DATA MINING FOR CARBON DIOXIDE ADSORPTION OVER AMINE MODIFIED ADSORBENTS FROM PUBLICATIONS IN LITERATURE

by

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ABSTRACT

DATA MINING FOR CARBON DIOXIDE ADSORPTION OVER AMINE MODIFIED ADSORBENTS FROM PUBLICATIONS IN LITERATURE

The aim of this thesis is to extract knowledge for carbon dioxide adsorption over amine modified adsorbents using two data mining techniques that are decision trees (DT) and artificial neural networks (ANN). The experimental data were collected from 30 papers published between 2002 and 2016. The data set consisted of 1356 data points with 26 attributes; the adsorption capacity (mmol CO_2/g adsorbent) and amino efficiency (CO_2/N ratio) were chosen as performance (output) variables. In DT analysis, the adsorption capacity and amino efficiency were classified in four groups, and the conditions leading to high adsorption capacity and amino efficiency were identified. Training and testing accuracies for adsorption capacity were 83.4% and 82%, respectively; while these values were 80.8 % and 77.3 % for the amino efficiency; from which the analysis for both output variables could be considered as successful. ANN analysis was also used to model the same data to develop predictive models; tansig function was used as the activation function and trainlm and trainbr were used as the training algorithms for training and testing, respectively. The optimal network topology was determined as 26-10-1 (10 neurons in one hidden layer) for adsorption capacity and 26-9-1 (nine neurons in hidden layer) for amino efficiency. The R^2 and RMSE values for adsorption capacity were respectively found to be 0.97 and 0.118 for training, and 0.90 and 0.250 for testing. Similar results were obtained for the amino efficiency. The R^2 and RMSE were 0.97 and 0.0230 respectively for training while R^2 was 0.83 and RMSE was 0.053 for testing. These results indicate that ANN models were also successful. The relative significances of input variables were also calculated by using the optimal neural network topology and change of mean square error method. Operational variables had greater significance on both amino efficiency and adsorption capacity relative to the adsorbent properties.

ÖZET

LİTERATÜRDE YAYINLANMIŞ MAKALELERDEN AMİNLE MODİFİYE EDİLMİŞ ADSORBANLAR ÜZERİNDE KARBONDİOKSİT TUTULUMU İÇİN VERİ MADENCİLİĞİ

Bu tezin amacı, karar ağaçları ve yapay sinir ağları gibi veri madenciliği tekniklerini kullanarak aminle modifiye edilmiş adsorbanların karbondioksit adsorpsiyonu için bilgi çıkarmaktır. 2002 ve 2016 yılları arasında yayınlanmış 30 makaleden deneysel veriler toplanmış, 26 değişken ve 1356 veri noktasından oluşan bir veri seti oluşturulmuştur. Adsorpsiyon kapasitesi (mmol CO_2/g adsorbent) ve amin verimi (CO_2/N oranı) ise performans (çıktı) değişkenleri olarak seçilmiştir. Karar ağaçları kullanarak analiz yapılırken hem adsorpsiyon kapasitesi hem de amin verimi için dörder sınıf tanımlanmış, her iki değişken için de en yüksek değerleri veren koşullar saptanmıştır. Karar ağaçlarının eğitim ve test için doğruluk oranları adsorpsiyon kapasitesi için sırasıyla 83.4% ve 82%, amin verimliliği için ise 80.8 %ve 77.3% bulunmuştur ki; bu değerler karar ağaçlarıyla yapılan analizin başarılı olduğunu göstermektedir. Tahmin edebilme gücü olan modeller geliştirmek için ise aynı set yapay sinir ağları kullanılarak modellenmiş, bunun için aktivasyon fonksiyonu olarak tansig, eğitim ve test algoritmaları olarak sırasıyla trainlm ve trainbr kullanılmıştır. Tahmin edebilme gücü en uygun sinir ağ yapısı adsorpsiyon kapasitesi için 26-10-1 (bir gizli katmanda 10 nöron), amin etkinliği için ise 26-9-1 (bir gizli katmanda dokuz nöron) olarak bulunmuştur. Adsorpsiyon kapasitesi için yapılan modelde R2 ve RMSE değerleri eğitim için sırasıyla 0.97 ve 0.118, test için ise 0.90 ve 0.250 olarak hesaplanmıştır. Amin etkinliği için ise R^2 ve RMSE değerlerinin eğitim için sırasıyla 0.97 ve 0.023, test için ise 0.83 ve 0.053 olduğu görülmüştür. Bu sonuçlar yapay sinir ağlarıyla geliştirilen modellerin de başarılı olduğunu göstermektedir. Bu modeller ayrıca RMSE değişimi yöntemiyle birlikte değişkenlerin göreceli önem analizleri için de kullanılmıştır. Operasyon değişkenlerinin her iki analiz için de adsorpsiyon özelliklerinden daha yüksek öneme sahip oldukları belirlenmiştir.

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R^2	Coefficient of determination

LIST OF ACRONYMS/ABBREVIATIONS

AEAPS	N-(2- aminoethyl)-3aminopropyltrimethoxysilane
APTES	3-aminopropyltriethoxysilane
cal.t	Calcination time
cal.T	Calcination Temperature
CART	Classification and regression tree
CO_2%	Flux CO_2 concentration
DEA	Diethanolamine
MEA	Monoethanolamine
MW	Molecular weight
P	Pressure
p. size	Pore size
p.vol	Pore volume
PEI	Polyethylenimine
PE-MCM-41	Pore expanded MCM-41
PE-SBA-15	Pore expanded SBA-15
pre.T	Pretreatment temperature
pri.	Primary amine
RMSE	Root Mean Square Error
SBET	Pore area
SC	Calcined SBA-15
sec.	Secondary amine
SP	Non-calcined SBA-15
STP	Standard temperature pressure
T	Adsorption temperature
TEPA	Tetraehylenepentamine
tert.	Tertiary amine
TRI	(3-trimethoxysilylpropyl)diethylenetriamine
pMONO-silane	3-aminopropyltrimethoxysilane
sMONO-silane	N-methylaminoproyltrimethoxysilane
tMONO-silane	N,N-dimethylaminopropyltrimethoxysilane

1. INTRODUCTION

Climate change and global warming, led by emission of greenhouse gases such as carbon dioxide, ozone, methane and nitrous oxide into the atmosphere, are the growing concerns of this century; hence the research efforts to improve the techniques for the diminution of greenhouse gases especially carbon dioxide emissions to the environment have continuously increased in recent years. One of these research areas is CO_2 capture from diversity of sources mainly fossil fuel-fired power plants by using some effective sorbents.

In spite of the fact that fossil fuel power plants have significant detrimental effect on environment, it is accepted that fossil fuel leads the resource of energy for years to come. Hence, development of effective methods for the sequestration and capture of CO_2 is crucial. There are three approaches being investigated on this matter: pre-combustion, post-combustion and oxy-fuel combustion processes. In pre-combustion capture, fuel is partially oxidized in steam and air and the resulting syngas subsequently undergoes the water-gas shift reaction converting CO and water to hydrogen and CO_2. CO_2 is then separated from the hydrogen stream and stored. In oxy-fuel combustion, oxygen is used for the combustion. In this way, the resulting flue gas mainly constitutes of CO_2 and water, making the separation of CO_2 easy. Finally, in the post-combustion capture, CO_2 is separated from the flue gas that is obtained through the combustion of fuel with air stream. Although separation of CO_2 is much easier due to the higher concentrations in the pre- and oxy-combustion methods, post-combustion approach is the most widely used technology due to the high investment costs of gasification and air/oxygen separation involved in the former methods (Benson and Orr, 2008).

Amine-based regenerative chemical absorption process using aqueous monoethanolamine (MEA) solutions is the most conventional and mature technology that is employed for the capture of CO_2 in the post-combustion approach. However, despite of the high reactivity and kinetics, aqueous MEA systems are still far from being used in large-scale capture processes due to the high regeneration costs, and finding a cost-

effective process for CO_2 capture from the flue gas is still one of the main interests in the field.

Adsorption of CO_2 is one of the most frequently considered alternatives to wet systems. Compared to other applications, the adsorption process using novel solid sorbents has versatile advantages, such as lower energy requirement, convenient handling conditions, high selectivity and capacity, etc. Using dry solid sorbent instead of aqueous amine-based processes significantly reduce the regeneration energy requirement for CO_2 capture due to the absence of large amounts of water. Moreover, solid sorbent heat capacity is lower than that of aqueous amine solvent. The other factors that favor the dry solid sorbents are adsorption and desorption kinetics and high CO_2 selectivity (Yang, 2003; Kohl and Nielsen, 1997).

The major challenge for CO_2 capture is to achieve it at the high volumetric flow rates of flue gas at atmospheric pressure with extensive amount of CO_2 at low pressure and 100-150 °C range of temperature (Choi *et al*., 2011).

In the literature, development of new solid sorbents for CO_2 capture from flue gas with the most efficient performance and desired economics have been investigated by numerous groups of researchers. Flue gas includes impurities inside such as oxides of nitrogen and sulfur, and these impurities reduce the sorbent performance, therefore it is important to understand the behavior and characterization of different sorbent materials (Lee *et al*., 2008). However, it is quite difficult to analyze the works in the literature, to observe and understand the relation between sorbent types and operating variables with the naked eyes because of the complexity and size of the data accumulated over the years. Therefore, data mining tools, which have been developed to extract knowledge from complex of datasets, can be also applied for this subject. This gives opportunity to discover meaningful correlations, trends and patterns by using statistical and mathematical methods (Romero and Ventura, 2007; Larose, 2005).

There are various data mining tools that can be used to perform various tasks such as clustering (like k-mean clustering), classification (like decision tree) and prediction (like artificial neural networks). Selection of the most appropriate data mining tool is critical for

the extraction of the desired knowledge successfully. An effective approach would be to use various tools together to maximize the benefit for the specific problem in hand.

In this work, a comprehensive database of CO_2 capture from flue gas was constructed by using the experimental data published in various papers in last decade. Then this database is analyzed using decision trees to deduce heuristics for best performance and artificial neural networks to develop predictive models for future works. The thesis consists of five chapters. In the Thesis Background (Chapter 2), published articles on carbon dioxide adsorption of amine modified sorbents are reviewed, and the data mining techniques used in this thesis are summarized. The database construction process and the computational details on data mining tools are explained in Computational Works (Chapter 3). In Results and Discussion (Chapter 4), the results of decision trees and neural network analysis are presented and discussed. In Conclusion and Recommendations (Chapter 5) the major conclusions and recommendations are summarized.

2. THESIS BACKGROUND

2.1. Carbon Dioxide Adsorption on Amine-Supported Adsorbent

CO_2 adsorption is the most effective way in order to capture carbon dioxide from flue gas. Amines are widely used as the functionalized adsorbents for carbon dioxide adsorption. The chemical reactions involved in carbon dioxide capture on amine-functionalized sorbent are indicated as follows:

Formation of zwitterion and carbamate:

$$RR'NH + CO_2 \leftrightarrow RR'NH^+COO^- \text{ (Zwitterion)} \quad (2.1)$$

$$RR'NH^+COO^- + RR'NH \leftrightarrow RR'NCOO^- \text{ (Carbamate)} + RR'NH_2^+ \quad (2.2)$$

The overall reaction is

$$2RR'NH + CO_2 \leftrightarrow RR'NCOO^- + RR'NH_2^+ \quad (2.3)$$

In the presence of water:

$$RR'NH + CO_2 + H_2O \leftrightarrow RR'NH_2^+ + HCO_3^- \quad (2.4)$$

R′ refers to hydrogen for the primary amine in the above equations.

The reaction of primary and secondary amine with CO_2 is to form zwitterion first and then to form carbamate. On the other hand, the reaction of tertiary and sterically hindered amines with carbon dioxide is to form bicarbonate but not carbamate. The carbon dioxide capture technology is an energy intensive process and the overall cost is high. The major concerns of selection of adsorbent are cost, adsorption rate, carbon dioxide adsorption capacity and thermal stability of adsorbents. Thus the process is usually maintained at

viable conditions in order to achieve desirable and high adsorption capacity (Yu *et al.,* 2012).

2.2. Influencing Factors on CO_2 Adsorption over Amine-Supported Adsorbent

2.2.1. Adsorbent Type and Adsorbent Properties

In order to increase carbon dioxide adsorption capacity and achieve high selectivity, surface of the porous materials is modified by incorporating basic sites that are capable of chemically interacting with CO_2. The common modifying functional substances are various amine groups and since these groups constitute the active sites of the adsorbent, the amount of these functional groups is quite determining on adsorbents' performance (Samanta *et al.,* 2012). On the other hand, although support materials do not usually interact with CO_2 at the conditions of interest, their pore size and structure are closely related to the amount of amine loaded onto the support, so they may still affect the adsorption capacities.CO_2 adsorption of different amine-supported mesoporous silicas, which were SBA-15 and MCM-41, were compared. Polyethylenimine (PEI) was impregnated on these silica sorbents. According to their study, adsorbent pore properties were determined for both MCM-41 and SBA-15. Pore size was 6.1 nm for 50 wt % PEI-SBA-15 and 0 nm for 50 wt % PEI-MCM-41. Surface area was found to be higher for 50 wt % PEI-SBA-15. It was obvious that SBA-15 silica had larger pore and surface area. CO_2 adsorption experiment was carried out in two stage process and CO_2 removal was achieved at first stage at 75 °C. It was reported that the CO_2 adsorption capacity was 140 mg/g sorbent for 50 wt % PEI-SBA-15 and 89.2 mg/g sorbent for 50 wt % PEI-MCM-41. It was concluded that under same experimental conditions, when the same amount of amine was impregnated on the sorbent surface, SBA-15 sorbent exhibited better adsorption capacity due its larger pores (Ma *et al.,* 2009).

Adsorption capacity of a series of mesoporous silica materials were investigated. MCM-41, MCM-48, SBA-15, SBA-16 and KIT-6 sorbents were modified by 50 wt % of PEI by impregnation method. The properties of these materials were measured by nitrogen adsorption isotherms and it was found out that pore size varies in decreasing order KIT-6 > SBA-15 > SBA-16 > MCM-48 >MCM-41. Accordingly, adsorption capacities were found

as 135 mg/g adsorbent, 129 mg/g adsorbent, 127 mg/g adsorbent, 119 mg/g adsorbent, 111 mg/g adsorbent for 50 wt % containing KIT-6, SBA-16, SBA-15, MCM-48, MCM-41 respectively. KIT-6 and SBA-16 sorbents showed the highest adsorption capacities due to their high pore sizes (Son et *al.,* 2008).

Adsorption kinetics affects primarily the adsorption performance in several processes. An adequate adsorbent should have high adsorption rate and equilibrium adsorbent capacity. As mentioned above, pore structure and size are closely related to the amount of amine loaded onto the mesoporous silica, so these two properties are quite determining on the adsorption capacity. On the other hand, diffusion of CO_2 within the pores of the adsorbent is closely related to the rate of adsorption, so adsorbent properties like pore structure and size as well as surface area may influence the adsorption capacity through the kinetics of adsorption. Correspondingly, larger pores resulted in a considerable increase in the adsorbent's CO_2 capture performance (Son *et al.,* 2008).

Conventional MCM-41 and pore expanded MCM-41 silicas' CO_2 adsorption performances were investigated in order to determine best performance. These supports were modified with (3-trimethoxysilylpropyl)diethylenetriamine (TRI) by grafting method. The experimental results showed that under the same grafting conditions, pore expanded PE- MCM-41 silica was grafted with larger amount of amine than MCM-41 silica. As a result, in terms of CO_2 adsorption performance, PE-MCM-41 had a significantly higher equilibrium capacity and adsorption rate. These results were mainly due to the larger pore diameter and volume of PE-MCM-41 (9.4 nm and 0.87 cm^3/g, respectively), compared to MCM-41 silica (Harlick and Sayari, 2006).

In addition to the mentioned physical properties of the adsorbent, calcination conditions such as calcination temperature and time were also reported to influence the adsorption capacity through the concentration of hydroxyl concentration (Yue *et al.,* 2008).

Wei *et al.* (2008) reported the adsorption performance of SBA-16 functionalized with N-(2-aminoethyl)-3aminopropyltrimethoxysilane (AEAPS). The adsorption performance was improved by the hydrolysis of the calcined SBA-16. The adsorbents, which had fine particle size, demonstrated good accessibility and high surface area. It was

found that maximum CO_2 adsorption capacity was 0.727 mmol/g at 333 K with a particle size range of 0.124-0.15 mm.

CO_2 adsorption performance of amine containing SBA-15 silica was investigated. Mesoporous material was prepared in two ways. Firstly, part of solid was recovered, washed with distilled water, then air dried and denoted as SP. The remaining part of the solid was calcined at 550 °C for 6 h and denoted as SC. Different amount of amines and mix of TEPA and diethanolamine (DEA) were impregnated on both sorbents in order to understand the effect of hydroxyl group concentration on adsorption capacity. DEA contains two hydroxyl groups. More hydroxyl group on the sorbent could result in a change in the mechanism of amine reacting with CO_2 and an increase in the capacity. An adsorbent which contained 30% of TEPA, 20% DEA and 50% SP, had 3.9 m^2/ g surface area and its adsorption capacity was found as 163 mg/g. CO_2 adsorption capacity of DEA modified SP and SC was 20.8 mg/g and 9.2 mg/g respectively. CO_2 capacity of DEA modified SP was larger than DEA modified SC due to the difference in the distribution of DEA in two sorbents (Yue *et al.,* 2008).

2.2.2. Amine Type

Amine supported materials exhibit high adsorption capacity and fast carbon dioxide adsorption rate. Several microporous/mesoporous materials loaded with basic nitrogen functionality or organic amine functionality are frequently employed in order to remove CO_2 from flue gas efficiently. Adsorption of CO_2 using amine-functionalized sorbents involves chemical reaction and therefore it is necessary to know how the nature of amine influences the capacity and kinetics.

Primary and secondary amines do react directly with CO_2, while tertiary amines do not directly react with CO_2. The zwitterion reaction mechanism of CO_2 adsorption for primary and secondary amines involves two steps; formation of zwitterion and deprotonation of zwitterion. The reaction between sterically hindered primary and secondary amine produces bicarbonate therefore CO_2 loading can increase to 1 mol/mol amine while CO_2 capacity for primary and secondary amine is 0.5 mol/mol amine. Amine type (primary, secondary, tertiary), nitrogen content, molecular weight, steric hindrance,

and the linearity of amine are the crucial factors on carbon dioxide adsorption process (Samanta *et al.,* 2012).

Sayari *et al.* (2012) investigated the adsorption capacities of PE-MCM-41 modified by grafting primary 3-aminopropyltrimethoxysilane (pMONO-silane) secondary N-methylaminoproyltrimethoxysilane (s-MONO-silane) and tertiary N,N-dimethylaminopropyltrimethoxysilane (tMONO-silane) amines. Amine content was 4.6, 3.67 and 3.25 mmol/g for pMONO-silane, sMONO-silane, tMONO-silane respectively. The equilibrium molar CO_2/N ratio (amino efficiency) was calculated under a reacting environment of %5 CO_2 in balance N_2 at 25 °C and 1 atm. It is found out that primary amine showed the highest CO_2/N molar ratio (0.5) compared to secondary and tertiary amines. Thus primary amine containing PE-MCM-41 silica exhibited the highest adsorption capacity. Secondary amine had weaker interaction with CO_2 than primary amine therefore secondary amine containing silica showed lower CO_2 capacity. Tertiary amine containing silica hardly captures CO_2. Primary and secondary amines show high reactivity.

CO_2 adsorption performance of pore-expanded mesostructured SBA-15 silica was examined by *Sanz et al*. (2013). pMONO-silane and TRI were grafted on the support surface, while PEI and tetraethylenepentamine (TEPA) were impregnated on PE-SBA-15 surface. In addition to this, pMONO-silane and TRI modified PE-SBA-15 materials were additionally impregnated with PEI and TEPA. Three different types of modification method were applied. They measured the amine-modified adsorbent properties and nitrogen content was different for all materials. Nitrogen content was 4.4 % and 6.8 % for pMONO-silane and TRI grafted PE-SBA-15, respectively. Adsorption experiments were carried out at 45 °C and 1 bar. Adsorption capacities were found as 65.7 and 71.4 mg CO_2 per g for pMONO-silane and TRI -grafted PE-SBA-15, respectively. Adsorption capacity of 50%-TEPA-impregnated PE-SBA-15 was 164 mg CO_2 per g at 45 °C and 1 bar and its nitrogen content was 14.1 %, while that of 50% PEI-impregnated PE-SBA-15 was 138 mg CO_2 per g under the same conditions and its nitrogen content was 13.2 %. PEI and TEPA impregnated sorbents showed higher adsorption capacities over grafted materials. In addition, these adsorbent's pore diameters were 12.8 and 10.6 for PEI-PE-SBA-15 and TEPA-PE-SBA-15, respectively. Amino efficiency (C/N) was found to be 0.33 and 0.37 for PEI-PE-SBA-15 and TEPA-PE-SBA-15, respectively. Since TEPA impregnated PE-

SBA-15 had higher nitrogen content, higher efficiency (ratio of captured carbon dioxide (mol) /nitrogen content (mol)) and it was exhibited higher adsorption capacity, at the end of this study it was concluded that nitrogen content of modified amine and pore diameter were the essential factors which had dominating effect on the adsorbent performance (Sanz *et al.,* 2013).

Adsorption performance of SBA-15 was investigated. SBA-15 was grafted with pMONO-silane and TRI while PEI and TEPA were impregnated on SBA-15 silica. CO_2 adsorption experiments were conducted under pure stream, diluted stream (15% CO_2) and in humid stream (5% water). All prepared adsorbents were characterized and it was found that chain length was increased for grafted samples, while organic content was increased for impregnated samples. In addition to this, it was observed that nitrogen content was increased for longer grafted organosilane chains and higher impregnated organic amounts. pMONO-silane containing SBA-15 and TRI containing SBA-15 adsorbents contain 3.7% and 5.3% nitrogen, had 286 m^2/g and 227 m^2/g surface area and 7.1 nm and 6.8 nm pore diameter, respectively. PEI and TEPA impregnated SBA-15 had higher nitrogen content compared to grafted ones. Adsorption capacities of these adsorbents were experimented at 25 °C. At the end of these experiments, CO_2 uptake was found as 1.74 mmol/g and 1.4 mmol/g for pMONO-silane containing SBA-15 and TRI containing SBA-15; respectively, which showed nitrogen dependence. 50% PEI impregnated SBA-15 and 50% TEPA impregnated SBA-15 had 2.22 mmol/g and 1.72 mmol/g CO_2 uptake. 50% PEI impregnated SBA-15 contains 8.53% nitrogen but it has similar adsorption capacity with grafted materials due to lower efficiency in CO_2 capture of the amino groups contained. This was a clue for viscous nature of PEI hindering CO_2 diffusion, as a result of which amino groups cannot react with CO_2 in the deep pores (Sanz Perez *et al.,* 2013).

A sterically hindered amine can be explained as the primary amine in which the amino group is attached to tertiary carbon atom. If the amine is secondary or tertiary in which the amino group attached to a secondary or tertiary carbon. In addition to this, it was showed that steric hindrance controls the carbon dioxide and amine reaction. The study showed that especially, in aqueous amino alcohols, steric hindrance has an effect on adsorption rate at high CO_2 loadings (Sartori and Savage, 1983).

2.2.3. Amine modification method

Type of interactions between amine groups and the support is significant for capturing CO_2 from flue gas streams and to determine the amount of amine loading on the adsorbent structures. In this project, amine attachment methods were collected under two titles, such as impregnation and grafting. Carbon dioxide adsorption capacity depends on the amine density and total nitrogen content. Thus, modified nitrogen content is restricted by the concentration of the hydroxyl groups on the sorbent surface, if grafting method is applied. On the other hand, impregnation method offers many advantages to overcome these amine-loading limitations. More amine loadings can be achieved during impregnation method by physical incorporation into the porous structure. Accordingly, nitrogen content and CO_2 uptake are generally higher for impregnated samples than grafted materials. However CO_2 capture efficiencies are lower in impregnated materials than grafted materials due to diffusion limitations. Impregnated materials show lower amine distribution (Sanz *et al.,* 2013).

On the other hand, organic functional groups are covalently bonded on sorbent surface through a chemical reaction between aminosilane molecules and sorbent surface silanol groups during grafting, as a result of which grafted materials exhibit high thermal stability. CO_2 adsorption of functionalized SBA-15 silica was experimented using two different amine modification methods, namely grafting with APTES and impregnating with PEI. CO_2 adsorption experiments were conducted at 25 °C for APTES-grafted and PEI-impregnated samples. It was reported that CO_2 uptake was 1.74 mmol CO_2/ g for the impregnated conventional sample, while it was 2.12 mmol CO_2/g for grafted material. On the other hand, nitrogen content was 8.53% and 4.97 % for PEI-impregnated and APTES-grafted SBA-15, respectively. Although PEI impregnated material had higher nitrogen content, it showed lower CO_2 uptake compared to APTES-grafted materials due to the diffusion limitation (Garcia *et al.,* 2015).

Adsorption characteristics of PEI impregnated SBA-15 was investigated. Materials were prepared with different PEI loadings on the mesoporous silica (10, 30, 50, and 70 wt %). CO_2 adsorption strongly depends on PEI content and pure CO_2 adsorption isotherms

showed that 50 wt % PEI had the highest capacity (89.8 mg CO_2 per g sample) at 75 °C and 1 bar (Sanz *et al.,* 2010).

2.2.4. Flue Gas Stream Composition (Selectivity of CO_2)

The selectivity can be described as the ratio of the CO_2 capacity to that of the other component at a given flue gas composition and has a direct impact on the purity of CO_2 captured. Flue gas streams from fossil fuel fired power plants contain 10-15% CO_2, 70-75% N_2, 8-10 % H_2O, 3-4% O_2, and trace amounts of SO_x and NO_x. Adequate sorbent for CO_2 separation should exhibit high CO_2 selectivity over these components of the gas (Samanta *et al.,* 2012).

CO_2 adsorption performance of APTES-grafted SBA-15 is significantly affected by CO_2 partial pressure and temperature. APTES-modified SBA-15 molecules had great advantages in terms of chemical interaction at low partial pressures. However, CO_2 capture capacity of the adsorbent decreased when the partial pressure decreased from 0.1 MPa to 0.005 MPa. But still adsorbent was stable at low partial pressure (Wang *et al.,* 2007).

TRI-grafted pore-expanded MCM-41 (PE-MCM-41) was studied. It was figured out that selectivity for CO_2 over N_2 and O_2 was high. Two different feed compositions were studied, namely pure CO_2 and a stream with CO_2:N_2 = 10:90 and it was observed that adsorption capacities under CO_2:N_2 = 10:90 mixture was 40% lower than pure CO_2 at 75 °C (Serna-Guerrero *et al.,* 2010).

2.2.5. Temperature and Pressure

Adsorption of carbon dioxide is an exothermic process. Therefore, adsorption capacity should decrease with increasing temperature due to mechanism of thermodynamically controlled process. Adsorption capacity of PEI modified mesoporous sorbent of MCM-41 was experimented. According to their study, PEI modified MCM-41's adsorption capacity was tested with changing temperature. In spite of the fact that adsorption is an exothermic reaction high adsorption rate was detected at higher temperatures. At 50 °C, adsorption capacity was 44 mg/g-adsorbent for MCM-41-PEI-50,

while 112 mg/g-adsorbent was captured when the temperature was increased to 75 °C, originating from the fact that adsorption was diffusion-controlled. At lower temperatures, some of the amine sites within the silica pore channels were not accessible but as the temperature increased these sites also reacted with CO_2 and adsorption capacity increased (Xu *et al.,* 2002).

Adsorption temperature and pressure significantly affect adsorbent stability and CO_2 capture capacity of adsorbent through adsorbent-adsorbate interactions. Optimum interactions between adsorbent-adsorbate should neither be too weak or too strong. For more comprehensive account on CO_2 adsorbents in general, the temperature should be in between 25 and 75 °C and as for total pressure, it should be between 1-2 bar (Choi *et al.,* 2009).

Amine grafted pore expanded mesoporous silica's CO_2 capture performance were investigated from very low pressure to 1 bar at 298, 308, 318, 328 K. TRI was grafted on PE-MCM-41 sorbent. Amine content was found as 7.9 mmol amine/g sorbent. Column breakthrough measurements were used to determine adsorption capacity and it was found that CO_2 adsorption capacity decreased when the temperature rose from 298 to 328 K and the pressure from 0.01 to 0.05 bar. The CO_2 adsorption capacity was the highest at 298 K (Belmabkhout *et al.,* 2010).

CO_2 capture performance of mesoporous SBA-15 modified by TEPA with different amounts was investigated. The adsorption measurements were performed at different temperatures. Adsorption capacity was increased with increasing temperature from 35 °C to 75 °C (Yue *et al.,* 2006).

Sanz Perez *et al.* (2013) investigated the adsorption performances of pMONO-silane and TRI as well as PEI and TEPA-impregnated SBA-15 at 25 °C and 110 °C. Since adsorption is an exothermic process, both physical and chemical adsorption decreases when temperature increases. pMONO-silane adsorption capacity was 1.4 and 0.46 mmol/g at 25 °C and 110 °C respectively. On the other hand, TRI grafted sample's adsorption capacity was 1.74 and 0.58 mmol/g at 25 °C and 110 °C respectively. Both adsorbent adsorption capacities drastically decreased when the temperature increased. Adsorption is

completely physical for SBA-15 sorbent which did not contain any amine. Adsorption capacity of 50% PEI impregnated SBA-15 were highly affected by temperature change. 50% PEI impregnated SBA-15 adsorbent had high amino content (8.3%), which contributed to chemisorption and its surface area was low demonstrating that the physically adsorbed CO_2 was low. Adsorption capacity of this sorbent was 1.72 and 1.15 mmol/g at 25 °C and 110 °C, respectively. It was observed that chemical and physical adsorption were both exothermic for both materials. However, interaction between amine group and carbon dioxide increases with temperature increase due to CO_2 diffusion into pores. 50% TEPA-impregnated SBA-15, on the other hand, showed the highest adsorption capacity due to its highest nitrogen content (15.4%). This adsorbent showed the maximum CO_2 adsorption capacity at 80 °C therefore it can be concluded that positive effects of temperature increase such as higher mobility, CO_2 diffusion was higher than negative effect of temperature increase (Sanz Perez *et al.,* 2013).

2.2.6. Presence of Water

Carbon dioxide stoichiometry is affected by water presence if water is included in the carbon dioxide capture reaction, the maximum amount of carbon dioxide captured per mole of amine can reach to 1 mole. On the other hand, this number can at most reach to 0.5 moles; if water is not involved in carbon dioxide capture reaction. Since flue gas also contains water vapor, it is critical to understand the influence of water on the capture characteristics of the adsorbents. Moisture is known to adversely affect CO_2 adsorption capacity in several physical adsorbents (Samanta *et al.,* 2012), but the effect of water on the capacity of chemisorbents could not still be clarified despite of the theoretical basis mentioned above.

CO_2 working performance was investigated with and without moisture by using PEI modified molecular sieve MCM-41. The PEI loading resulted in improvement of CO_2 adsorption capacity and CO_2 separation selectivity. Simulated flue gas contained CO_2, O_2, N_2 and the moisture was added into flue gas to make the humid flue gas. Therefore, flue gas contained 8-20% moisture (water vapor) and the experiments were run at 75 °C under ambient pressure. It was concluded that under a reacting environment containing 5% CO_2, the adsorption capacity was 20% lower than that for moist flue gas which included 6 %

moisture. CO_2 adsorption capacity increased with increasing moisture concentration (Xu *et al.,* 2005).

APTES and TRI grafted SBA-15 materials were tested and it was suggested that CO_2 adsorption increased with increasing surface density of amine. Aminosilane modified SBA-15 was placed in a tube and heated to 150°C and the adsorbent was saturated with water vapor. APTES and TRI grafted adsorbents' pore areas and volumes were found as 616 m^2/g, 0.76 cm^3/g and 183 m^2/g, 0.29 cm^3/g, respectively. The adsorption experiments were conducted under dry and humid conditions at 333 K. It was found that adsorption capacity of APTES grafted material was 0.1 mmol/g under humid condition and 0.15 mmol/g without water. On the other hand, TRI grafted material showed an adsorption capacity of 0.35 mmol/g under humid condition and 0.39 mmol/g without water (Hiyoshi *et al.,* 2005).

The tolerance of pore expanded MCM-41 silica loaded by TRI to moisture in the feed. The measurements were performed under both equilibrium and dynamic conditions. The experiments showed that the moisture presence enhances the CO_2 uptake at equilibrium. The CO_2 adsorption capacity was detected as 2.05, 2.19 and 2.51 mmol/g for 0%, 27% and 74% relative humidity, respectively. Improvement of CO_2 adsorption capacity in wet streams could be explained by reaction mechanism of CO_2 and amines. Under dry conditions, carbamate is produced with the ratio of 0.5 CO_2/N while bicarbonate is produced (CO_2/N=1) in the presence of moisture (Serna-Guerro *et al.,* 2010).

2.3. Data Mining Methods for Knowledge Extraction

Data mining is the science of finding new and useful correlations, patterns and trends hidden within the large amount of data by using various statistical and mathematical techniques. Exploratory data analysis of large data sets presents suitable ways to find hidden complex relationships by utilizing graphical and numerical tools. The results were found by data mining techniques should be clear and suitable for interpretation and explanation, hence the techniques that will be employed should be selected accordingly (Larose and Larose, 2014).

For example, the decision tree method is simple, user friendly and provides intuitive results and explanation. On the other hand, neural networks are comparatively complex; it can be used for prediction but not easy for interpretation of the results. Description, estimation, prediction, classification, clustering are the main tasks of data mining tasks to accomplish (Larose and Larose, 2014).

Data mining is based on developing algorithms that can indicate understandable relationships in complex data sets. Exploring knowledge process by evaluating selected applications, constructing data sets and cleaning data by removing outliers and missing values, implementing data mining methods and analyzing patterns to reach desirable outcomes are the basic data mining steps. The given data set is split into training and test sets; the training set includes the class feature and it is used to structure a model and test set is used to calculate the accuracy of the model. Regression method is used for prediction of a value by using linear or nonlinear models (Baydogan, 2015).

On the other hand, clustering is used to group the data according to similarity or dissimilarity of instances. Features can be grouped as a discrete and continuous and values of feature properties should be examined accurately to achieve desirable model (Baydogan, 2015).

Data mining is the part of knowledge detection work to obtain unknown patterns. Data analysis should include all available collected variables. The large amount of data can be automatically analyzed by using data mining tools. There are two different types of data mining methodologies such as verification-oriented and discovery-oriented. Discovery-oriented techniques include prediction and description methods that identify pattern in data automatically (Rokach and Maimon, 2008).

In order to obtain prediction for new and unknown data, prediction-oriented methods are widely used; these techniques are used to construct the model by using training data, then the model is used for prediction. In addition to prediction-oriented methods, verification oriented techniques are based on the testing and deciding a hypothesis proposed by the users on the other hand. Different kind of data mining techniques

(verification, discovery, prediction, description, classification, regression) can be seen from Figure 2.1 (Rokach and Maimon, 2008).

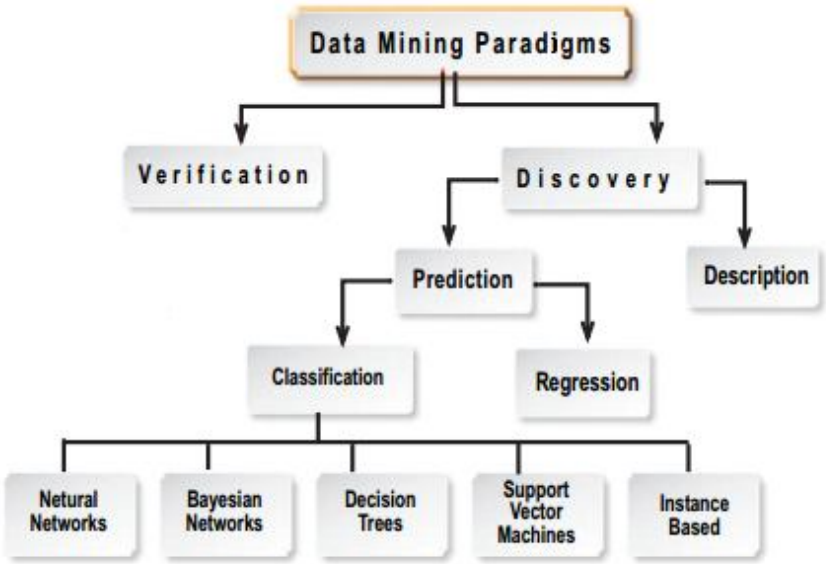

Figure 2.1. Data mining methods (Rokach and Maimon, 2008).

2.3.1. Prediction by Artificial Neural Network

Artificial neural network was developed based on the working principles of biological neural networks; it is formed by certain number of neurons that interact with each other. The model depends on three basic operations, which are multiplication, summation and activation.

Once artificial neural network model is constructed, it should be capable of predicting the outcome of the untested input conditions within certain ranges. Artificial neural network has great advantage with its high capacity of learning. They can be used to make classification, clustering, data processing and decision making.

In each neuron, the input value is multiplied with individual weight first; then all weighted inputs and bias are summed before following through a transfer function at the

exit of artificial neuron. The whole process can be seen from the Figure 2.2 (Krenker *et al.,* 2011) on working principle of artificial neuron.

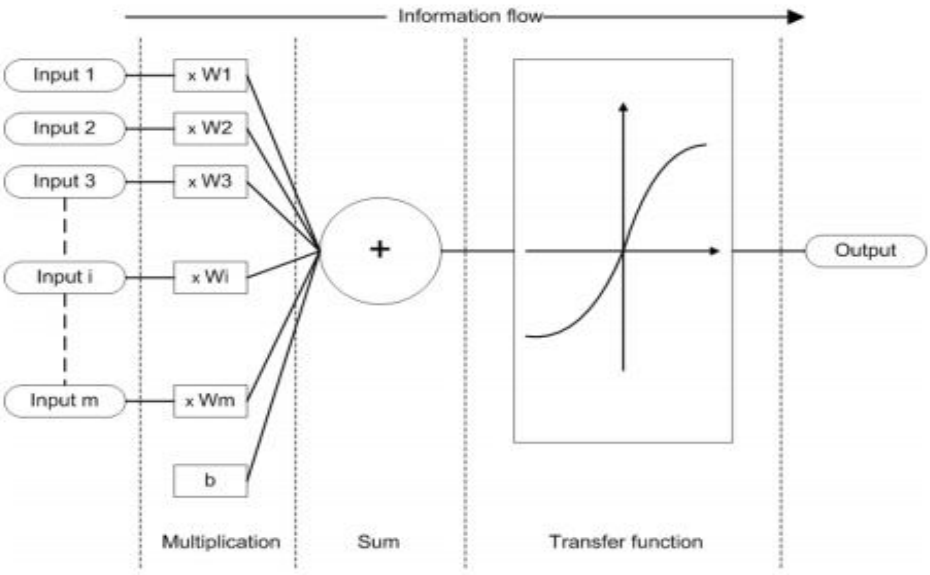

Figure 2.2. Working principle of artificial neuron (Krenker *et al.,* 2011).

For each artificial neuron, input, which brings information, is multiplied by its weight. The multiplied inputs and bias pass through the artificial neuron structure and process information with output efficiency formulation as indicated below (Krenker *et al.,* 2011):

$$y(k) = F\left(\sum_{i=0}^{m} w_i\ (k).x_i\,(k) + b\right) \tag{2.5}$$

Where:

x_i (k) = input value in discrete time

w_i (k) = weight value in discrete time

b = bias

F = transfer function

y_i (k) = output value in discrete time

Artificial neural network is combination of two or more artificial neurons. Artificial neurons can connect to each other. This kind of interconnection can be observed in two class of neuron structure: feed-forward and recurrent. In feed-forward structure, inputs and outputs carry the information in one way. While in recurrent networks, information can progress both in opposite and direct way (Krenker *et al.,* 2011).

Feed- forward artificial neural network can result in complicated and long results. On the other hand, backward transfer type of recurrent artificial neural network creates impressive networks. In recurrent artificial neural network, there is connection in every way between the artificial neurons. Network memorizing capability is significantly better in recurrent artificial neural network type. This memory ability depends on input significance; recurrent artificial neural network can measure whether the inputs are worth to remember or not (Krenker *et al.,* 2011).

Neural Network workflow contains following primary steps: collecting data, creating the network, configuring the network, initializing the weights and biases, training the network, validating the network, and using the network. The data collection is the main step and it should be performed outside of the neural network (Baela *et al.,* 2016).

After collecting the data set by extracting knowledge from the literature, preprocessing may be required in order to obtain final form of data. It should be noted that the data set must cover the range of inputs since the network does not have capability to predict out of this range. After preprocessing step, the data set needs to be divided into training and testing subsets. Than the network, weights and biases need to be configured. In this way, optimal network can be obtained (Baela *et al.,* 2016).

During application of training process, a neural network can obtain different solutions. It means that, even the same neural network model used, each time, different output values will be obtained for same inputs. In order to prevent any defects during this process, each network topology is trained certain number of times to ensure the compensation on the effects of random initialization of the neural network weights and the

best performance is recorded. The early-stopping technique is applied in order to avoid over learning of the neural network (Günay and Yildirim, 2011).

2.3.2. Classification by Decision Tree

Decision tree is one of the main classification methods in data mining process. Decision tree takes the values and attributes into consideration in order to predict patterns of different classes. Decision tree is useful tool and it provides many advantages by illustration of classification in the form of trees. Decision tree are widely used in many areas such as psychology, computer science, medicine etc. (Han *et al.,* 2012).

Decision trees have three types, which are classification trees, regression trees, CART (Classification and Regression Tree). According to data set, one or more decision trees can be obtained based on splitting attributes. Each decision tree contains splitting nodes; ideally pure nodes should be obtained. In order to measure impurity of nodes the GINI index, the entropy can be used (Han *et al.,* 2012).

First of all, GINI index is the quality criteria which based on the parent nodes (n) that are split into the children partitions (p). The proportion of the class j that are distributed to node i for f (i, j) gives this index. The GINI index is given by:

$$GINI(split) = \sum_{i=1}^{p} \left(\frac{\mathrm{ni}}{\mathrm{n}} GINI(i) \right) \tag{2.6}$$

The maximum split node is achieved when GINI index is zero.

Secondly, entropy is the maximum energy reduction at nodes during node splitting. Entropy regards to class labels therefore if the class labels for the given records are all same, entropy is equal to zero. The entropy formula is defined as:

$$Entropy(i) = -\sum_{j=1}^{m} (\mathrm{f(i,j)}.\log_2[f(i,j)]) \tag{2.7}$$

Where f (i, j) is the proportion of the class j for the attributed node i (Gorunescu, 2011).

Data classification depends on two basic steps which are learning step to build a data structure and a classification step to predict class labels. During the execution of first step, a structure of classifier is built depending on how the data classes are described (Han *et al.,* 2012).

In the second step, the built model is used for classification by measuring accuracy of the predicted class labels. Generally test set is processed in order to find accuracy, rather than training set. If the training is used in order to determine the accuracy of predicted values, the result would not be true due to classifiers can over fit the data. A typical decision tree is shown in Figure 2.4 (Han *et al.,* 2012).

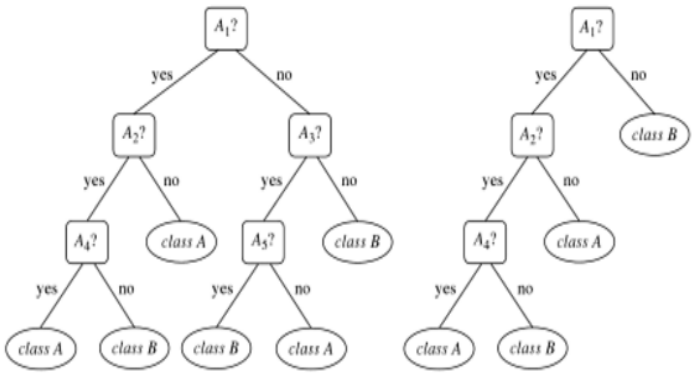

Figure 2.3. Decision tree sample (Han *et al.,* 2012).

Decision tree is described as a predictive model which illustrates classifiers and regression models. A decision tree includes nodes and each internal node splits the values into two or more sub-classes. Generally, decision trees should not be preferred with complex structures because the complexity has negative effect on the accuracy. The total number of nodes, tree depth and number of attributes are the tree complexity (Rokach and Maimon, 2008).

Decision tree algorithm stops creating new nodes when no further splits exist. On the other hand, some data sets include wide variety of attributes that's why decision tree

cannot make a split. In addition to this, prior to application of tree, some requirements must be followed. If the training data set is lack of subset records, classification for this subset would be impossible. Two main algorithms are used during building decision tree in order to measure purity of lead node. These algorithms are CART (Classification and regression trees) and C4.5 algorithm. CART algorithm has specific mechanism which depends on processing each node to get optimal split. At the end of this process, there will be no remaining nodes and the tree will be achieved. CART would calculate the error rate for the whole decision tree. However it should be taken into consideration that, even if the minimum entire error rate is achieved on the training data set, the model that we had at the end can be too complex or overfitting (Larose, 2005).

Secondly, the C4.5 algorithm finds maximum splitting value until no further splits would remain. There are differences between CART and C4.5 algorithms. CART algorithm creates a binary tree; while C4.5 algorithm creates a tree includes several variables. The determination of purity for splitting variables is completely different for these two algorithms. The C4.5 algorithm selects optimal split to obtain the largest information gain. Even if C4.5 and CART divide the categorical values in different way, the dividing process for numerical value are quite similar for both algorithms. Decision trees are used in order to build decision rule (Larose, 2005).

3. COMPUTATIONAL WORKS

3.1. Experimental Data Collection

The published articles in the literature from 2002 to 2016 were examined in order to construct the data base for CO_2 adsorption; the time period of 13 years should be sufficient to represent the carbon dioxide adsorption on amine modified adsorbents literature adequately. The articles, which are available in online sources such as Science Direct, Wiley, American Chemical Society, The Royal Society of Chemistry, Taylor and Francis and Springer, were used to construct the data set. The number of articles over the years was presented in Figure 3.1.

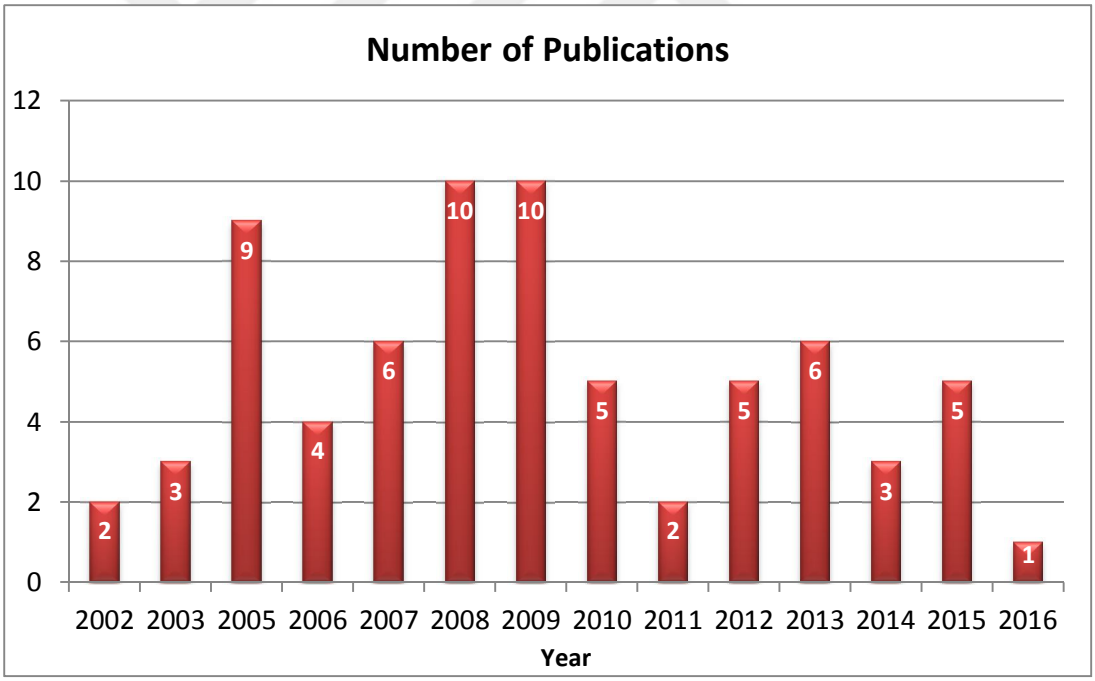

Figure 3.1. Number of publication from 2002-2016.

Various experimental studies on carbon dioxide adsorption of amine functionalized adsorbents reported numerous attributes and parameters which affect the performance of the adsorbents and carbon dioxide capture capacity. These parameters can be classified as follows: support type, support pretreatment conditions, support properties, sorbent preparation method, amine properties, and operational variables.

71 articles on carbon dioxide adsorption were evaluated. Some articles were removed from the list because they had missing values of some variables, hence they were not suitable for the analysis we performed. At the end, 30 of them were found to be suitable to create database for this project. The data set was constructed by extracting the data from these 30 articles on carbon dioxide adsorption from amine modified adsorbent. The final database includes 1356 experimental data with 26 input values and 2 output values. These outputs were extracted from same articles. All of these values and the attributes are shown as below in the Table 3.1 to 3.11.

First of all, the database contained five different types of sorbent material; they all have mesoporous structures. The support types and number of data points involving these materials are given in Table 3.1. MCM-41 and SBA-15 were most commonly used sorbents in the literature for carbon dioxide adsorption.

Table 3.1. Sorbent types in input variables.

Variable	Alternatives	Data Number
Sorbent Type	**MCM-41**	740
	MCM-48	12
	SBA-15	594
	SBA-12	4
	SBA-16	6

The support pretreatment conditions, especially calcination temperature and time are important because they influence the support properties, which are also crucial on carbon dioxide capture performance. These properties were identified as surface area, pore size, pore volume. These properties were usually tested before the modification of amine on the support surface. In the literature, the highest calcination temperature was 550 °C while the longest calcination time was 8 hours. In some articles, the calcination was not applied, therefore calcination time and temperature were set 0 °C and 0 hour. The detailed information of the calcination conditions can be seen from Table 3.2.

Table 3.2. Data number of calcined sorbent with calcination temperature and time.

Variable	Data Number of Calcined Sorbent	Calcination Temperature (°C)	Calcination Time (hr)
Calcination Conditions	1237	400	5
		500	6, 7
		540	5, 6, 8
		550	4, 5, 6, 8

Surface area, pore volume and pore size were found for each material from the articles before the amine loading. They directly impact the amount of amine which was loaded on the support surface and then the retained carbon dioxide amount. These support properties are mainly dependent on support type, and Table 3.3 shows their ranges for each support.

Table 3.3. Surface area, pore size and pore volume of the support.

Variable	Alternatives	Surface area (m^2/g)	Pore size (diameter) (nm)	Pore volume (cm^3/g)
Support Physical Properties	**MCM-41**	864-1506	2.3 - 33	0.62 - 3.09
	MCM-48	1290	2.58	1.15
	SBA-15	428-950	5.8 - 71	0.61-2.29
	SBA-12	1347	3.8	0.842
	SBA-16	479	4.3	0.48

Modification of the surface enhances adsorbent's basicity and carbon dioxide interaction therefore affects adsorbent capture capacity. Modification is performed through amine groups on the support surface; the impregnation and grafting methods are used commonly for this purpose. During the construction of data set, only the articles, which include impregnation and grafting methods, were used. Table 3.4 summarizes the number of data of the modification method through all type of sorbents; grafting method was used more frequently than impregnation method in the literature.

Table 3.4. Modification method of amine through overall data set.

Variable	Alternatives	Data Number
Modification Method of Amine (Overall Data Set)	**Impregnation**	586
	Grafting	887

Table 3.5 illustrates the number of data of the modification method through each sorbent. It is obvious from table that MCM-48, SBA-12, SBA-16 were modified by grafting method, while SBA-15 and MCM-41 were modified by either grafting or impregnation method. The highest number of data points belongs to modification of MCM- 41 by grafting.

Table 3.5. Modification method of amine through each sorbent.

Variable	Alternatives	Grafting (Data Number)	Impregnation (Data Number)
Modification Method of Amine (Based on support type)	**MCM-41**	575	252
	MCM-48	12	0
	SBA-15	290	334
	SBA-12	4	0
	SBA-16	6	0

Amine properties are another set of significant variables on carbon dioxide capture performance of the adsorbent. As can be seen in Table 3.6, mostly primary amine is used for modification in carbon dioxide adsorption experiments.

In addition to this, linearity of the amine structure, sterically hindered, amine type such as primary, secondary and tertiary can also be effective in the determination of the capacity so it is involved in Table 3.6.

Table 3.6. Amine properties of input variables.

Variable	Alternatives	Data Number
Amine Properties	**Primary**	305
	Secondary	111
	Tertiary	8
	Linear	947
	Primary + Secondary	508
	Primary + Secondary + Tertiary	424
	Sterically Hindered	417

In Table 3.6, sterically hindered amine type is indicated as well. Steric hindrance is an indication of how crowded the surroundings of the nitrogen atom on which CO_2 would adsorb. If amine is sterically hindered, it was labeled as 1 in the database; while 0 if the steric hindrance was not observed.

Table 3.7 contains the range of the molecular weight of amines used for modification of the support surface; in addition to the range of the nitrogen content of the sorbents. The amine, which was used during the modification process, directly affects the nitrogen content of the adsorbent.

Table 3.7. Range of amine properties.

Variable	Alternatives	Range
Amine Properties	**Molecular Weight (g)**	58- 800
	N content (mmol/gsorbent)	1.11 – 14.86

Operational variables like pretreatment temperature, adsorption temperature, pressure, flux carbon dioxide concentration, relative humidity, pre-hydration conditions are also significant for the carbon dioxide capture performance of the adsorbent. These variables are given in Table 3.8 and 3.9.

Table 3.8. Range of the operational variables.

Variable	Alternatives	Range
Operational Variables	**Pretreatment Temperature**	25-200 °C
	Adsorption Temperature	0-100 °C
	Adsorption Pressure	0.01-25.06 bar
	Flux CO_2 Concentration	0.1-100 %
	Relative Humidity	0-78 %

As can be seen from Table 3.8, adsorption temperature varies between 0 °C and 100 °C. On the other hand adsorption pressure range is in between 0.01 and 25.06 bars. Flux CO_2 concentration and relative humidity ranges are 0.1-100 % and 0-78 %, respectively.

The last operational variable which is the presence or absence of pre-hydration; the pre-hydration was used in 45 experiments in the data set (Table 3.9). The data points were marked as "1" when pre-hydration method was applied and "0" for the cases without pre-hydration.

Table 3.9. Data number of pre-hydration method.

Variable	Alternatives	Data Number
Operational Variables	**Prehydration**	45

Finally, CO_2 adsorption capacity, which is the output variable, is reported in two ways: the ratio of carbon dioxide over nitrogen (amino efficiency) and the CO_2 adsorption capacity in mmol CO_2/g adsorbent. Output variables are illustrated in Table 3.10.

Table 3.10. Output variables.

Output Variable	Range	Data Number
Amino efficiency (CO_2/N)	0.02-0.88	1356
CO_2 adsorption capacity (mmol CO_2/g adsorbent)	0.05- 5.77	1356

The distribution of output variables on different sorbent types can be seen from Table 3.11. It is clear from the table that SBA-15 had output range in between 0.05-5.77 mmol CO_2/g adsorbent, while MCM-41 had the output range between 0.12-5.29 mmol CO_2/g adsorbent. On the other hand, the highest CO_2/N ratio was recorded for SBA-12 sorbent with a range in between 0.68-1.04.

Table 3.11. Output variables based on the sorbent type.

Input Variable	Output: Amino efficiency (CO_2/N)	Output: CO_2 adsorption capacity
MCM-41	0.04-0.88	0.12-5.29
MCM-48	0.08-0.84	0.06-0.34
SBA-15	0.02-0.83	0.05-5.77
SBA-12	0.68-1.04	0.38-0.49
SBA-16	0.16-0.24	0.37-0.73

3.2. Computational Details

MATLAB R2014a was used to implement the computational work in this thesis. Two basic methods were used in calculations. Neural Network Modeling was used to develop models for the predictions of unstudied conditions. On the other hand, Decision Tree Modeling was implemented to develop heuristics to determine the best conditions for the carbon dioxide adsorption.

3.2.1. Neural Network Modeling

Data collection is the main step for neural network modeling and data were extracted from the literature by examining several articles therefore data set was built. After collecting the data set by extracting knowledge from the literature, preprocessing was applied to obtain final data.

Once data were collected and preprocessing work was executed, then neural network model was applied to the whole data set. There were two forms of output values gathered in the data set: amino efficiency (CO_2/N) and adsorbent capacity (mmol CO_2/g). The input

variables were the same for both output variables. Same neural network MATLAB code was applied to both of them and the results were reported. Main steps of neural network creation can be seen from Figure 4.2.

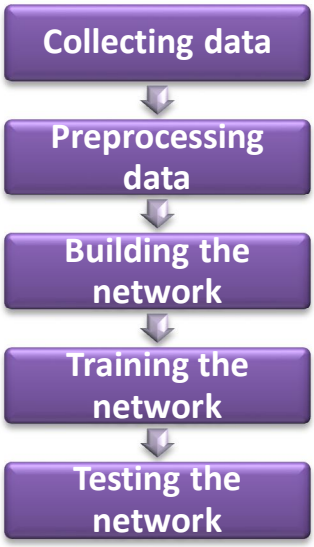

Figure 3.2. Neural network creation main steps.

The number of neurons in the hidden layer was changed and numerous neural network models were analyzed and evaluated for training and testing. If the neuron number is too low it could lead poor representation of the data while too many neuron numbers lead to overfitting of the model. Large networks can be established by high neuron numbers and the large networks have an advantage on memorize the training examples. Hence, training error is decreased if the number of neurons is high. However, large neuron numbers have an adverse effect on predicting the new situations due to lack of generalization ability. Therefore optimum neuron number was determined by checking the root mean square error for testing of different topologies.

In order to prevent the negative effect of random initialization of the neural network weights, each neural network was trained ten times. Testing R^2 and RMSE values of each model were compared to check ability of network to predict the unknown data. RMSE of testing was computed by applying 10-fold cross validation method in order to test the accuracy of the model predictions on the unknown data: the data set was randomly divided into 10 subsets, the nine subsets was used to train the network while the remaining set was

used for testing. This procedure was repeated 10 times and the RMSE for testing was determined taking the average of 10 tests. Calculation of RMSE is shown in Equation 3.1 and R^2 is shown in Equation 3.2.

$$RMSE = \sqrt{\frac{1}{N} \times \sum_{i=1}^{N} (t_i - p_i)^2} \tag{3.1}$$

Where N is the number of experiments and p_i and t_i predicted and target value respectively.

$$R^2 = 1 - \frac{SS_{res}}{SS_{res}} = 1 - \frac{\sum_{i=1}^{N}(t_i - p_i)^2}{\sum_{i=1}^{N}(t_i - t_{average})^2} \; where \; t_{average} = \frac{\sum_{i=1}^{N} t_i}{N} \tag{3.2}$$

The significance of input variables on carbon dioxide adsorption were also analyzed using neural networks in order to understand the relative importance of the input variables and their effect on the carbon dioxide adsorption. In order to find significance of the input variables, the change root mean square error method was used. During input significance determination process, one input variable was removed and the network was trained with the remaining variables. The difference in RMSE of this model with a model containing all input variables was used as the indicator of the significance of that input variable (larger the difference, more significant the variable). This procedure was repeated for all input variables, and changes of RMSEs from the full model were compared to determine the relative significance of input variables (Günay and Yildirim, 2011).

During the neural network modeling using MATLAB, “tansig” activation function was used. On the other hand, “trainbr” (Bayesian Regularization Algorithm) and “trainlm” (Levenberg- Marquardt Algorithm) functions were used as training and testing algorithms respectively. The fastest training function was “trainlm” and the “trainbr” function has ability to determine the optimal regularization parameters and the weights and biases. The “mapminmax” function normalizes the data so that all data falls in the range [-1,1] . When the network inputs and targets are scaled to be in a range [-1,1], “trainbr” algorithm conclude the best performance (Baela *et al.,* 2016).

3.2.2. Decision Tree Modeling

Decision tree classification was used to find out the conditions and rules that led to high carbon dioxide adsorption capacities.

Decision tree modeling process involved the following steps and considerable attention was given on these steps in order to obtain clear results:

- Classify the outputs clearly
- Separating the whole data into two parts as training and testing data set
- Creating decision trees for training data set
- Applying the results for training data set into testing data set
- Finding different values, nod numbers and complexity of decision trees

Firstly, experimental data were called from excel file and saved in the MATLAB workspace. The total data set was divided randomly into two training and testing sets. Training set was used for building the decision tree structure while test set was used to evaluate the generalization ability. Decision tree model was applied to both output values, which were amino efficiency (the ratio of carbon dioxide over nitrogen content) and adsorption capacity.

Nominal categorization in decision tree was carried out in the ranges of outputs and these ranges involve each output one by one. The ranges of the ratio of carbon dioxide over nitrogen were from 0 to 0.9 while the range was 0 to 6 for adsorption capacity. The outputs were classified into four levels which were low, moderate, high and very high. Total data set was divided into two sets randomly and three fourth of the data were used for constructing (training) the decision tree. Remaining was used for testing to evaluate generalization ability.

The comparison of the nod numbers and complexity of the decision trees was used to find the optimum prune and splitmin values. In order to obtain optimum results for operating conditions, relationship between these parameters were found with numerous tries. Splitmin value is an important parameter and it shows the impure nodes must have

the number of assigned splitmin value or more. Splitmin value was selected as 20 and it means that the node is not branched further if the number of data points is less than 20. In addition to this, prune value was used for reducing tree by removing branch and leaf nodes. Best prune value was chosen in order to prevent the complexity of the tree. Higher number of nodes can result in too large tree therefore overfitting can occur. The cases cannot be clearly distinct if decision tree has small number of nodes.

The best performing decision tree was found by evaluating the results and error percentages. The simplicity of a decision tree and nominal error rate indicates the best decision tree model therefore simple decision trees were chosen. General rules and heuristics were deducted at the end of analysis to achieve the highest carbon dioxide capture performance.

4. RESULTS AND DISCUSSIONS

Artificial neural network and decision tree methods were performed in order to analyze the experimental data extracted from the published articles in the literature on the carbon dioxide adsorption. The output results which were carbon dioxide capture performance were defined in two ways: the ratio of carbon dioxide over nitrogen and CO_2 adsorption capacity. MATLAB modeling was same for both variables and the same procedure was applied.

4.1. Neural Network Analysis for CO_2/N ratio

The neural network model was constructed for the ratio of carbon dioxide over nitrogen first. Various network topologies were tested and the best performing structure was determined. Then this structure was used for input significance.

4.1.1. Determining Optimum Artificial Network Topology

The optimum neural network topology was determined by using value of testing RMSE and R^2 because they indicated the ability of network to predict unknown data. Ability of network to estimate unknown data are more precious than prediction ability of training data. 10-fold cross validation technique was performed to obtain the testing RMSE and R^2. Tangent sigmoid function was used as transfer function in order to normalize inputs and targets between -1 and +1. trainlm and trainbr, were used for as training and testing algorithms, respectively.

During 10-fold cross validation process, the dataset was randomly divided into 10 groups; one group was estimated using the network constructed from the remaining nine subsets. This procedure was repeated 10 times and RMSE were summed up to compare different structures. Training RMSE values were determined by the error between the experimental data points and predictions on the total data while testing RMSE values were calculated by 10-fold cross validation method.

Several network topologies were tested and compared with their RMSE values of testing and training. Both one and two-hidden-layer topologies were tested and it was found that two-hidden-layer structure has no practical superiority over the single-layer structures. Then one-hidden layer networks with the number of neurons changing from two to 10 were employed, and the training and testing errors were compared to decide the best structure representing the experimental data.

The training and testing errors of nine networks with the increasing number of neurons in the first hidden layer are compared in Figure 4.1. The notation of "a, b, c" are the number in the x-axis that is used to label the neural networks as a: number of input variables, b: number of hidden layer, c: number of output. This notation indicates that 26 input variables were processed through the increasing number of neurons (from two to10 neuron) in one hidden layer and one output variable.

The blue bars in Figure 4.1 display the training error which indicates the prediction accuracy of that particular network while testing error, which represents the generalization accuracy, is shown with red bars in Figure 4.1.

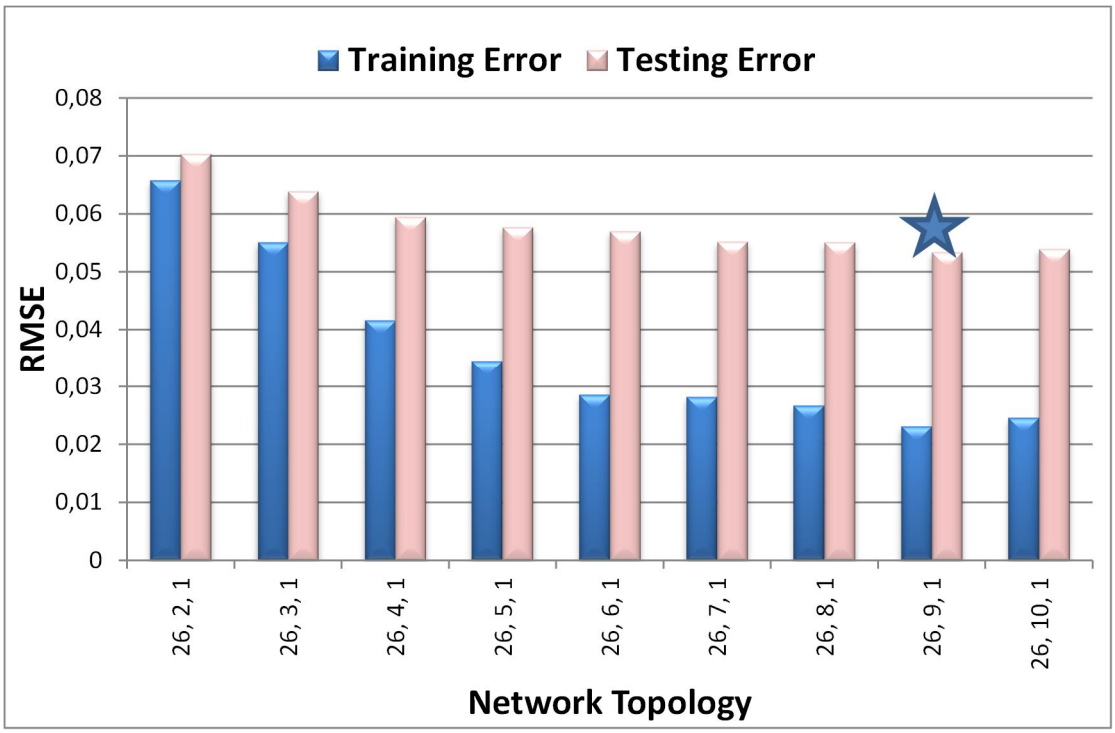

Figure 4.1. Training and testing errors of different neural network topologies for CO_2/N ratio.

Figure 4.1 shows that there is a drastic decrease in training RMSE values first with the larger network size (increase in neuron number) and then it does not change significantly with further increase in neuron number. Normally testing error should decrease first and then increase again as an indicator of overfitting. However, this kind of great change in trend was not observed in the neural network structures up to 10 neurons. Although number of data are still high enough to test higher number for neurons, the performance of the structures having seven or more neurons does not change significantly, and their fitness for representing the data are sufficiently good. Hence the structure of 26, 9, 1 exhibits the minimum RMSE of testing (0.053) and low training RMSE (0.023) was assumed to be optimum and the input significance was analyzed with this structure. The experimental versus predicted CO_2/N ratio was given in Figure 4.2 for optimal network (26, 9, 1) for both training and testing. It can be seen from the Figure 4.2 that successful modeling was achieved.

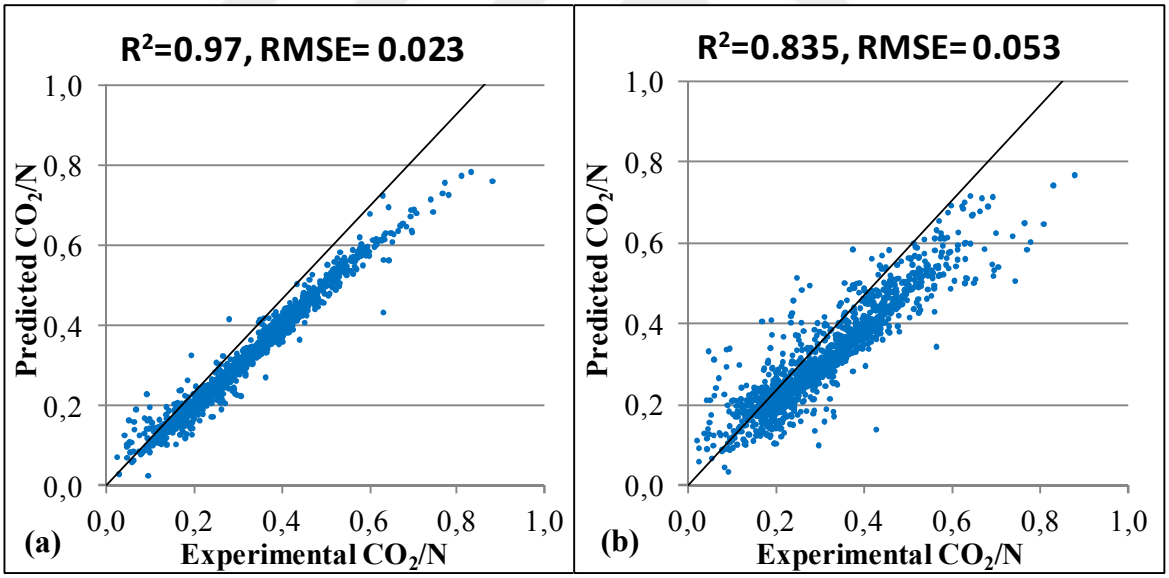

Figure 4.2. Experimental versus predicted CO_2/N ratio for: (a) training, (b) testing data by the optimal neural network topology.

4.1.2. Analyzing input significance for CO_2/N ratio

Relative significance of input variables was analyzed by evaluating results for one hidden layer with nine neuron neural network model. In order to achieve this, change of root mean square error method was employed: the method involves removing one or a

group of variables from the network and retraining it with remaining variables. RMSE values were calculated for each run. The differences between RMSE for original model (it was 0.023) and the value calculated in the absence of a variable were accepted as an indicator of the significance of that variable for the output. High RMSE values show the high significance of that variable.

Input significance analysis was performed six times in order to minimize the deviations due to random initialization, and then the average value of each variable was calculated. In addition to this, Table 4.1 shows the results of input significance neural network of CO_2/N ratio.

As can be seen from Table 4.1, adsorbent variables were found to have 34.33% significance while the operating variables had 65.67% significance. These are expected results; especially temperature, pressure and CO_2 concentration has to be important; hence the model can be considered as successful. Amine type has considerable effect on how efficient the amino group is during adsorption process. It can be seen from table 4.1 that the total significance of amine type and properties, which was the summation of primary, secondary, tertiary, linearity, molecular weight of amine, steric hindrance of amine and nitrogen content, was 19.5%. Total significance of amine properties was quite high and comparable to most important parameter (pressure).

During adsorption process, not all amino groups in the amine modified material are expected to be useful (Sanz *et al.,* 2010). The number of moles of CO_2 adsorbed per mole of amino groups gives amino efficiency (Sayari *et al.,* 2012). By analyzing the distribution of amino groups in the sorbent structure, it may be understood how efficient the amino groups are. Molecular weight of amine (chain length) may have considerable effect on diffusion therefore is expected to affect amino efficiency.

When high molecular weight-amines are deposited on the external surface of the mesoporous silica, they may block the pore entrance due to their long chain lengths and this may hinder the access of CO_2 into the pores, where amino groups are located, leading to smaller CO_2/N ratios (Sanz *et al.,* 2012). In addition to this, molecular weight of the

amine was estimated to have a relative significance of 1.87 % on the determination of the amino efficiency, pointing out the effect of amine chain length.

Table 4.1. Input significance results of neural network for CO_2/N ratio.

Input Variable	**RMSE (found)**	**RMSE Difference**	**Relative Significance%**	**Group Significance %**
Support type	0.027	0.004	2.94	Adsorbent Variables 34.33
Calcination conditions	0.026	0.003	2.42	
Surface area	0.025	0.002	1.91	
Pore size	0.026	0.003	2.66	
Pore volume	0.026	0.003	2.62	
Modification method of amine	0.026	0.003	2.20	
Primary amine	0.025	0.002	1.63	
Secondary amine	0.025	0.002	1.72	
Tertiary amine	0.025	0.002	2.12	
Linearity of amine	0.024	0.001	0.96	
MW (Molecular Weight) of amine	0.025	0.002	1.87	
Steric hindrance of amine	0.025	0.002	1.44	
N content	0.036	0.013	9.84	
Pretreatment T(°C)	0.026	0.003	2.58	Operational Variables 65.67
T °C Adsorption	0.039	0.016	11.96	
P (bar)	0.064	0.041	30.01	
CO_2 concentration (%)	0.045	0.022	16.04	
RH % (relative humidity)	0.027	0.004	3.50	
Prehydration	0.025	0.002	1.58	

Table 4.1 shows that whether the amino groups involved are primary, secondary, or tertiary has an input significance of 5.47 % in total, the distribution being 1.63, 1.72, and 2.12 %, respectively. Primary and secondary amines are known to react with CO_2 under anhydrous conditions. However, in multi-functional amine structures or under conditions where adsorption is controlled by kinetics, some of the amine structures may not take part in the CO_2 adsorption, even though they are primary or secondary. On the other hand, tertiary amines do not react with CO_2 under anhydrous conditions even though they are accessible by the CO_2 molecules. Thus tertiary amine effect is actually negative but apparently significant (2.12%). In humid adsorption conditions tertiary amines are also active (Samanta *et al.,* 2012).

Examination of CO_2/N ratio with respect to adsorbent properties such as pore size, volume and surface area revealed that their significance were found as 2.66%, 2.62, and 1.91% respectively. Surface area is usually associated with physical adsorption (Sanz Perez *et al.,* 2013); the higher the surface area, usually the higher the adsorption capacity is. So, our finding of the relatively smaller significance of the surface area on amino efficiency makes sense, if the chemical interaction of amines with CO_2 is considered. In addition, it was reported that higher surface area of PE-MCM-41 material resulted in low CO_2/N ratio due to reaction of amine with support surface and lose its ability (Franchi *et al.,* 2005). Pore size and volume, on the other hand, were found to be more significant on the determination of C/N ratio. This was also expected since these two properties were reported to control adsorption kinetics as well as the amount of amine loaded (Son *et al.,* 2008). Adsorption capacity was found to be the highest for the adsorbent, which had the largest pores. Normally, from a diffusion point of view, it may be foreseen that amino efficiency might be higher for larger pore sizes. Larger pores permit mobility of amino groups and improve CO_2 diffusion therefore amino efficiency is increased (Sanz *et al.,* 2013). However, there is still the probability of the presence of inefficient amino groups due to their orientations even if the diffusion of CO_2 is not problematic.

Adsorption temperature has an essential effect on adsorption capacity and amino efficiency. Kinetic effect becomes dominant if the adsorption capacity is increased with increasing temperature. Since the adsorption temperature allows higher mobility, CO_2 diffusion is achieved to the areas which are not easily accessible at low temperature. As a

result, the possibility of reaction between amine groups which are located inside of the pores and CO_2 is increased. It was observed that at low temperatures PEI impregnated on the external surface of material and diffusion limitation occurs. On the other hand, PEI enters inside the pores and becomes more active for CO_2 at high temperatures (Sanz *et al.,* 2010). Significance of adsorption temperature on amino efficiency was calculated as 11.96%.

It should be noted that these relative significance are found within the limits of this experimental data set, hence results are empirical. The relatively low significance of a variable may not actually indicate that it is unimportant for the process. It may be due to the fact that it may not be changed much through the data set; for example if the optimum value of a variable is well established, and adopted in all works that are used to construct the data set, the significance would be low even though this variable is actually important. Hence the significance values in Table 4.1 should be considered as the indicator of whether changes in the value of a variable may produce changes in performance or not.

4.2. Neural Network Analysis for CO_2 adsorption capacity

The neural network model was also constructed for the CO_2 adsorption capacity. Similar to CO_2/N ratio, the optimal network topology was found first, and this structure was used for input significance.

4.2.1. Determining Optimum Artificial Network Topology

10 neural networks with 26 inputs and one output variable (adsorption capacity) were built in different structures with different number of hidden layer and neurons. Single layer structure also showed better performance compared to two hidden layers for adsorption capacity as in the CO_2/N case. Same approach for CO_2/N was taken into consideration by calculating optimum neural network for capacity in all steps. 10-fold cross validation technique was performed to obtain the testing RMSE and R^2. The RMSE and R^2 values of testing were compared and they were used to find the optimal network.

Similar to previous section, “a, b, c” notation of represents the 26 input variables (a) introduced through different number of neurons (b, increased from 2 to 11) in the first hidden layer with one input variable (c), which was the adsorption capacity in this case. Figure 4.3 illustrates the comparison of training and testing errors of 10 networks with the increased number of neurons.

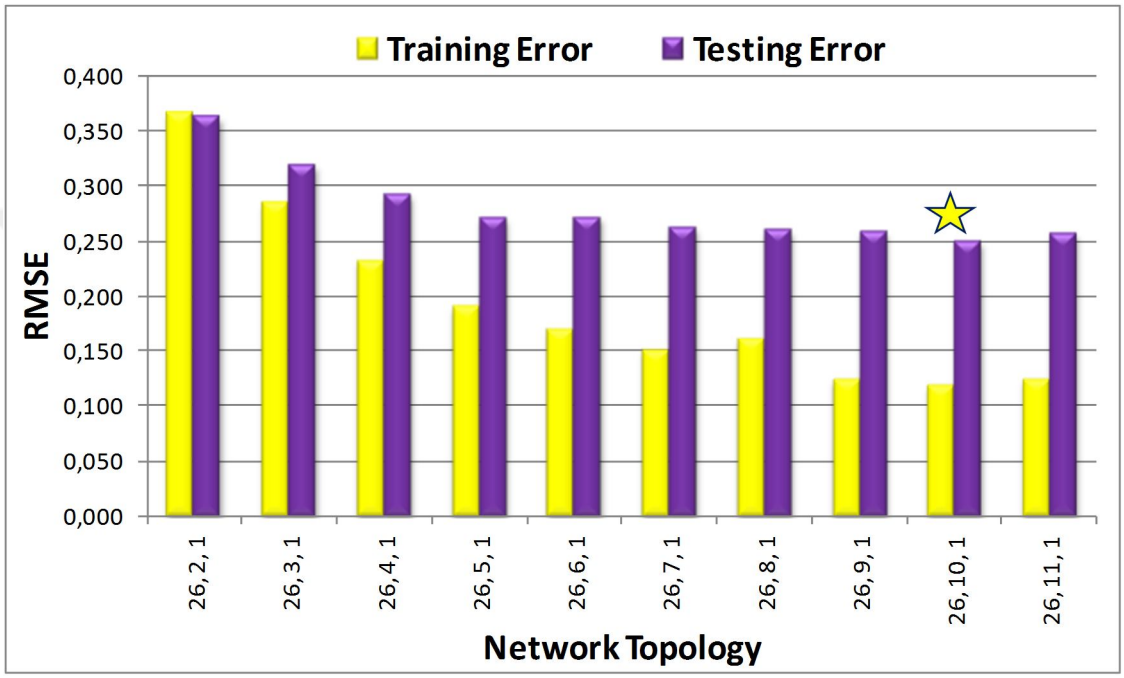

Figure 4.3. Training and testing errors of different neural network topologies for CO_2 adsorption capacity.

The yellow bars in Figure 4.3 show the training error of that specific network while the purple bars indicate the testing error, which is the indicator of generalization accuracy. It can be seen from Figure 4.3 that there is a sharp decrease of the training RMSE with the increase in neuron number. As the network gets larger, decrease in training RMSE decelerates.

Normally, the testing error decreases first with the increasing network size, and then, once the training error reaches the minimum, it starts to increase again due to overfitting. However there was no sharp change in testing RMSE for this work for the number of neurons from seven to 11. The network structure of 26, 10, 1 displays the minimum RMSE

of testing (0.25) with an obvious low RMSE of training (0.118). This structure was used to determine significance of input variables.

The experimental versus predicted CO_2 adsorption capacity plots of optimal network (26, 10, 1) for both training and testing are shown in Figure 4.4. It indicates considerably successful fitting and quite satisfactory RMSE and R^2 values for both training and testing.

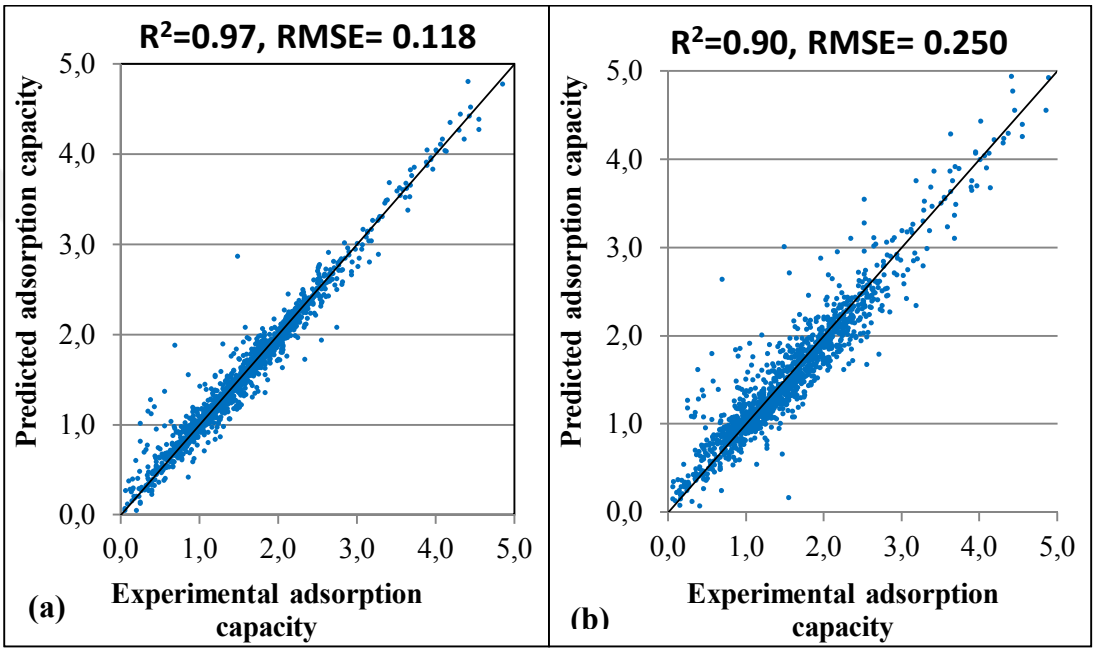

Figure 4.4. Experimental versus predicted CO_2 adsorption capacity for: (a) training, (b) testing data by the optimal neural network topology.

4.2.2. Analyzing input significance for adsorption capacity

Neural network model was used to calculate the relative significances of input variables and to analyze the results. A procedure similar to the one followed for CO_2/N ratio (Section 4.1) was performed in order to find the input significance results for CO_2 adsorption capacity. As mentioned earlier, input significance calculations was processed by removing one or a group of variables from the network and then retraining the whole network with remaining variables. Then the RMSE value in the absence of a variable is compared with the RMSE value found for full model (0.118) as the significance of that variable.

Table 4.2 illustrates the relative significance of inputs. It is seen from Table 4.2 that operational variables had 57.34% of relative significance in total while adsorbent variables had 42.66% of relative significance. Operational variables had much effect on the carbon dioxide adsorption capacity than adsorbent variables as it was calculated for CO_2/N ratio.

Table 4.2. Input significance results of neural network of CO_2 adsorption capacity.

Input Variable	**RMSE (found)**	**RMSE Difference**	**Relative Significance%**	**Group Significance %**
Support type	0.1311	0.0131	1.97	Adsorbent Variables 42.66
Calcination conditions	0.1380	0.0200	3.00	
Surface area	0.1306	0.0126	1.89	
Pore size	0.1313	0.0133	2.00	
Pore volume	0.1302	0.0122	1.84	
Modification method of amine	0.1351	0.0171	2.56	
Primary amine	0.1335	0.0155	2.33	
Secondary amine	0.1194	0.0014	0.21	
Tertiary amine	0.1260	0.0080	1.20	
Linearity of amine	0.1246	0.0066	1.00	
MW (Molecular Weight) of amine	0.1230	0.0050	0.75	
Steric hindrance of amine	0.1228	0.0048	0.72	
N content	0.2727	0.1547	23.20	
Pretreatment T(°C)	0.1264	0.0084	1.25	Operational Variables 57.34
T °C Adsorption	0.1849	0.0669	10.03	
P (bar)	0.3304	0.2124	31.86	
CO_2 concentration (%)	0.1832	0.0652	9.78	
RH % (relative humidity)	0.1362	0.0182	2.74	
Prehydration	0.1292	0.0112	1.67	

The most important adsorbent variable was found as the nitrogen content with 23.2%. It is much higher than for the case of CO_2/N ratio as expected; adsorption capacity does not have information regarding to N contents as CO_2/N does, hence it is normal that it was affected from N content more. Carbon dioxide adsorption depends on nitrogen functionality and its amount in the adsorbent. According to Sanz *et al.* (2013) study, nitrogen content of 50 wt % of TEPA modified PE-SBA-15 sorbent was found as 14.1 %, which was the highest compared to other adsorbents. They concluded that higher nitrogen content led to higher adsorption capacity. In this thesis, we also observed same trend in our analysis.

Primary and secondary amines directly interact with CO_2 while tertiary amine does not if water is not added. The effect of tertiary amine is crucial but it has negative effect on carbon dioxide capture process. In humid adsorption conditions tertiary amines are inactive (Samanta *et al.,* 2012). As can be seen from Table 4.2, relative significance of primary amine (2.33%) was higher than secondary (0.21%) and tertiary amine (1.20%). Primary amine modified adsorbents exhibit high reactivity over secondary and tertiary amine-modified ones. Primary amine containing silica sorbent exhibited highest carbon dioxide capture capacity compared to secondary and tertiary amine containing silica sorbent (Sayari *et al.,* 2012).

Adsorbent physical properties such as pore size, pore volume, surface area are found to have 5.73 % significance in total. According to the study by Son *et al.* (2008) adsorption capacity is also the highest for the adsorbent which had the largest pores. Pore diameter was detected as the most important variable by taking into consideration its effect on controlling adsorption kinetics. Mesoporous structures offer ability for organic amine to enter into pore space and good mass diffusion of CO_2 molecules into the sorbent structure. In addition, surface functionalization and diffusion of reagents to the surface depend on pore size and pore volume (Samanta *et al,* 2012).

As in shown Table 4.2, the relative significance of sorbent type was 1.97%. Based on the literature studies proving the inactivity of mesoporous silica structures towards CO_2 under the conditions of interest, it may be argued that if two different supports (e.g. MCM-41 or SBA-15) are modified by the same amount of identical amines under the same

conditions, they will probably adsorb similar amounts of CO_2 at identical reaction conditions. Similar findings that CO_2 adsorption capacity is mainly dependent on pore size and volume rather than type of sorbent were reported before (Son *et al.,* 2008).

Studies with impregnation and grafting as amine modification method were extracted in this thesis and shown as one attribute in data set. Significance of method of amine modification was found as 2.56%. Impregnation method has ability to load more amine on support surface and it provides higher CO_2 uptake rate. On the other hand, amine loading on support surface is restricted in grafting method but it has more thermal stability compared to impregnation. Effect of both type of modification method on carbon dioxide capture is essential but it cannot be generalized whether one of these methods is always better than other. According to Garcia *et al.* (2015) study, it was observed that grafted SBA-15 material showed higher CO_2 adsorption capacity compared to PEI impregnated SBA-15 material.

On the other hand, the operational variables had more dramatic effects on the results. As expected, pressure, CO_2 concentration and the temperature are the major variables affecting the adsorption capacity. These results are understandable since the adsorption process is highly dependent on adsorption temperature, pressure and CO_2 concentration. Adsorption pressure was found to be the most important variable with 31.86% significance. CO_2 adsorption performance of adsorbent is greatly affected by CO_2 partial pressure therefore it is valuable to understand the influence of this attribute (Wang *et al.,* 2007). The significance of CO_2 concentration was detected as 9.78 % which can be seen from Table 4.2.

Adsorption of carbon dioxide is an exothermic process. Thus, under the conditions where adsorption is purely controlled by thermodynamics adsorption capacity should decrease with increasing temperature. However, when kinetic effects are dominating, the reverse may also be true. The reason for this phenomenon is that the amine sites can exist in the sorbent channels like nanosized particles and the access to some of those may be restricted at low temperatures. In both ways, adsorption temperature has a significant effect on carbon dioxide adsorption process (Xu *et al.,* 2002). It can be seen from Table 4.1 that

significance of temperature was found comparatively high with 10% which is consistent with literature data.

CO_2 adsorption capacity is affected by presence of water in adsorption process. However, the findings about the effect water are quite contradicting; in some experiments adsorption capacity increased under moist conditions, in some decreased or remained the same. The significance of relative humidity was determined as 2.74%. CO_2 adsorption capacity of mesoporous adsorbent was increased with increasing relative humidity (Serna-Guerro *et al.,* 2010). On the other hand, it was also shown that under moist conditions adsorbed amount of CO_2 decreased (Hiyoshi *et al.,* 2005).

4.3. Decision Tree Classification for CO_2/N ratio

The data base including 1356 instances with 26 attributes were classified according to their CO_2/N ratio into four classes representing low, moderate, high, very high amino efficiencies. The ranges and number of data points in classes are: 0-0.22 (low), consisting 361 data points; 0.22-0.30 (moderate), consisting 342 data points; 0.30-0.40 (high), consisting 319 data points; 0.40-0.90 (very high) consisting 334 data points. These divisions were chosen because they are sufficient to distinct the good and bad performance, and lead to an approximately equal number of data points in each class, hence it will not create class imbalance problem. Then, they were divided randomly into two parts which were training and testing sets. Three fourth of the total data including 1017 data was used to build decision tree and to train it while, one fourth of the total data including 339 data was used for testing set which test the generalization ability of the decision tree.

The ranges of input variables leading to very high CO_2/N ratio were predicted by applying decision tree analysis to develop heuristics which improve adsorption performance. In order to reach optimal decision tree, different prune and split min values were investigated. First, large tree were constructed and then different levels of prune value was applied until reaching minimum error rate. If the tree size is increased, training error decreased continuously while testing error decreased first and then increased due to model overfitting. Split min value was detected as 20 and optimal prune value found as 3.

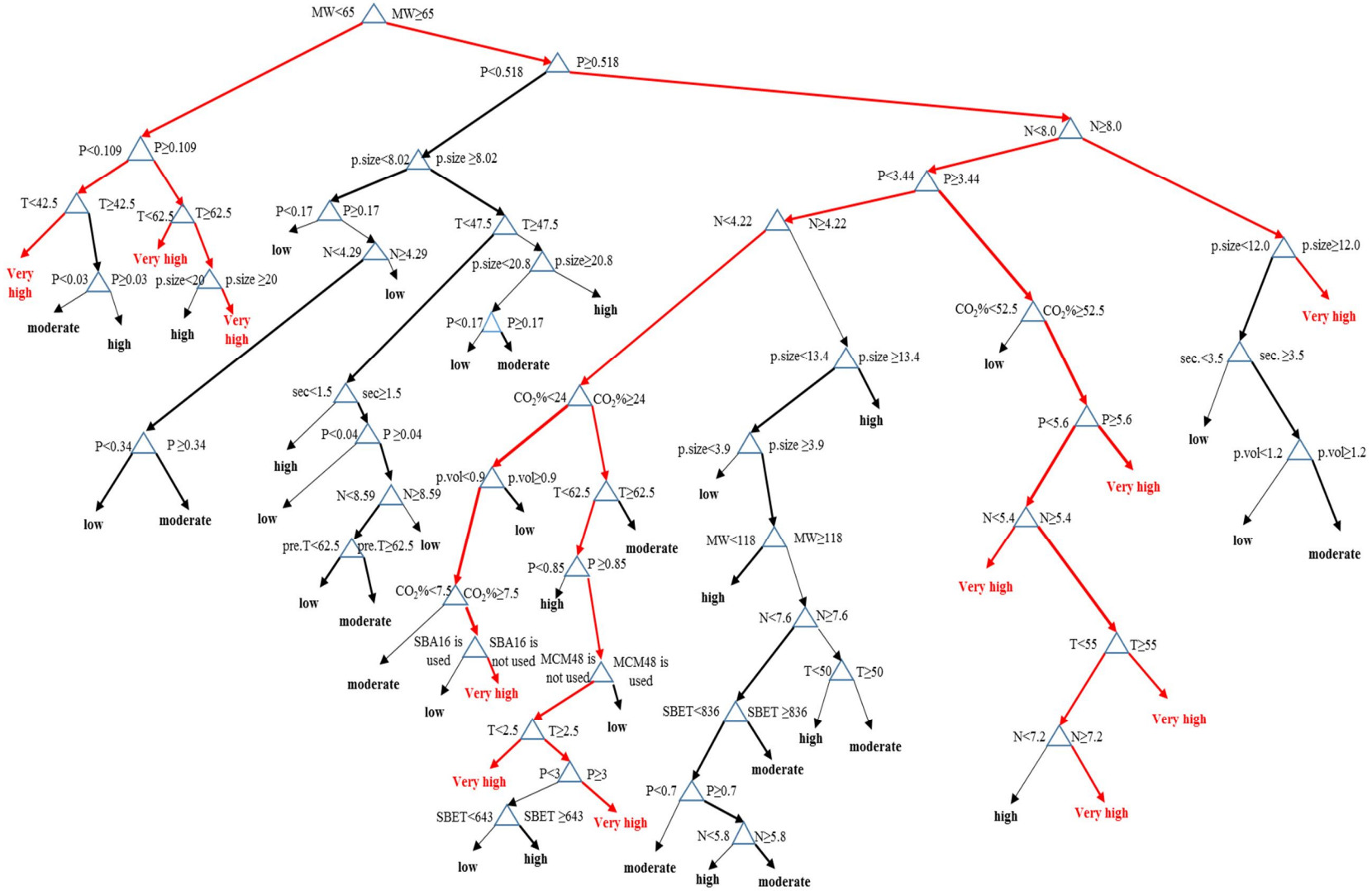

Figure 4.5. Optimal decision tree for total data set of CO_2/N ratio.

The optimal decision tree was illustrated in Figure 4.5. Training and testing errors were 19.2% and 22.7% respectively. Testing error showed that the tree was able to predict the CO_2/N levels reasonably well. It can be concluded from testing error that the model results were successful since these data points were not used during model construction. As can be seen from Figure 4.5, the first division at the top was according to molecular weight of amine, which was modified on the sorbent surface. The decision point for molecular weight of amine was 65 g/g mol and classification process continues in the sub branches with adsorption pressure, adsorption temperature, nitrogen content, pore size and CO_2 flux concentration.

If the molecular weight of amine was higher than 65 g/g mol, tree showed that high amino efficiency level was not possible at the pressures less than 0.518 bar. If the molecular weight of amine was higher than 65 g/g mol and the pressure was higher than 0.518 bar, tree suggested that the high CO_2/N ratio depends on other variables; the four most significant variables were molecular weight, pore size, adsorption temperature and adsorption pressure. In this division (MW was higher than 65 g/g mol and P was higher than 0.518 bar) certain conditions like the nitrogen content was lower than 8 mmol/g sorbent, pressure was higher than 3.44 bar, flux CO_2 concentration was higher than 52.5%, pressure was less than 5.6 bar, nitrogen content was less than 5.4 g/gmol were suggested by tree to reach very high levels. In same division, the tree also showed that if nitrogen content was higher than 8 mmol/g sorbent pore size must be higher than 12 nm to achieve highest amino efficiency. There were six other branches and possibilities towards very high CO_2/N ratio in the same main branch. It can be seen that adsorption temperature, molecular weight, pressure and pore volume were the dominant parameters.

If molecular weight was lower than 65 g/g mol, there had three braches which led to high CO_2/N ratio with different combinations. In this division (molecular weight of amine was lower than 65 g/gmol), pressure was the decision point which had a value of 0.109 bar. Tree suggested that if the pressure was higher than 0.109 bar and temperature was lower than 62.5 °C, very high level of CO_2/N ratio may be achieved. In the same division, there was one other branch which had highest CO_2/N ratio. On the other hand, highest CO_2/N ratio was accomplished when molecular weight was lower than 65 g/g mol, pressure was lower than 0.109 bar and temperature was lower than 42.5 °C.

Table 4.3. Classification accuracies of CO_2/N ratio training data classes.

Experimental Data		**Predictions for Training**				
CO_2/N ratio	Number of data	0-0.22 (low)	0.22-0.30 (moderate)	0.30-0.40 (high)	0.40-0.90 (very high)	Classification Accuracy (%)
0-0.22 (low)	251	**211**	28	7	5	84.1
0.22-0.30 (moderate)	263	24	**202**	29	8	76.8
0.30-0.40 (high)	259	5	24	**190**	40	73.4
0.40-0.90 (very high)	244	2	1	22	**219**	89.8

Table 4.4. Classification accuracies of CO_2/N ratio testing data classes.

Experimental Data		**Predictions for Testing**				
CO_2/N ratio	Number of data	0-0.22 (low)	0.22-0.30 (moderate)	0.30-0.40 (high)	0.40-0.90 (very high)	Classification Accuracy (%)
0-0.22 (low)	110	**89**	15	3	3	80.9
0.22-0.30 (moderate)	79	9	**53**	14	3	67.1
0.30-0.40 (high)	60	0	8	**39**	13	65.0
0.40-0.90 (very high)	90	0	0	9	**81**	90.0

The distribution of training and testing errors among tree classes for the optimum tree are shown in Table 4.3 and Table 4.4 respectively. Accuracy of training classification

was 81%. It can be seen from Table 4.3 that 822 of 1017 data points were correctly classified during training. The accuracy of testing classification was 75.7% which is quite successful since 262 of 339 data were classified accurately. It should be noted that even the wrong classes were placed mostly to the neighboring classes indicating that the success of the tree is actually higher than as it was indicated by the correct classification rate. The lowest and highest CO_2/N ratio classification accuracies are high as expected since the model predicts outer classes better.

It should be noted that these split values are calculated by learning algorithm of the decision tree therefore they are not the exact physical limits; they are just the center point between the values in two branches.

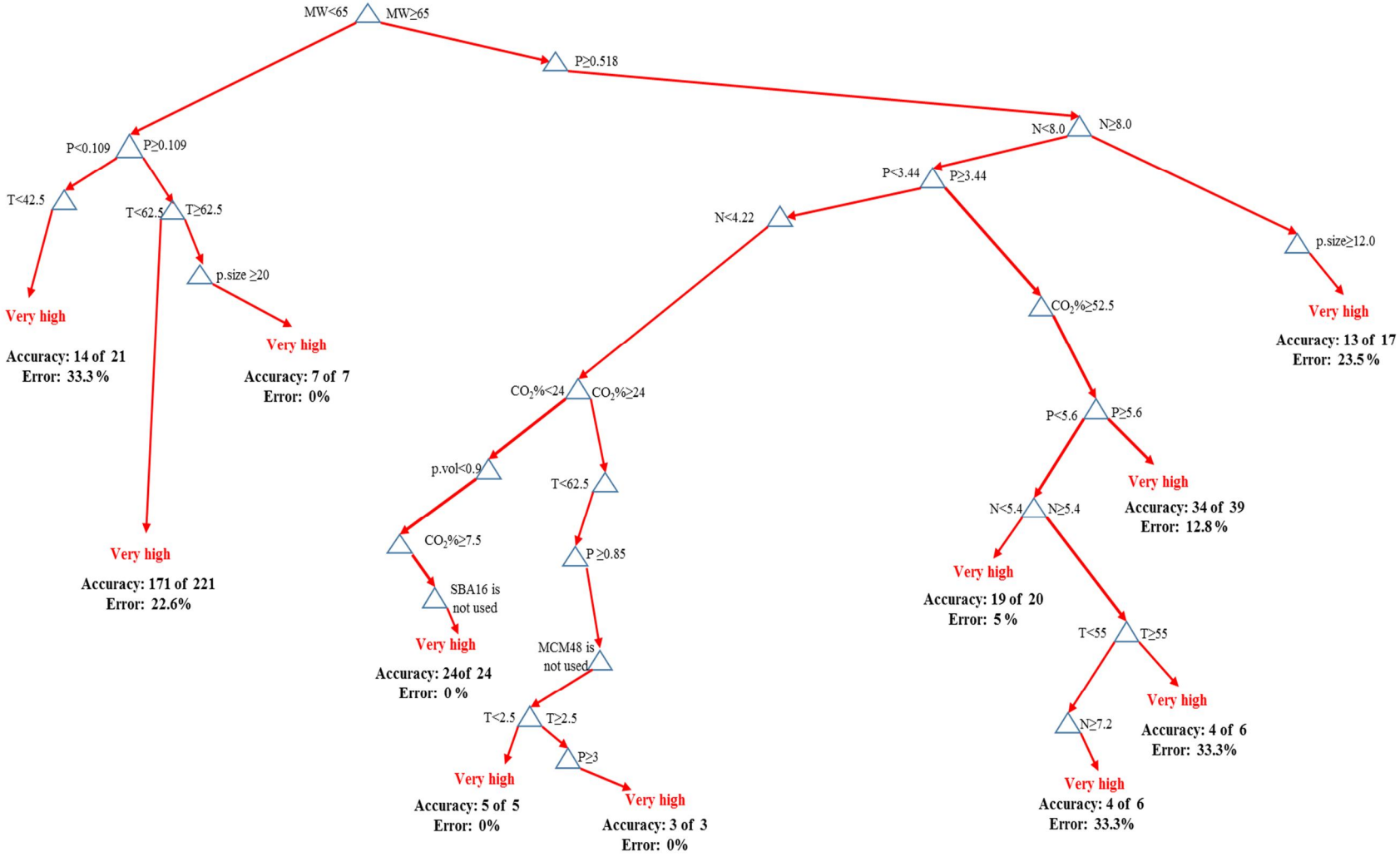

Figure 4.6. Branches of decision tree leading the highest (0.40-0.90) CO_2/N ratio.

Branches of decision tree leading the highest amino efficiency and accuracy of each branch was showed in Figure 4.6. The heuristics leading to very high CO_2/N ratio improved from the decision tree analysis were illustrated in Table 4.5. It can be seen from Table 4.5 that there are 11 different combinations and ranges of input variables which leads to high CO_2/N ratio. In Table 4.5, rows from left to right indicate conditions for very high (0.40-0.90) CO_2/N ratio and the last columns indicate the accuracy of prediction which was the ratio of correctly predicted number of data points over total data for each node that led to very high CO_2/N ratio. In spite of the fact that the rules in Table 4.5 are empirical, they could lead future studies. It should be noted that the rows verified by high number of data points could be considered as heuristics for high amino efficiency. On the other hand, the rows include moderate number of data points could be used with cautions (Tapan *et al.,* 2016).

Table 4.5. Conditions for maximum CO_2/N ratio determined by decision tree.

<table>
<tr><th colspan="6">Variables and their ranges leading very high CO_2/N ratio</th><th>Accuracy of classification (correct data/total data)</th></tr>
<tr><td rowspan="7">MW≥65,P≥0.518</td><td colspan="5">N≥8, p.size≥12</td><td>13/17</td></tr>
<tr><td rowspan="6">N<8</td><td rowspan="3">P≥3.44, CO_2%≥52.5</td><td colspan="3">P≥5.6</td><td>34/39</td></tr>
<tr><td rowspan="2">P<5.6</td><td rowspan="2">N≥5.4</td><td>T≥55</td><td>4/6</td></tr>
<tr><td>T<55, N≥7.2</td><td>4/6</td></tr>
<tr><td colspan="2">N<5.4</td><td>19/20</td></tr>
<tr><td rowspan="3">P<3.44, N<4.22</td><td rowspan="2">CO_2%≥24, T<62.5, P≥0.85, MCM48 is not used</td><td>T≥2.5, P≥3</td><td>3/3</td></tr>
<tr><td>T<2.5</td><td>5/5</td></tr>
<tr><td colspan="3">CO_2%<24, p.vol<0.9, CO_2%≥7.5, SBA16 is not used</td><td>24/24</td></tr>
<tr><td rowspan="3">MW<65</td><td rowspan="2">P≥0.109</td><td colspan="4">T≥62.5, p.size≥20</td><td>7/7</td></tr>
<tr><td colspan="4">T<62.5</td><td>171/221</td></tr>
<tr><td colspan="5">P<109, T<42.5</td><td>14/21</td></tr>
</table>

Although they are not completely conclusive, some heuristics mat may be drawn from this table can be summarized.

It can be seen from tree that, at high adsorption pressure, the best combination seems to depend on whether nitrogen content lower than 8 mmol/g sorbent or not, if the amine

has high molecular weight(MW≥65). The tree indicated the following set of rules for both cases. If nitrogen content of adsorbent is higher than 8 mmol/g sorbent, pore size must be higher than 12 nm. If nitrogen content of adsorbent is lower than 8 mmol/g sorbent, adsorption pressure becomes important. In this case, if the adsorption pressure is higher than 3.44 bar, flux CO_2 concentration must be higher than 52.5%.

On contrary, if the adsorption pressure is lower than 3.44 bar, nitrogen content should be lower than 4.22 mmol/g sorbent and flux CO_2 concentration, pore volume, adsorption temperature and pressure becomes dominant.

If the molecular weight of amine was lower than 65 g/gmol, pressure and temperature becomes dominant. If pressure and temperature is high, pore size should be taken into consideration carefully and needs to be higher than 20 nm.

4.3.1. Decision tree results of CO_2 adsorption capacity

Same procedure for decision tree analysis of CO_2/N ratio in previous section was applied on CO_2 adsorption capacity analysis. As for amino efficiency analysis, 1356 total data with 26 attributes were classified as low, moderate, high and very high levels according to their adsorption capacity values. The ranges were 0-1 mmol CO_2/g adsorbent (low) consisting 310 data, 1-1.5 mmol CO_2/g adsorbent (moderate) consisting 392 data, 1.5-2 mmol CO_2/g adsorbent (high) consisting 313 data, 2-6 mmol CO_2/g adsorbent (very high) consisting 341 data. 1017 data was used training data set, while 339 data was used for testing set.

Decision tree analysis of capacity was applied and some heuristics were developed by taking very high adsorption capacities into consideration. Optimal results were taken from the analysis for 20 split min and 4 prune value and decision tree was shown in Figure 4.7.

Decision tree was obtained with 16.6% training error and 18.0% testing error. It can be deduced from testing and training errors that decision tree model and analysis for adsorption capacity was quite satisfactory, and better than the case of CO_2/N.

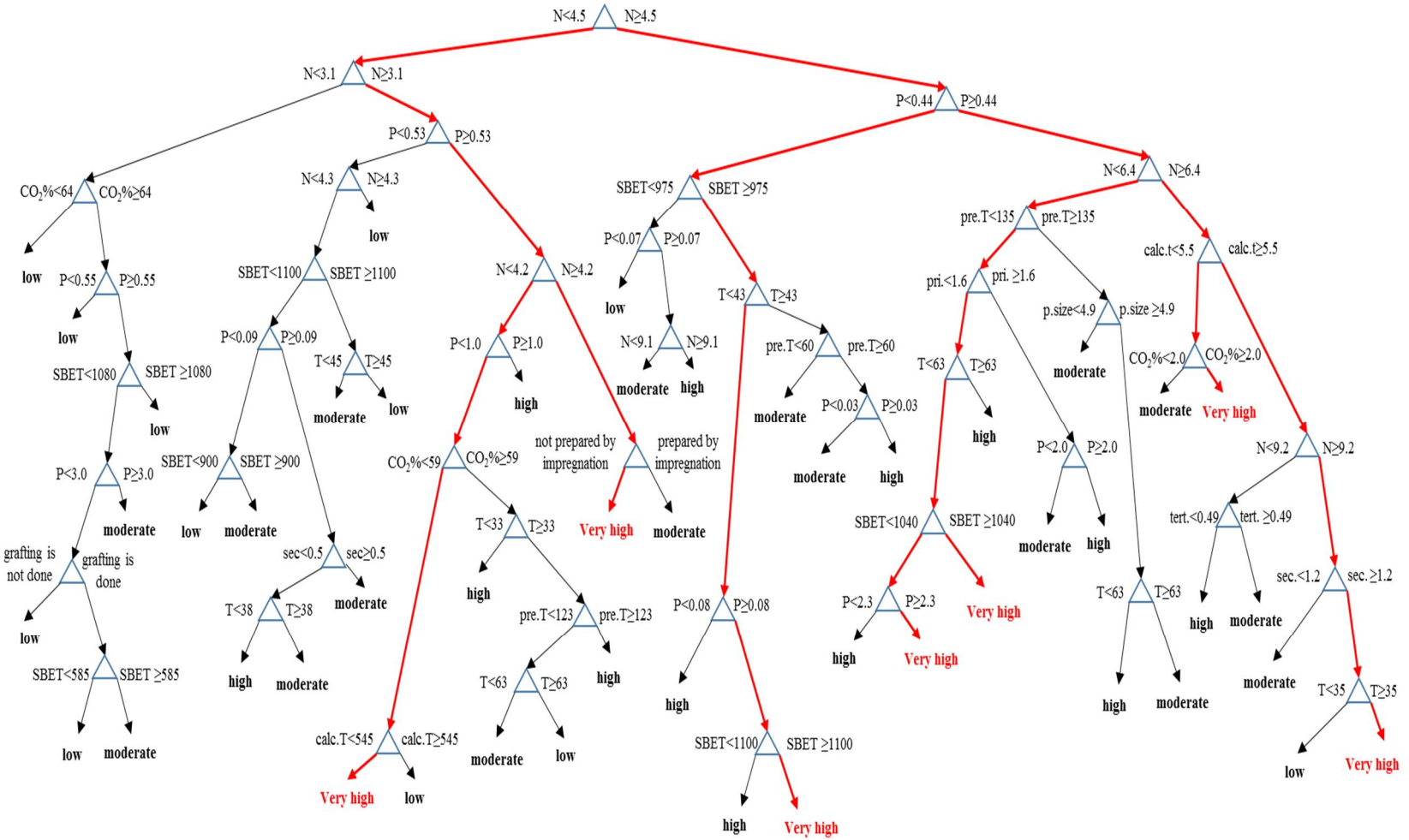

Figure 4.7. Optimal decision tree for total data set of CO_2 adsorption capacity.

Figure 4.7 reveals that the data first divided at the top according to nitrogen content of an adsorbent. It is well known from many studies that nitrogen content is very effective on amount of captured carbon dioxide by reacting with carbon dioxide (Sanz *et al.,* 2013). Decision point for nitrogen content at the top was 4.5 mmol/g sorbent. It was impossible to achieve very high CO_2 adsorption capacity when nitrogen content was less than 3.2 mmol/g sorbent. If nitrogen content was between 3.1 mmol/g and 4.5 mmol/g ($3.1 \leq N < 4.5$), tree suggested that there were two branches which led to the highest capacity. One of these two branches was for nitrogen content between 4.2 and 4.5 mmol/g and pressure was higher than 0.53 bar. In this division, tree indicated that amine needed to be grafted on the support surface in order to achieve the highest adsorption capacity. If nitrogen content was between 3.1 mmol/g and 4.5 mmol/g, pressure must be higher than 0.53 bar, otherwise the highest adsorption capacity cannot be reached.

Decision tree showed that if nitrogen content was higher than 4.5 mmol/g, division continued with pressure and in this division there were five branches and combination towards the highest capacity. Tree suggested that, in this division (nitrogen content was higher than 4.5 mmol/g), the highest CO_2 adsorbent capacity depends on adsorption pressure, presence or absence of primary amine, nitrogen content, surface area, and adsorption temperature.

If the nitrogen content was higher than 4.5 mmol/g and pressure was higher than 0.44 bar there were four combinations for achieving very high level of performance. In this division, tree suggested that nitrogen content higher than 9.2 mmol/g, calcination time was higher than 5.5 h, temperature was higher than 35 °C, high secondary amine led the highest adsorption capacity. On the other hand, in this division (nitrogen content was higher than 4.5 mmol/g and pressure was higher than 0.44 bar), if nitrogen content was lower than 6.4 mmol/g, pretreatment temperature, primary amine, surface area and adsorption temperature became dominant. In the literature, the significance of adsorption temperature and pressure were also indicated as relatively important parameters on adsorption performance and temperature effect on adsorption capacity is variable, depending whether the adsorption is controlled by thermodynamics or kinetics (Xu *et al.,* 2002).

Tree suggested that, when the nitrogen content was higher than 4.5 mmol/g and pressure was lower than 0.44 bar, surface area cannot be lower than 1100 m^2/g to achieve high capacity. In this division adsorption temperature and surface area were significant variables to determine the highest adsorption performance.

Table 4.6. Classification accuracies of CO_2 adsorption capacity training data classes**.**

Experimental Data		**Predictions for Training**				
CO_2 adsorption capacity	Number of data	0-1 (low)	1-1.5 (moderate)	1.5-2 (high)	2-6 (very high)	Classification Accuracy (%)
0-1 (low)	228	**203**	20	1	4	89.0
1-1.5 (moderate)	274	27	**210**	28	9	76.6
1.5-2 (high)	246	2	23	**186**	35	75.6
2-6 (very high)	269	0	1	19	**249**	92.6

Table 4.7. Classification accuracies of CO_2 adsorption capacity testing data classes.

Experimental Data		**Predictions for Testing**				
CO_2 adsorption capacity	Number of data	0-1 (low)	1-1.5 (moderate)	1.5-2 (high)	2-6 (very high)	Classification Accuracy (%)
0-1 (low)	82	**72**	6	0	4	87.8
1-1.5 (moderate)	118	15	**90**	9	4	76.3
1.5-2 (high)	67	0	6	**49**	12	73.1
2-6 (very high)	72	0	0	5	**67**	93.1

The distribution of training and testing errors among tree classes for the optimum tree are shown in Table 4.6 and Table 4.7, respectively. Accuracy of training classification was 83.4%.

It can be seen from Table 4.6 that 848 of 1017 data points were correctly classified during training. While accuracy of testing classification was 82.5% which is quite successful since 278 of 339 data were classified accurately shown in Table 4.7. This results show how good models classify and predict the data.

Figure 4.8 illustrates branches of decision tree that have the highest adsorption capacity with accuracy information for each branch. Table 4.8 shows the conditions for high performance.

It is seen from the top of tree that nitrogen content should not be lower than 3.1 mmol/g sorbent. Decision point for nitrogen content is 4.5 mmol/g sorbent and tree suggested that the high performance could be achieved whether nitrogen content is lower or higher than this value (as long as higher than 3.1 mmol/g) if some other conditions are met.

If nitrogen content is in between 3.1 and 4.5 mmol/g sorbent, adsorption pressure becomes dominant and it should not be less than 0.53 bar.

If nitrogen content is higher than 4.5 mmol/g sorbent, tree suggested different rules. If pressure is lower than 0.44 bar, surface area must be higher than 1100 m^2/g and temperature must be lower than 43 °C. On contrary, if pressure is higher than 0.44 bar, pretreatment temperature, presence of primary amine, adsorption temperature and surface area becomes important. In this case, nitrogen must be lower than 6.4 mmol/g sorbent and pretreatment temperature must be higher than 135 °C to achieve very high level.

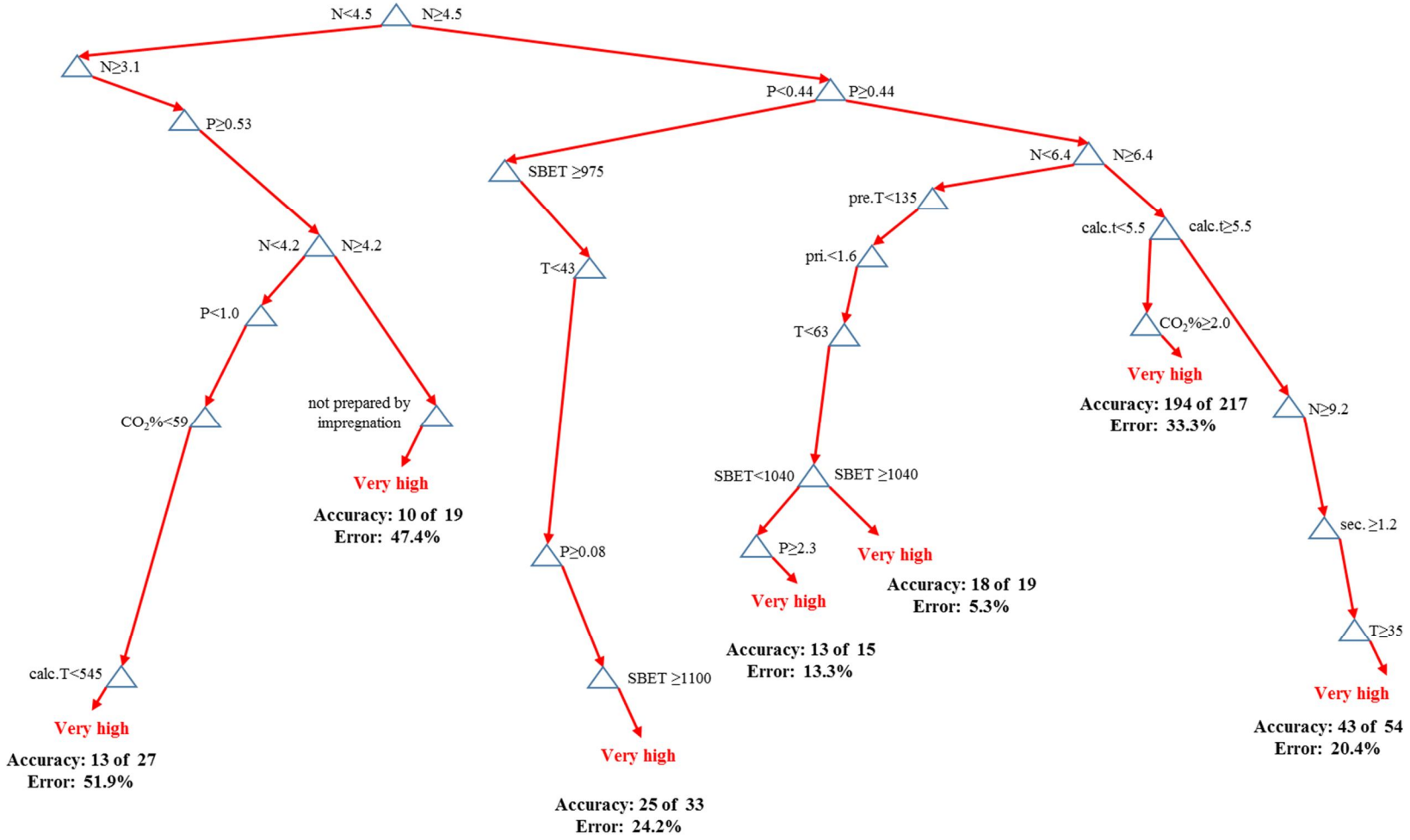

Figure 4.8. Branches of decision tree leading the highest (2-6) CO_2 adsorption capacity.

Table 4.8. Conditions for maximum CO_2 adsorption capacity.

Variables and their ranges leading very high mmol CO_2/g adsorbent capacity				**Accuracy of classification (correct data/total data)**
N≥4.5	P≥0.44	N≥6.4	calc.t≥5.5, N≥9.2, sec. ≥1.2, T≥35	43/54
			calc.t<5.5, CO_2%≥2.0	194/217
		N<6.4, pre.T<135, pri.<1.6, T<63	SBET ≥1040	18/19
			SBET<1040, P≥2.3	13/15
	P<0.44, SBET ≥975, T<43, P≥0.08, SBET ≥1100			25/33
N<4.5, N≥3.1, P≥0.53	N≥4.2, not prepared by impregnation			10/19
	N<4.2, P<1.0, CO_2%<59, calc.T<545			13/27

It can be seen from Table 4.8 that rows from left to right explain conditions for the highest adsorption capacity and the accuracy of prediction was shown in the last column. There were seven different combinations and ranges of inputs, which led to very high adsorption capacity.

5. CONCLUSION AND RECOMMENDATIONS

5.1 Conclusion

In this thesis, the experimental data for carbon dioxide adsorption on amine modified mesoporous sorbents were collected from the published articles between the years 2002 to 2016. The final database consisted of 30 articles and 1356 experimental data with 26 input variables and 2 output variables. Two kinds of data mining techniques that were decision tree and artificial neural networks were applied to the final data set to extract knowledge for carbon dioxide adsorption.

Firstly, neural network analysis was applied and it was quite successful for predicting results in unknown conditions. The best performing neural network topology was found as 26, 9, 1 which indicated 26 input variables and nine neurons in the first hidden layer for amino efficiency (CO_2/N ratio) analysis. 10-fold cross validation technique was used for testing model. R^2 value and RMSE was 0.83 and 0.053 respectively for testing neural network analysis of CO_2/N ratio. On the other hand, the best neural network topology for adsorption capacity analysis was found as 26, 10, 1. R^2 value and RMSE was 0.90 and 0.250 respectively for testing neural network analysis of capacity.

Input significance for amino efficiency and adsorption capacity calculated by using neural network showed that the most important factor was pressure with approximately 30% relative significance. The order of significance decreased in the order: pressure > flux carbon dioxide concentration > adsorption temperature > nitrogen content > others. Amino efficiency analysis showed that the group significance of for operational variables was 65.6 %, while adsorbent variables have the relative significance of 34.4 %. On the other hand, input significance analysis for adsorption capacity showed that operational variables had the relative significance of 57.3 % while the significance of adsorbent variables was 42.7 %.

Optimum decision tree structure for the entire database was also determined according to simplicity of decision tree and an acceptable error rate. Splitmin value was 20

for CO_2/N ratio and CO_2 adsorption capacity; whereas prune value was 3 and 4, respectively. The data points were divided in four levels; which were low, moderate, high and very high for both analysis. The decision tree analysis for CO_2/N ratio was accomplished with 19.2% training error and 22.7% testing error which was quite successful. It was observed from the decision tree that first decision point is the molecular weight of amine followed by pressure, nitrogen content, adsorption temperature, flux carbon dioxide concentration and pore size and so on. Some heuristics were also developed for very high (0.4–0.9) CO_2/N ratio from decision tree analysis. Same procedure was applied to CO_2 adsorption capacity decision tree analysis. Decision tree was achieved with 16.6% training and 18.0% testing error. First division of decision tree at the top was according to nitrogen content of an adsorbent this time. Then decision tree was divided into branches according to pressure, adsorption temperature, pore area, flux carbon dioxide concentration, which were quite similar to the results of CO_2/N ratio analysis. The conditions that are required to achieve very high (2-6 mmol CO_2/g adsorbent) adsorption capacity were also determined.

As a result, artificial neural network analysis seemed to have high prediction ability for both capacity and CO_2/N ratio analysis. Hence it could be used for extracting knowledge from published experimental data and direct the future studies. On the other hand, decision tree, as a widely used classification technique due to its simplicity and interpretability, was converted into set of rules that may be used in future studies.

5.2. Recommendations

In the light of this thesis, some recommendations can be stated in order to improve current methods and build better models to lead future researches.

- In order to achieve wider range of dataset to lead in detailed learning, more data can be collected by evaluating more articles. This will improve the prediction ability of model therefore model accuracy would increase.
- Other machine learning tools such as clustering can be applied to the dataset first, instead of applying neural network directly. The subset formed by clustering may be more suitable for neural network modeling.

- Input variables analysis can be performed to eliminate the ineffective variables, and data mining tools may be implemented by taking only the significant variables into consideration. This would provide quicker learning and increase the model capability.
- Other adsorbent types can be added to the data set. Then this data set can be analyzed to understand the common and different aspects of different types of adsorbent. And only chemisorption data can be used.

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APPENDIX A: ARTICLES INVOLVED IN DATABASE

Table A.1. Articles Involved in Database.

Number of articles	Reference
1	Sanz-Perez *et al.,* 2013
2	Zheng *et al.,* 2005
3	Belmabkout *et al.,* 2010
4	Harlick and Sayari, 2006
5	Serna- Guerrero *et al.,* 2008
6	Belmabkout and Sayari, 2010
7	Serna- Guerrero *et al.,* 2010
8	Zelenak *et al.,* 2008
9	Kim *et al.,* 2005
10	Belmabkout and Sayari, 2009
11	Wang *et al.,* 2007
12	Hiyoshi *et al.,* 2005
13	Zelenak *et al.,* 2008
14	Kim *et al.,* 2008
15	Ma *et al.,* 2009
16	Sanz *et al.,* 2010
17	Wei *et al.,* 2008
18	Sayari *et al.,* 2012
19	Xu *et al.,* 2002
20	Franchi *et al.,* 2005
21	Harlick and Sayari, 2007
22	Yan *et al.,* 2013
23	Wang and Yang, 2011
24	Sanz *et al.,* 2015
25	Sanz *et al.,* 2013
26	Sanz *et al.,* 2013
27	Sanz *et al.,* 2012
28	Chang *et al.,* 2009
29	Garcia *et al.,* 2015
30	Loganathan *et al.,* 2016