Prediction of Adsorption Isotherm of Methane Gas onto Activated Coconut Shell Charcoal by Neuro-Fuzzy Logic Model

By

Nur Amalina binti Ya'acob @ Ali

Dissertation submitted in partial fulfillment of
the requirements for the
Bachelor of Engineering (Hons)
(Chemical Engineering)

JANUARY 2005

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CERTIFICATION OF APPROVAL

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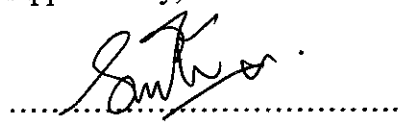
Approved by,



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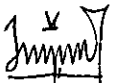
CERTIFICATION OF ORIGINALITY

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



NUR AMALINA BINTI YA'ACOB @ ALI

ABSTRACT

ANG (Adsorption Natural Gas) is a technology in which natural gas is adsorbed by a porous adsorbent material (i.e. activated carbon) at relatively low pressure (3.5 MPa up to 5.0 Mpa) that is applied on ANG vehicle. This technology, which the storage vessel is filled with a suitable adsorbent material, will have greater energy density compared to the same storage vessel without the adsorbent when filled to the same pressure. Besides that, natural gas is found as a potentially attractive fuel for vehicle use. It is because it is normally cheaper than diesel and gasoline and the vehicle has a less adverse effect compared to liquid-fuel vehicles which emitting more CO_2 as well as several other air pollutants. However, natural gas has a problem to be utilized at ambient temperature since it is difficult to liquefy because it comprises mostly of methane gas, which having a very low critical temperature (191 K). Therefore, this project is mainly to predict the adsorption isotherm of methane gas onto Activated Coconut Shell Charcoal using Neuro-Fuzzy Logic design system.

From the modeling done, the prediction of adsorption isotherm at three different temperatures (273 K, 303 K and 323 K) for methane gas onto activated coconut shell charcoal was successfully implemented by using Neuro-Fuzzy module system. The software used was Fuzzytech 5.52 Professional Demo software. The reference data used was taken from research done by E.Loren Fuller,Jr entitled Characterization of Porous Carbon Fibre and Related Materials. From the simulation done, the objective of this project has been achieved due to average error between experimental/reference data and Neuro-Fuzzy Logic data gained is less than 3%. The isotherm plotted between Neuro-Fuzzy Logic data and experimental data shown almost similar to each other. It can be concluded that the equilibrium model of adsorption isotherm of methane gas onto activated coconut shell charcoal was fitted with the experimental data at different temperature, which in this case were 273 K, 303 K and 323 K. Therefore, from the model developed, it is easier to predict the adsorption isotherm at other temperature but limited within the temperature range (273 K- 323 K) and pressure up to 760 Torr.

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CHAPTER 1
INTRODUCTION

1.1 Background of Study

World is facing problem in having surplus of natural gas and natural gas is one of the important energy resources. Thus, natural gas is found as a potentially attractive fuel for vehicle use because the it is normally cheaper than diesel and gasoline. Beside that, the feasibility of natural gas vehicle is well established. From environmental point of view, natural gas vehicle has a less adverse effect compared to liquid-fuel vehicles which emitting more CO_2 as well as several other air pollutants. However, since natural gas comprises mostly of methane, it has a transportation/storage problem since it is very difficult to liquefy due having a very low critical temperature (191K).

Historically, there have been two alternatives for storing natural gas on vehicle that are:

- *Liquefied Natural Gas (LNG)*: This option gives advantage in giving high methane density but from practical point of view, it is not suitable to use in vehicles due to the low temperature required (113K) that needs more cost for cooling system.
- *Compressed Natural Gas (CNG)*: This is the most common system used for this moment that stores natural gas is carried out at room temperature. However, this storage needs very high pressure (around 20MPa) that makes the vessel necessary to use of heavy steel cylinder and big size. The worse case comes when the vehicle crash, which it can be somewhat dangerous consequences (i.e. explosion).

Thus ANG technology developed that used adsorption approach was widely employed in order to improve the utilization of methane as well as natural gas in variety real world applications. This gas adsorption process that used activated carbon as the adsorbent materials in storage vessels for storing natural gas at relatively low pressure (3.5 MPa up to 5.0 MPa) and at room temperature. This gas adsorption technology is one of practical consequence to engineers and chemists in many ways. It is because advantages of using ANG as an automotive fuel over gasoline and diesel are lower vehicle emission, lower

maintenance and saving in fuel cost. Besides that, in relation to the use of CNG, ANG inherent safety which means if an ANG vessels is punctured and the fuel ignited, it tends to burn in a controlled way with the desorbing gas tending to cool the remaining mass (limit the emission rate). However, the key important of this ANG technology is it provides a maximum gas storage density that becomes the main requirement for storing the maximum volumes of gas per volume of storage tank (vessel).

1.2 Problem Statement

1.2.1 Problem Identification

Natural gas is difficult to be utilized at ambient temperature and pressure since it has lower energy density. Therefore, it is crucial to develop a gas storage technology for getting high energy density, especially to meet demand as an auto alternative fuel. Thus, adsorption technology was applied. For this purpose, a suitable development of the adsorbent is necessary to maximize gas uptake per storage volume. Among the available adsorbents, activated carbons exhibit the largest adsorptive capacity. The basic step of development of ANG technology is to obtain adsorption isotherm of natural gas prior studying dynamic flow of adsorption and desorption process.

1.2.2 Significant of the Project

This project is related directly to predict the adsorption isotherm of natural gas onto activated carbon where in this case is activated coconut shell charcoal. Thus, due to difficulty to obtained natural gas equilibrium data, methane gas equilibrium data was used since natural gas mainly consists of methane component. The prediction was done by using Neuro-Fuzzy Logic

1.3 Objectives and Scope of Study

1.3.1 Objectives

One objective has been identified to focus on the deliverables within the given time frame. The main objective of this research project is to predict adsorption isotherm of methane gas onto Activated Coconut Shell Charcoal using Neuro-Fuzzy Logic design system.

1.3.2 Scope of Study

1.3.2.1 To model equilibrium of methane onto Activated Coconut Shell Charcoal

1.3.2.2 To fit equilibrium data at different temperature range (273 K, 303 K and 313 K) using Neuro-Fuzzy Logic.

1.3.3 Feasibility of the Project within the Scope and Time Frame

Abide by the suggested milestone, the project scope has been narrowed down to make it feasible to be completed in Week 14 (Please refer to Appendix 1).

CHAPTER 2
LITERATURE REVIEW

2.1 Adsorption Natural Gas (ANG) Principle and Characteristic

ANG is a technology in which natural gas is adsorbed by a porous adsorbent material such as activated carbon at relatively low pressure, 3.5 MPa up to 5.0 MPa. This technology that the storage vessel is filled with a suitable adsorbent material will have greater energy density compared to the same storage vessel without the adsorbent when filled to the same pressure. Thus, it can be said that ANG at low pressure can reach almost the same energy density of Compressed Natural Gas at high pressure (20 MPa). The characteristic of ANG is shown in Figure 1. Theoretically, the amount of natural gas stored of ANG at 3.5 MPa is near 210v/v that actually at one-six the pressure. It stores about two-third the amount of CNG at 20MPa. But because of relatively low pressure, ANG has some obvious advantages in weight of storage vessel, shape of the vessel, safety and cost. [6]

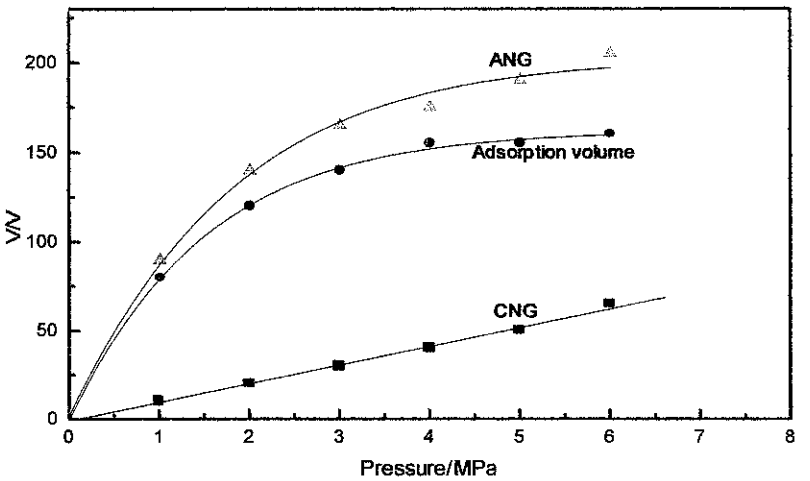

Figure 2.1: ANG Characteristic

2.2 Theory of Adsorption

Adsorption process is a process, which involves separation of a substance from one phase accompanied by its accumulation or concentration at the surface of another. The adsorbing phase is the adsorbent, and the material concentrated or adsorbed at the surface

of that phase is the adsorbate. Once the absorbate molecules was introduce to the adsorbent, it molecules quickly find their way to the surface of every pore in the adsorbent. These molecules can either bounce off or stick to the surface. Gas molecules that stick to the surface are said to be adsorbed. The strength with which adsorbed molecules interact with the surface determines if the adsorption process is to be considered physical (weak) or chemical (strong) in nature that are:

I. Physisorption

Physical adsorption (physisorption) is the most common type of adsorption. Physisorbed molecules are fairly free to move around the surface of the sample. As more gas molecules are introduced into the system, the adsorbate molecules tend to form a thin layer that covers the entire adsorbent surface.

II. Chemisorption

Many gases react with surfaces by chemically bonding. In contrast to physisorption, chemical adsorption (chemisorption) involves the formation of strong chemical bonds between adsorbate molecules and specific surface locations known as chemically active sites. Chemisorption is thus used primarily to count the number of surface active sites which are likely to promote chemical and catalytic reactions.

2.3 Adsorbent (Activated Carbon)

Diffusion of gases in carbon adsorbents has been intensively investigated with various techniques such as pulse chromatographic, gravimetric uptake, batch column adsorption, volumetric, gas permeation and isotope exchange methods. The overall transport rate in adsorbent is generally controlled by diffusion inside the micro pores and the corresponding diffusivities are concentration dependent, as would be inferred from generally heterogeneous nature of the adsorptive-adsorbent interactions. The most

common industrial adsorbents are activated carbon, silica gel, and alumina, because they present enormous surface areas per unit weight. Activated carbon is produced by roasting organic material to decompose it to granules of carbon such as coconut shell, wood, and bones are common sources. Besides that, activated carbon has been identified as one of the best tools that can reduce risks to human health. It also becomes such an effective adsorbent material due to its large number of large and deep pores. So, larger surface area exists relative to the size of the actual particle and its visible exterior surface. Hoehn (1996) found that approximate ratio for activated carbon is 1 gram AC equal to 100 m^2 of surface area [5]. Typically, the activated carbon is in the form of powder, granules, or extruded pellets. It was found that both gases will adsorb at 3-5 MPa while desorb at 0.14 Mpa at 298.15 K.

2.4 Adsorption Isotherm

Isotherm represents empirical relationship between the amounts of contaminants adsorbed per unit weight of activated carbon. Generally, isotherm is mainly to evaluate the activated carbon used during adsorption process. Technically, adsorption isotherm is the variation of number of occupied adsorption sites per total number of possible sites with pressure at a given temperature. It is because at constant temperature, adsorbate and the surface come to a dynamic equilibrium (chemical potential of the free adsorbate equal to the chemical potential of the surface bound adsorbate)

There are three instrument methods in common use today for measuring adsorption isotherm data. These volumetric methods use the "GAS LAWS" to calculate the volume of gas adsorbed at measured relative pressures and are known as:

1) Static, (classic) fully equilibrated,
2) Continuous Flow, or quasi-equilibrated,
3) Dynamic or Chromatographic.

There are many types of adsorption isotherms used in this technology. The simplest isotherm used is Langmuir Isotherm (LI). It was found that like BET (Bruneur, Emmett

& Teller) Isotherm, Dubinin-Radushkevich Isotherm (D-R) also was used in this technology application. Details are stated below:

2.4.1 Type of Isotherm ([1],[2], [3])

For gas-solid interface physisorption, isotherm interpretation is a useful indication of the mechanisms of surface coverage and/or pore filling. It should be kept in mind that the overall shape of an isotherm is governed by nature of the gas-solid system, the pore structure of the adsorbent and the operational temperature. Linearity of the isotherm is generally observed only at very low surface coverage and therefore cannot be easily detected at the temperatures and with the techniques normally used for studying the complete range of p/p^o(e.g. 77K for nitrogen adsorption). The deviation from linearity may be caused on the scale of surface heterogeneity and the magnitude of the adsorbate-adsorbate interactions. There are six major types of isotherms in the IUPAC classifications, which still provide a useful basis for adsorption mechanism.

2.4.1.1 Type I isotherms

The main feature of reversible this type of isotherm is the long plateau, which indicates a relatively small amount of multiplayer adsorption on the open surface. Micropore filling may take place either in pores of molecular dimensions at very low p/p^o or in wider micropores over a range of higher p/p^o.

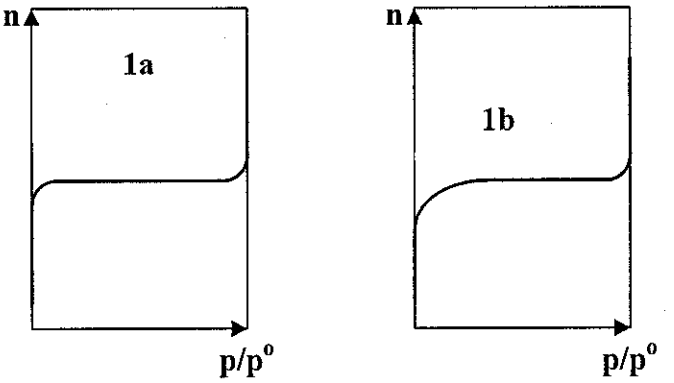

Figure 2.2: Type I isotherm

2.4.1.2 Type II isotherms

A truly reversible of this type of isotherm is normally associated with monolayer-multilayer adsorption on an open and stable external surface of a powder, which may be non-porous, macroporous or even, to a limited extent,microporous(**Type IIa**). The isotherm is smooth,non stepwise character is often associated with energetic heterogeneity in the adsorbent-adsorbate interactions. A sharp point b and a corresponding high value of C(BET) usually indicate a formation of a well defined monolayer, while the absence of an identifiable Point B is a clear sign of a significant overlap of monolayer and multiplayer adsorption. Increase of temperature leads to smoothing of the isotherm, which may be generally assigned to an increase in mobility of the adsorbed molecules or alternatively to a decreased degree of localization.

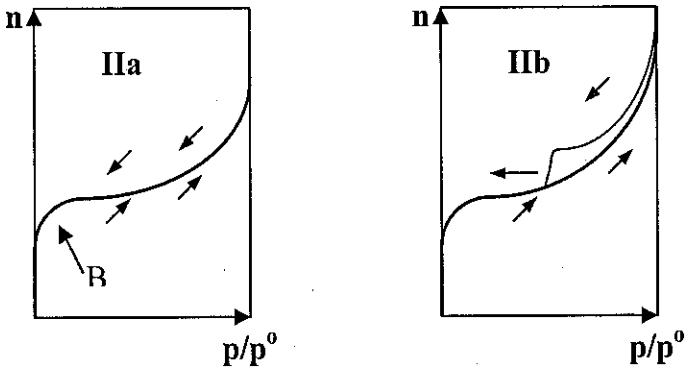

Figure 2.3: Type II Isotherm

Type IIb shown that there is no plateau at high p/p^{o}. It was obtained with combines of plates-like particles, which therefore possessed non-rigid slit shaped pores. Due to delayed capillary condensation, multiplayer adsorption is able to proceed on the particle surface until reaching high p/p^{o}. Then, once condensation has happened, the state of the adsorbate is changed and the desorption curve therefore follows different path until the condensate becomes unstable at a critical p/p^{o}.

2.4.1.3 Type III isotherms

This type of isotherms is confined to a few systems in which the overall adsorbent-adsorbate interactions are weak. The monolayer density tends to be unevenly distributed on the adsorbent surface with a relatively high concentration of molecules located on the most active areas. So that, as pressure increases, the average monolayer concentration is increases too. But then, before it can become close packed over the complete surface, the monolayer coverage is overtaken by a form of co-operative multiplayer adsorption (the molecules are bunched around the most favorable sites). Below figure shows that the isotherm curve remains convex to the p/p^o axis with C (BET)<2.

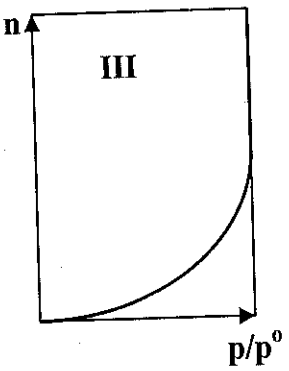

Figure 2.4: Type III Isotherm

2.4.1.4 Type IV isotherms

For this type of isotherm, the main characteristic feature is the hysterisis loop. Two types of hysterisis loop is shown below (IVa and IVb). For IVa , the loop is relatively narrow. Besides that the adsorption and desorption branches being almost vertical and nearly parallel. Generally, it is due to the location of the adsorption branch is governed by delayed condensation. For IVb, the loop is broad and the desoprtion branch is being much steeper compared to adsorption branch. It is because the steep desorption branch is dependent on network percolation effects. For IVc, it was less common and completely reversible isotherm. If the riser is almost vertical at a characteristic **p/p^o**, reversible pore filling and emptying appear to occur in a narrow range of uniform near cylindrical

pores of critical size. Besides that, the reversibility is being dependent on the adsorptive and the operational temperature.

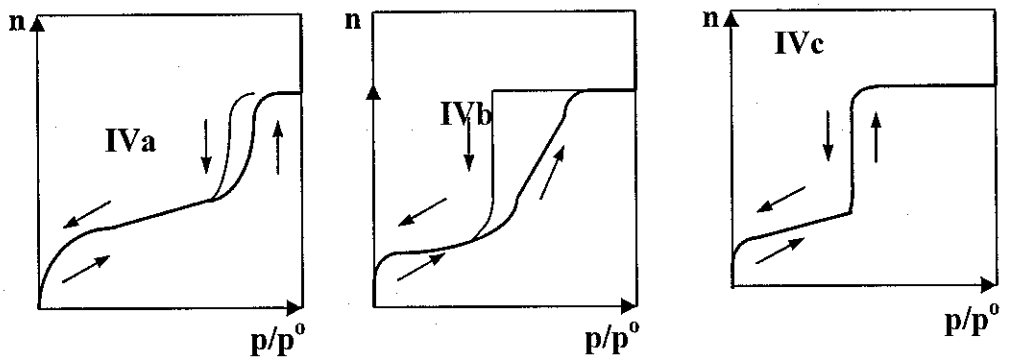

Figure 2.5: Type IV Isotherm

2.4.1.5 Type V isotherms

For initial section of this type of isotherm, it looks like very similar to that of Type III isotherm for a similar gas-solid system. But in this case, the sharp increase in adsorption at higher p/p^o is dependent on the pores size. For example, the ultramicropores in a molecular sieve carbon are filled with water at a much lower p/p^o than are the wider pores in supermicroporous carbon.

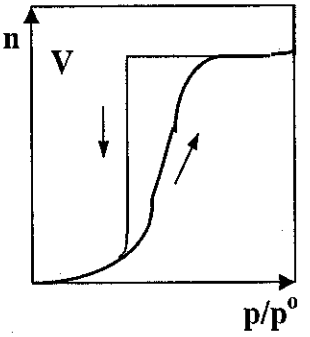

Figure 2.6: Type V Isotherm

2.4.1.6 Type VI isotherms

The highly distinctive form of isotherm is due to a stepwise layer-by-layer adsorption process. Such isotherm is given by the adsorption of simple non-polar molecules (e.g. argon, krypton and xenon) on uniform surfaces. The steps become less sharp as the temperature increased. The vertical riser can be neglected as the

adsorbed layer boundaries and the centers of the inflection points as the layer capacities.

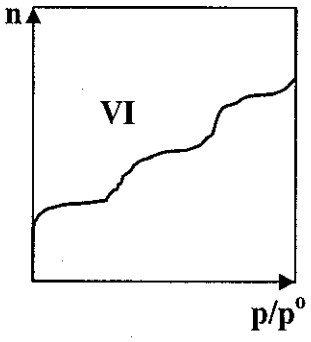

Figure 2.7: Type VI Isotherm

2.4.2 Isotherm Analysis [2,3]

2.4.2.1 Empirical methods

Many different equations have been applied to physisorption isotherms on microporous adsorbents. The first and best-known empirical equation was proposed by **Freundlich** (1926) in the form of

$$n = kp^{1/m} \qquad \text{where} \quad k,m \text{ constants}(m>1) \qquad (3.1)$$

According to equation (3.1), the plot of In [n] against In [p] should be linear. In general, activated carbons give isotherms that obey the Freundlich equation in the middle range of pressure (Brunuer, 1945). Even so, the agreement is usually weak at high pressures and low temperatures. It because are partly due to the fact that Freundlich isotherm does not giving a limiting values of n as $p \rightarrow \infty$.

It is impossible to achieve an improved fit at higher pressures by combination of the Freundlich and Langmuir equations, **Sips equation**:

$$n/ n_L = (kp)^{1/m} /[1+ (kp)^{1/m}] \qquad (3.2)$$

where n_L is limiting adsorption capacity.

Equation (3.2) has been applied as generalized Freundlich isotherm to multisite occupancy by long chain hydrocarbons. However, as in the case of the Freundlich isotherm itself, the Sips equation does not reduce to Henry's Law as $p \rightarrow 0$.

Another empirical approach is **Toth Equation**:

$$n/ n_L = p /(b+ p^m)^{1/m}$$

which also contains three adjustable parameters (n_L, b and m) but has the advantage that it appears to give the correct limits for both $p \rightarrow 0$ and $p \rightarrow \infty$. Even this equation is was originally proposed for monolayer adsorption (Toth, 1962), this equation actually gives more extensive range of fit when applied to Type I isotherm (Rudzinski and Everett,1992).

2.4.2.2 Langmuir Isotherm (LI) theory

The original derivation of the Langmuir equation (Langmuir,1916) is a kinetic one. The adsorbent surface is pictured as an array of N^s equivalent and independent sites for localized adsorption (one molecule per site). The total number of possible site is pictured pf N^a. Thus, the fractional coverage of a surface, θ is $\theta = N^a/N^s$.

From the kinetics theory of gases, the rate of adsorption is dependent on the pressure and the fraction of bare sites(1- θ). The rate of desorption is dependent on θ an on activation energy. Thus, at equilibrium, both rates are equal and results zero net rate of adsorption:

$$\mathbf{dN^a/dt = \alpha p(1- \theta) - \beta \theta \exp(-E/RT) = 0}$$

where α, β = rate constant for adsorption and desorption, respectively.

From above, Langmuir isotherm equation was derived:

$$\mathbf{\theta = Kp/(1+Kp)} \qquad \text{where } K = \alpha/ \beta [\exp(E/RT)]$$

p = pressure of the adsorbate

The assumptions made for this isotherm are stated below:

I. Adsorption cannot proceed beyond the point at which adsorbates are one layer thick on the surface (monolayer).
II. All adsorption sites are equivalent.

III. The adsorption and desorption is independent of the population of neighboring sites.

IV. Energy of adsorption is uniform.

At high adsorbate pressure and thus high fractional coverage, this isotherm fails to predict experimental results and cannot provide a correct explanation of adsorption. It is because this isotherm only considers monolayer case.

2.4.2.3 Dubinin-Radushkevich Isotherm (D-R)

Dubinin was the pioneer of the concept of micropore filling. His approach was based on the early potential theory of Polanyi, in which the physisorption isothem data were expressed in the form of temperature-invariant 'characteristic curve'. In 1947, Dubinin and Radushkevich put forward an equation for te characteristic curve in terms of the fractional filling, W/Wo of the micropore volume,Wo. This relation is usually expressed in the form

$$W/W_o = \exp [-(A/E)^2]$$

where A = Polanyi adsorption potential (adsorption affinity),

$$= -RT \ln (p/p^o)$$

E = characteristic energy of the system

Then, the isotherm equation is obtained by combining both equation above with introduction of a scaling factor,β, it becomes:

$$W/W_o = \exp \{-[RT \ln (p^o/p)]^2/(\beta E_o)^2\} \qquad (3.3)$$

With another parameter that is:

Structural Constant: $B= 5.304(R/E_o)^2$

By arranging equation 3.3, Dubinin-Radushkevich Isotherm equation becomes:

$$\mathbf{\log_{10}[W/W_o] = -D\log_{10}^2(p^0/p)}$$

where $D = 0.434B(T/\beta)^2$

Thus, equation above also can be expressed in the form of:

$$\mathbf{\log_{10}[n] = \log_{10}(n_p(mic)) - D \log_{10}^2(p^0/p)}$$

Therefore, a plot $\log_{10}[n]$ against $\log_{10}^2(p^o/p)$ should be linear with the slope D and intercept $\log_{10}(n_p(mic))$.

2.4.2.4 Brunauer_Emmett-Teller (BET) Equation

This equation is mostly used in determination of the surface area of adsorbent that is :

$$\frac{1}{W((P_o/P)-1)} = \frac{1}{W_mC} + \frac{C-1}{W_mC}\frac{P}{P_o}$$

where:

W = the weight of adsorbed at a relative pressure,P_o/P

W_m= the weight of adsorbate constituting a monolayer of surface coverage

C = BET constant is related to the energy of adsorption in the first adsorbed layer

2.5 Literature Review on Neuro-Fuzzy Logic Module

In general, a neuro-fuzzy system is a fuzzy system that uses a learning algorithm derived from or inspired by neural network theory in order to determine its parameters (fuzzy sets and fuzzy rules) by processing data samples. Modern neuro-fuzzy systems are usually represented as special multilayer feedforward neural networks (see for example models like ANFIS [14], FuNe [13], Fuzzy RuleNet [17], GARIC [9], or NEFCLASS and NEFCON [15]). However, fuzzifications of other neural network architectures are also considered, for example self--organizing feature maps [10, 18]. In those neuro--fuzzy networks, connection weights and propagation and activation functions differ from common neural networks. Although there are a lot of different approaches [11, 12, 15, 16], we usually use the term *neuro--fuzzy system* for approaches that display the following properties:

I. A neuro-fuzzy system is based on a fuzzy system which is trained by a learning algorithm derived from neural network theory. The (heuristical) learning

procedure operates on local information, and causes only local modifications in the underlying fuzzy system.

II. A neuro-fuzzy system can be viewed as a 3-layer feedforward neural network. The first layer represents input variables, the middle (hidden) layer represents fuzzy rules and the third layer represents output variables. Fuzzy sets are encoded as (fuzzy) connection weights. It is not necessary to represent a fuzzy system like this to apply a learning algorithm to it. However, it can be convenient, because it represents the data flow of input processing and learning within the model. *Remark:* Sometimes a 5-layer architecture is used, where the fuzzy sets are represented in the units of the second and fourth layer.

III. A neuro-fuzzy system can be always (i.e.\ before, during and after learning) interpreted as a system of fuzzy rules. It is also possible to create the system out of training data from scratch, as it is possible to initialize it by prior knowledge in form of fuzzy rules.
Remark: Not all neuro-fuzzy models specifiy learning procedures for fuzzy rule creation.

IV. The learning procedure of a neuro-fuzzy system takes the semantical properties of the underlying fuzzy system into account. This results in constraints on the possible modifications applicable to the system parameters. *Remark:* Not all neuro-fuzzy approaches have this property.

V. A neuro-fuzzy system approximates an n-dimensional (unknown) function that is partially defined by the training data. The fuzzy rules encoded within the system represent vague samples, and can be viewed as prototypes of the training data. A neuro-fuzzy system should not be seen as a kind of (fuzzy) expert system, and it has nothing to do with fuzzy logic in the narrow sense.

CHAPTER 3
METHODOLOGY/PROJECT WORK

3.1 Procedure of Neuro-Fuzzy logic approach

In order to establish the Neuro-fuzzy logic system in the Fuzzytech 5.52 Professional Demo software, some studies need to be performed in the first step. The leak of knowledge and experience as the system is used for the first time require range of time to be familiarized. After the system or software being studied and understood, than the prediction isotherm model was developed based on knowledge and equilibrium data gathered . Here the rules of fuzzy logic were created and adjusted to get the best forecasting data. Figure below is a simplified diagram showing the system design approach.

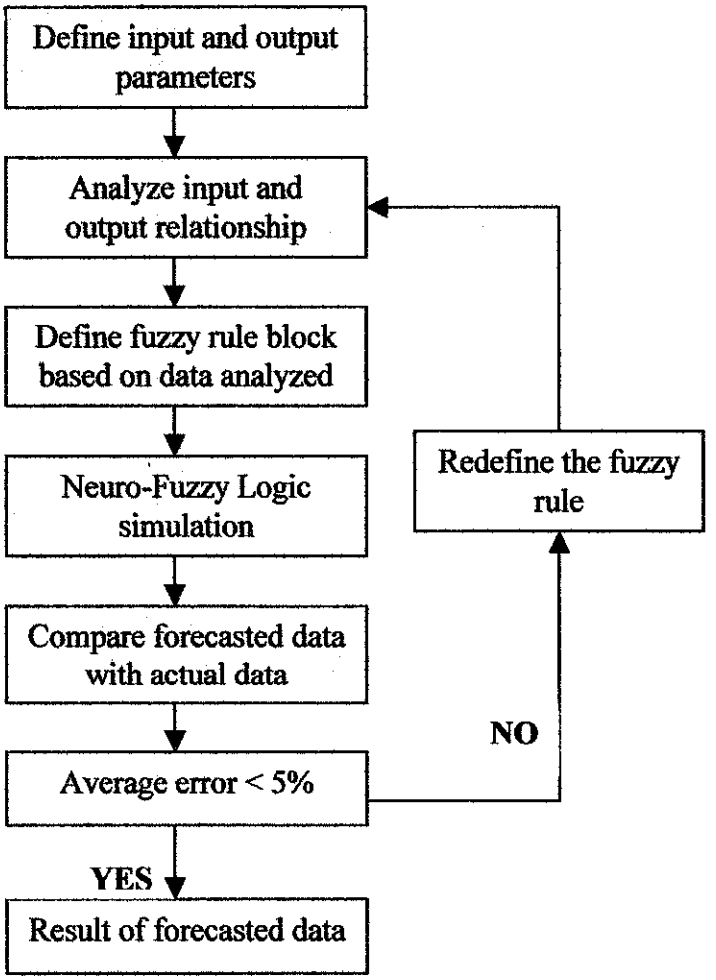

Figure 3.1: Flowchart of system design approach

From the Figure 3.1, the fuzzy system is reviewed several times before the final result determined. The revision done after comparing the forecast data and the actual equilibrium data that gathered from paper written by E.Loren Fuller,Jr.[7]. This is done in order to ensure reliability and accuracy of forecast data that produced by the system.

3.2 Neuro-Fuzzy Logic Implementation

In order to predict the adsorption isotherm of methane onto activated coconut char, Neuro-Fuzzy logic model was developed by using FuzzyTech Software. Neuro–Fuzzy system is developed based on the historical data that was set as the rule of the system which in this case was the experimental equilibrium isotherm data. The data parameters used for this model were:

i. Temperature (K)
ii. Pressure (kPa)
iii. Amount Adsorbed, Q ($mol.kg^{-1}$)

After extracting and gathering as per stated above data parameters, the Neuro-Fuzzy system model was developed first by generating a complete fuzzy logic system prototype via Fuzzy Design Wizard (FDW). The FDW has an ability to extract information from sample data file that must be in the fuzzy TECH data format. The data should be saved in CSV (comma delimited) format thru Excel. Besides that the data should be arranged as per shown below:

Temperature	**Pressure**	**Q**

Figure 4.1: Sequence of Data input

Where in this case,

Temperature = Input 1,

Pressure = Input 2

Q = Output.

All those variables were defined in perspective of name, range, number of terms and terms name. After that, the defuzzification method for output variable was determined.

For this research, the method chose was CoM since it was used in most control applications. Generally, there are several methods can be used to generate the output from the Neuro Fuzzy logic system that are:

a. CoM: Center of Maximum
b. Fast CoA: Center of Area
c. MoM / MoM BSUM: Mean of maximum defuzzification for pattern recognition application
d. CoA BSUM: Variants of MoM and CoA which have been optimized for efficient VLSI implementation
e. Hyper CoM: Used for fuzzy application, which not only positive experience in the form of recommendations but also negative experience in the form of warnings and prohibition.

Finally, the generation of the system prototype was completed after defining rule blocks which in this case only 1 rule block was used with zero (0) Degree of validity of rules (DoS). The reason for creating a complete but totally false (0) rule set is that the Neuro-Fuzzy training can only start with an existing rule set. Below is the generated complete fuzzy logic system prototype via FDW:

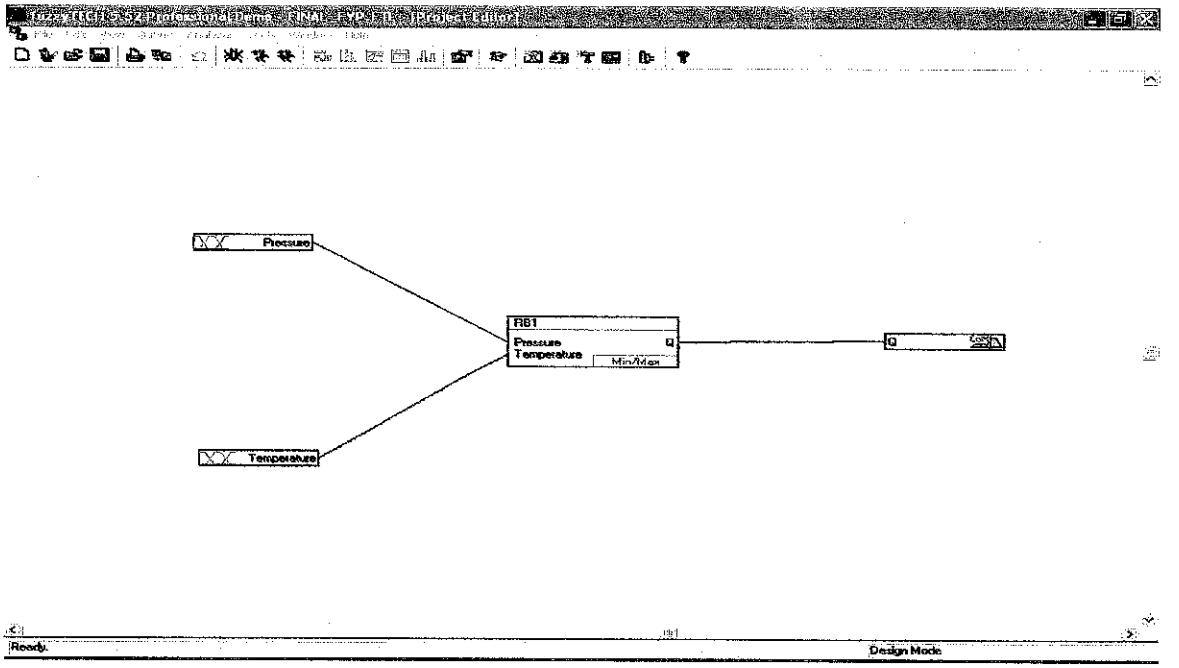

Figure 4.2: Neuro-fuzzy logic system prototype

From the generated prototype, there were three membership functions that can be extracted. They were temperature, pressure and Q (please refer to Appendix 2,3 and 4). There were three terms for temperature (Low, Medium, High) while five terms for pressure and Q (Very low, Low, Medium, High, Very High). Initially, all the terms were divided equally based on the range defined. However, those terms will be changed (if required) in order to achieve small average errors or almost no difference exists between experimental data and Neuro-Fuzzy data.

After Neuro-fuzzy logic system prototype for prediction of methane adsorption isotherm has been developed, the prediction was proceed with the Neuro-Fuzzy Training of Fuzzy system. The steps of developments are stated below:

i. Open the components of the fuzzy logic system to be trained

The components that should be opened prior training process are Temperature Editor (Appendix 2), Pressure Editor (Appendix 3), Q editor (Appendix 4), Spreadsheet Rule Editor (Appendix 5), Interactive Debug Mode (Appendix 6) and 3-D plot Window (Figure 12). Besides that, DoS (Degree of validity of rules) was set at 0.01 values via Rule Block Utility (Appendix 9).

ii. Configure the Neuro-Fuzzy Module

In this step, the Neuro was configured in perspective of learning method (in this case was Random Method), Selection Mode (Random), Learn Parameters (Step Width (Dos): 0.1; Step Width (Term): 1% and Winner Neuron:1), Stop Conditions (Max Steps:100 ; Max Deviation From: 1.99% to 1% ; Factor :0.75 ; Average Deviation:0.1%). Please refer to Appendix 7 for Neuro Configuration Window.

iii. Train with the sample data

By choosing Neuro Learning from tools toolbar, the training window will be looked like as per Appendix 8. The training will start as the▶ icon was clicked. The training will terminate as the one of stop conditions met. Before exit the training window, the Neuro-Fuzzy system for adsorption isotherm was updated by clicking icon indicated with 1984.

iv. Evaluate the system performance

In this step, initially the system was evaluated by using Interactive Debug Mode. One point of isotherm was selected in order to compare between experimental data and Neuro-Fuzzy Data. Then the overall Neuro-Fuzzy Data was compared with Experimental data by looking at the graph plotted and average error calculated (will be discussed at results section).

v. Manual Optimization

If there is some points that far away deviated from the experimental data value and average error was quite big (for this case > 5%), the neuro-fuzzy system will be reviewed and redesigned in order to decrease the error and to increase the accuracy a part of reliability of the model/system. For this research, the model was reviewed on three part that were:

a. Degree of validity of rules (DoS)
b. Limit/range of pressure membership function
c. Limit/range of Q membership function

CHAPTER 4
RESULTS AND DISCUSSION

4.1 Adsorption Isotherm Analysis

The prediction is mainly on the adsorption isotherm of methane onto activated coconut shell charcoal. It because the natural gas is mainly consists of methane and the activated coconut shell charcoal is one of the common activated carbon used for methane adsorption. The prediction was done at three different temperatures that are 273 K, 303 K and 323 K. The pressure range was from 5 kPa up to reference pressure at 760 Torr. Twenty-one (21) points of adsorption data of each temperature was taken in order to generate the isotherm model/system. Those data was taken from experimental data obtained by E.Loren Fuller,Jr entitled Characterization of Porous Carbon Fiber and Related Materials[7].

The prediction was done by using Neuro-Fuzzy Logic system. Basically Fuzzy logic and neural network are natural complementary tools in building intelligent systems. While neural networks are low-level computational structure that performs well when dealing raw data, fuzzy logic deals with reasoning on higher level by using linguistic information acquired from domain experts. However, fuzzy system lacks the ability to learn and cannot adjust them to a new environment On the other hand, although neural networks can learn, they are opaque to the user. That why integration of both systems was made in order to made the neural network becomes more transparent and fuzzy system become capable of learning. A Neuro-Fuzzy system is a neural network that is functionality equivalent to a fuzzy inference model. It can be trained to developed IF-THEN fuzzy rules and determine membership functions for input and output variables of the system. Expert knowledge can be incorporated into the structure of the Neuro-Fuzzy system. At the same time, the connectionist structure avoids fuzzy inference, which entails a substantial computational burden. From the studies done, this Neuro-Fuzzy Logic approach has it owns benefits and limitations. The benefits that has been identified were:

i. Avoidance of explicit programming

ii. Reduced need of experts
iii. This approach is adaptable to changed inputs
iv. No need for refined knowledge base
v. It is dynamic and improved with use since it can be tuned closer to specification in order to be more precisely in generating output by predicting the output.
vi. Able to process erroneous or incomplete data
vii. Allow inclusion of common sense into the problem solving domain

There are some limitations have been identified by earlier researcher such as:

i. This approach cannot explain their inference due to the "black box" nature makes accountability and reliability issues difficult to determine.
ii. Sometimes it becomes time consuming due to requirement of repetitive training in order to achieve the best model.
iii. In highly complex system, this approach may become an obstacle to the verification of system reliability. Besides that the fuzzy reasoning mechanism cannot learn from their mistakes.

However, this approach was chosen for this research due to the simplicity of the model.

4.2 Results

The model was reviewed in order to achieve targeted average error of <5%. The final limit of range for all parameters contributed to the prediction of methane adsorption isotherm onto activated coconut char were stated below:

For temperature (Input 1), the membership function was divided into three terms that were:

i. Low : 273 K – 289 K
ii. Medium : 285.5 K – 310.5 K
iii. High : 298 K- 323 K

For pressure (Input 2), the membership function was divided into five terms that were:

i. Very Low : 5.000 kPa – 23.7780 kPa
ii. Low : 5.000 kPa – 24.2820 kPa
iii. Medium : 19.05 kPa – 96.7480 kPa
iv. High : 24.2828 kPa – 100.7960 kPa
v. Very High : 96.748 kPa – 105 kPa

For Amount Adsorbed (Q), the membership function also was divided into five terms that were:

i. Very Low : (0 – 97) $mol.kg^{-1}$
ii. Low : (75 – 461.24) $mol.kg^{-1}$
iii. Medium : (97 – 77.31) $mol.kg^{-1}$
iv. High : (461.24 – 987.6) $mol.kg^{-1}$
v. Very High : (773.1 – 1000) $mol.kg^{-1}$

After the system of the prediction of adsorption isotherm was developed, both Neuro-Fuzzy data and experimental data were compared between each other in order to test the reliability and accuracy of the system. Tables and graphs below showed the final results of Nero-Fuzzy system developed.

Table 4.1: Isotherm data of Neuro-Fuzzy Logic and Experimental approaches at 273 K

Neuro-Fuzzy		Experimental	
Pressure (kPa)	Q ($mol.kg^{-1}$)	Pressure (kPa)	Q ($mol.kg^{-1}$)
5.0931	118.7000	5.0931	111.2079
7.3983	152.9200	7.3983	155.1738
9.9181	194.8600	9.9181	198.2777
14.9039	267.6600	14.9039	267.2438
19.8361	327.4800	19.8361	336.21
24.6611	403.0600	24.6611	398.7106
29.915	456.6200	29.915	450.4352
34.8472	504.8200	34.8472	502.1598
40.2083	555.2400	40.2083	556.0396
45.0333	598.9400	45.0333	599.1435
50.3944	645.7800	50.3944	646.5577
54.9514	684.2000	54.9514	685.3512
59.9372	724.8200	59.9372	728.455
65.4056	767.7600	65.4056	762.9381
70.2306	804.3200	70.2306	797.4212
75.3236	841.7200	75.3236	836.2146
80.3094	877.1200	80.3094	870.6977
85.7778	914.7400	85.7778	905.1808
90.6028	942.3000	90.6028	935.3535
95.6958	968.1400	95.6958	965.5262
100.7889	990.3200	100.7889	993.5437

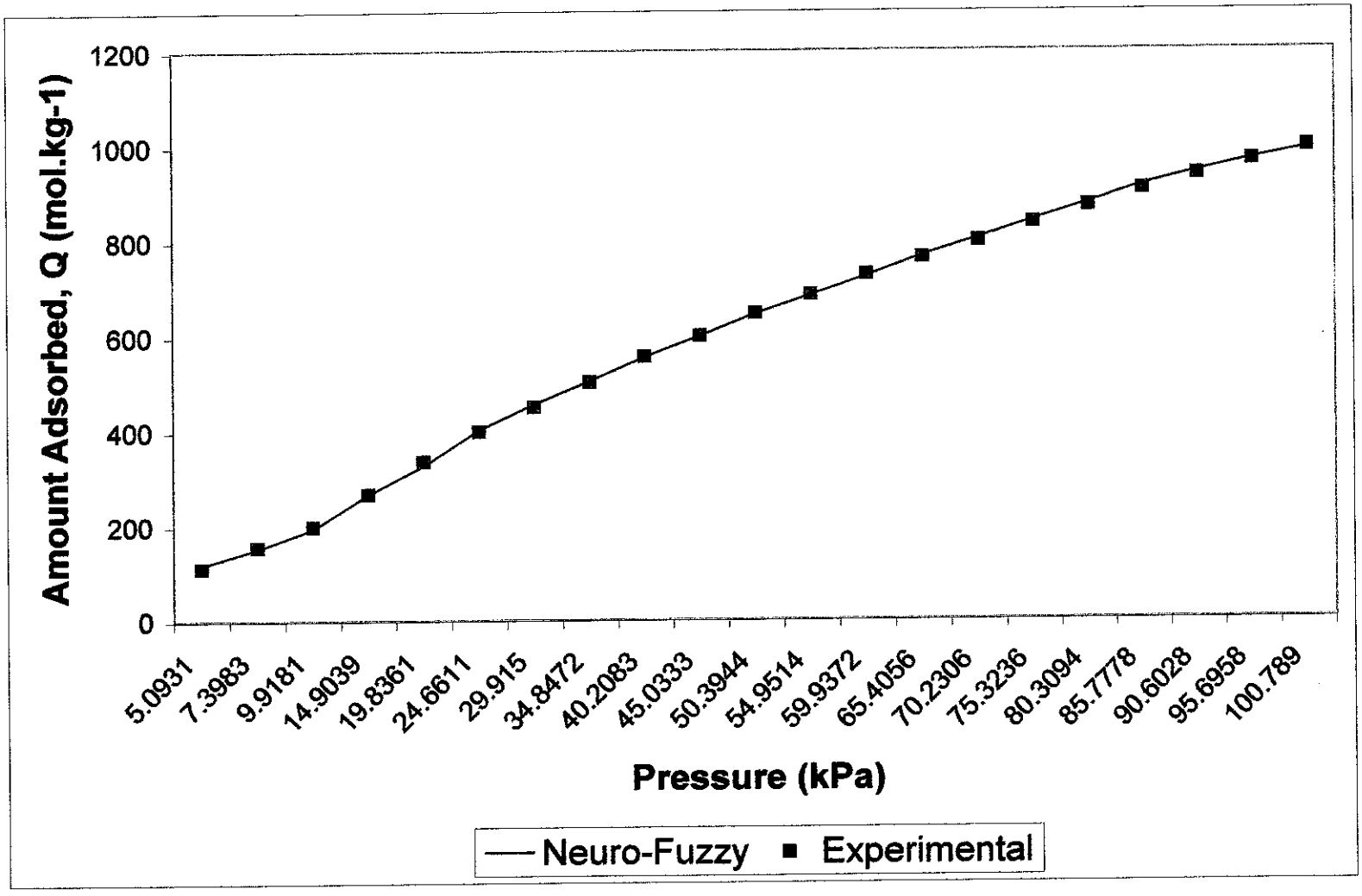

Figure 4.3: Adsorption Isotherm between Neuro-Fuzzy Prediction and Experimental Data at 273 K

Table 4.2: Isotherm data of Neuro-Fuzzy Logic and Experimental approaches at 303 K

Neuro-Fuzzy		Experimental	
Pressure (kPa)	Q ($mol.kg^{-1}$)	Pressure (kPa)	Q ($mol.kg^{-1}$)
5.0931	57.0800	5.0931	51.7246
7.3983	76.0600	7.3983	73.2765
9.9181	107.1600	9.9181	99.1388
14.9039	142.7400	14.9039	137.9323
19.8361	170.4200	19.8361	174.5706
24.6611	201.3200	24.6611	211.2088
29.915	246.2200	29.915	245.6919
34.8472	275.1600	34.8472	280.175
40.2083	318.0800	40.2083	310.3477
45.0333	346.3600	45.0333	340.5204
50.3944	370.4600	50.3944	370.6931
54.9514	391.200	54.9514	396.5554
59.9372	418.7800	59.9372	422.4177
65.4056	445.6800	65.4056	443.9696
70.2306	466.3400	70.2306	469.8319
75.3236	487.9400	75.3236	495.6942
80.3094	511.7800	80.3094	521.5565
85.7778	541.7200	85.7778	543.1085
90.6028	571.3600	90.6028	568.9708
95.6958	591.3200	95.6958	590.5227
100.7889	603.8800	100.7889	607.7642

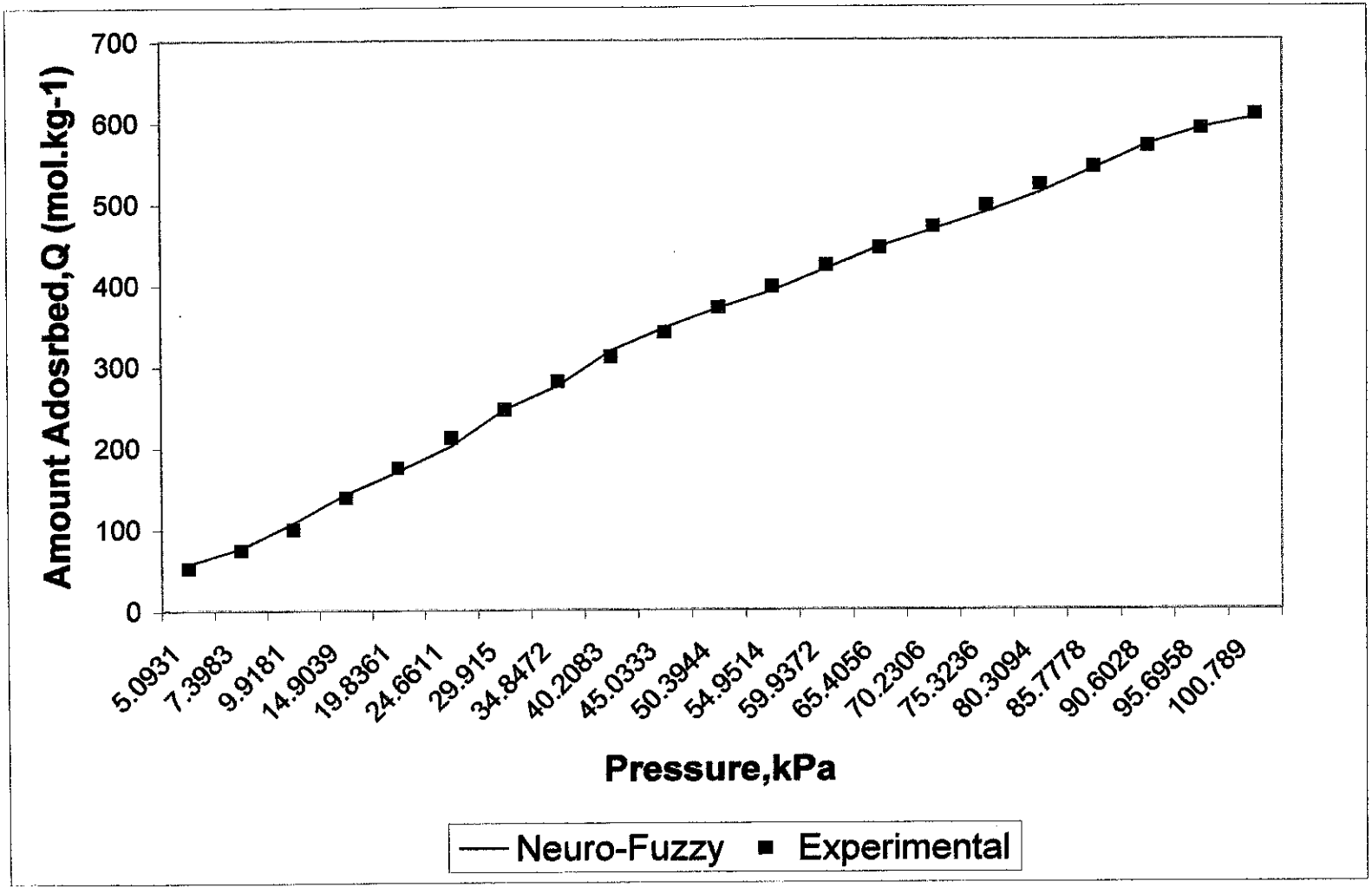

Figure 4.4: Adsorption Isotherm between Neuro-Fuzzy Prediction and Experimental Data at 303 K

Table 4.3: Isotherm data of Neuro-Fuzzy Logic and Experimental approaches at 323 K

Neuro-Fuzzy		Experimental	
Pressure (kPa)	Q ($mol.kg^{-1}$)	Pressure (kPa)	Q ($mol.kg^{-1}$)
5.0931	30.7800	5.0931	30.1727
7.3983	41.7400	7.3983	47.4142
9.9181	61.6400	9.9181	68.9662
14.9039	100.9600	14.9039	92.6733
19.8361	115.7800	19.8361	120.6908
24.6611	144.3000	24.6611	146.5531
29.915	169.7200	29.915	172.4154
34.8472	191.5400	34.8472	191.8121
40.2083	214.9000	40.2083	215.5192
45.0333	235.7600	45.0333	241.3815
50.3944	258.4200	50.3944	262.9335
54.9514	277.4800	54.9514	284.4854
59.9372	298.0600	59.9372	306.0373
65.4056	320.2200	65.4056	323.2788
70.2306	339.5400	70.2306	344.8308
75.3236	359.6800	75.3236	366.3827
80.3094	379.1200	80.3094	383.6242
85.7778	402.1200	85.7778	405.1762
90.6028	421.9200	90.6028	422.4177
95.6958	431.1400	95.6958	435.3488
100.7889	450.9400	100.7889	452.5904

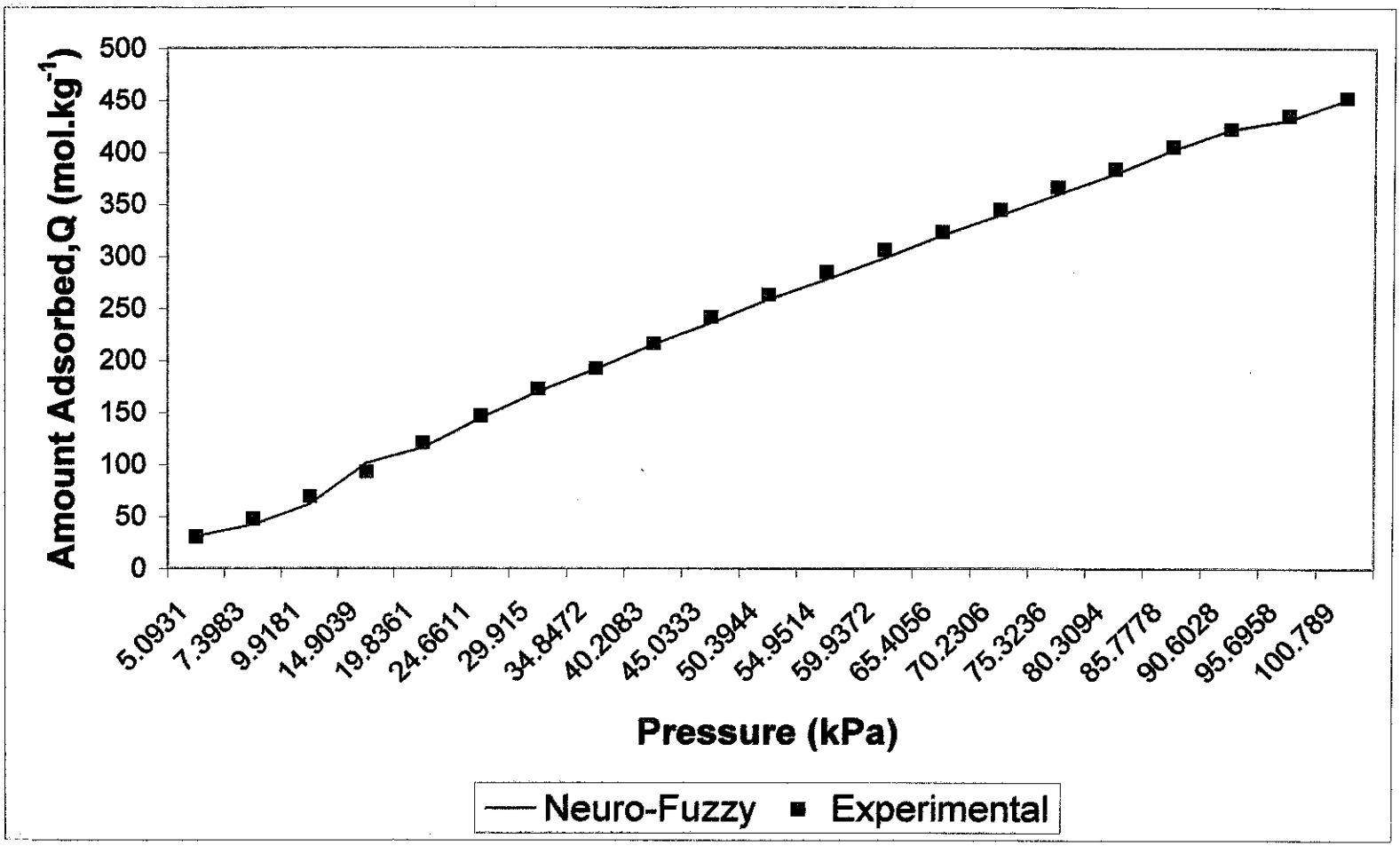

Figure 4.5: Adsorption Isotherm between Neuro-Fuzzy Prediction and Experimental Data at 323 K

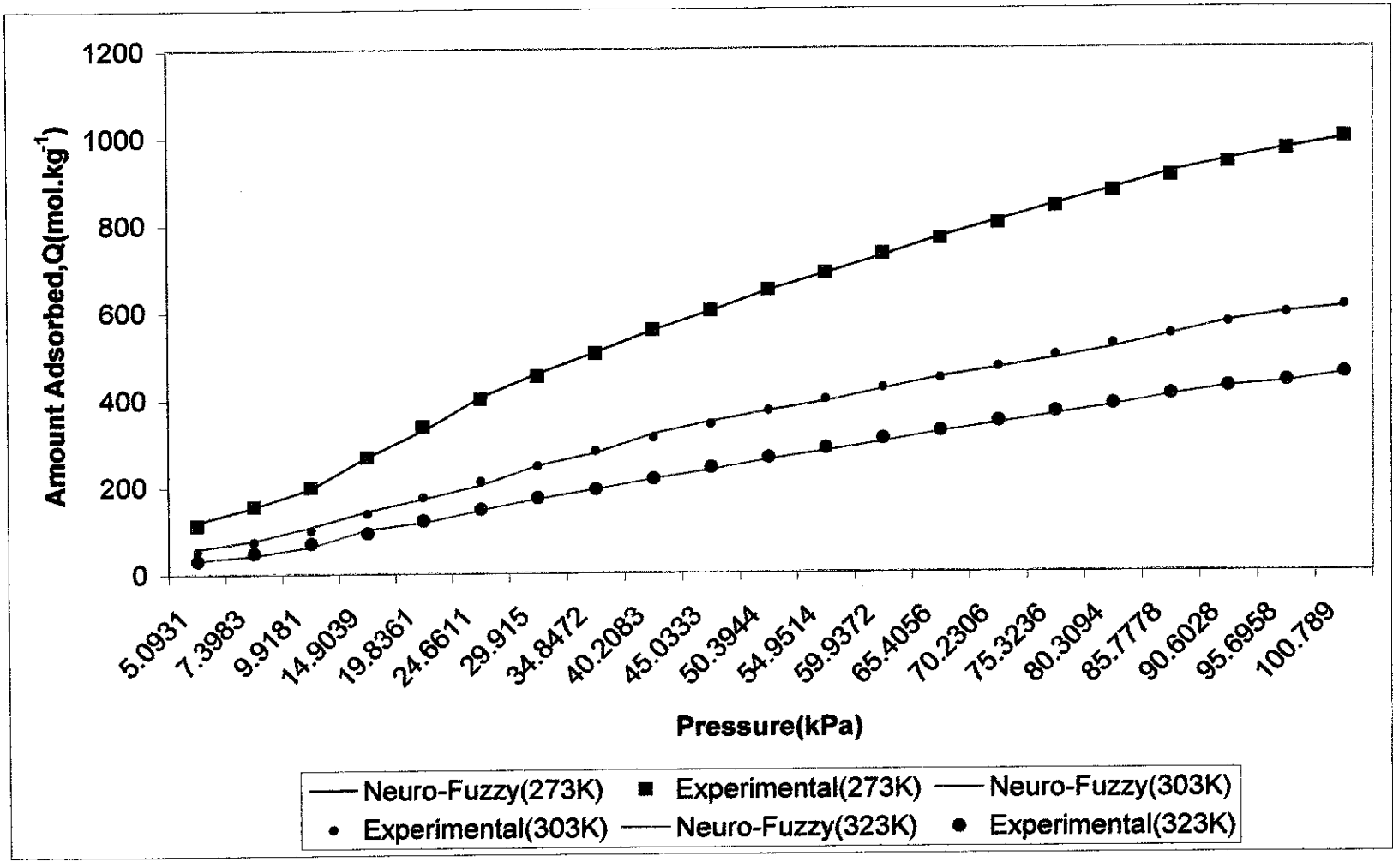

Figure 4.6: Adsorption Isotherm between Neuro-Fuzzy Prediction and Experimental Data

Results indicated in Figure 4.3, Figure 4.4 and Figure 4.5 were combined for better view of adsorption isotherm of methane gas onto activated coconut shell charcoal as per shown in Figure 4.6. It can be seen that the amount of methane adsorbed onto the activated coconut shell charcoal increases as the pressure increases. It is because increasing pressure indicates the increment of number of methane molecules to be adsorbed. Thus it shown the direct relationship between the amounts adsorbed respective to pressure. However, the amount of adsorbed decreases as the adsorption temperature increases. Therefore, it indicates the inversely proportional relationship between temperature and amount of adsorbate adsorbed. From Figure 4.6, it also shown that the Neuro-Fuzzy data (forecasted data) almost equal with the actual data which obtained experimentally. The review done on the pressure, Q and DoS was successfully developed Neuro-Fuzzy Logic system that was fit at the temperatures that had been chosen. It was justified more due to unseen Neuro-Fuzzy point(s) deviates far away from the experimental value and also the calculated average error that will be discussed in the next section later.

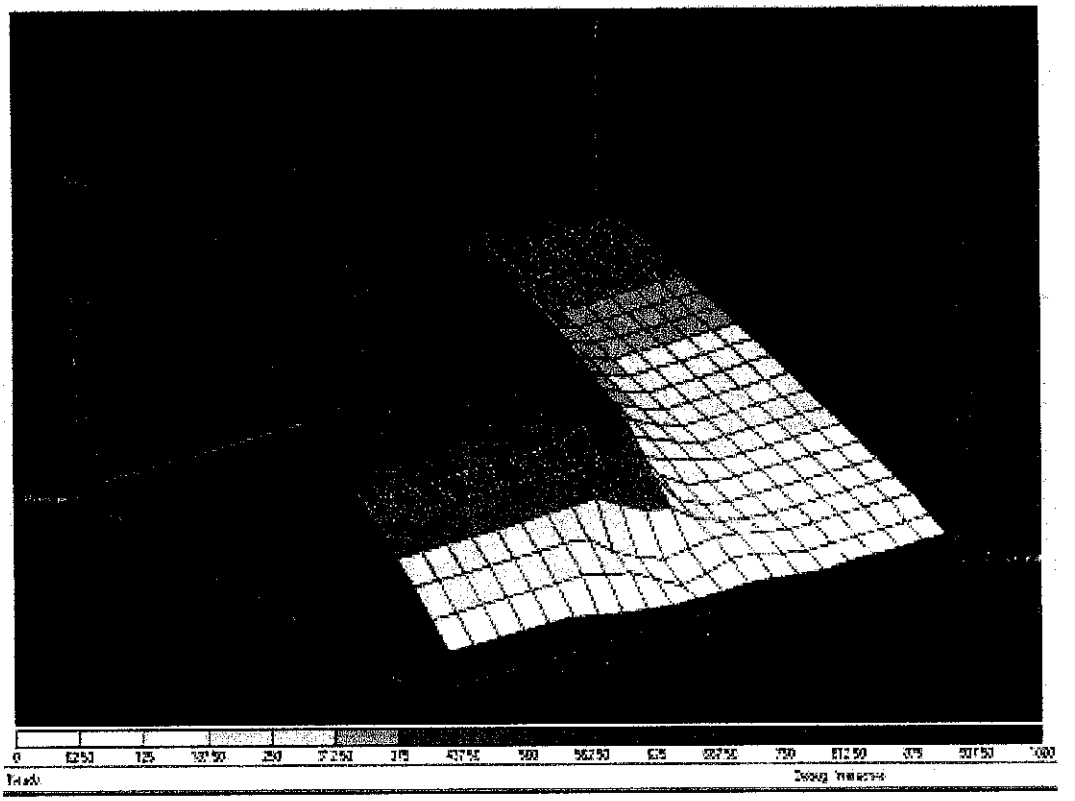

Figure 4.7: 3-D Plot of Predicted Isotherm Produced from Neuro-Fuzzy Module

Figure 4.7 shown the 3-D plot of predicted isotherm produced from Neuro-Fuzzy Module/system. The plot shows the similar representation as Figure 4.6 but in three-dimension perspective. The ability to rotate and see the isotherm plot from many angles gives credits to new isotherm representation over the conventional representation (Figure 4.6).

4.3 Error Analysis

This error analysis is done in order to ensure the accuracy and the reliability of the model developed. The error of each isotherm points is simply calculated by using formula per stated below:

Error (%) = |(Experimental-Neuro-Fuzzy)/(Experimental)|x 100%

Below is a sample of error calculation for the isotherm points for adsorption of methane onto activated coconut char.

Table 4.4: Error calculated for 273 K data points

Pressure	Neuro-Fuzzy (Q)	Experimental (Q)	Error (%)	Absolute Error (%)
5.0931	118.7000	111.2079	-6.737	6.737
7.3983	152.9200	155.1738	1.452	1.452
9.9181	194.8600	198.2777	1.724	1.724
14.9039	267.6600	267.2438	-0.156	0.156
19.8361	327.4800	336.21	2.597	2.597
24.6611	403.0600	398.7106	-1.091	1.091
29.915	456.6200	450.4352	-1.373	1.373
34.8472	504.8200	502.1598	-0.530	0.530
40.2083	555.2400	556.0396	0.144	0.144
45.0333	598.9400	599.1435	0.034	0.034
50.3944	645.7800	646.5577	0.120	0.120
54.9514	684.2000	685.3512	0.168	0.168
59.9372	724.8200	728.455	0.499	0.499
65.4056	767.7600	762.9381	-0.632	0.632
70.2306	804.3200	797.4212	-0.865	0.865
75.3236	841.7200	836.2146	-0.658	0.658

80.3094	877.1200	870.6977	-0.738	0.738
85.7778	914.7400	905.1808	-1.056	1.056
90.6028	942.3000	935.3535	-0.743	0.743
95.6958	968.1400	965.5262	-0.271	0.271
100.7889	990.3200	993.5437	0.324	0.324

Average error for each temperature is calculated by using equation per stated below:

Average Error (%) =Σ Error / no. of points

Table 4.5: Percentage Average Error Between Experimental Data and Neuro-Fuzzy

Average Error(%)		
273 K	**303 K**	**323 K**
1.043	2.252	2.759

For this research, 5 % maximum of the average error calculated was chosen due to the similarity shown between Neuro-Fuzzy data (forecasted data) and experimental data (actual data). If after completed one training system of a sample data, the average error will be calculated per shown above. If the average error obtained is greater than 5%, reviewing of some parameters (either input or output) will be done until the average error gained is less than 5%.

CHAPTER 5

CONCLUSION AND RECOMMENDATIONS

5.1 Conclusion

The prediction of adsorption isotherm for methane gas onto activated coconut shell charcoal was successfully implemented by using Neuro-Fuzzy module system. The software used was Fuzzytech 5.52 Professional Demo software. The reference data used was taken from research done by E.Loren Fuller,Jr entitled Characterization of Porous Carbon Fibre and Related Materials. From the simulation done, the objective of this project has been achieved due to average error between experimental/reference data and Neuro-Fuzzy Logic data gained is lees than 5%. The isotherm plotted between Neuro-Fuzzy Logic data and experimental data shown almost similar to each other. It can be concluded that the equilibrium model of adsorption isotherm of methane gas onto activated coconut shell charcoal was fitted with the experimental data at different temperature, which in this case were 273 K, 303 K and 323 K. Therefore, from the model developed, it is easier to predict the adsorption isotherm at other temperature but limited within the temperature range (273 K- 323 K) and pressure up to 760 Torr.

For Neuro-Fuzzy systems itself, it can be summarized that the combinations of both fuzzy logic and neural network constitutes a powerful means for designing intelligent systems which in this case is adsorption isotherm. Besides that, the domain knowledge can be put into a Neuro-fuzzy system by human experts in the form of linguistic variables and fuzzy rules. For this system, when a representative set of examples is available, a Neuro-fuzzy system can automatically transform it into a robust set of fuzzy IF-THEN rules and thereby reduce our independence on expert knowledge when building the intelligent systems.

5.2 Recommendations

For better use of the model developed, it is recommended to do further study on getting optimum temperature, pressure and adsorption capacity for ANG Technology. Other than that, the model can be analyzed by using the types of activated for instance activated carbon fiber, activated carbon monolith and others. Besides that, instead of using this Neuro-Fuzzy module, the adsorption isotherm of methane onto various type of activated carbon can be obtained experimentally by using AUTOSORB-1C equipment. Thus, it can be compared equally basis with the experimental data used for generating Neuro-Fuzzy model.

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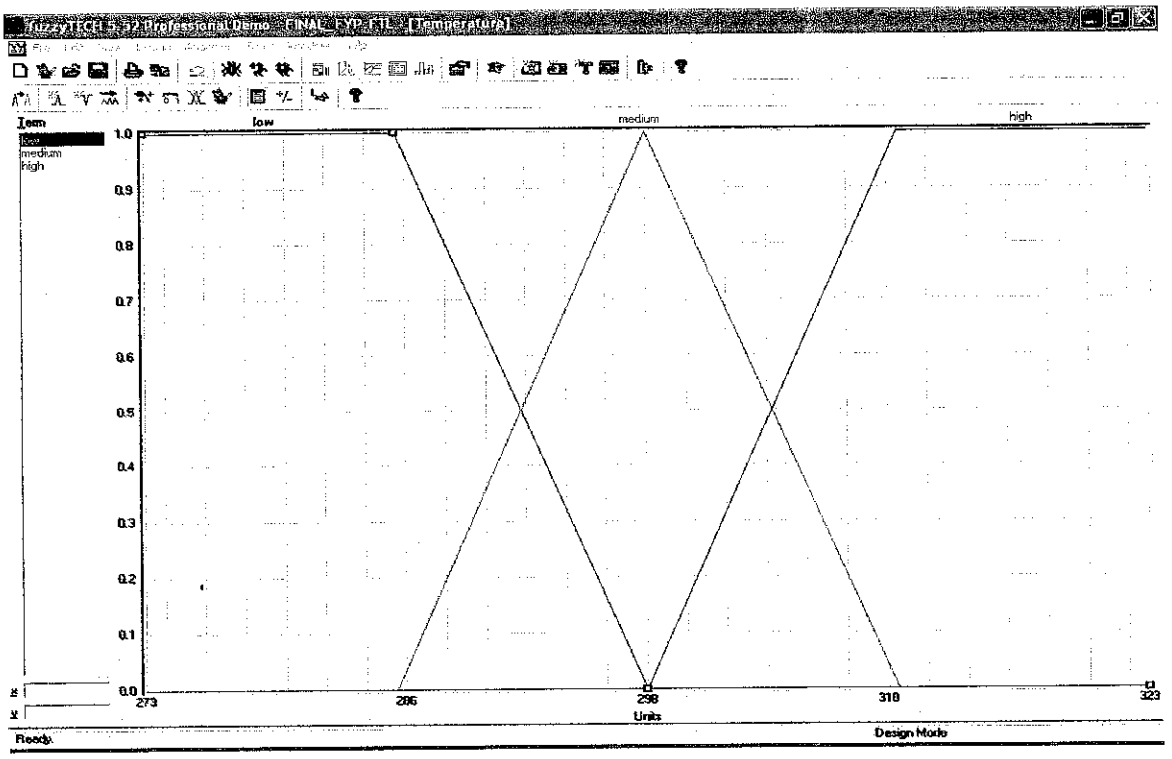
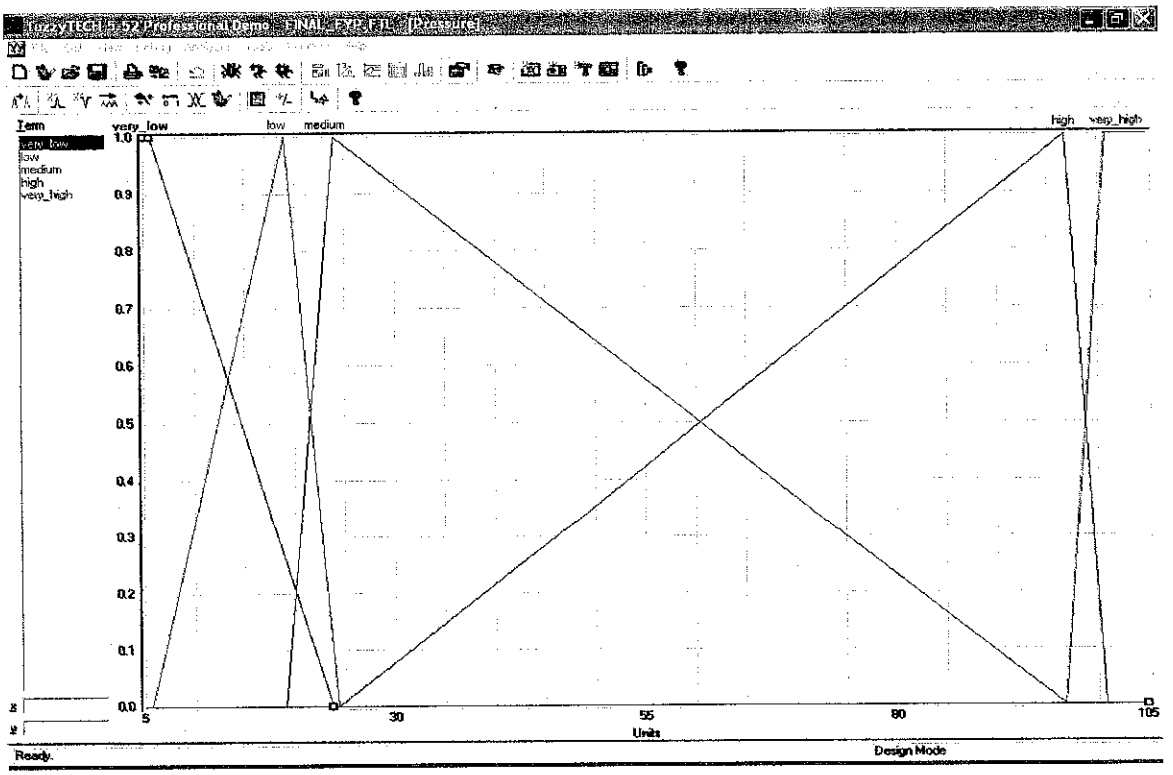
APPENDICES

No	Detail/Week	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15
1	Selection of Project Topic	■														
	-Topic assigned to student															
	-First meeting with supervisor															
2	Preliminary Research Work		■	■												
	-Introduction to project scope and objectives															
	-Literature review															
	-Project Planning															
3	Submission of Preliminary Report			●6/8												
4	Project Work				■	■	■	■								
	-Literature Review															
	-Practical work (simulation)															
5	Submission of Progress Report							●3/9								
6	Project work continue								■	■	■	■				
7	Submission of Dissertation Final Draft														●27/10	
8	Oral Presentation															
9	Submission of Project Dissertation															●3/11

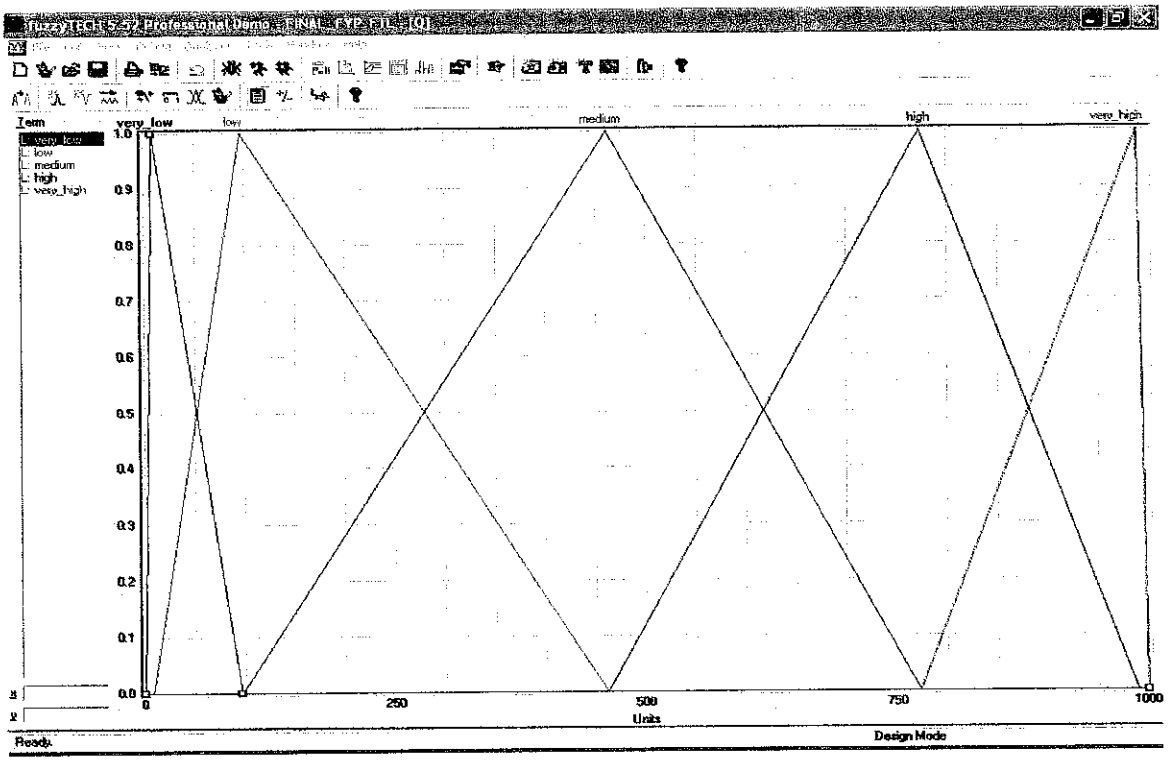
Appendix 1: Gantt Chart of Planning



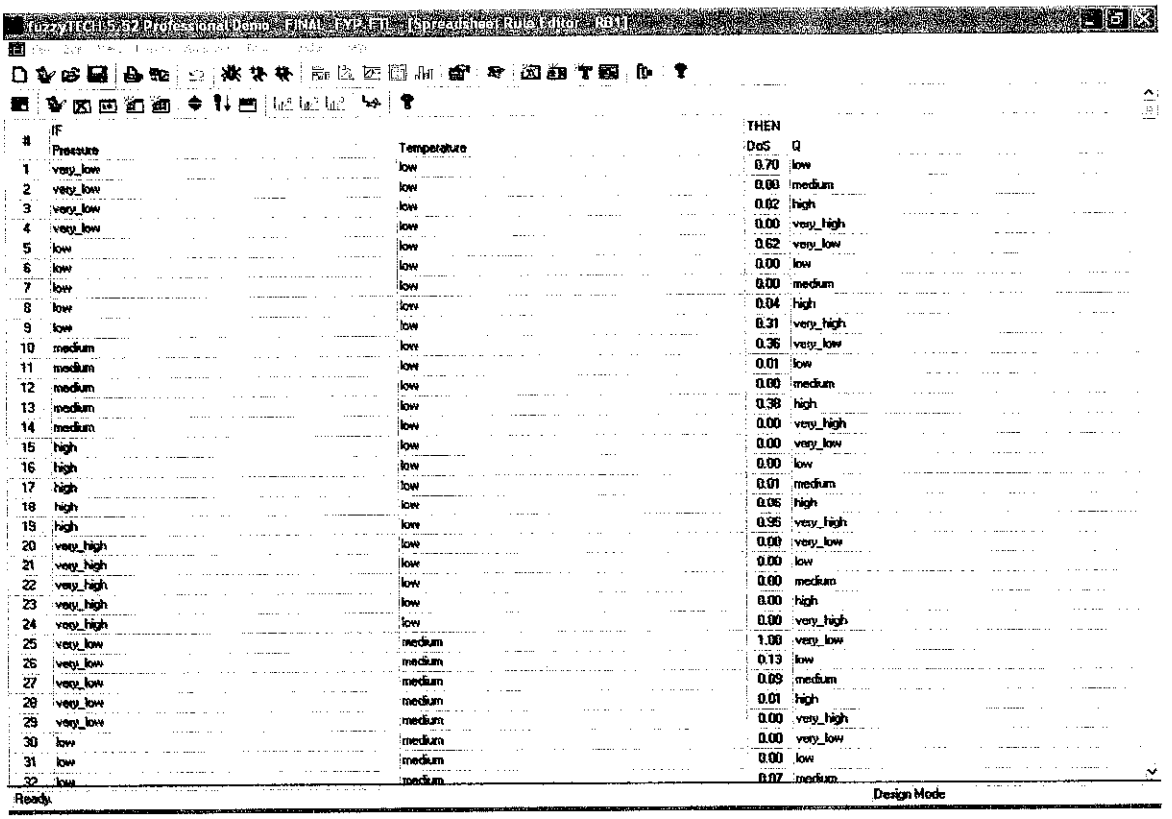
Appendix 2: Temperature (Input) Editor



Appendix 3: Pressure (Input) Editor



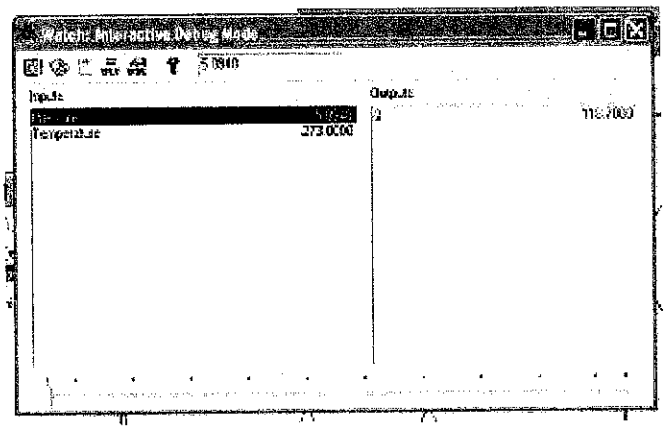
Appendix 4: Amount Adsorbed, Q (Output) Editor



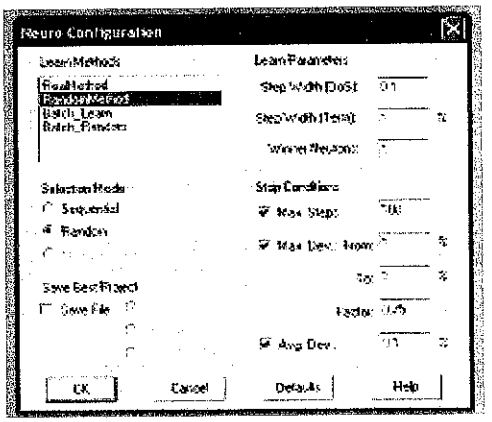
#	IF Pressure	Temperature	THEN DoS	Q
1	very_low	low	0.70	low
2	very_low	low	0.00	medium
3	very_low	low	0.02	high
4	very_low	low	0.00	very_high
5	low	low	0.62	very_low
6	low	low	0.00	low
7	low	low	0.00	medium
8	low	low	0.04	high
9	low	low	0.31	very_high
10	medium	low	0.36	very_low
11	medium	low	0.01	low
12	medium	low	0.00	medium
13	medium	low	0.38	high
14	medium	low	0.00	very_high
15	high	low	0.00	very_low
16	high	low	0.00	low
17	high	low	0.01	medium
18	high	low	0.06	high
19	high	low	0.95	very_high
20	very_high	low	0.00	very_low
21	very_high	low	0.00	low
22	very_high	low	0.00	medium
23	very_high	low	0.00	high
24	very_high	low	0.00	very_high
25	very_low	medium	1.00	very_low
26	very_low	medium	0.13	low
27	very_low	medium	0.09	medium
28	very_low	medium	0.01	high
29	very_low	medium	0.00	very_high
30	low	medium	0.00	very_low
31	low	medium	0.00	low
32	low	medium	0.07	medium

Ready
Design Mode

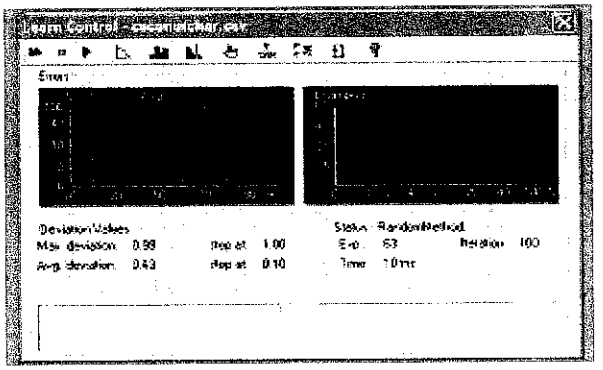
Appendix 5: Spreadsheet Rule Editor



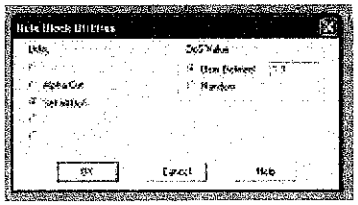
Appendix 6: Interactive Debug Mode



Appendix 7: Neuro Configuration



Appendix 8: Neuro Learning Control



Appendix 9: Rule Block Utility