The Study of Direct Methanol Fuel Cell Parameters by Taguchi Method

by

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(Chemical Engineering)

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CERTIFICATION OF APPROVAL

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Approved by,

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September 2012

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.

(ADIBAH HANI BINTI AZIT)

ABSTRACT

Technologically advanced human societies require specialized tools and equipment to enable their diverse and mobile activities. Portable electronic devices like laptop, PDA, hand phone, etc. are now an essential tool for many people in their daily lives. The rechargeable batteries used to power the portable electronic devices could be improved upon with regards to its power density, and there is a crucial need for an efficient, renewable and more environmentally friendly power sources. Many researchers have shown that the direct methanol fuel cell (DMFC) is an appropriate alternative to rechargeable battery technology, although many factors must be resolved before it can be commercialized. This paper gives an overview on the possibilities for using the DMFC as portable electronic devices power source along with its optimum operating parameter which include the temperature and methanol concentration that will give significant impact towards efficiency of the DMFC itself. A 5cmx5cm single cell of direct methanol fuel cell (DMFC) which is manufactured by H-Tec Education, a German company is used. The cell is using the standard Nafion membrane. In this study, the Taguchi method using Qualitek-4 software is used to find the optimal process parameters for DMFC. Through this study, not only the optimal process parameters for DMFC can be obtained, but also the main process parameters that affect the whole performance of the DMFC itself. Experimental results are provided to confirm the effectiveness of this approach. It is expected that, by integrating all optimum operating parameters, the tested DMFC's efficiency to be increased to 70-80% compared to current studies which gives only up to 30-40% efficiency. These will approximately producing around 0.7 to 0.9 V for each single cell of DMFC.

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CHAPTER 1 : INTRODUCTION

1.1 Background of Study

Portable electronic devices with the increasing functionality call for high-energy density power sources. Current batteries, even the most advanced Li-ion batteries, are unlikely to keep pace with these growing power and energy demands. The rechargeable battery is the major source of power for most lithium-based, e.g., lithium or lithium-polymer. There is a disadvantage in using a rechargeable battery as a power source as the battery needs an external electrical power source to charge, and this is a limitation to the mobility of the device because it can only be used with an existing electrical source and has limited battery capacity.

In remote areas where there is no electric power grid, running a device on portable batteries is problematic. An important issue regarding electrical power plants is that many of them use fossil fuel to generate electricity. In 2000, about 6.2 billion tons of carbon was emitted into the atmosphere as CO_2, of which approximately 40% was emitted during the production of electricity. This also leads to issues relating to non-renewable energy and environmental problems. In addition, the major focuses of human civilization in the 21st century are on finding alternative sources of energy, the environment and information technology [1] as people worldwide try to build a relationship between living a modern life and being in harmony with the nature.

Alternative sources of energy that are efficient, renewable and environmentally friendly remain one of the biggest challenges for the world today, and they are still largely in the research and development stages. The prospect of fuel cells seems to potentially be the answer to that challenge. It was discovered in 1839, when William Grove invented the fuel cell system. The fuel cell is an electrochemical device that converts chemical energy into electrical energy [2].

Fuel cells are a unique energy source to the industry and population. Like a combustion engine, as long as a fuel supply is provided, fuel cells can provide an indefinite amount of energy. And like batteries, fuel cells rely on electrochemistry to produce energy, contain no external moving parts, and work silently. In addition, fuel cells produce nearly no particulate emissions and harmful products that may affect the environment [3].

Several types of fuel cells are currently being developed in the industry, including Phosphoric Acid Fuel Cells (PAFC), Polymer Electrolyte Membrane Fuel Cells (PEMFC), Alkaline Fuel Cells (AFC), Molten Carbonate Fuel Cells (MCFC), Solid-Oxide Fuel Cells (MOFC), and, the focus of this report, Direct Methanol Fuel Cells (DMFC). DMFCs have several advantages over the other types of fuel cells. One advantage is that they can work at temperatures below 100ºC, a suitable working temperature, as opposed to PAFCs operating temperature of 200ºC or MCFCs operating temperature of 650ºC.

Another advantage is the use of methanol in the fuel cell; because methanol is a liquid at room temperature, it is easy to store and refill as a fuel source as opposed to hydrogen. In addition, Lu et al. [4] discovered that methanol has a high energy density compared to hydrogen, which can be a promising asset as a power source for portable devices and micro power sources.

1.1.1 The DMFC

Direct-methanol fuel cells or DMFCs are a subcategory of proton-exchange fuel cells in which methanol is used as the fuel. DMFCs consists of several parts: an anode and cathode bipolar plates, two gaskets, an anode and cathode gas diffusion layer (GDL), an anode and cathode catalyst layer, and a Proton Exchange Membrane (PEM).

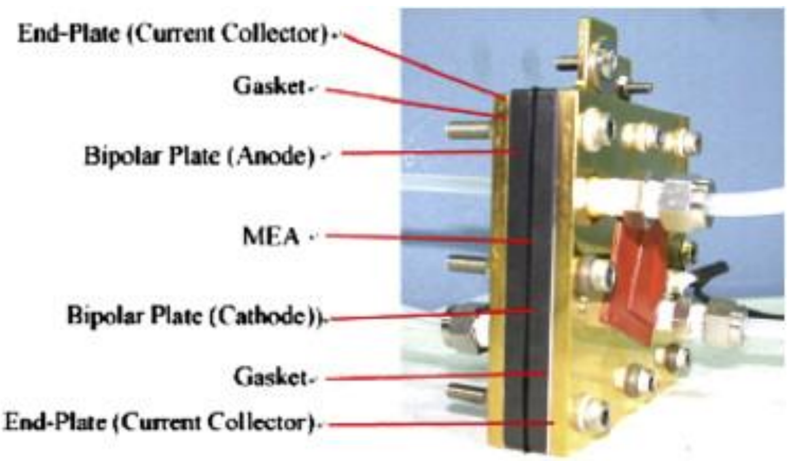

Figure 1. 1 : Basic Components of Direct Methanol Fuel Cell

The bipolar plates on the outside of the cell, usually constructed from metal or graphite, allow methanol to flow on the anode side and oxygen on the cathode side through a unique flow pattern. The methanol flowing through the anode bipolar plate makes contact with the anode GDL and disperses to the anode catalyst layer where it reacts, producing carbon dioxide, protons, and electrons, while the oxygen being supplied to the cathode GDL and then to the cathode catalyst layer, reacts with protons and electrons arriving from the anode to form water. The gaskets, typically made from Teflon, must be about the same width of the catalyst layer and GDL combined in order to prevent the methanol and oxygen from leaking out of the fuel cell. The PEM, the catalyst layer, and the GDLs are prepared together, forming a Membrane Electrode Assembly (MEA).

1.1.2 The Reaction

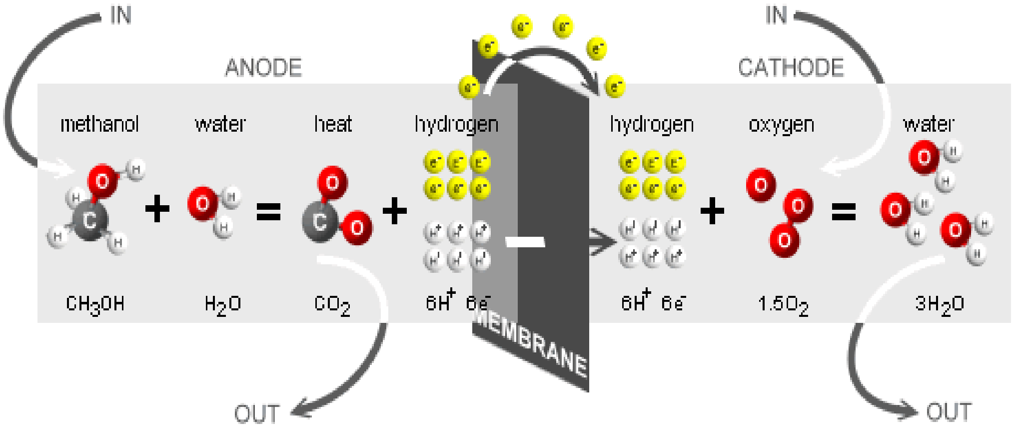

Figure 1. 2 : Mechanism of Direct Methanol Fuel Cell

The DMFC relies upon the oxidation of methanol on a catalyst layer to form carbon dioxide. Water is consumed at the anode and is produced at the cathode. Protons (H^+) are transported across the proton exchange membrane - often made from Nafion - to the cathode where they react with oxygen to produce water. Electrons are transported through an external circuit from anode to cathode, providing power to connected devices.

The half-reactions are:

Table 1. 1 : Half Reaction for DMFC

	Equation
Anode	$CH_3OH + H_2O \rightarrow 6\ H^+ + 6\ e^- + CO_2$ oxidation
Cathode	$\frac{3}{2}O_2 + 6\ H^+ + 6\ e^- \rightarrow 3\ H_2O$ reduction
Overall reaction	$CH_3OH + \frac{3}{2}O_2 \rightarrow 2\ H_2O + CO_2$ redox reaction

Methanol and water are adsorbed on a catalyst usually made of platinum and ruthenium particles, and lose protons until carbon dioxide is formed. As water is consumed at the anode in the reaction, pure methanol cannot be used without provision of water via either passive transport such as back diffusion (osmosis), or active transport such as pumping. The need for water limits the energy density of the fuel.

Currently, platinum is used as a catalyst for both half-reactions. This contributes to the loss of cell voltage potential, as any methanol that is present in the cathode chamber will oxidize. If another catalyst could be found for the reduction of oxygen, the problem of methanol crossover would likely be significantly lessened. Furthermore, platinum is very expensive and contributes to the high cost per kilowatt of these cells. During the methanol oxidation reaction carbon monoxide (CO) is formed, which strongly adsorbs onto the platinum catalyst, reducing the surface area and thus the performance of the cell. The addition of another component, such as ruthenium or gold, to the catalyst tends to ameliorate this problem because, according to the most well-established theory in the field, these catalysts oxidize water to yield OH radicals: $H_2O \rightarrow OH\bullet + H^+ + e^-$. The OH species from the oxidized water molecule oxidizes CO to produce CO_2 which can then be released as a gas: $CO + OH\bullet \rightarrow CO_2 + H^+ + e^-$.

Using these OH groups in the half reactions, they are also expressed as:

Table 1. 2 : Half Reaction of DMFC when using OH Groups

	Equation
Anode	$CH_3OH + 6\ OH^- \rightarrow 5\ H_2O + 6\ e^- + CO_2$ oxidation
Cathode	$\frac{3}{2}O_2 + 3\ H_2O + 6\ e^- \rightarrow 6\ OH^-$ reduction
Overall reaction	$CH_3OH + \frac{3}{2}O_2 \rightarrow 2\ H_2O + CO_2$ redox reaction

1.1.3 Methanol crossover

Methanol crossover happens when methanol molecules diffuse through the membrane and are directly oxidized by oxygen on the positive electrode [5]. Methanol crossover from the anode to the cathode is a very serious problem that severely reduces cell voltage, current density and fuel utilization, and hence cell performance [7]. Of the total chemical energy contained in methanol, less than 30% can be exploited as electricity, with the rest being converted into heat as the result of methanol crossover and the irreversibility of electrode reactions especially in the anode [6], [7] and [8]. Although methanol has a high energy density (about 1.8 kWh kg^{-1} or 1.7 kWh L^{-1}), it must be diluted in order to reduce methanol crossover.

A consequence of dilution is that the cell stack dimensions must be proportionally increased. With increasing dimensions, it is important to have an appropriate estimate of the relationship between dimensions and power requirements, as the cell will be used in portable electronic devices.

The second effect of methanol cross-over is on the kinetics of the electro-reduction of oxygen. To date, there is no clear understanding of the mechanism of this effect, which slows down the rate of reaction. However, the rate of reactions not only can be accelerated by adding more platinum–ruthenium catalyst [8], [9] give negative effect on the cost, but it can also be reduced by the selection of proper membranes and oxygen tolerant cathodes.

1.2 Problem Statement

1.2.1 Problem Identification

The rechargeable batteries used to power the portable electronic devices could be improved upon with regards to power density and there is crucial need for efficient, renewable and more environmentally friendly power sources. In addition, the disadvantages of rechargeable batteries have led many researchers to seek alternative power sources to replace battery technology. On the other hand, researches have shown that direct methanol fuel cell (DMFC) is an appropriate alternative to rechargeable battery technology.

Thus, research in this project on the effect of DMFC‘s efficiency at elevated temperature and various concentrate ion for portable electronic devices application are crucial.

1.2.2 Significant of the Project

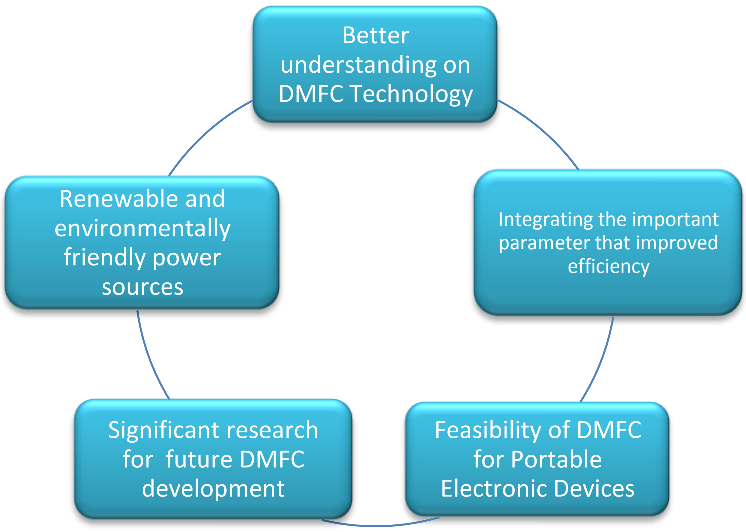

Figure 1. 3 : Significance of the project

This project is done basically to understand in depth on DMFC Technology as there is still lacks of current research and development on DMFC Technology that has been done generally in Malaysia and specifically in UTP. Besides that, this project is also relevant as it will give significant information for next researchers to continue the development of DMFC as well as can help the manufacturer to get clear details on the optimum operating parameter for DMFC that will be used later in portable electronic devices. Apart from that, with the successful research on this project, it can help other researches to foresee the feasibility of the DMFC to replace current rechargeable batteries and indirectly able to make the DMFC as another renewable and environmental friendly type of power source.

1.3 Objective

The main objective of this research is to analyze the performance of DMFC towards selected operating parameter which includes methanol concentration, temperature and air flow rate and to use Taguchi method in order to determine the optimum DMFC parameter for portable electronic devices application.

1.4 Scope of the Study

The project involved experimental work. A passive single cell DMFC which is developed by H-Tech Education is used in order to visualize the real effect of operating parameter towards DMFC's efficiency. Parameters involved during the experiment are methanol concentration, temperature and air flow rate. The result will be tabulated graphically and will be analyzed to predict its effect at different manipulated parameters.

1.4.1 The relevancy of the Project

The market for portable fuel cells increased rapidly at the beginning of the millennium, especially in 2001 and 2002, because a few companies, e.g., Ball Aerospace and Smart Fuel Cell, began producing portable fuel cells in greater volumes. The technology of choice for portable fuel cells is the polymer electrolyte membrane fuel cell (PEMFC), and a majority of units sold in 2005 were PEMFC units. The small portable electronic markets on the other hand are dominated equally by PEMFC and DMFC technologies.

Currently, DMFC has an edge due to the market activities of one or two large companies. The fastest growing market in small portable electronic devices is mobile phones. These are used not only for constant voice communication but also in various other communication modes, e.g., email, text and multi-media messaging, as an entertainment center with downloaded music, movies and games, as well as a lifestyle device that enables credit card transactions and airline ticketing. Forces that drive the increased capabilities of mobile phones and that ultimately lead to the need for the longest "talk" and/or "usage" time are competition among device manufacturers, mobile operators' desire to increase Average Revenue per User (ARPU) and convergence of content on mobile platforms.

The direct methanol fuel cell (DMFC) portable power market for notebook computers, mobile phones and other portable electronic devices is expected to grow significantly. Leading electronics manufacturers and innovative start-up companies are introducing products. Micro fuel cells are anticipated to work in combination with thin film batteries, creating hybrid power systems. Hybrid markets are expected to achieve market growth as the batteries are less expensive than the micro fuel cells. The micro fuel cells are useful for charging thin film batteries.

The main problem of these emerging economies is the lack of readily available electrical power. The answer to this problem as well as to the need for longer talk or usage times is a power pack with a direct methanol micro fuel cell (DMFC).

1.4.2 Feasibility of the project within the scope and time frame

The project is divided into planning and experimenting stages. Planning stage is more on finding information through journal, articles and gets the idea on how to carry out the experiment. Parameters to be tested during the experiment need to be identified during these stages.

Experiment stage involves totally experimental work. Results of the experiment will be tabulated graphically and expected data to be collected such as current density of each investigating parameter is determined. The data obtained will further analyze and discuss.

CHAPTER 2 : LITERATURE REVIEW

Interest in using fuel cells to power portable equipment for commercial applications is relatively recent [10, 11]. This is perhaps partly due to the success of Li based batteries in powering laptop computers, mobile phones and the like. This chapter will discuss in detail regarding DMFC's market potential and its performance based on selected parameters which include methanol concentration, operating temperature and the effect of the oxidant gas.

2.1 Direct Methanol Fuel Cell for Portable Electronic Devices

The requirement for higher energy density, higher specific energy or longer operational time between recharges was generally well served by the Li-ion battery and nickel-based batteries especially those based on metal hydrides. Safety and environmental factors were key considerations in addition to the high energy density of these batteries. There is now growing pressure on battery manufacturers to increase further the energy density for the next generation of portable electronic equipment, which will require much higher energy densities, if the equipment is to be conveniently portable. This is not just due to marketing and product differentiation; it is a technological requirement for high bandwidth applications, which demand much more power.

While many obstacles remain in DMFC commercialization, the use of DMFCs for powering laptop computers has recently passed the demonstration phase. For example, many companies in fields including fuel cell technology (Antig, DMFC Corp., DTI energy, Energy Visions Inc., INI Power, MTI Micro Fuel Cells, Neah Power, Plug power, and Smart Fuel Cell), communication and electricity (Fujitsu, IBM, LG, Motorola, NTT, Sanyo, Samsung, Sony and Toshiba) have announced various DMFC prototypes for laptop computer power supply. In addition, these companies have also announced commercialization plans in the near future. The prototypes introduced by many companies worldwide are summarized below and their features are listed in table below:

Table 2. 1 : DMFC prototypes and their features for powering laptop computers introduced by many companies worldwide

Companies	Announcing date (month, year)	Power output (W)	Specification (W: weight) (V: volume)	Concentration of fuel solution (wt.% of MeOH solution)	Impressive technologies
Toshiba	3, 2003	12 (average)	W: 900 g (without fuel solution)	3–6	Developing a system for fuel dilution using produced water
		20 (max)	V: 825 ml (275 × 75 × 40 mm)		
NEC	6, 2003	14 (ave)	W: 893 g (including 298 g of fuel solution)	10	Fuel cell's size reduction due to higher power density
		24 (max)	V: 2916 ml (270 × 270 × 40 mm)		
Fujitsu	1, 2004	15	n.g.	30	Their new membrane help lead to smaller and more efficient fuel cells
SAIT (Samsung)	6, 2004	20	n.g.	n.g.	Applying nanomaterials technology
Antig	3, 2005	10	W: 435 g	10–15	DMFC module fit into a standard laptop optical drive bay
			V: 730 ml (190 × 128 × 30 mm)		
Sanyo Electric and IBM	5, 2005	12 (DMFC only)	W: 2.2 kg	n.g.	Docking bay type and hybrid with Li-polymer battery
			V: 1218–4111 (270 × 282 × 16 to 54 mm).		
		72 (combined with Li-polymer battery)			
LG Chem.	9, 2005	25	W: less than 1 kg	n.g.	Lifetime of more than 4000 h
			V: less than 1 l in the core volume		
Panasonic	1, 2006	13 (DMFC only)	W: 450 g (without fuel)	n.g.	Hybrid with Li-ion battery
		20 (combined with Li-ion battery)	V: 400 ml		
Antig and their partner	9, 2006	16 W (80 Wh)	W: 800 g (without fuel)	n.g.	Power supply for a wide range of portable applications
			V: 1527 ml (218 × 68 × 103		
Samsung Electronics	12, 2006	20 (max)		n.g.	Docking station type and high power output

n.g.: not given.

2.2 Effect of Temperature

Temperature has a large influence on the electro kinetics of the reaction; with an increase in temperature, the ohmic resistance and activation resistance decreases [12]. In a standard DMFC, the operating temperature is usually between 50ºC and 90ºC, whereas a DMFC in completely passive conditions operates at room temperature. Figure 2.1 shows a correlation with increasing temperature and the effect on performance; as the temperature increases, overall performance of the DMFC increases due to an increase in the electrochemical kinetics [13]. While an increase in temperature usually improves performance, there are situations where a temperature increase is detrimental, depending on membrane thickness and molarity.

Field's research shows that a temperature increase to a DMFC with 5M methanol decreases in performance at higher current densities. The reasoning behind the loss in performance is an increase in methanol crossover due to the weakening of the PEM. Chen mentions that at higher temperatures, the rate of methanol diffusion across the PEM may be higher than the catalytic efficiency, causing a decrease in performance [14].

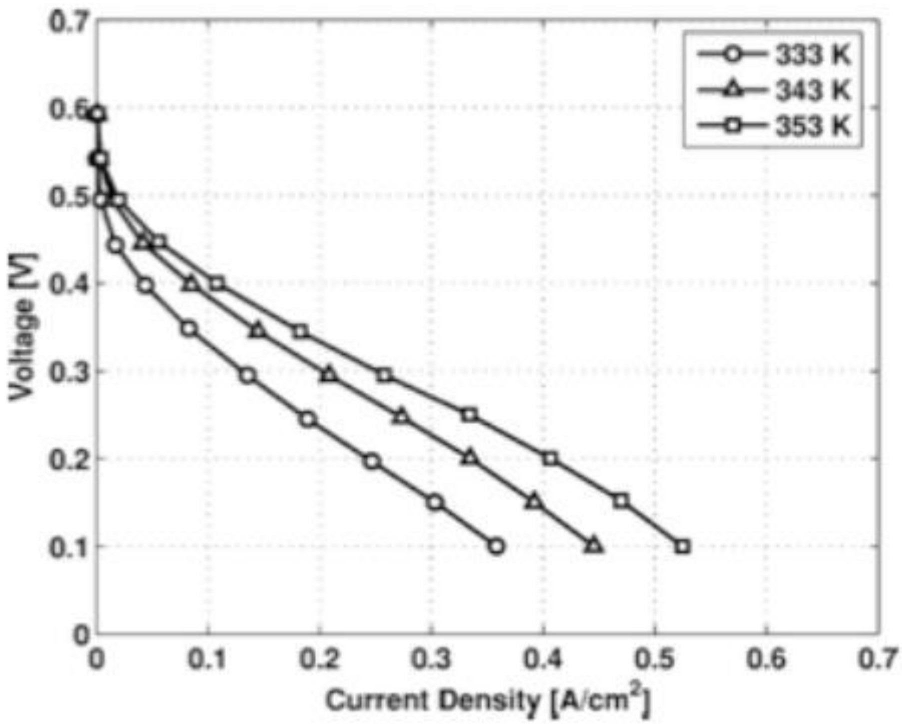

Figure 2. 1 : Polarization Curve with Varying Temperature

2.3 Effect of Concentration

One of the largest issues in DMFCs is methanol crossover. Methanol crossover occur when unreacted methanol on the anode is carried over to the cathode, resulting in a short circuiting current and hence causing a decrease in the overall fuel cell voltage as well as fuel loss. While standard DMFCs obtain a high power density at lower methanol molarities (1M or 2M), passive DMFCs can reach high power densities at higher molarities. Figure 2.2 shows the polarization curves of a passive DMFC at different methanol concentrations. At low current densities, lower concentrations give a higher voltage and OCP. However, Figure 2.2 also indicates that the maximum power density is attainable with 4M methanol, decreasing onward.

The reasoning for this phenomenon is due to the passive fuel cell’s reliance on diffusion of methanol, improving its mass transfer to the anode catalyst layer. A higher methanol concentration is also directly correlated to the operating temperature of a passive DMFC; a higher molarity leads to a higher permeation rate through the MEA, allowing more methanol to react with oxygen. Because the reaction on the cathode side is exothermic, the increase in reacting methanol will cause the operating temperature of the passive DMFC to increase.

The increase in temperature, which speeds up the kinetics in the reacting methanol and oxygen, decreases the internal resistance, and therefore improves performance, in a similar fashion to standard DMFCs [15]. It is important to note that there is no clear indication of the best methanol molarity due to the several variables that can affect the performance of a passive DMFC, including thickness, operating temperature and catalyst composition. Bae et al., determined that the optimal power density was obtained at 5M.

Arico et al. [16] found that a 1 M concentration of methanol is the best for an active system, providing a balance between a good supply of reactant and power gain, while Dohle et al. [17] found 2 M was best in their active system, illustrating that the optimum concentration is very much dependent on channel design. Ge et al. [18] discovered a concentration between 1 and 2 M was best for their active system DMFC, with a concentration below 1 M resulting in very low power, while concentrations above 2 M causing an increase in methanol crossover and rapidly decreasing performance.

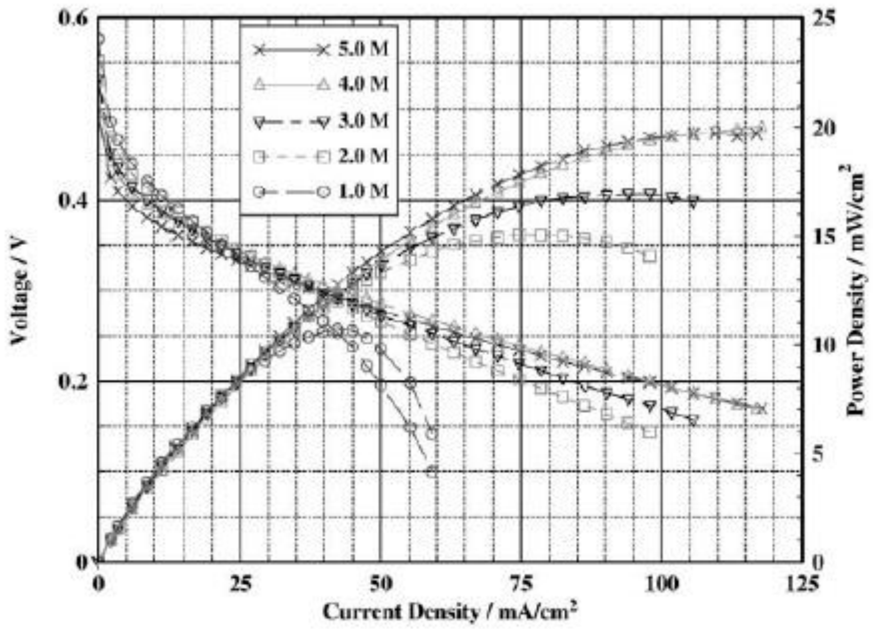

Figure 2. 2 : Methanol Molarity Comparison

2.4 Taguchi Method

The Taguchi method is a well-known technique that provides a systematic and efficient methodology for process optimization. It has been widely used for product design and process optimization worldwide. This is due to the advantages of the design of experiment using Taguchi's technique, which includes simplification of experimental plan and feasibility of study of interaction between different parameters. Lesser number of experiments is required in this method. As a consequence, time as well as cost is reduced considerably. Taguchi proposes experimental plan in terms of orthogonal array that gives different combinations of parameters and their levels for each experiment. According to this technique, the entire parameter space is studied with minimal number of necessary experiments only [19]. Based on the average output value of the quality characteristic at each parameter level, main effect analysis is performed. Analysis of variance (ANOVA) is then used to determine which process parameter is statistically significant and the contribution of each process parameter towards the output characteristic. With the main effect and ANOVA analyses, possible combination of optimum parameters can be predicted. Finally, a confirmation experiment is conducted to verify the optimal process parameters obtained from the process parameter design. The detail of the Taguchi method is later explained in the next chapter.

CHAPTER 3 : METHODOLOGY

This research will involved two stages of experimental works in order to find out the effect of the selected operating parameter towards DMFC's efficiency and performance as well as to use the Taguchi method to determine the optimization parameter of the DMFC for powering up a portable electronic device respectively. The ranges of the process parameters were selected in light of the data available in the literature as per discuss in the chapter before.

3.1 Research Methodology

3.1.1 Direct Methanol Fuel Cell

As shown in Figure 3.1 and 3.2, this experiment was conducted on a single cell passive DMFC. The test cell was manufactured by H-Tech Education. This cell passive DMFC is using standard Nafion membrane which was sandwiched between two electrical current collectors, which were made of 316 stainless steel plates of 1.0 mm in thickness. A 200-nm platinum layer was sputtered onto the surface of the current collectors to reduce the contact resistance with the electrodes. The cell was held together between an anode and a cathode fixture, both of which were made of transparent acrylic plates.

The passive DMFC came with a built in 3.0 ml methanol solution reservoir. The access of methanol to reaction areas purely depends on methanol diffusion process. Methanol was diffused into the catalyst layer from the built-in reservoir, while oxygen, from the surrounding air, was diffused into the cathode catalyst layer through the opening of the cathode fixture.

Voltage and current measurements were made using a digital multimeter.

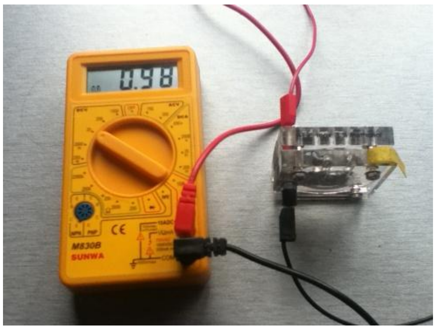

Figure 3. 1: Multimeter

Figure 3. 2 : Direct Methanol Fuel Cell manufactured by H-Tech

3.1.2 To determine the effect of selected operating parameter towards efficiency and performance of DMFC

In this part, a customized DMFC as mentioned before is tested at various elevated temperature and various concentration. Parameters such as current density, methanol concentration, and cell's voltage will be tabulated graphically. This graphical information will show the efficiency of the DMFC based on the cell's voltage that being produced according to its respective operating parameter.

Currently, the temperature of 15°C, 30°C, 45°C, 60°C and 75°C, will be chosen to represent range of elevated temperature on DMFC. This 5 temperature values are considered to be used in this experiment based on the studies made by other researcher in the past and it will be used to see the effects of elevated temperature on DMFC efficiency for portable electronic devices.

After completed with the temperature, the experiment is continued with varying the concentration methanol at constant temperature. This is done to get the optimum molarity of methanol solutions in order to produce the highest voltage. The results obtained which is in term of current density, cell's voltage and power density will be used to determine the efficiency and performance of DMFC.

Methanol Solution Preparation

The methanol solution is prepared for 0.1M, 0.5M, 0.7M, 1.0M, 2.0M, 3.0M and 5.0M. The dilution process follows this equation,

$$v_{stock} = v_{solution} \frac{c_{target}}{c_{stock}}$$

Where v_{stock} is the volume of master solution that is needed for dilution, $v_{solution}$ is a known volume to dilute the solution, c_{target} is concentration of dilution and c_{stock} is concentration of master solution.

Once the dilute solutions are prepared, they will be covered properly to eliminate any gases or foreign particles from dissolve into the solutions.

Operating Temperature

In order to demonstrate the real operating temperature for the DMFC, each of the methanol solution is kept in a water bath which has been heated to its respective temperature. Before the methanol solution is tested using DMFC, the temperature is again checked by using thermometer in order to make sure that the desired temperature is still maintained. This is done to reduce the error make during the experiment.

Figure 3. 3 : The temperature of the water bath is pre-set

Figure 3. 4 : The methanol solution is kept in the water bath until it reach the desired temperature

3.1.3 To use Taguchi method in order to determine optimum parameter for DMFC optimization

a) Selection of the DMFC parameters and their levels

Only three DMFC parameters i.e. methanol concentration, operating temperature and air flow rate were investigated in this study. Based on the result that were obtained on the DMFC performance before, the range of the methanol concentration was selected to be 0.7M, 1M and 2M and the temperature was selected in the range between 30 – 60°C. The air flow rate was chosen to be 0, 200 and 400ml/min respectively. The selected DMFC process parameters along with their levels are given in Table 3.1. Each parameter had two levels.

Table 3. 1 : DMFC parameters and their levels

Symbol	Parameter	Unit	Level 1	Level 2	Level 3
A	Methanol Concentration	M	0.7	1.0	2.0
B	Temperature	°C	30.0	45.0	60.0
C	Air flow rate	ml/min	0	200	400

b) Selection of orthogonal array

The selection of an appropriate orthogonal array (OA) depends on the total degrees of freedom of process parameters. Degrees of freedom are defined as the number of comparisons between process parameters that need to be made to determine which level is better and specifically how much better it is. In this study, since each parameter has three levels therefore, the total degrees of freedom (DOF) for the parameters are equal to 8. Basically, the degrees of freedom for the OA should be greater than or at least equal to those for the process parameters. The standard *L*9 orthogonal array has three 3 level columns with 8 DOF. Therefore, an *L*9 orthogonal array with three columns and nine rows was appropriate and used in this study. The experimental layout for the DMFC parameters using the *L*9 OA is shown in Table 3.2. Each row of this table represents an experiment with different combination of parameters and their levels.

Table 3. 2 : Taguchi's L9 Orthogonal Array

Experiment Number	Column/Parameter		
	P1	**P2**	**P3**
1	1	1	1
2	1	2	2
3	1	3	3
4	2	1	2
5	2	2	3
6	2	3	1
7	3	1	3
8	3	2	1
9	3	3	2

c) The result for optimization is then being analyzed using main effect analysis, ANNOVA and signal to noise ratio (S/N). A Taguchi software namely Qualotek-4 is used for this purpose.

3.4 Key Milestone and Gantt Chart

Table 3. 3 : FYP II Gantt Chart and Milestone

Activities	Week 1 17th Sept	Week 2 24th Sept	Week 3 1st Oct	Week 4 8th Oct	Week 5 15th Oct	Week 6 22nd Oct	Week 7 29th Oct	Week 8 5th Nov	Week 9 12th Nov	Week 10 19th Nov	Week 11 26th Nov	Week 12 3rd Dec	Week 13 10thDec	Week 14 17th Dec
Study on the detail of DMFC	■													
Preparing methanol solution		■												
Experiment : Effect of Methanol Concentration		■	■	■										
Experiment : Effect of Operating Temperature					■	■	■							
Submission of Progress Report								★						
Experiment : Determine the optimum DMFC parameter using Taguchi's method								■	■	■				
Pre-Edx/Poster Presentation											★			
Submission of Dissertation													★	
Submission of Technical Report													★	
Oral Presentation														★

★ Key Milestone

■ Process

CHAPTER 4 : RESULTS AND DISCUSSION

Several different experiments were conducted for this research as per discuss in the previous chapter. In this chapter, the result for each experiment will be clearly shown and a detail analysis is done to have a better understanding on the outcome of the research project.

4.2 Expected Result

4.2.1 The performance of DMFC using different methanol concentration

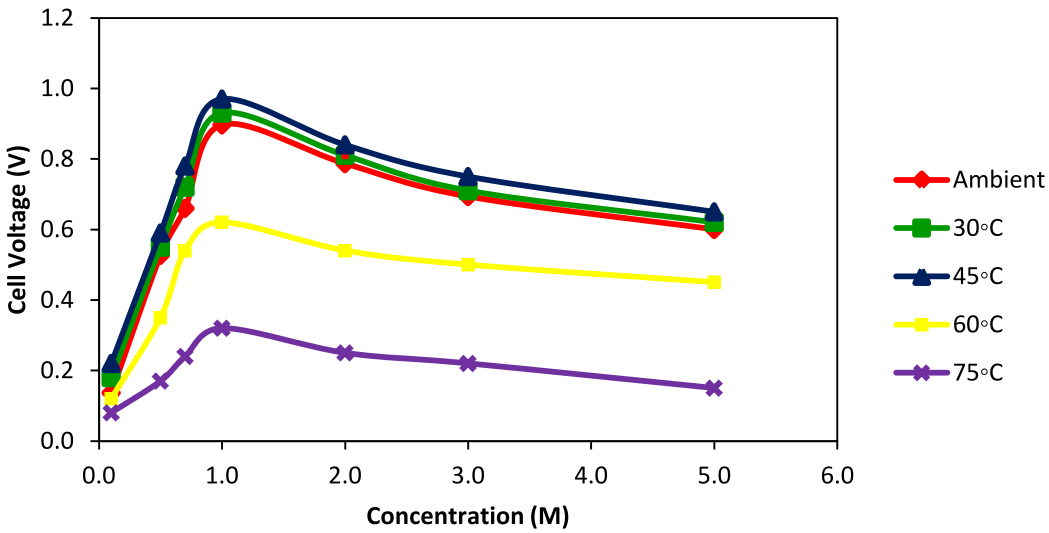

Figure 4. 1 : The performance of DMFC using different methanol concentration

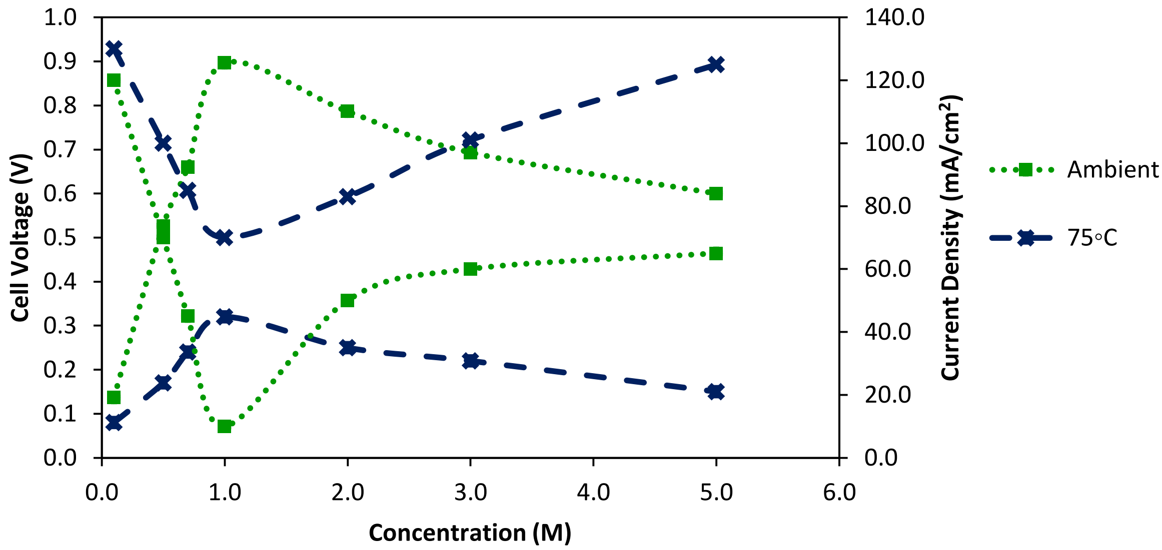

Figure 4. 2: Current density profile at different methanol concentration

Table 4. 1 : The performance of DMFC using different methanol concentration

Temperature	**Ambient**	**30◦C**	**45◦C**	**60◦C**	**75◦C**
Concentration (M)	**Average Voltage (V)**				
0.1	0.14	0.18	0.22	0.12	0.08
0.5	0.53	0.55	0.59	0.35	0.17
0.7	0.66	0.72	0.78	0.54	0.24
1.0	0.90	0.91	0.95	0.62	0.32
2.0	0.79	0.81	0.84	0.54	0.25
3.0	0.69	0.71	0.75	0.50	0.22
5.0	0.60	0.62	0.65	0.45	0.15

Figure 4.1 shows the performance of the DMFC tested with various methanol concentrations ranging from 0.1 M to 5.0 M. Each data point represents typical steady state voltages that were taken after continuous operation for 5 min at the indicated current density. It can be seen the cell voltage exhibited a tremendous increase when the methanol concentration was increased from 0.5 M to 1.0 M. As the methanol concentration increases, sufficient methanol can be delivered to the anode CL so that the mass transport polarization at the anode can be reduced. In the cases when the methanol concentration was increased from 1.0 to 5.0 M, although the cell performance kept improving, the increments became progressively smaller toward the highest methanol concentration.

Too high methanol concentration will lead to a higher rate of methanol crossover, which in turn lowers the cell voltage as a result of the increased mixed potential. It can be seen that the open circuit voltages decrease with increasing methanol concentration. This agrees well with the experimental results reported by Surampudi et. al. It has been noted that the open circuit voltage of the DMFC at higher methanol concentrations is attributed to the higher methanol crossover than the lower methanol concentration. These results show that the highest cell voltage which is 0.95V are obtained with 1.0 M methanol while somewhat lower voltages are obtained with both the higher concentration, 5.0M methanol, and lower concentration, 0.5 M. The lower performance of the cell at concentrations less than 0.5 M is due to the concentration polarization effects. When the methanol concentration is too low, the rate of methanol transport to the anode becomes too low, resulting in a larger mass transport polarization, which not only lowers the cell voltage but also leads to a limiting current density.

Detailed performance parameters measured with different methanol concentrations are listed in Table 4.1. Clearly, the lower performance at low current densities can be attributed to the fact that methanol crossover from the anode to the cathode becomes larger with increasing methanol concentration. At higher current densities, however, the mechanism leading to better performance of the DMFC with a higher methanol concentration is more complicated. The performance behavior similar to that shown in Figure 4.1 and Table 4.1 was also reported in many previous papers studying the effect of methanol concentrations on the performance of passive DMFCs. The higher performance at higher current densities was traditionally attributed to the improved mass transfer with higher methanol concentration.

By changing methanol concentration, optimal operating conditions were revealed. It was found that 1.0 M methanol was a suitable fuel concentration reducing diffusion polarization and methanol crossover.

4.2.2 The performance of DMFC at different operating temperature

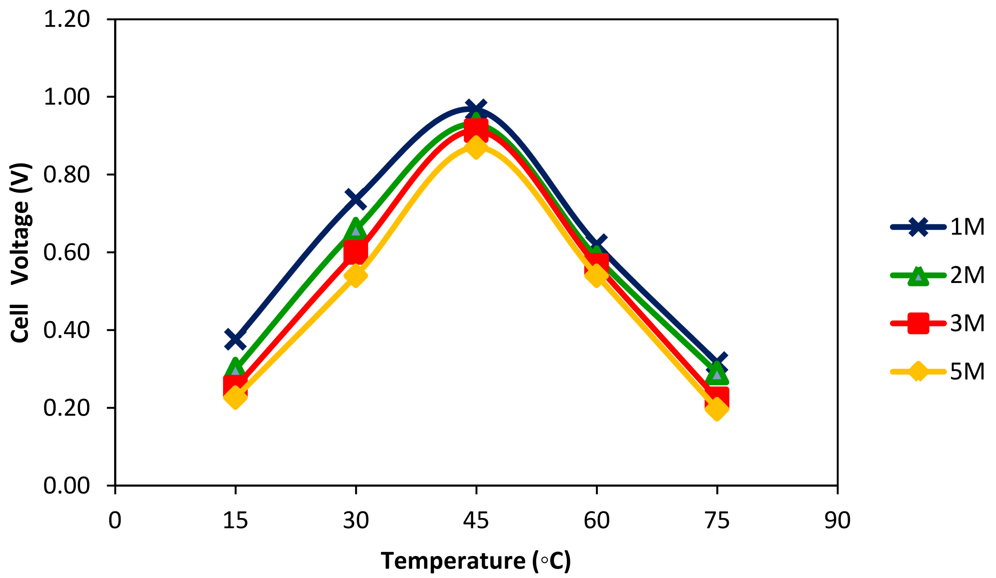

Figure 4. 3 : The performance of DMFC at different operating temperature

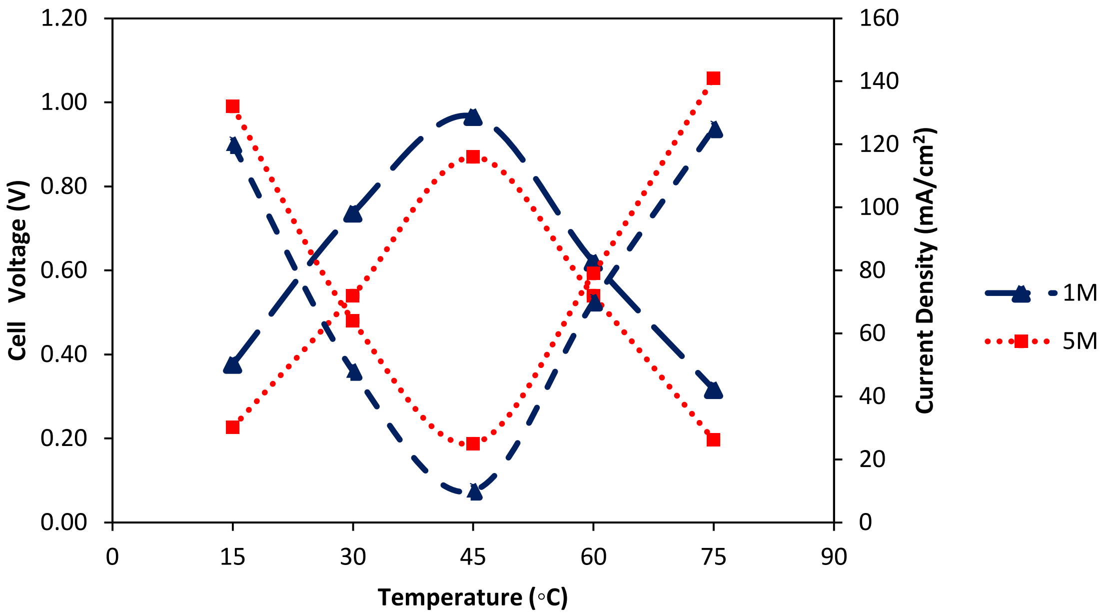

Figure 4. 4: Current density profile at elevated temperature

Table 4. 2: The performance of DMFC at different operating temperature

Concentration (M)	**1M**	**2M**	**3M**	**5M**
Temperature,◦C	**Average Voltage (V)**			
15.0	0.38	0.30	0.25	0.23
30.0	0.74	0.66	0.60	0.54
45.0	0.97	0.93	0.91	0.87
60.0	0.62	0.59	0.57	0.54
75.0	0.32	0.29	0.22	0.20

The operating temperature variation of DMFC with methanol concentration, however, has never been reported in the literature. Figure 4.3 shows the cell operating temperature variation with time after the methanol solution with different concentrations was injected into the reservoir. It should be mentioned that the temperatures shown in Figure 4.3 and Table 4.2 were measured under open circuit conditions. It is interesting to note from Figure 4.3 that the cell voltage increased with increasing temperature up to 45◦C. Over these temperatures, the performance decreased and was unstable. The increase in the temperature increased the open-circuit voltage and also reduced the activation overvoltage according to the Arrhenius relation, thus resulting in a higher performance. However, the performance reached a maximum just below the boiling temperature of the solution at 45◦C under atmospheric pressure. This suggests that boiling of the solution reduces the cell performance. Small bubbles of the vapor formed in the catalyst layer and diffusion layer may obstruct mass transfer of the liquid methanol.

Although the high temperature results in the high reaction kinetics in the fuel cell, which improves cell performance, the large water loss from the cathode at the higher cell temperature will lower both the water content in the membrane and the anode, which in turn greatly increases the cell resistance and lowers the anode performance, thus lowers the cell performance. Therefore, operating DMFC at an appropriate temperature is preferred.

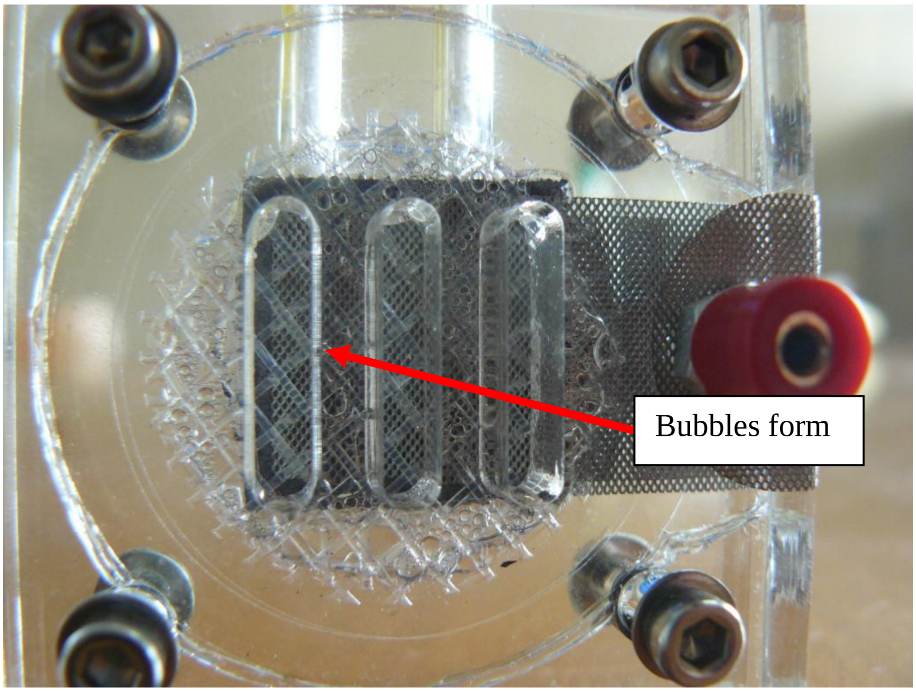

Figure 4. 5: Small bubbles form obstruct the mass transfer of liquid methanol

4.2.3 DMFC Optimization

a) Result

The results, in terms of average voltage were obtained after conducting the test for all nine experiments. The experimental results for DMFC test under the application of selected parameters are summarized in Table 4.3. In the latter, the results were analyzed by employing main effects analysis and ANOVA. Finally, a signal to noise ratio (S/N) analysis was carried out to confirm the estimated combination of parameters and level for DMFC optimization.

Table 4. 3 : Experimental result for DMFC optimization

Experiment Number	Operating Temperature (°C)	Methanol Concentration (M)	Air Flow Rate (ml/min)	Average Voltage (V)
1	30.00	0.70	0.0	0.71
2	45.00	0.70	200.0	0.79
3	60.00	0.70	400.0	0.68
4	30.00	1.00	200.0	0.91
5	45.00	1.00	400.0	0.97
6	60.00	1.00	0.0	0.80
7	30.00	2.00	400.0	0.62
8	45.00	2.00	0.0	0.64
9	60.00	2.00	200	0.53

b) Main Effects

The average value of DMFC test for each factor i.e. A, B and C at each level i.e. level 1, level 2 and level 3 was obtained and the result is summarized in Table 4.4. Figure 4.6, Figure 4.7 and Figure 4.8 presents the main effect graph for average voltage at specified condition. This graph is based on the average voltage presented in Table 4.4. The quality characteristics investigated in this study was “the-bigger-the-better” owing to the fact that higher voltage reading represents higher power density for the fuel cell. It can be seen from Figure 4.6, Figure 4.7and Figure 4.8 that the combination of parameters and their levels $A_2B_2C_3$ yield the optimum quality characteristic.

Table 4. 4 : Levels average for main effects analysis

Symbol	Parameters/Factors	Average Voltage (V)		
		Level 1	Level 2	Level 3
A	Operating Temperature	0.73	0.89	0.60
B	MeOH Concentration	0.75	0.80	0.67
C	Air Flow Rate	0.72	0.74	0.76

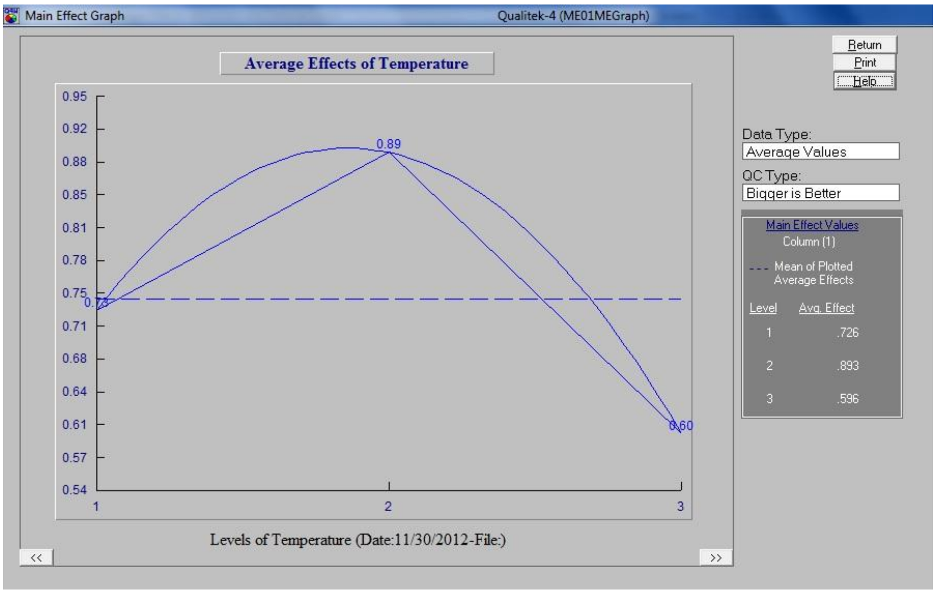

Figure 4. 6: Main Effect graph for Operating Temperature [from Qualitek-4]

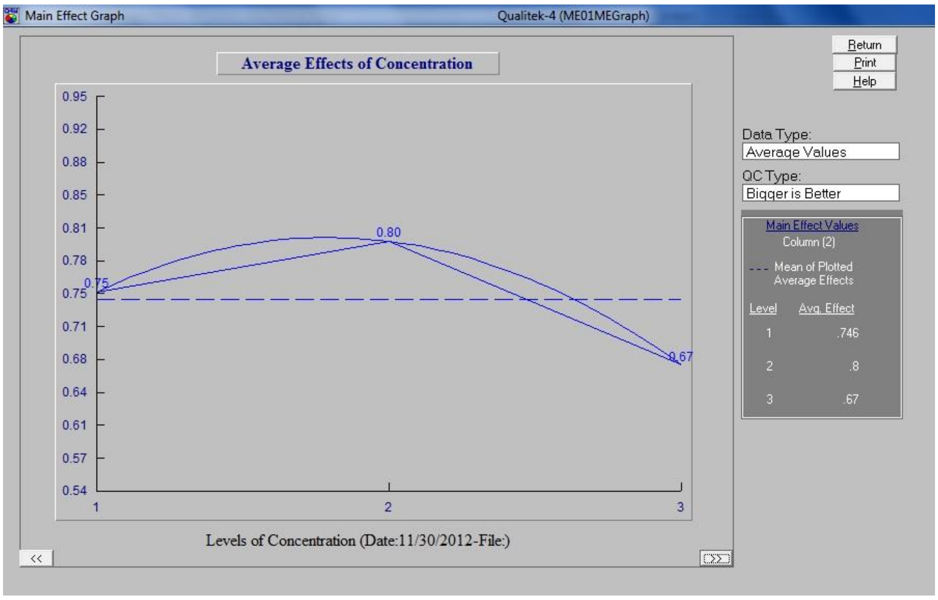

Figure 4. 7: Main Effect graph for MeOH Concentration [from Qualitek-4]

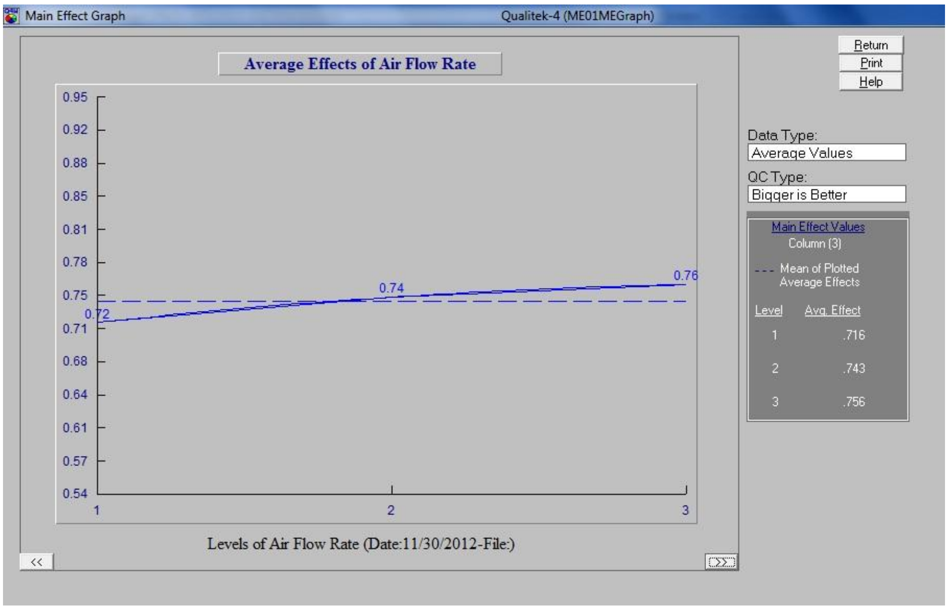

Figure 4. 8: Main Effect graph for Air Flow Rate [from Qualitek-4]

c) Analysis of Variance (ANOVA)

The purpose of the analysis of variance (ANOVA) was to investigate which parameters significantly affected the quality characteristic. In order to perform *ANOVA*, the total sum of squared deviations, *SSr* was calculated from the following formula :

$$\mathrm{SSr} = \sum_{j=1}^{n} {y_i}^2 - \mathrm{C.F}$$

Where,

n	:	number of experiments in the orthogonal array
y_i	:	cell voltage at respective condition
C.F	:	correction factor

C.F was calculated as:

$$C.F = \frac{T^2}{n}$$

Where,

T	:	total of the cell voltage

It should be noted that each test experiment was conducted for three times and thus the value of n is 21 (9 experiments x 3 runs).

Statistically, there is a tool called *F* test to see which process parameters have significant effect on the quality characteristic. Usually, when $F > 4$, it means that the change of the process parameter has significant effect on the quality characteristic. Table 4.5 shows the results of *ANOVA* for the DMFC. The *F*-ratios were obtained for 99% level of confidence. In addition to this, percent contribution of each parameter was also calculated. It can be seen from Table 4.5 that change in the value of all the three parameters, within the range investigated in this study, affect the cell voltage and thereby the DMFC performance significantly since the *F*-ratios are higher than 4.

From table 4.5, the right-most column of ANOVA represents the relative influence of factors and interactions to the variability of results. It can also be seen from this table that the contribution of parameter i.e. operating temperature, to the quality characteristic is maximum (82.4%). The contribution of other parameters in descending order is methanol concentration (15.86%) and air flow rate (1.48%), respectively. Thus, based on the main effect and ANOVA analyses, the optimal combination of parameters and their levels for achieving maximum cell voltage is $A_2B_2C_3$ i.e. operating temperature at level 2 (45^{o}C), methanol concentration at level 2 (1.0 M) and air flow rate at level 3 (400ml/min).

Table 4. 5: ANOVA Table for DMFC Optimization

Symbol	Parameters/Factors	DOF	Sum of Squares	Variance (V)	F-Ratio (F)	Contribution (%)
A	Operating Temperature	2	0.132	0.066	1326.89	82.404
B	MeOH Concentration	2	0.025	0.012	256.223	15.862
C	Air Flow Rate	2	0.002	0.001	24.889	1.484
	Other/Error	2	0.001	0.001		0.25
	Total	8	0.16			100.00

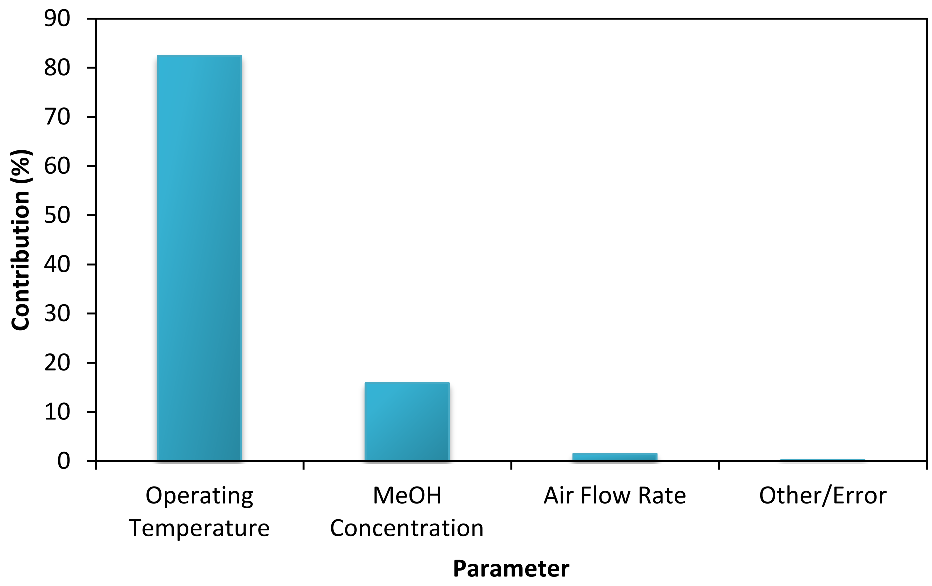

Figure 4. 9: Significant Factor bar chart based on ANOVA analysis

d) Signal to Noise Ratio (S/N)

The signal to noise ratio measures the sensitivity of the quality investigated to those uncontrollable factors (error) in the experiment. The higher value of *S/N* ratio is always desirable because greater *S/N* ratio will result in smaller product variance around the target value. As mentioned earlier the quality characteristic used in this study was "the-bigger-the-better", i.e. the higher cell voltage of the DMFC under respective condition results in better performance. In order to perform *S/N* ratio analysis, mean square deviation (*MSD*) for "the-bigger-the-better" quality characteristic and *S/N* ratio were calculated from the following equations:

$$MSD = \frac{1}{n}\sum_{i=1}^{n}\frac{1}{{y_i}^2}$$

$$\frac{S}{N} = -\ 10\log_{10}(MSD)$$

where,

yi : is the cell voltage for *i* th experiment.

Using the above two formulae the S/N ratios for the nine experiments were calculated and the results are presented in Table 4.6. It can be seen from this table that experiment number 5 yields the largest S/N ratio and for this experiment the combination of parameters and their levels is $A_2B_2C_3$ as indicated in Table 4.6. This result match with those obtained from main effect analysis and ANOVA. Thus, this signal to noise ratio (S/N) result confirm that combination of $A_2B_2C_3$ i.e. operating temperature at level 2 (45^{o}C), methanol concentration at level 2 (1.0 M) and air flow rate at level 3 (400ml/min) is the best for DMFC optimization as it has the highest *S/N* ratio value which significantly result in smallest product variance around the target value.

Table 4. 6: S/N ratio response for DMFC Cell Voltage

Experiment Number	Average Voltage (V)	MSD	S/N
1	0.71	1.9837	-2.974833026
2	0.79	1.6023	-2.047458174
3	0.68	2.1626	-3.349821746
4	0.91	1.2075	-0.819172154
5	0.97	1.0628	-0.264565315
6	0.8	1.5625	-1.93820026
7	0.62	2.6014	-4.15216621
8	0.64	2.4414	-3.87640052
9	0.53	3.5599	-5.514482608

e) Optimum Performance

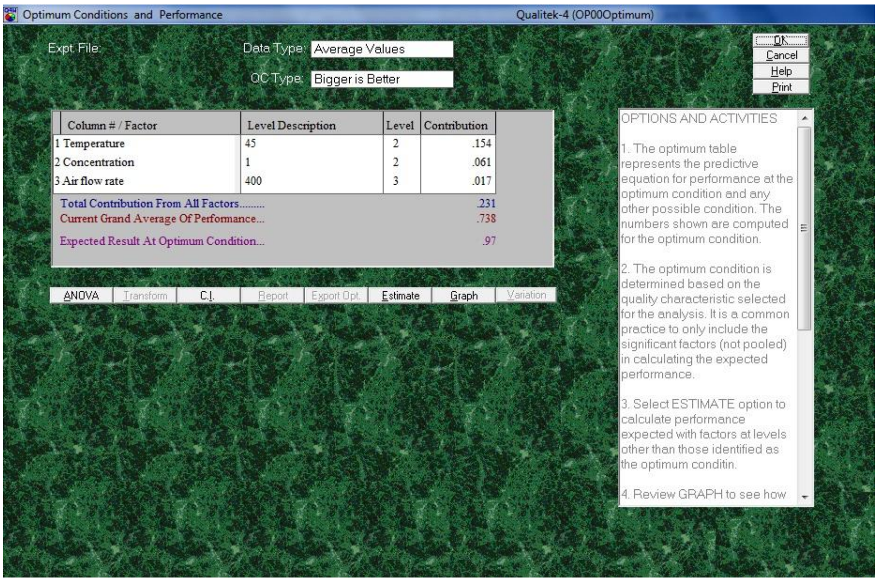

Figure 4. 10: Optimum performance [Qualitek-4]

Figure 4.9 shows the estimation made by Taguchi software which is Qualitek-4. The optimum table represents the predictive equation for performance at the optimum condition and any other possible condition. The numbers shown are computed for the optimum condition. Thus the optimum value for each parameter is as follows:

1. Operating temperature at level 2 ($45^{o}C$)
2. Methanol concentration at level 2 (1.0 M)
3. Air flow rate at level 3 (400ml/min)

This agrees with the result from main effect, ANOVA and signal to noise ratio (S/N) analysis made before. From this result, the expected cell voltage at optimum condition is 0.97V.

CHAPTER 5 : CONCLUSION AND RECOMMENDATION

Conventional batteries are soon becoming inadequate for the increasing power and complexity of portable electronic devices and computers. The DMFC is capable of replacing the conventional battery without recharging from the AC mains. It is smaller, better, less-costly, environmentally safe and much more efficient and mobile and can be used either in the plane, train, and car or in remote areas where there is no electricity as in some parts of emerging economies. The refueling of the DMFC is fast and the fuel can last several months. The product is cost competitive due to the large market size and economies of scale. The DMFC systems are eventually far less expensive than the alternative battery technologies in the long run.

In this project, the result shows that the performance of DMFC increased with increasing of methanol concentration but lower performance is seen at higher concentration as the methanol crossover rate is also increased. At elevated temperature, DMFC shows the best performance at 45◦C with 0.93V. The performance of DMFC is directly proportional to the temperature. Higher temperatures result in better DMFC performance. But, as the temperature reached the methanol boiling point (65◦C), the performance decreased greatly as more methanol is loss through the phase change from liquid to vapor. Besides that, the bubbles present from the boiling of methanol blocked the movement of liquid methanol from anode to cathode and indirectly gives a lower performance to the DMFC.

For optimization, Taguchi method is the best method to get an accurate result as well as help to reduce cost and time. This is because Taguchi method provides simplification on the design of experiment where it helps to reduce number of experiment through the orthogonal array design which contains selected parameters and levels. In addition, Taguchi method also provide a systematic analysis approach in order to determine the optimum parameter for the DMFC optimization through main effect, ANOVA, signal to noise ratio calculation.

For this research, after conducting the main effect analysis, it can be found that the combination of parameter and level at temperature of 45◦C, 1.0 M methanol concentration and 400ml/min of air flow rate gives the best performance for DMFC. Based on the ANOVA analysis, the operating temperature is the most significant parameter that affects the DMFC performance as no matter how much concentration of methanol is used but if the condition of temperature is too high which near or exceed the boiling point of methanol, this will automatically reduce the cell performance. The signal to noise ratio (S/N) confirm that combination of $A_2B_2C_3$ i.e. operating temperature at level 2 (45^oC), methanol concentration at level 2 (1.0 M) and air flow rate at level 3 (400ml/min) is the best for DMFC optimization as it has the highest *S/N* ratio value which significantly result in smallest product variance around the target value.

With the 0.97V cell voltage produce from the optimization of DMFC, it is expected that in order to power up a 4V portable electronic device, we just need a cell stack consist of 4 single cell DMFC. This helps to reduce the manufacturing cost as well as increased the power density of the DMFC which indirectly proves that DMFC is a promising sustainable power sources which are able to replace current rechargeable batteries.

Lastly, the author hopes that this project which mainly focus on fuel cell technology will indirectly helps in promoting efficient, renewable and more environmentally friendly power sources towards the academic society and normal community especially in Malaysia and specifically in UTP.

Recommendation

As this is the first Direct Methanol Fuel Cell experimental research in UTP, it is hoped that in the future many more research in this field can be done especially focusing more on:

1. Developing our own UTP Direct Methanol Fuel Cell
2. Study on different type of membrane towards DMFC performance
3. Study on both active and passive DMFC
4. Study on DMFC fluid flow design
5. Developing the DMFC membrane

Besides that, the authors do hope that UTP especially the Chemical Engineering department realize the importance of developing this fuel cell technology so that we can be the upfront for the research and development in this field.

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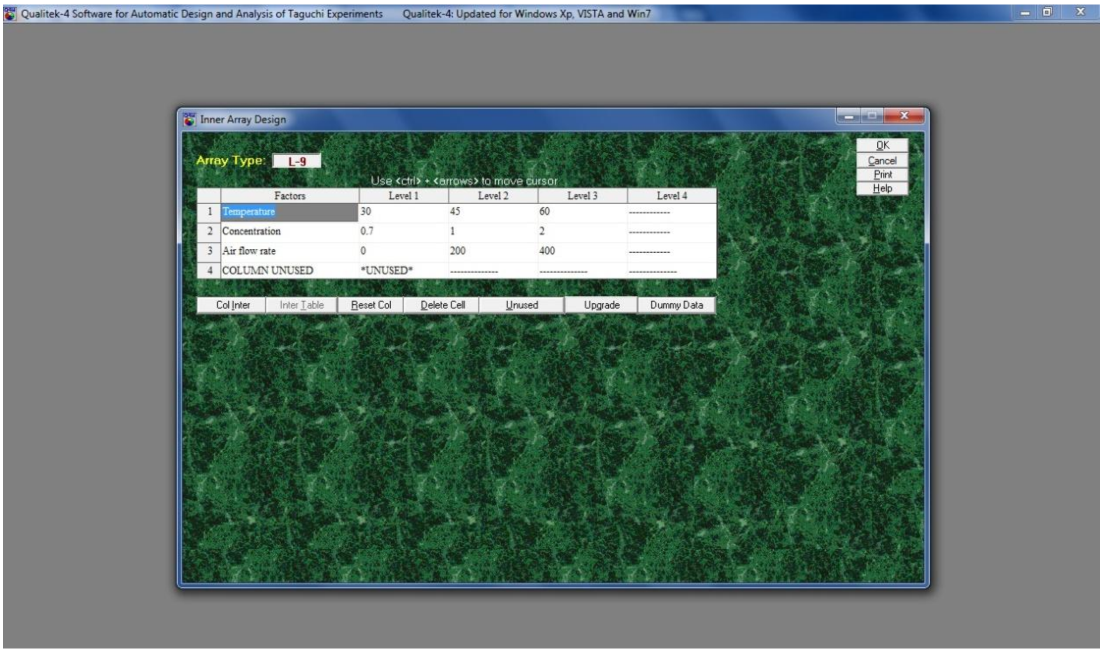
APPENDIXES

A. Qualitek-4 Result

1) Taguchi Orthogonal L9 Array



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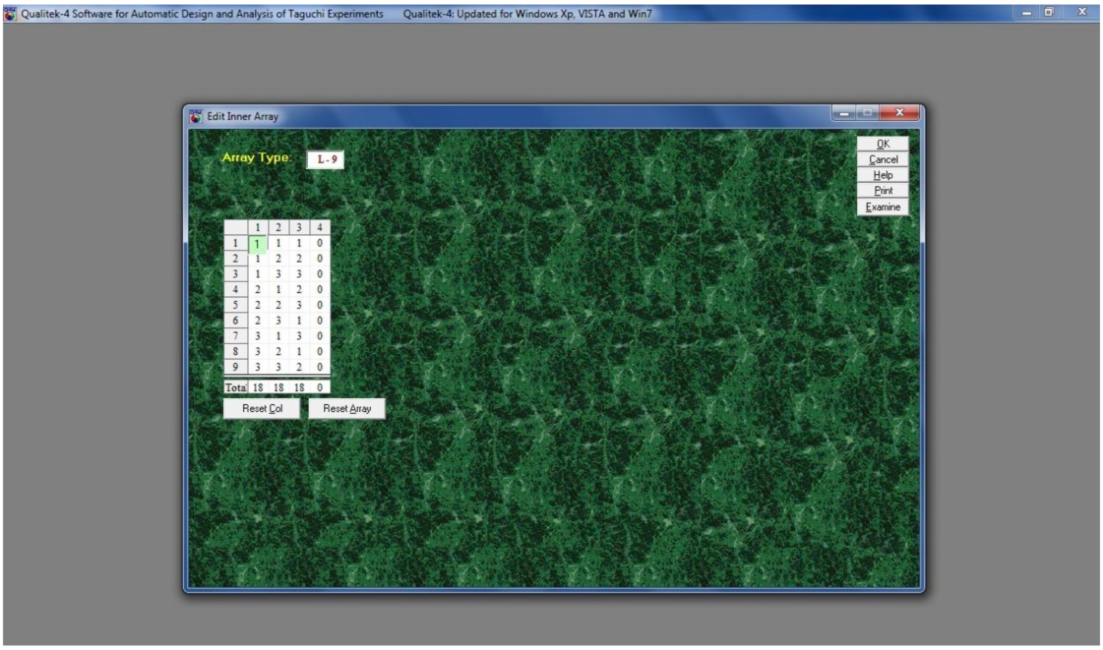
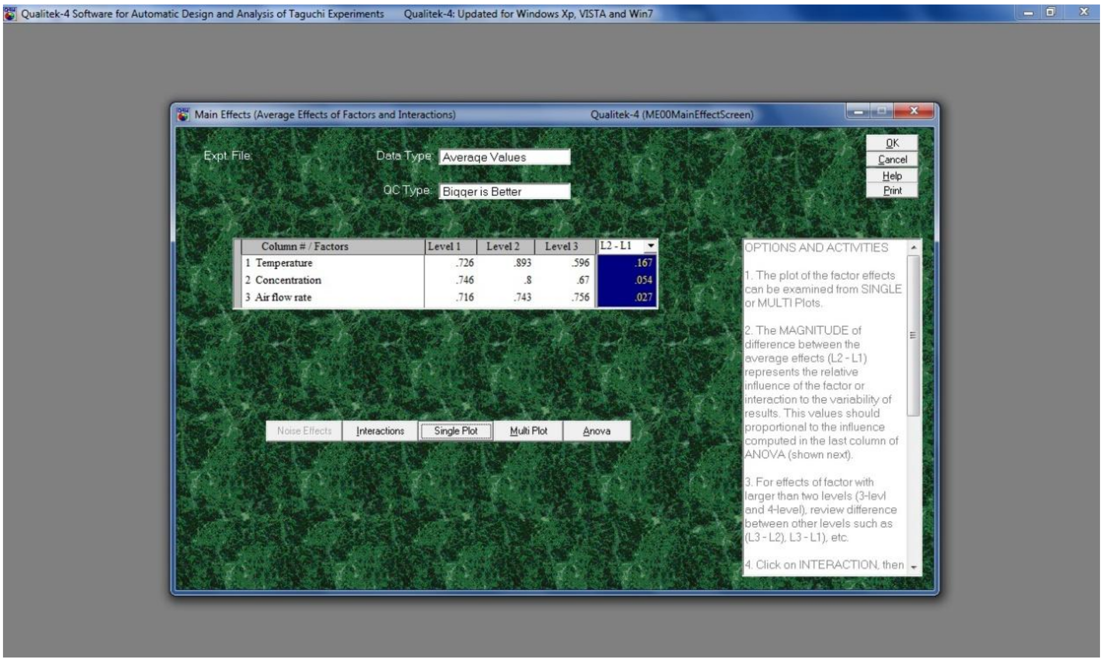


(Array)

2) Main Effect Analysis



3) ANNOVA