selectivity (Table 3.9).

$$CH_4 \text{ Conversion } (\%) = \frac{F_{CH_4,in} - F_{CH_4,out}}{F_{CH_4,in}} x\ 100$$

3.2. Computational Details

In this thesis, computational work was carried out by using MATLAB R2010b. Different approaches were applied in order to obtain knowledge from the database about steam methane reforming and to benefit from this knowledge in future studies as well to predict any new data related with steam methane reforming. Knowledge for the conditions leading best performance was extracted by Decision Tree Modeling. Effectiveness of classifications and predictions for new unknown data were determined by Neural Network Modeling. MATLAB codes according to objectives of the thesis were written separately and numerous works on these codes were performed to reach optimized consequences.

3.2.1. Decision Tree Modeling

Decision trees predict responses to data as a classification method. To predict this response, the decisions in the tree from the root (beginning) node down to a leaf node are followed. The leaf node contains the response as nominal.

While writing code of decision tree model, a big attention was paid to these following steps:

- calling data from excel file,
- classification of outputs properly,
- dividing total data into two parts as training and testing data set,
- creating decision trees for training data set and applying them for testing data set,
- taking different prune and splitmin values, nod numbers and complexity of decision trees into consideration.

Using a separate MATLAB Code, experimental data were called from its own excel file and saved in the workspace or memory of the MATLAB, which is an easy way to work

on the data without losing any time. The computer program saved the data as inputs and outputs.

Since decision tree gives nominal results, nominal categorization was carried out on output values as “0-50, 50-60, 60-70, 70-80, 80-90, 90-100” in terms of range that includes each output one by one (i.e. “56” as an output value should be in “50-60”).

Then, total database were divided as training and testing data set. Two third of total data were assigned as training data while remaining one third of total data were separated as testing data.

Decision trees were created by modifying some parameters in MATLAB. Diverse prune and splitmin values were tried and nod numbers and complexity of the decision trees were compared. Since optimum results were searched, relationship between these parameters should be found after some trials. The meaning of “Splitmin” is that impure nodes must have as the number of assigned splitmin value or more observations to be split (i.e. when data are scanned and splitmin value is 50, the aim of this parameter is to find at least 50 data that give the same result.). Splitmin values in codes were selected as 10, 25, 50, 100, 150, etc. The function of “prune” is reducing a phylogenetic tree by removing branch and leaf nodes. Trees are pruned based on an optimal pruning scheme that first prunes branches giving less improvement in error cost. Some branches which are contrary to generalizations are pruned according to given prune level. Prune values in codes were 0, 1, 2, 3, 4, 5, 6, 7, 8, 9 and 10.

The same model of training data set was applied to testing data. Error percentages for training and testing data as well as node number of each decision tree were measured as a result of running MATLAB code. Error analysis for training data set is done by detecting how the decision tree verifies its own predictions. Error analysis for testing data set is realized by detecting how the same decision tree predicts the unseen data set.

By observing decision tree results and error percentage amounts, the best decision was made. Since the best decision is parallel with simplicity of decision tree and nominal error rate, the optimal solution with lower error rate and simple decision tree should be preferred. According to these optimal solutions, rule deduction was applied and a general rule was obtained at the end of the analysis.

3.2.2. Neural Network Modeling

The work flow for the general neural network design process in MATLAB has seven primary steps (Beale *et al*., 2015):

(i) Collect data
(ii) Create the network
(iii) Configure the network
(iv) Initialize the weights and biases
(v) Train the network
(vi) Validate the network (post-training analysis)
(vii) Use the network

First of all, the experimental data should be collected as accurate as the MATLAB program can analyze. After collecting, preprocessing of data and dividing them into subsets should be carried out. The reason of these requirements is that certain preprocessing steps on the network inputs and targets make the neural network training more efficient. If the input is very large, then the weight must be very small in order to prevent the transfer function from becoming saturated. It is standard practice to normalize the inputs before applying them to the network. Generally, the normalization step is applied to both the input vectors and the target vectors in the data set. As a result of this normalization, the network output always falls into a normalized range. When training multilayer networks, the general practice is to first divide the data into three subsets as (Beale *et al*., 2015)

(i) The training set, which is used for computing the gradient and updating the network weights and biases.
(ii) The validation set, on which the error is monitored during the training process. The network weights and biases are saved at the minimum of the validation set error.
(iii) The test set, which has error not used during training, but it is used to compare different models.

If the error on the test set reaches a minimum at a significantly different iteration number than the validation set error, this might indicate a poor division of the data set. Four functions can be used while dividing data into training, validation and test sets. These

four functions are dividerand (the default), divideblock, divideint, and divideind. The data division is normally performed automatically when training the network. The divide function is accessed automatically whenever the network is trained, and is used to divide the data into training, validation and testing subsets. In 'dividerand' (the default), the data are randomly divided into the three subsets according to the division parameters of MATLAB program (Beale *et al*., 2015).

Network inputs might have associated processing functions which transform user input data to a form that is easier or more efficient for a network (Beale *et al*., 2015):

- *mapminmax* transforms input data so that all values fall into the interval [−1, 1] to speed up learning for many networks.
- *removeconstantrows* removes the rows of the input vector that correspond to input elements that always have the same value, because these input elements are not providing any useful information to the network.
- *fixunknowns* recodes unknown data (represented in the user's data with NaN values) into a numerical form for the network and preserves information about which values are known and which are unknown.

Many transfer functions are included in the Neural Network Toolbox software. The most common transfer functions are as the following (Beale *et al*., 2015).

- The linear transfer function (purelin), in which neurons are used in the final layer of multilayer networks that are used as function approximators.
- The Log-Sigmoid transfer function (logsig), which takes the input, which can have any value between plus and minus infinity, and squashes the output into the range 0 to 1.
- The Tan-Sigmoid transfer function (tansig), which takes the input, which can have any value between plus and minus infinity, and squashes the output into the range -1 to 1.

The next step is to create the network. The following call to feedforwardnet creates a two-layer network with 10 neurons (default) in the hidden layer. The default setting is 10, which means one hidden layer with 10 neurons. In some cases, two hidden layers should be applied to offer necessary results. However, mostly, one hidden layer produces

excellent results. Larger number of neurons in the hidden layer means more power of the network, which causes more computation and is more likely to produce overfitting (Beale *et al*., 2015).

After creating neural network, it must be configured. The configuration step consists of examining input and target data, setting the network's input and output sizes to match the data, and choosing settings for processing inputs and outputs that will enable best network performance. The configure command configures the network object and also initializes the weights and biases of the network. The configure command must not be applied, since the train command will automatically configure the network and initialize the weights. In this project, "trainlm" (Levenberg-Marquardt Algorithm) and "trainbr" (Bayesian Regularization Algorithm) functions will be used in training and testing respectively. "trainlm" (Levenberg-Marquardt Algorithm) is the fastest training function and performs better on function fitting (nonlinear regression) problems than on pattern recognition problems. "trainbr" (Bayesian Regularization Algorithm) is preferred in testing, because it is desirable to determine the optimal regularization parameters in an automated fashion. In this framework, the weights and biases of the network are assumed to be random variables with specified distributions. The regularization parameters are related to the unknown variances associated with these distributions. The trainbr algorithm generally works best when the network inputs and targets are scaled so that they fall approximately in the range [−1, 1], which means that the "tansig" transfer function is more suitable to combine with (Beale *et al*., 2015).

Each time, a neural network trained can result in a different solution due to different initial weight and bias values and different divisions of data into training, validation, and test sets. As a result, different outputs can be obtained for the same neural network model of the same input. To ensure that a neural network of good accuracy has been found, retrain several times. Thus, each network topology was trained 10 times not to be affected negatively from random initialization of the neural network weights. To prevent overlearning of the neural networks, the early-stopping technique was applied during the training of the neural networks by using some random data points among the training set as the validation data. Independent of the neural network training method, the optimal network topology was always determined by testing the performances of several networks according to their generalization accuracies which shows the ability of the network to

predict the data unseen during the training process. The root mean square error (RMSE) of testing was obtained at the end of the each run of MATLAB code. The root mean square error (RMSE) measured the degree of the generalization accuracy by dividing the entire data randomly into 4 subsets and using the data acquired from 3 sets to train the network to predict the outcome of the remaining one set. The errors between these predictions and the corresponding experimental results were calculated and after applying this method 4 times covering all the data points, the RMSE was used as the indicator to determine the optimal neural network topology (Günay, 2012).

The coefficient of determination (R^2) which is related with fitness of the model was also obtained together with corresponding RMSE values. Although RMSE was not used in decision making, R^2 gives some idea of the suitability of the database to construct a single model. The R^2 value is an indication of the relationship between the outputs and targets. If $R^2 = 1$, this indicates that there is an exact linear relationship between outputs and targets. If R^2 is close to zero, then there is no linear relationship between outputs and targets (Günay, 2012).

"the change of root mean square error" technique was used to test the significance. The technique includes beginning with the removal of one of the input variables or article or experiment, training the network with the remaining input groups or articles or experiments and observing the difference between the RMSE value of the model calculated without this variable or article or experiment and the value obtained when all is included, respectively. Here, the difference indicates the significance of the parameter. By repeating this technique for each one, the importance of each input variable, article and experiment can be sorted (Günay, 2012).

Neural network model in MATLAB was employed on the entire network. Two different models were applied for training and testing and one more model was applied separately for test of significance of the input variables. Three activation or transfer functions (purelin, logsig and tansig) and several combinations of hidden layer numbers and neuron numbers were experienced on the models. R values of each model were compared as a result of running MATLAB code. As in decision tree, R^2 analysis for training data set is done by detecting how the model verifies its own and R^2 analysis for testing data set is realized by detecting how the same model predicts unprocessed data set.

By observing values of training and testing models, the best network model was selected and the importance of each input variable was decided.

4. RESULTS AND DISCUSSIONS

The analysis on the experimental data in this thesis was performed by two methods: decision trees and artificial neural networks. As mentioned in Chapter 3, the experimental data were exctracted from published articles in the literature. The database constructed is pre-analyzed first and some datapoints were excluded from the database because they did not fit the purpose of study. For example if a unique variable is used in one work (for example a promoter that was not used by anyone else), that part of work was exluded because it has no use for generalization. After final state of the database was decided, it was divided into five subsets according to the most common parameters. This way, it was possible to analyze the entire dataset as well as the dataset belonging the most common variables. Since Ni, Rh and Ru metal base catalysts are preferred in these studies, their data were modeled separately. Within catalyst preparation methods, incipient to wetness impregnation is the most frequently used method, so one dataset, which involved experiments using catalyst prepared by this method, was also created. Lastly, a dataset containing the data obtained in packed bed reactor was also separately analyzed because it is the most common reactor configuration for the steam reforming of methane process. Thus, six different datasets were analyzed, their decision trees were obtained and general knowledge about each of them was extracted from these decision trees. By changing effective parameters in MATLAB, optimum decision trees were selected. At this point, “splitmin” and “prune” values were manipulated for each data set. Up to 150 in splitmin value and between 0-10 in prune value were used in decision tree analysis. The complexity, training and testing error percentages were compared. Since the best decision is parallel with simplicity of decision tree and nominal error rate, the optimal solution with lower error rate and simple decision tree was preferred. Using these optimal solutions, some general rules were deducted at the end of the analysis for each data set.

Neural network model was also applied to the entire database. First of all, the neural network structure with sufficiently high prediction and generalization accuracies in representing the experimental data was searched. Three activation or transfer functions (linear, logistic sigmoid, hypberbolic tangent) were applied on the models. Then, the number of neurons in the hidden layer was adjusted. Thus, many neural network models

were analyzed for training and testing. Each network model was trained 10 times so that it is not affected negatively from random initialization of the neural network weights. RMSE and R^2 values of each model were compared. By considering the results of training and testing, the optimal network model was selected and was used to analyze the significances of 59 input variables as well as effects of 421 experiments and 59 articles on CH_4 conversion. The success criteria for the prediction of the results of the experiments and papers was based on two points, the RSME values should be smaller than 15 and R^2 values should be higher than 0.5.

4.1. Decision Tree and Knowledge Extraction Results

4.1.1. CH_4 Conversion Results of Total Data

The total database was composed of 5552 experiments and they were divided randomly into two parts as training and testing. As mentioned before, training data were two third of the total data, while remaining one third of total data were used for testing. In other words, numbers of training and testing data were 3701 and 1851, respectively. The optimal decision tree was found by starting with a large tree first and then pruning it from the less important branches until the minimum testing error was found. Splitmin value was decided as “100” and prune value was “8”. As a result of running decision tree code in MATLAB, the optimal decision tree was obtained with 63 nod numbers, 20.83% training error and 22.91% testing error (Figure 4.1). The rule deduced for the methane conversion from this tree is also represented in Table 4.1.

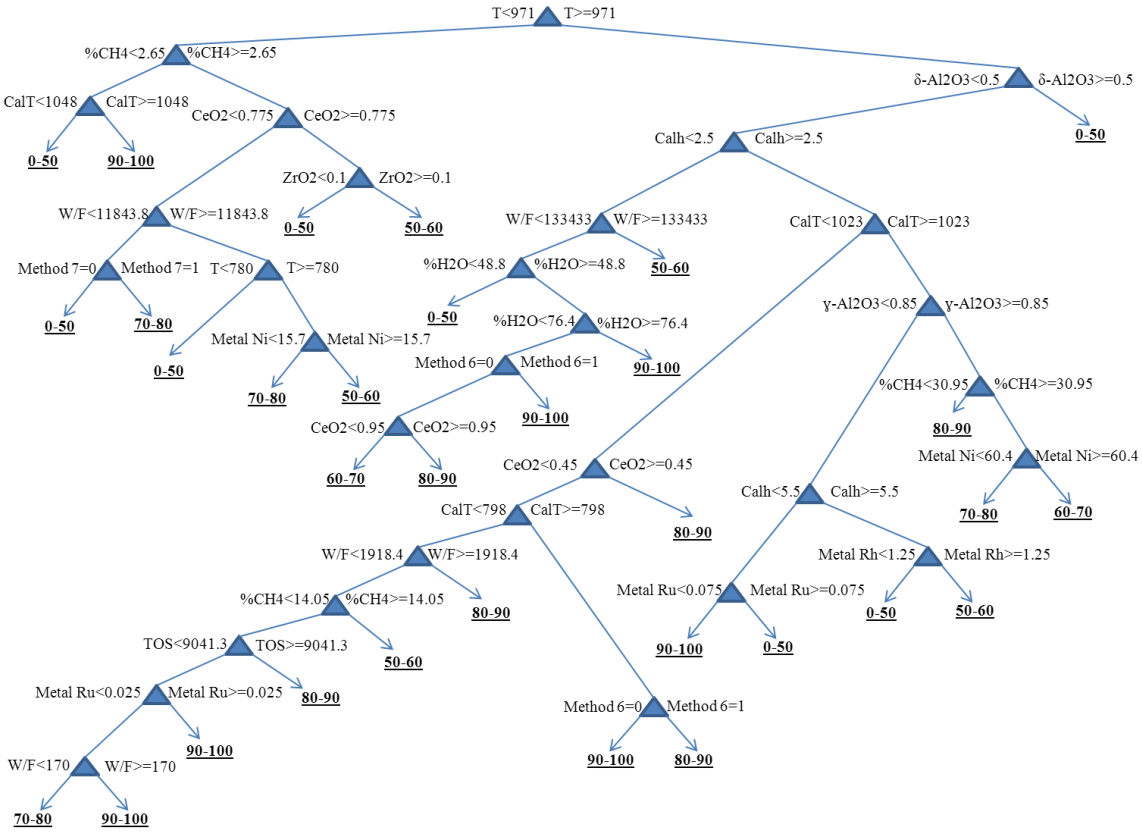

Figure 4.1. Decision tree of total data.

Table 4.1. Deduction rule conditions of total data for CH_4 conversion.

T<971	**%CH4<2.65**	CalT<1048											0-50
		CalT>=1048											**90-100**
	%CH4>=2.65	CeO2>=0.775	ZrO2<0.1										0-50
			ZrO2>=0.1										50-60
		CeO2<0.775	W/F<11843.8	Method 7=0									0-50
				Method 7=1									70-80
			W/F>=11843.8	T<780									0-50
				T>=780	Metal Ni>=15.7								50-60
					Metal Ni<15.7								70-80
T>=971	δ-Al2O3>=0.5												0-50
	δ-Al2O3<0.5	**Calh<2.5**	W/F>=133433										50-60
			W/F<133433	%H2O<48.8									0-50
				%H2O>=48.8	**%H2O>=76.4**								**90-100**
					%H2O<76.4	**Method 6=1**							**90-100**
						Method 6=0	CeO2<0.95						60-70
							CeO2>=0.95						**80-90**
		Calh>=2.5	**CalT>=1023**	**ɣ-Al2O3>=0.85**	**%CH4<30.95**								**80-90**
					%CH4>=30.95	Metal Ni>=60.4							60-70
						Metal Ni<60.4							70-80
				ɣ-Al2O3<0.85	**Calh<5.5**	Metal Ru>=0.075							0-50
						Metal Ru<0.075							**90-100**
					Calh>=5.5	Metal Rh<1.25							0-50
						Metal Rh>=1.25							50-60
			CalT<1023	**CeO2<0.45**	**CeO2>=0.45**								**80-90**
					CalT<798	**Method 6=1**							**80-90**
						Method 6=0							**90-100**
						W/F>=1918.4							**80-90**
						W/F<1918.4	%CH4>=14.05						50-60
							%CH4<14.05	**TOS>=9041.3**					**80-90**
								TOS<9041.3	**Metal Ru>=0.025**				**90-100**
									Metal Ru<0.025	W/F<170			70-80
										W/F>=170			**90-100**

It can be seen that the training error was smaller than testing error as expected, since verifying the decision tree itself is much easier than predicting a never-before-seen data set.

Figure 4.1 reveals that the data were first divided at the top of the tree according to the reaction temperature indicating that this variable was the most significant factor determining the CH_4 conversion level. Low temperatures ($T < 971K$) leaded to lower CH_4 conversions while higher temperatures ($T \geq 971K$) resulted in higher CH_4 conversions for total data set. This division is acceptable and reasonable since the reaction mechanism requires higher temperature due to endothermic nature of the reaction. However, it should be noted here that 971K was the split value calculated by the learning algorithm of the decision tree; it is not an exact physical limit. The same situation is valid for the values of all other parameters in the data set; hence, they should be treated as some empirical approximations. The second decision point to be able to obtain higher conversion levels was the amount of δ-Al_2O_3 support. It is well known that supports make the structure of the catalyst more active, but the amount should be taken carefully. For this data set, it should be lower than 0.5 (which means that 50% of support part of the catalyst) for desired results. Other essential input variables were calcination time, W/F ratio, calcination temperature, composition of H_2O, co-precipitation catalyst preparation method, CeO_2 support, γ-Al_2O_3, CH_4 composition, amount of Ru metal base and time on stream. W/F ratio, co-precipitation catalyst preparation method, CeO_2 support, γ-Al_2O_3, CH_4 composition, amount of Ru metal base and time on stream were already known as common variables in the steam reforming of methane process.

By following the decisions in the tree from the root (beginning) node down to a leaf node, all other rules can be constructed, since the leaf node contains the response. All constructed rules are summarized in Table 4.1. From the table, the conditions leading higher and better conversion level of methane can be obtained by following the regions with dark color (could be interpreted as rules deduced from the tree for higher conversions). There seem to be many options to reach the desirable conversion levels; this is the results of having huge amount of data with a great range of possibilities of variables and conversions. It should not be forgotten that the word rule does not imply any theoretical rule; instead, it is just a statement that explains the empirical patterns derived from the database. However, these rules were valid for at least 100 experiments in the data

due to the splitmin value, so they are reliable with this reality as well acceptable lower error percentages.

4.1.2. CH_4 Conversion Results of Ni Metal Base Data

The data of Ni based catalysts were analyzed separately by using a splitmin value of "75" and pruning level of "5". From 2284 experiments in the training set, a training error of 21.41% was calculated while the testing eror for 1142 experiments in the testing was 24.52%. Related decision tree had 65 nod numbers as indicated in Figure 4.2.

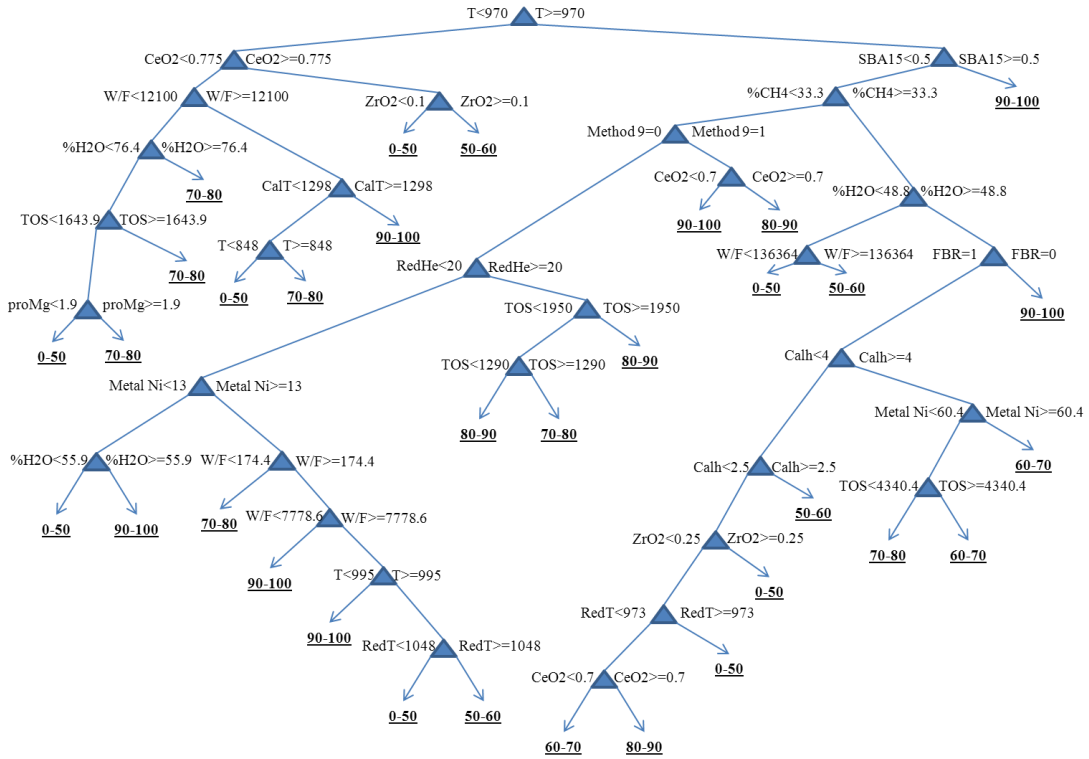

Figure 4.2. Decision tree of Ni metal base data.

Table 4.2. Deduction rule conditions of Ni metal base data for CH_4 conversion.

T<970	CeO2>=0.775	ZrO2<0.1								0-50
		ZrO2>=0.1								50-60
	CeO2<0.775	W/F<12100	%H2O>=76.4							70-80
			%H2O<76.4	TOS>=1643.9						70-80
				TOS<1643.9	proMg<1.9					0-50
					proMg>=1.9					70-80
		W/F>=12100	**CalT>=1298**							**90-100**
			CalT<1298	T<848						0-50
				T>=848						70-80
T>=970	**SBA15>=0.5**									**90-100**
	SBA15<0.5	**%CH4>=33.3**	%H2O<48.8	W/F<136364						0-50
				W/F>=136364						50-60
			%H2O>=48.8	**FBR=0**						**90-100**
				FBR=1	Calh>=4	Metal Ni>=60.4				60-70
						Metal Ni<60.4	TOS>=4340.4			60-70
							TOS<4340.4			70-80
					Calh<4	Calh>=2.5				50-60
						Calh<2.5	ZrO2>=0.25			0-50
							ZrO2<0.25	RedT>=973		0-50
								RedT<973	CeO2<0.7	60-70
									CeO2>=0.7	**80-90**
		%CH4<33.3	**Method 9=1**	**CeO2>=0.7**						**80-90**
				CeO2<0.7						**90-100**
			Method 9=0	**RedHe>=20**	**TOS>=1950**					**80-90**
					TOS<1950	TOS>=1290				70-80
						TOS<1290				**80-90**
				RedHe<20	**Metal Ni<13**	%H2O<55.9				0-50
						%H2O>=55.9				**90-100**
					Metal Ni>=13	W/F<174.4				70-80
						W/F>=174.4	**W/F<7778.6**			**90-100**
							W/F>=7778.6	**T<995**		**90-100**
								T>=995	RedT<1048	0-50
									RedT>=1048	50-60

Since this data set contains only Ni based catalysts, the number of items was fewer. Hence, the splitmin and prune could be decreased. Error percentages went up a little, but they are acceptable since the trees leading smaller errors would be too large and complex for generalization.

The data were first divided at the top of the tree according to the reaction temperature as in total data. This is expected results because Ni is the most often used active metal in the total data base. Temperatures higher than 971K gave higher CH_4 conversions for this data set. The second decision point was the amount of SBA-15 support that has been started to use in steam reforming of methane nowadays; this indicates that the researches about this process are improving performance and making the presence of this support significance. All the other rules obtained are summarized in Table 4.2. CeO_2, W/F ratio, composition of CH_4, composition of H_2O, fixed bed reactor type, He as reduction medium, calcination time, time on stream, Ni metal base, ZrO_2 support and reduction temperature also affected the results.

4.1.3. CH_4 Conversion Results of Rh Metal Base Data

Training and testing data numbers for this catalyst were 449 and 224, respectively. Taking complexitiy and error percentges into consideration, splimin values and prune values were chosen as “3” and “4” respectively. Error percentages decreased to 6.68% for training data and 8.93% for testing data. Our analysis resulted in a 41 nodes decision tree for Rh metal base data as shown in Figure 4.3. Following these nodes one by one, the information was tabulated as shown in Table 4.3. The regions with dark color will give the more desirable conversion levels as in the previous tables.

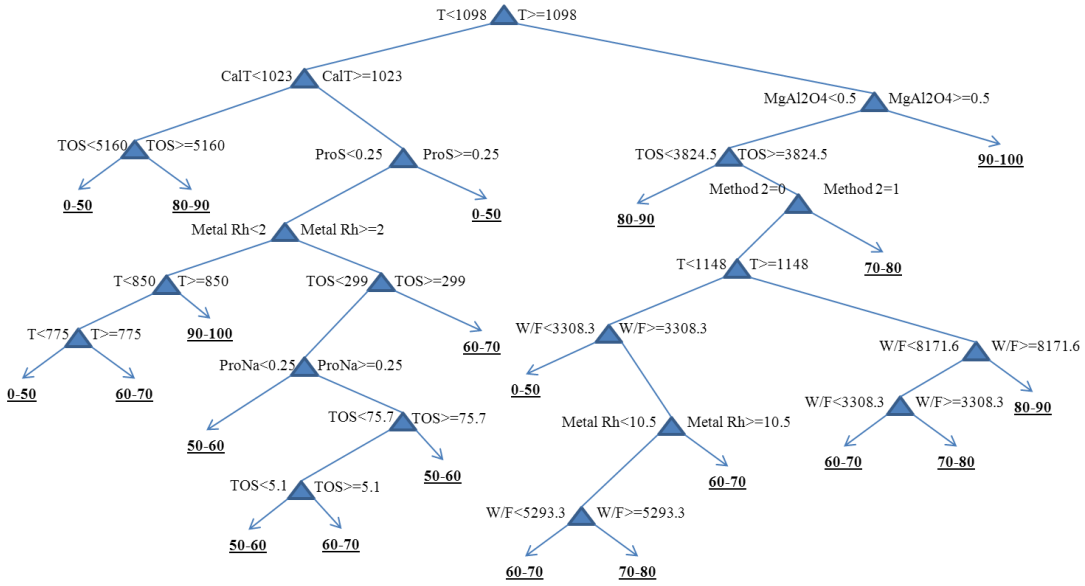

Figure 4.3. Decision tree of Rh metal base data.

For this data set, experiment number was very low, thus it could be possible to use a smaller splitmin value and a pruning level. While studying less data, complexity of tree begin at minimum values of parameters. If splitmin value is very low, error percent also becomes low. If you could extract knowledge for as much as experiment individually, your rule would contain whole data set and verifying and predicting become. Therefore, training and testing error decreased.

First division point was again temperature for Rh metal base data, but with a higher value as 1098K. Remaining division points were $MgAl_2O_4$ support, calcination temperature, time on stream, S promoter, incipient to wetness impregnation catalyst preparation method, amount of Rh metal base and W/F ratio.

Table 4.3. Deduction rule conditions of Rh metal base data for CH_4 conversion.

T>=1098	**MgAl2O4>=0.5**							**90-100**
	MgAl2O4<0.5	**TOS<3824.5**						**80-90**
		TOS>=3824.5	Method 2=1					70-80
			Method 2=0	T<1148	W/F<3308.3			0-50
					W/F>=3308.3	Metal Rh>=10.5		60-70
						Metal Rh<10.5	W/F<5293.3	60-70
							W/F>=5293.3	70-80
				T>=1148	**W/F>=8171.6**			**80-90**
					W/F<8171.6	W/F<3308.3		60-70
						W/F>=3308.3		70-80
T<1098	**CalT<1023**	TOS<5160						0-50
		TOS>=5160						**80-90**
	CalT>=1023	ProS>=0.25						0-50
		ProS<0.25	**Metal Rh<2**	**T>=850**				**90-100**
				T<850	T<775			0-50
					T>=775			60-70
			Metal Rh>=2	TOS>=299				60-70
				TOS<299	ProNa<0.25			50-60
					ProNa>=0.25	TOS<75.7		50-60
						TOS>=75.7	TOS<5.1	50-60
							TOS>=5.1	60-70

4.1.4. CH_4 Conversion Results of Ru Metal Base Data

Compared to Ni and Rh metal base data, Ru metal based data consisted of lower number of experiments as 299 in training data and 149 in testing data. Since splitmin value is in parallel with the number of experiments, decreasing in experiments made splitmin value smaller as "3". In addition to splitmin, increasing prune value for small data sets is not required, so "2" was sufficient for Ru metal base data set. Training error was 8.03% and testing error was 14.77% for decision tree with 17 nodes in Figure 4.4.

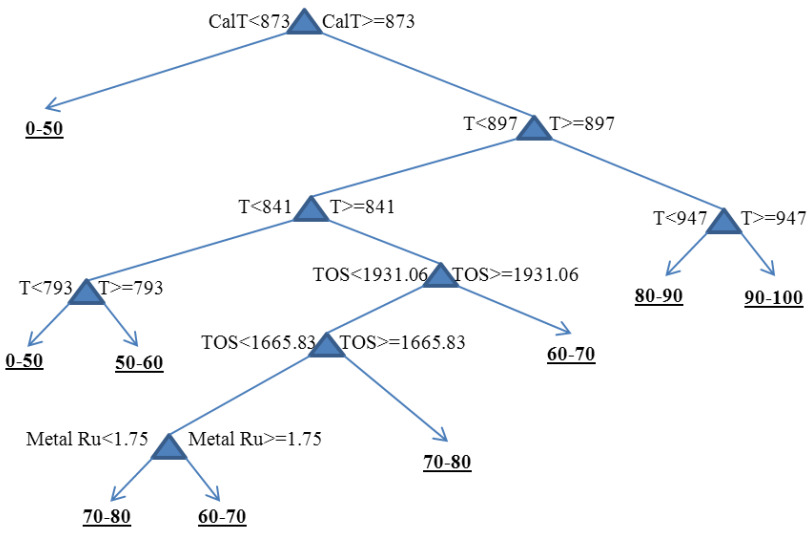

Figure 4.4. Decision tree of Ru metal base data.

Table 4.4. Deduction rule conditions of Ru metal base data for CH_4 conversion.

<table>
<tr><td>CalT<873</td><td colspan="5"></td><td>0-50</td></tr>
<tr><td rowspan="8">CalT>=873</td><td rowspan="2">T>=897</td><td>T<947</td><td colspan="4"></td><td>80-90</td></tr>
<tr><td>T>=947</td><td colspan="4"></td><td>90-100</td></tr>
<tr><td rowspan="6">T<897</td><td rowspan="2">T<841</td><td>T<793</td><td colspan="3"></td><td>0-50</td></tr>
<tr><td>T>=793</td><td colspan="3"></td><td>50-60</td></tr>
<tr><td rowspan="4">T>=841</td><td>TOS>=1931.06</td><td colspan="3"></td><td>60-70</td></tr>
<tr><td rowspan="3">TOS<1931.06</td><td>TOS>=1665.83</td><td colspan="2"></td><td>70-80</td></tr>
<tr><td rowspan="2">TOS<1665.83</td><td>Metal Ru>=1.75</td><td>60-70</td></tr>
<tr><td>Metal Ru<1.75</td><td>70-80</td></tr>
</table>

Although error percentages should decrease with lower splitmin and prune value, lack of generalizaton rules in the data prevented this favourable opportunity. Then, the optimal decision tree had to be decided as Figure 4.4. Increasing complexity of the tree didn't help extract most informative rule. However, error results were still at an acceptable level.

First division point was calcination temperature for Ru metal base data. Remaining division points were temperature, time on stream and amount of Ru metal. Since the range of temperature within the data set was not large, the most important variable was determined as calcination temperature. As a consequence of less data, a simpler deduction rule table was created for Ru metal base data in Table 4.4.

4.1.5. Results of Incipient to Wetness Impregnation Method Data

The most commonly used catalyst preparation method was incipient to wetness impregnation, Thus, a respectable amount of data existed in this type of data set; 1987 data points in the database were generated over the catalyst prepared by this method. In this section, the dataset containing these experiments were analyzed to see whether some rules could be deduced for this catalyst preparation method or not. For this subset, 1325 of total data points were randomly separated for training and the remaining 662 data points were used for testing. Optimal results were taken from the analysis for "10" splitmin and "7" prune value leading a 55 nodes decision tree. Training error was 11.47% while testing error was found as 14.50%; both are quite low. The optimal decision tree is shown in Figure 4.5, and the rules created from this tree for CH_4 conversion are given in Table 4.5.

For this data set, the value of the temperature is also the first decision points to as in total data set, but the division is in a lower values. If the catalyst is preparing with incipient

to wetness impregnation method, the presence of δ-Al_2O_3 seems to be the second decision points. γ-Al_2O_3, Ni metal base, H_2O composition, Rh metal base, ZrO_2 support, Ni metal base, time on stream, Mo promoter are the other variables that sould be considered.

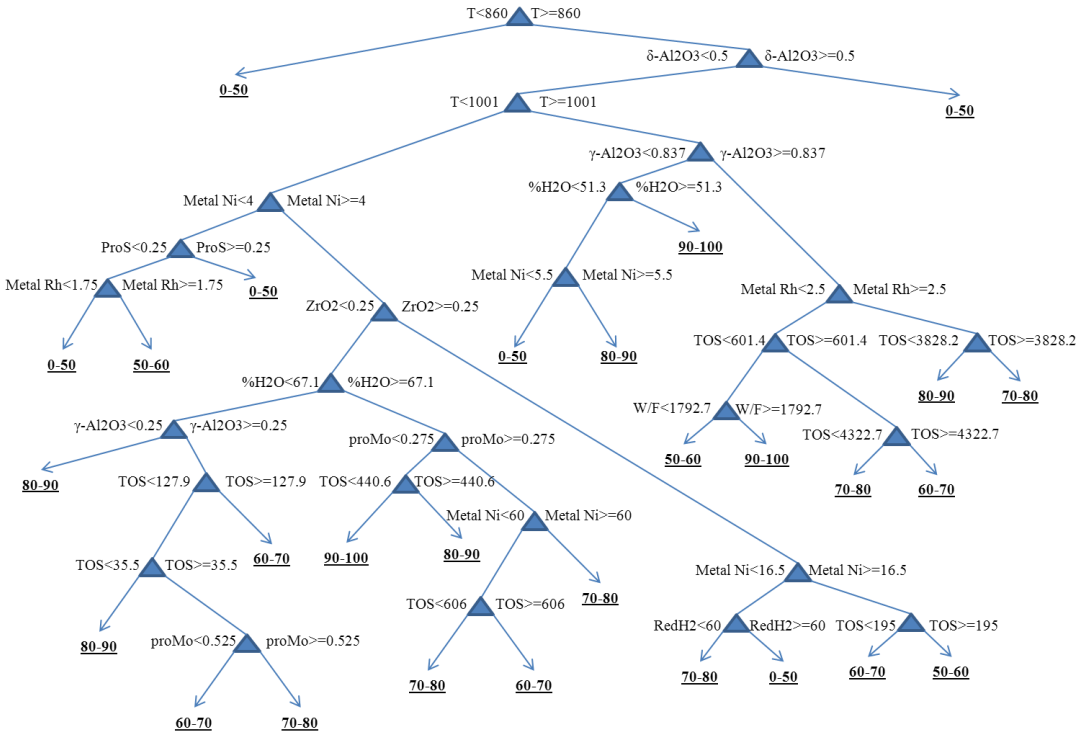

Figure 4.5. Decision tree of incipient to wetness impregnation data.

Table 4.5. Deduction rule conditions of incipient to wetness impregnation method data.

T<860										0-50
T>=860	δ-Al2O3>=0.5									0-50
	δ-Al2O3<0.5	T>=1001	γ-Al2O3<0.837	% H2O>=51.3						90-100
				% H2O<51.3	Metal Ni<5.5					0-50
					Metal Ni>=5.5					80-90
			γ-Al2O3>=0.873	Metal Rh>=2.5	TOS>=3828.2					70-80
					TOS<3828.2					80-90
				Metal Rh<2.5	TOS>=601.4	TOS>=4322.7				60-70
						TOS<4322.7				70-80
					TOS<601.4	W/F<1792.7				50-60
						W/F>=1792.7				90-100
		T<1001	Metal Ni<4	ProS>=0.25						0-50
				ProS<0.25	Metal Rh<1.75					0-50
					Metal Rh>=1.75					50-60
			Metal Ni>=4	ZrO2>=0.25	Metal Ni>=16.5	TOS>=195				50-60
						TOS<195				60-70
					Metal Ni<16.5	RedH2>=60				0-50
						RedH2<60				70-80
				ZrO2<0.25	% H2O>=67.1	proMo<0.275	TOS>=440.6			80-90
							TOS<440.6			90-100
						proMo>=0.275	Metal Ni>=60			70-80
							Metal Ni<60	TOS>=606		60-70
								TOS<606		70-80
					% H2O<67.1	γ-Al2O3<0.25				80-90
						γ-Al2O3>=0.25	TOS>=127.9			60-70
							TOS<127.9	TOS<35.5		80-90
								TOS>=35.5	proMo<0.525	60-70
									proMo>=0.525	70-80

4.1.6. CH_4 Conversion Results of Packed Bed Reactors Data

The packed bed reactors are the most common configuration in steam reforming of methane, hence there are significant number of data points obtained in these reactor. The dataset containing 4752 experiments were divided into two parts as 3168 of total data points for training and the remaining 1584 data points for testing. Optimal results were taken from the analysis for "75" splitmin and "2" prune value leading a 67 nodes decision tree. Training error was 20.01% while testing error was found as 21.78%. The optimal decision tree is shown in Figure 4.6, and the rules created from this tree for CH_4 conversion are given in Table 4.6.

The testing and training errors are quite similar to those for entire data set as expected since most of the data are obtained in packed bed reactor. The temperature is again the first decision variable followed by CH_4 composition, Ni metal base, W/F ratio, and so on.

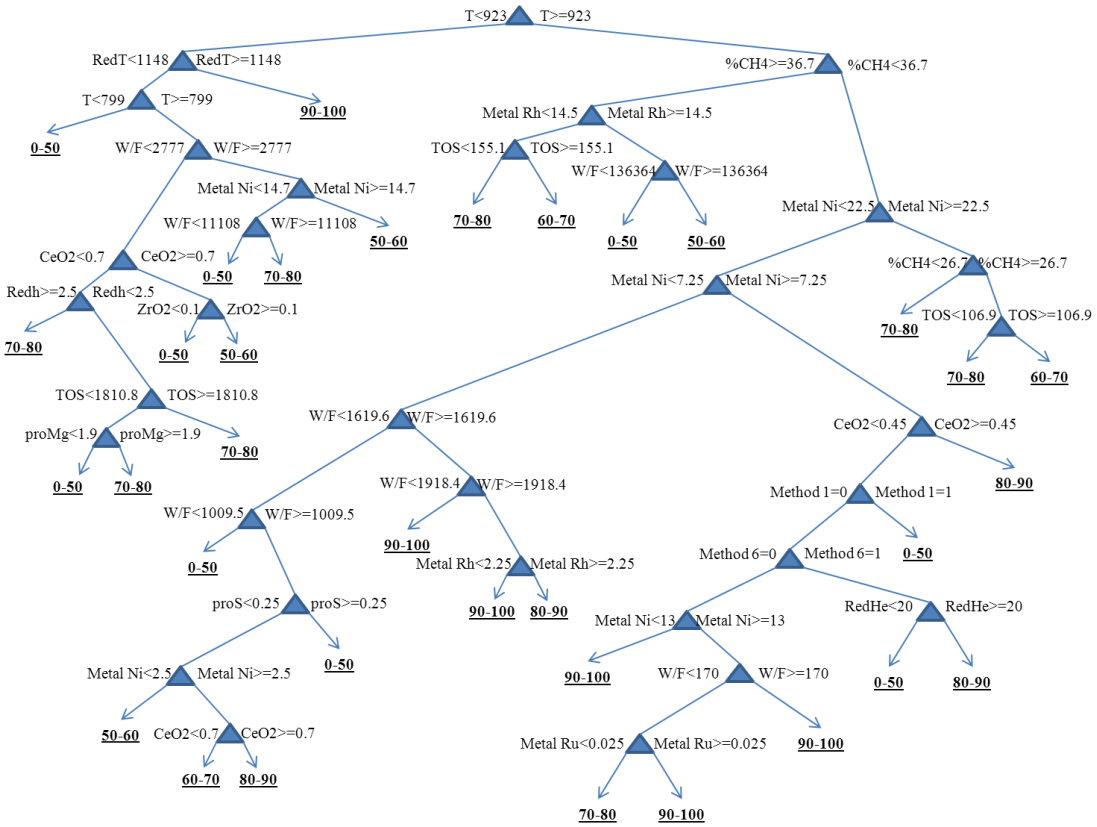

Figure 4.6. Decision tree of PBR data.

Table 4.6. Deduction rule conditions of packed bed reactors data for CH_4 conversion.

T<923	**RedT>=1148**										**90-100**
	RedT<1148	T<799									0-50
		T>=799	W/F>=2777	Metal Ni>=14.7							50-60
				Metal Ni<14.7	W/F<11108						0-50
					W/F>=11108						70-80
			W/F<2777	CeO2<0.7	Redh>=2.5						70-80
					Redh<2.5	TOS>=1810.8					70-80
						TOS<1810.8	proMg<1.9				0-50
							proMg>=1.9				70-80
				CeO2>=0.7	ZrO2<0.1						0-50
					ZrO2>=0.1						50-60
T>=923	%CH4>=36.7	Metal Rh>=14.5	W/F<136364								0-50
			W/F>=136364								50-60
		Metal Rh<14.5	TOS>=155.1								60-70
			TOS<155.1								70-80
	%CH4<36.7	Metal Ni>=22.5	%CH4<26.7								70-80
			%CH4>=26.7	TOS>=106.9							60-70
				TOS<106.9							70-80
		Metal Ni<22.5	**Metal Ni<7.25**	**W/F>=1619.6**	**W/F<1918.4**						**90-100**
					W/F>=1918.4	**Metal Rh>=2.25**					**80-90**
						Metal Rh<2.25					**90-100**
				W/F<1619.6	W/F<1009.5						0-50
					W/F>=1009.5	proS>=0.25					0-50
						proS<0.25	Metal Ni<2.5				50-60
							Metal Ni>=2.5	CeO2<0.7			60-70
								CeO2>=0.7			**80-90**
			Metal Ni>=7.25	**CeO2>=0.45**							**80-90**
				CeO2<0.45	Method 1=1						0-50
					Method 1=0	**Method 6=1**	RedHe<20				0-50
							RedHe>=20				**80-90**
						Method 6=0	**Metal Ni<13**				**90-100**
							Metal Ni>=13	**W/F>=170**			**90-100**
								W/F<170	Metal Ru<0.025		70-80
									Metal Ru>=0.025		**90-100**

4.1.7. Selectivity Results of Total Data

The database was also examined in terms of selectivity of CO and H_2 since the product distribution is also important in steam reforming of methane process. Splitmin and prune values were again adjusted with a desirable decision tree for selectivity of each product. The sum of the variables and results are in Table 4.7. There are less number of data points on selectivities compare to CH_4 conversion; almost in all publications, the conversion values were presented while the selectivity (and other performance measures) less frequently reported. As seen in Table 4.7, the training and the testing errors were again quite reasonable.

Table 4.7. Parameters and results related with selectivity.

Product	Training Data	Testing Data	Splitmin	Prune	Training Error %	Testing Error %	Node Number
CO	931	466	10	10	15.68	16.73	19
H_2	734	365	10	8	12.67	12.88	17

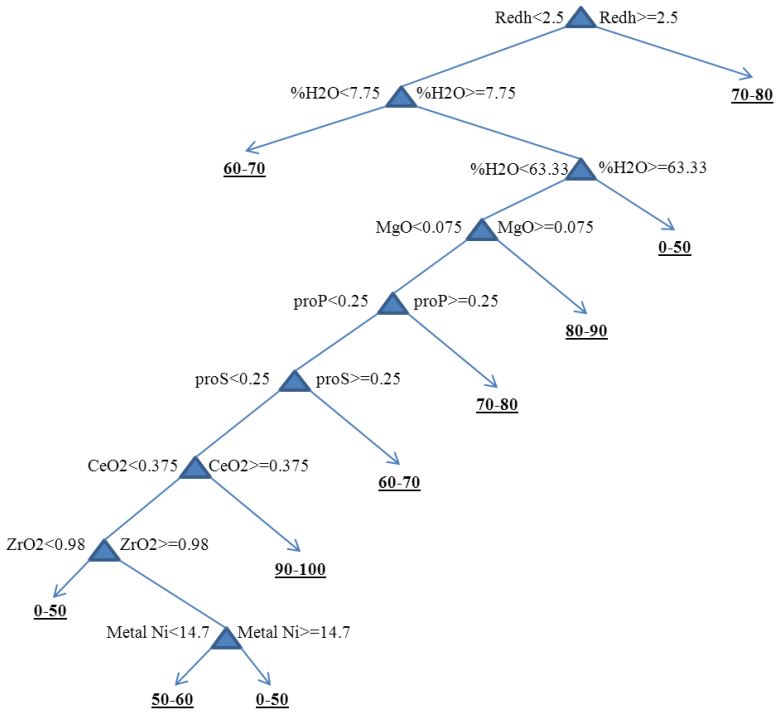

Figure 4.7. Decision tree of total data for CO selectivity.

Table 4.8. Deduction rule conditions of total data for CO selectivity.

Redh>=2.5									70-80
Redh<2.5	%H2O<7.75								60-70
	%H2O>=7.75	%H2O>=63.33							0-50
		%H2O<63.33	**MgO>=0.075**						**80-90**
			MgO<0.075	proP>=0.25					70-80
				proP<0.25	proS>=0.25				60-70
					proS<0.25	**CeO2>=0.375**			**90-100**
						CeO2<0.375	ZrO2<0.98		0-50
							ZrO2>=0.98	Metal Ni>=14.7	0-50
								Metal Ni<14.7	50-60

Obviously, the training error is smaller than testing error, as expected.

Figure 4.7 indicates the way of successful selectivity results for CO.

From Table 4.8, the best conditions for higher and better selectivity level of CO can be obtained by following the regions with dark color. Reduction time is a determinant parameter for high selectivity levels. Then, H_2O composition, MgO support, P promoter, S promoter and CeO_2 support make the selectivity levels increase.

Figure 4.8 is targeting successful selectivity results for H_2.

In Table 4.9, general rules exist for H_2 selectivity of total data. Rh metal base is favored in H_2 selectivity. Calcination time, reduction time, Ni metal base, reduction temperature and ZrO_2 support are also effective on the results.

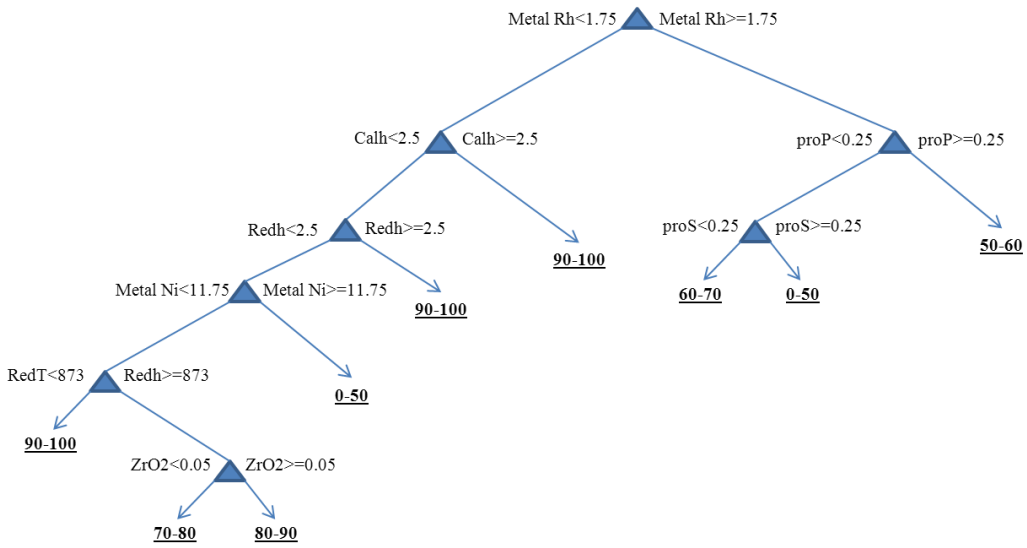

Figure 4.8. Decision tree of total data for H_2 selectivity.

Table 4.9. Deduction rule conditions of total data for H_2 selectivity.

Metal Rh>=1.75	proP>=0.25					50-60
	proP<0.25	proS>=0.25				0-50
		proS<0.25				60-70
Metal Rh<1.75	**Calh>=2.5**					**90-100**
	Calh<2.5	**Redh>=2.5**				**90-100**
		Redh<2.5	Metal Ni>=11.75			0-50
			Metal Ni<11.75	**RedT<873**		**90-100**
				RedT>=873	ZrO2<0.05	70-80
					ZrO2>=0.05	**80-90**

4.2. Neural Network Analyses and Results

The optimum neural network should be decided by using testing RMSE and R^2 because they show the ability of network to predict the unseen data. The RMSE of training was calculated by the error obtained between the experimental data points and the model predictions when whole data were included. On the other hand, the RMSE of testing, which was calculated by 4-fold cross validation analysis, was applied to test the generalization accuracy (prediction ability for the unseen data).

Activation function was selected as “tansig”. “trainlm“ (Levenberg-Marquardt Algorithm) and “trainbr” (Bayesian Regularization Algorithm) functions were used in training and testing, respectively. “trainlm” is selected as the fastest training function; “trainbr” is preferred in testing because it is desirable to determine the optimal regularization parameters in an automated fashion. The trainbr algorithm generally works best when the network inputs and targets are scaled so that they fall approximately in the range [−1, 1].

Too few neurons can lead to underfitting and too many neurons can contribute to overfitting. The increasing number of neurons will decrease the the training error but it will worsen the testing error after certain size. The reason is that the very large networks memorize the training examples, but they do not learn to generalize to new situations.

Various neural network topologies were tested and the neural network with 2 hidden layers and 16 neurons in each cause the RMSE and corresponding R^2 values are quite satisfactory for training and testing. In other words, 59 input variables introduced through 16 neurons in the first hidden layer and 16 neurons in the second hidden layer and 1 output

variable (CH_4 conversion) were created, and their accuracies of prediction were analyzed by using their root mean square error (RMSE) of training and testing .

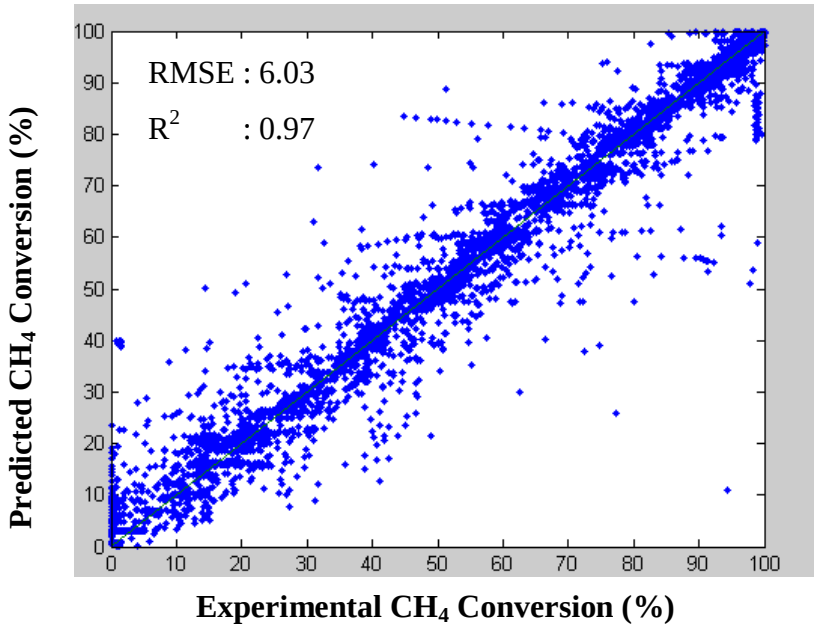

Figure 4.9. Training neural network results.

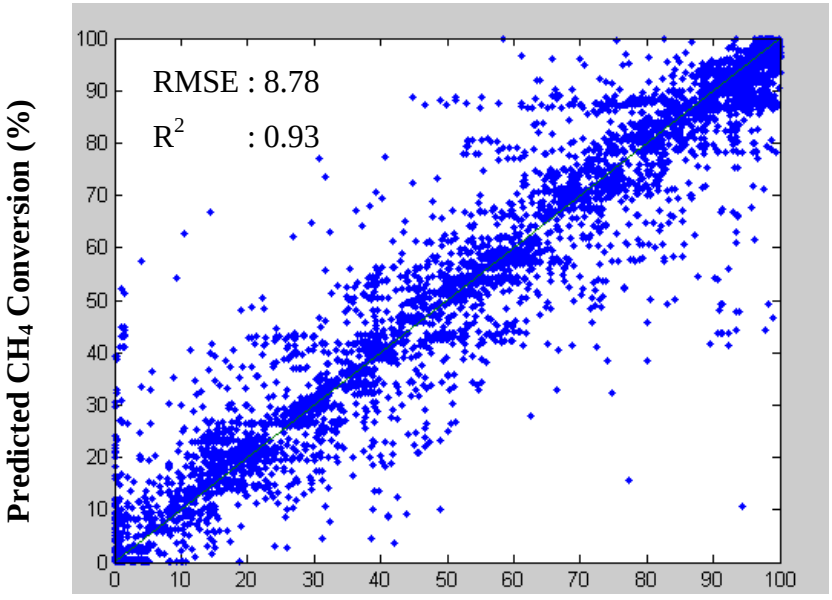

Figure 4.10. 4-fold testing neural network results.

The plot of the experimental versus predicted CH_4 conversions of training and testing for this optimal network is shown in Figure 4.9 and Figure 4.10. A considerable success was achieved with the training and testing R^2 values of 0.97 and 0.93 respectively, which indicates that the model exhibits excellent fits for both training and testing data with the training and testing RMSE values of 6.03 and 8.78, respectively.

Table 4.10. Input significance results of neural network.

Input Variable	RMSE (found)	RMSE difference	Relative Significance%	Group Significance %
Base Metal	8.95	3.11	29.9	Catalyst Design Variables 53.9
Support	7.54	1.70	16.3	
Promoters	6.38	0.53	5.1	
Reduction Conditions	5.95	0.11	1.0	
Calcination Conditions	5.94	0.10	0.9	
Catalyst Preparation Method	5.91	0.06	0.6	
Temperature	8.14	2.30	22.1	Operational Variables 46.1
W/F	6.53	0.69	6.7	
TOS	6.53	0.69	6.6	
Feed Compositions	6.51	0.67	6.4	
Pressure	6.11	0.26	2.5	
Reactor Types	6.02	0.18	1.7	

The relative significance of input variables were also analyzed by using 16-16 neural network model. By removing one variable from the input variables and retraining 16-16 network using the remaining variables, the difference between the RMSE in the absence and presence of that variable was determined as the indicator of its significance (larger the RMSE, higher the significance of variable). RMSE of the model when all input variables were included was 5.84. This procedure repeated for all the input variables and relative deviations from the RMSE of full model was used as the measure of relative significances. The results were listed in Table 4.10. The catalyst design variables were found to have 53.9% significance while the operating variables had 46.1% significance. Base metal, support and promoter types were the significant design variables. Temperature was the most effective operational variable. These results were expected since the support and

promoter are important variables on the catalyst structure because of the interaction with the base metals and leading parameter in operational variables is temperature for a highly endothermic steam reforming of methane process. Being the catalyst design conditions more significant than the operational variables is also an understandable result since the catalyst design conditions are usually changed in a wider range than the operational design conditions. The main reason behind this change is being in search of new catalytic properties for the process to solve the problems (such as coking and deactivation) of current catalysts.

It should be noted that the relative significances are valid within the limits of these variables in this experimental data set. Hence even a significant variable may be found as insignificant in this type analysis if it was not changed much though the database.

The prediction ability of the neural network model developed was also tested on the individual paper (to see whether it is possible or not to predict the outcome of one study in the literature using the others). At this analysis, one experiment from 421 experiments or one article from 59 articles was removed from the dataset, the model trained with the remaining data and used to predict the excluded experiment or paper; this procedure was repeated for all experiments and articles. Iteration numbers in MATLAB code were changed during the analysis since it affects the results. As a result, "25" was determined as the optimal one due to RMSE and R^2 values. 38 in 421 experiments and 11 out of 59 articles had R^2 values greater than 0.5 and RMSE values lower than 15; which seems a bad outcome, but it should be noticed that all these studies were experienced by different people under several set of conditions. Thus, they are not so bad at all. However, it should not be utilized sufficiently for practical purposes.

RMSE and R^2 results of all papers can be found in Table A.1 in which favorable results are in bold. Plots of the predicted versus experimental CH_4 conversions for the best predicted four publications are presented in Figure 4.11.

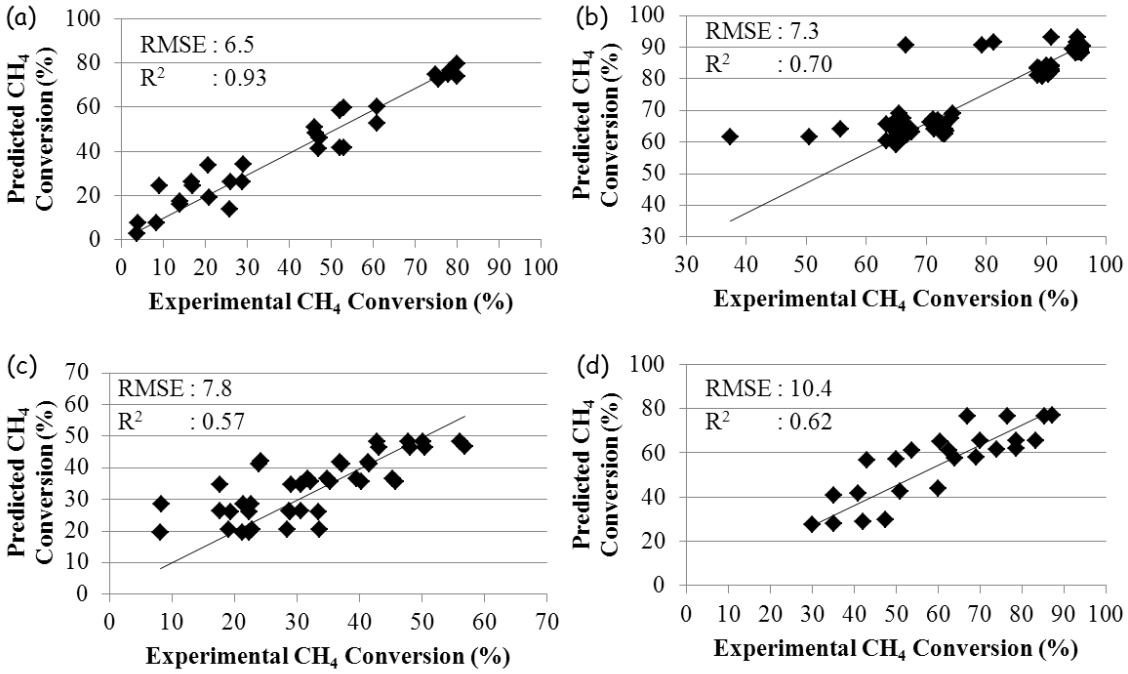

Figure 4.11. Experimental vs. predicted CH_4 conversion for (a) Jiménez-González *et al*., 2014, (b) Lee *et al*., 2012, (c) Soria *et al*., 2012, (d) Mbodji *et al*., 2012.

5. CONCLUSIONS AND RECOMMENDATIONS

In this thesis, the experimental data for steam reforming of methane were collected from the published articles between the years 2004 to 2014 using the databases of Science Direct, Wiley, ACS (American Chemical Society), and Springer, and analyzed by decision tree and neural networks. The final database consisted of 59 articles and 5552 experimental data with 59 input variables and 4 output variables. It was observed that the number of articles published in the year 2014 was the highest compared to other years. Also, it can be obviously seen that studies and publications have been increasing year by year since 2004, except 2010 and 2013.

Splitmin and prune parameters have an important effect on the decision tree selection. Several decision trees are obtained by trying different values of these parameters, and the most suitable values are selected in order to construct the tree and extract knowledge. Altough there are no definitive rules for selection of splitmin and prune value, the optimum decision tree was chosen according to simplicity of decision tree and an acceptable error rate. Number of data is not directly related with these parameters; however the decision tree analysis is usually successful in the experimental region having large number of data whereas smaller datasets were not easy to generalize.

The optimum decision tree structure performed on the entire database was achieved by using a splitmin value of 100 and a pruning level of 8. This tree had 63 nodes and with 20.83% training error and 22.91% testing error, both of which can be considered as acceptable. Tree suggested that first decision point is the reaction temperature followed by δ-Al_2O_3 support, CH_4 composition, and calcination and so on.

CH_4 conversion analysis of Ni metal base data was performed with 75 “splitmin” and 5 “prune” value. The decision obtained tree has 65 nod numbers with 21.41% training error and 24.52% testing error, which are quite similar to those obtained for the entire dataset. The first division was again based on the value of reaction temperature, but followed by SBA-15 and CeO_2 supports.

Because of less data, nod numbers and errors are decreasing for the other metal based datasets. Using 3 “splitmin” and 4 “prune” value, a decision tree was created with 41 nod

numbers and “temperature” as first division point for Rh metal base data in terms of CH_4 conversion. The training error and the testing error are 6.68% and 8.93%, respectively. As a result of CH_4 conversion analysis of Ru metal base data, 17 nod numbers exist in decision tree with 8.03% training error and 14.77% testing error for 3 “splitmin” and 2 “prune”. The general rule of the decision tree starts with calcination temperature.

The splitmin, prune, node number, training error, testing error and division point are 10, 7, 55, 11.47%, 14.50% and temperature for CH_4 conversion of incipient to wetness impregnation method data, respectively. The same parameters and results are 75, 2, 67, 20.01%, 21.78% and temperature for CH_4 conversion of packed bed reactors data.

A similar analysis was performed for the selectivity of various products. For CO selectivity, training error (15.68%) and testing error (16.73%) were in acceptable level. The results are 12.67% and 12.88% for H_2 selectivity, respectively.

As a results, the decision tree classification was found to be useful to derive some simple rules to determine favorable input variables for high conversion levels of methane steam reforming; it was proven that a simple procedure can be applied to the combination of various variables to extract some essential knowledge and experience from the published experimental data in the literature. Although consistency of decision tree classification with 100 percentage level could not be possible, the models developed were sufficient enough to guide the future studies about steam reforming of methane.

For the neural network analysis, adjustable parameters are activation functions, training functions, testing functions, hidden layer number and neuron number in these hidden layers. Several combinations of these parameters are performed until an optimal neural network model will be created with a better generalization capability.

For training of neural network model, 2 hidden layers and 16 neurons in each hidden layers were applied with “tansig” activation function and “trainlm” function. R^2 value was calculated as 0.97 and RMSE was 6.03. For testing of neural network model, R^2 and RMSE terms were calculated as 0.93 and 8.78 respectively.

The input significance analysis was also performed and the most significant input variable was found as base metal type with 29.9%. the order of importance for other variables fourn to be as temperature, support type, W/F ratio, time on stream, feed

compositions, promoter type, pressure, reactor type, reduction conditions, calcination conditions and catalyst preparation methods. As group significance, effect of the catalyst design variables (metal base, support type, promoter type, reduction conditions, calcination conditions and catalyst preparation methods) was 53.9% while the effect of operational variables (temperature, W/F ratio, time on stream, feed compositions, pressure and reactor type) was 46.1%.

To determine the effect of each experiment in total data, RMSE and R^2 values of 421 experiments were calculated by neural network algorithm while iteration number is "25" in MATLAB. Success level of experiments were 69.6% in terms of RMSE (lower than 15) and 9.03% in terms of R^2 (higher than 0.5).

The same procedure of experiments was applied to articles in order to find importance of each article while iteration number is "25" in MATLAB. For 59 articles, level of achievement of RMSE analysis in which the value was lower than 15 and R^2 analsis with higher than 0.5 values 44.07% and 18.64%, respectively.

Decision tree results are understandable and intuitive rules, whereas neural networks are relatively opaque to human interpretation since no straightforward procedure exists for translating the weights of a neural network into a compact set of decision rules. Also, neural networks require longer training times than decision trees.

Taking everything into consideration, in order to reach the best prediction method on any unknown data for the future studies, some recommendations can be stated. Other data mining tools such as clustering, support vector machines, etc. can be preferred. Also, the beginning time of the research may be extended as earlier than 2004. Resources may be improved in terms of literature field, patent field and other researching materials. Range and identity of input variables may be reviewed and their importance and effect on the reactions may be decided previously. Thus, dominant parameters may be analyzed carefully or ineffective parameters may be neglected.

APPENDIX A: ARTICLE RESULTS

Table A.1. Significance of articles.

Article	Data No	RMSE	Abs Error	R^2
Zeppieri *et al.*,2010	1	15.6	10.7	0.05
Lim and Bae, 2010	48	**3.1**	2.4	0.00
Halabi *et al.*,2010	79	26.4	19.7	0.00
Halabi *et al.*,2010	107	**2.1**	1.7	**0.86**
Avetisov *et al.*,2010	177	**8.9**	6.0	**0.69**
Jakobsen *et al., 2010*	185	54.2	53.7	0.00
Simsek *et al.*,2011	197	16.7	15.3	0.00
Chakrabarti *et al.*,2011	253	**14.9**	14.0	0.00
Soria *et al.*,2011	371	31.5	18.0	0.00
Kim *et al.*,2011	649	15.4	9.5	0.00
Prasad *et al.*,2011	923	**13.9**	11.3	0.35
Lee *et al.*,2012	1028	**7.3**	6.3	**0.70**
Abreu *et al.*,2012	1124	19.6	13.5	0.00
Soria *et al.*,2012	1265	**7.8**	6.0	**0.57**
Izquierdo *et al.*,2012	1307	16.2	11.6	0.00
Karakaya *et al.*,2012	1359	15.7	14.7	0.00
Arstad *et al.*,2012	1583	42.2	42.2	0.00
Miguel *et al.*,2012	1627	27.0	21.5	0.00
Mbodji *et al.*,2012	1697	**10.4**	9.0	**0.62**
Sekine *et al.*,2011	1721	**14.6**	12.1	0.36
Roh *et al.*,2012	1967	18.9	13.6	0.00
Tada *et al.*,2012	2427	17.2	12.4	0.00
Miguel *et al.*,2010	2430	63.4	62.2	0.00
Bej *et al.*,2013	2455	**10.7**	8.1	0.35
Amjad *et al.*,2013	2555	41.7	32.8	0.00

Table A.1. Significance of articles (cont.).

Oshima *et al.*,2013	2593	**10.3**	8.9	0.04
Obradović *et al.*, 2013	2603	17.1	11.0	0.00
Andrade *et al.*,2014	2903	**7.5**	6.5	**0.66**
Chu *et al.*,2014	2926	**4.0**	2.3	**0.81**
Mei *et al.*,2014	2960	25.1	20.7	0.00
Lee *et al.*,2014	3168	44.9	44.0	0.00
Sprung *et al.*,2014	3275	90.7	90.7	0.00
Huang and Huang, 2009	3414	15.1	14.0	0.39
Maluf and Assaf, 2009	3421	**11.9**	9.0	0.00
Xu *et al.*,2009	3651	16.5	9.3	0.00
Jiménez-González *et al.*, 2014	3786	**6.5**	5.0	**0.93**
Zhan *et al.*,2009	3816	**11.4**	7.3	0.00
Zhou *et al.*,2009	4052	18.7	17.8	0.00
Zhou *et al.*,2009	4259	23.4	20.7	0.00
Huang and Huang, 2008	4265	**12.8**	11.0	**0.56**
Zhou *et al.*,2008	4272	29.9	21.9	0.00
Nguyen *et al.*,2008	4313	**9.9**	9.1	0.10
Sutthisripok *et al.*,2008	4393	59.3	59.3	0.00
Jeon *et al., 2008*	4435	**5.9**	4.7	**0.56**
Purnomo *et al.*,2008	4447	**2.7**	2.2	0.00
Ma *et al.*,2008	4585	31.4	24.3	0.00
Wang *et al.*,2008	4625	**9.4**	5.7	0.00
Zhou *et al.*,2008	4795	35.9	25.3	0.00
Neto *et al.*,2007	5037	40.4	34.4	0.00
Wan *et al.*,2007	5085	**6.4**	5.5	0.00
Parizotto *et al.*,2007	5188	**13.4**	10.8	0.00
Li *et al.*,2007	5283	61.4	58.9	0.00
Jeong *et al.*,2006	5343	33.6	29.7	0.00
Djaidja *et al.*,2006	5381	**14.5**	9.6	0.00

Table A.1. Significance of articles (cont.).

Tong and Matsumura, 2005	5406	37.2	34.7	0.00
Urasaki *et al.*,2005	5433	20.1	19.9	0.00
Kusakabe *et al.*,2004	5454	32.8	28.0	0.00
Wang *et al.*,2004	5499	**4.6**	3.1	**0.78**
Matsumura and Nakamori, 2004	5527	**9.9**	7.7	0.00

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