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Optimization of Experimental Conditions based on the Taguchi Technique for the Production of Methanol via Saponification Process

By
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A THESIS
SUBMITTED TO THE POSTGRADUATE STUDIES PROGRAMME
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DEGREE OF MASTERS OF SCIENCE in CHEMICAL ENGINEERING
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PERAK

JULY 2007

Declaration

I hereby declare that the thesis is based on my original work except for quotations and citations which have been duly acknowledged. I also declare that it has not been previously or concurrently submitted for any other degree at UTP or other institutions.

Signature :

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Date : 25 JULY 2007

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Abstract

Methanol is a clean fuel energy. The demand of methanol is increasing since it can substitute the energy that is based on petroleum. Several technologies of methanol synthesis have already being developed, mostly in gas phase and heterogeneous system. Recent development for methanol synthesis technology is known as liquid phase methanol, but still, it involves heterogeneous system.

An alternative route to produce methanol at milder operating conditions is studied. This new one-pot reaction was developed and tested by using methyl acetate and calcium hydroxide as the raw materials. The liquid reactants were reacted in a reactor at milder operating conditions of temperature less than 60°C and at atmospheric pressure. This saponification process was tested to find the best combination of operating conditions that can produce the most yield of methanol at a maximum conversion of methyl acetate.

Taguchi robust design method with L_{16} orthogonal array was implemented to optimize experimental conditions for the production of liquid methanol. Reactor type, reactor volume, flow rate of reactants, reactants' concentrations and temperature were chosen as significant parameters in designing the experiment. Taguchi approach of design of experiment was used to evaluate both the main and interaction effects of the experimental variables. This methodology facilitated analysis of the experimental data to establish the optimum conditions for the process, understand the contribution of individual factors and to evaluate the response under optimal conditions.

Results showed that the optimum conditions for the saponification process of methyl acetate and calcium hydroxide in producing methanol was at a semi-batch system, at 2L volume, 25 cm^3/min of flow rate, 0.05M concentration of both methyl acetate and calcium hydroxide, and temperature of 50°C. Results also indicated that concentrations of reactants strongly influence the yield of methanol. It is found that reactants' concentrations were the most influencing parameters that affect the production of methanol, with 38.15% contribution from methyl acetate and 25.39% from calcium hydroxide.

The rate law of the saponification reaction was determined using the linearized least-squared method. The order of reaction with respect to calcium hydroxide and methyl acetate are found to be of 0.69 ± 0.03 and 0.94 ± 0.08 respectively. The rate constant, k is postulated as 0.097 ± 0.05 $(\text{mol/L})^{-0.6}$ s^{-1} at 50°C. The reaction is said to be a pseudo-first-order reaction with respect to the limiting reactant, methyl acetate. At these optimum conditions, the yield of methanol obtained was 32.95% with error of 0.72% compared to the expected value from the Qualitek-4 software.

This new experimental route proved that methanol can be produced via this saponification of methyl acetate and calcium hydroxide. Taguchi method was successfully applied to design the experiment for the process and it showed that of could save time and costs of reactants by 75% as compared to traditional statistical approach.

Abstrak

Metanol ialah sejenis bahan bakar yang bersih. Permintaan terhadap metanol telah meningkat memandangkan ia dapat menggantikan sumber tenaga yang berasaskan petroleum. Beberapa teknologi penghasilan metanol telah pun diiktiraf, kebanyakannya dalam fasa gas and sistem heterogen. Penemuan terkini untuk teknologi penghasilan metanol dikenali sebagai metanol fasa cecair, namun ia masih juga mengekalkan sistem heterogen.

Satu jalan alternatif dalam proses penghasilan metanol telah dikaji. Proses ini dibina dan diuji dengan menggunakan metil asetat dan kalsium hidroksida sebagai bahan tindakbalas. Bahan-bahan ini ditindakbalaskan di dalam sebuah reaktor dengan sistem homogen, pada kadar suhu yang kurang daripada 60°C dan tekanan atmosfera. Proses saponifikasi ini diuji untuk mencari kombinasi keadaan yang paling sesuai untuk menghasilkan metanol pada kadar yang paling tinggi dan pertukaran metil asetat kepada metanol yang paling tinggi.

Teknik Taguchi dengan janjang ortogonal L_{16} telah diaplikasikan untuk mengoptimakan keadaan eksperimen untuk kadar penghasilan metanol yang tinggi. Jenis reaktor, isipadu reaktor, kadar aliran, kepekatan bahan tindakbalas, dan suhu operasi telah dipilih sebagai parameter yang signifikan dalam merekabentuk eksperimen ini. Teknik Taguchi ini dapat memberikan tentang kesan yang diberikan oleh faktor utama dan hubungan di antara faktor secara individu dan secara kombinasi kepada kuputusan yang dikehendaki, iaitu kadar penghasilan metanol. Teknik ini membekalkan dan membolehkan analisa data-data daripada eksperimen dilakukan untuk mendapatkan keadaan yang optima untuk proses tersebut serta memberikan pemahaman tentang sumbangan oleh faktor individu dan juga boleh digunakan untuk mengkaji respon pada keadaan optima.

Keputusan yang didapati telah menunjukkan bahawa keadaan yang paling optima untuk proses saponifikasi antara metil asetat dan kalsium hidroksida untuk menghasilkan metanol adalah dengan menggunakan sistem separa-kelompok pada isipadu 2L, kadar aliran pada 25 cm^3/min, kepekatan kedua-dua bahan tindakbalas pada 0.05M, dan suhu reaktor pada 50°C. Keputusan juga menunjukkan bahawa kepekatan kedua-dua bahan tindakbalas tersebut mempunyai pengaruh yang besar dalam penghasilan metanol. Kajian mendapati bahawa kepekatan metil asetat menyumbang kepada 38.15% kadar pengaruh kepada proses saponifikasi ini, diikuti oleh kepekatan kalsium hidroksida dengan sumbangan sebanyak 25.39%.

Hukum kadar proses saponifikasi ini ditentukan dengan menggunakan kaedah regresi linear kuasa dua terkecil. Melalui pengiraan dengan menggunakan kaedah regresi ini, didapati bahawa aturan tindakbalas untuk tindakbalas ini berdasarkan kepada kalsium hidroksida dan metil asetat adalah bukan berada pada aturan pertama; iaitu masing-masing adalah pada 0.69 ± 0.03 and 0.94 ± 0.08. Pemalar kadar, *k*, telah diperoleh sebagai 0.097 ± 0.05 $(\text{mol/L})^{-0.6}$ s^{-1} pada suhu 50°C. Tindakbalas ini boleh dikatakan berada pada aturan pertama pseudo berdasarkan kepada metil asetat, yang merupakan bahan tindakbalas yang terhad. Pada keadaan optima ini, hasil metanol yang didapati adalah sebanyak 32.95% dengan ralat sebanyak 0.72% berbanding dengan nilai yang telah dijangkakan oleh Qualitek-4.

Proses baru dalam penghasilan metanol ini telah membuktikan bahawa metanol boleh dihasilkan melalui saponifikasi antara metil asetat dan kalsium hidroksida. Kaedah Taguchi telah berjaya diaplikasikan untuk merekabentuk eksperimen bagi proses saponifikasi ini dan didapati bahawa ianya dapat menjimatkan masa dan kos bahan mentah sebanyak 75% berbanding dengan kaedah statistik tradisional.

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Nomenclature

T	Total of all results from trials
$C.F.$	Correction factor
S	Sum of Squares
S_T	Total Sum of Squares
f	Degree of freedom
f_T	Total degree of freedom
V	Variance
P	Percentage contribution
r	Rate of reaction
E_a	Activation energy
α	Order of reaction with respect to calcium hydroxide
β	Order of reaction with respect to methyl acetate
C_A	Concentration of calcium hydroxide
C_B	Concentration of methyl acetate

CHAPTER 1: INTRODUCTION

1.1 Background of project

Energy is a major issue in the world due to its shortage and high demand. Energy consumption is estimated to be 3.18 x 10^{17} BTU per annum, and is projected to increase up to 5.97 x 10^{17} BTU in the year 2050. Thus, an alternative source of energy from renewable resources is crucial (Hugill, 2001).

Methanol is an alternative source of fuel. Due to its physical and chemical characteristics, it has inherent advantages as an automotive fuel. In addition, methanol is used in the petrochemical industry as raw materials to produce other important products for our daily lives usage. Methanol is also known as methyl alcohol, usually manufactured from synthesis gas consists of carbon dioxide, carbon monoxide and hydrogen. Methanol can be manufactured from a variety of carbon-based feedstocks other than natural gas, such as coal and biomass. Methanol is a colourless, neutral, polar liquid that miscible with water, alcohols, esters and most other organic solvents. It has lower emissions, higher performance, and lower risk of flammability compared to gasoline.

US Environmental Protection Agency claimed that methanol is one of a number of fuels that could substitute for gasoline or diesel fuel in passenger cars, light trucks, and heavy-duty trucks and buses. Emissions from methanol cars are low in reactive hydrocarbons, which form smog, and in toxic compounds. Methanol-fueled trucks and buses emit almost no particulate matter, which cause smoke and odor, and can also be carcinogenic, and much less nitrogen oxides than their diesel-fueled counterparts. Use of methanol would diversify the country's fuel supply and reduce its dependence on imported petroleum (EPA, 1997).

Methanol Institute has outlined that methanol has been widely used in our daily lives, for making polyester, cotton fabric, fertilizers, pesticides, medication, and also magnetic films for our computer disc. Recent emerging market for methanol is for the usage as hydrogen carrier for fuel cell vehicles, stationary fuel cell power plants, and portable fuel cell devices such as cellular phones. Besides, methanol can also be used as additive to remove harmful nitrates from wastewater treatment plant effluent by accelerating bacterial degradation and also as superior fuel for turbines used for electric power generation that significantly reduces NOx emmisions.

The efficiency of methanol synthesis is severely limited by thermodynamics because it is an extremely exothermic reaction (Zhang & Zhao, 2006). For example, at 573K and 50 bar, the theoretical maximum of a one-pass CO conversion process is around 20% (Reubroycharoen et al., 2004). Therefore, developing a low-temperature process for methanol synthesis will greatly reduce the production cost by utilizing the intrinsic thermodynamic advantage at low temperature (Zhang & Zhao, 2006)

Current route to synthesize methanol is through high temperature and high pressure process, basically using a technique introduced by a German chemist, Pier M. in 2003. The process operated at up to 250-350 bar and 320-450 °C.

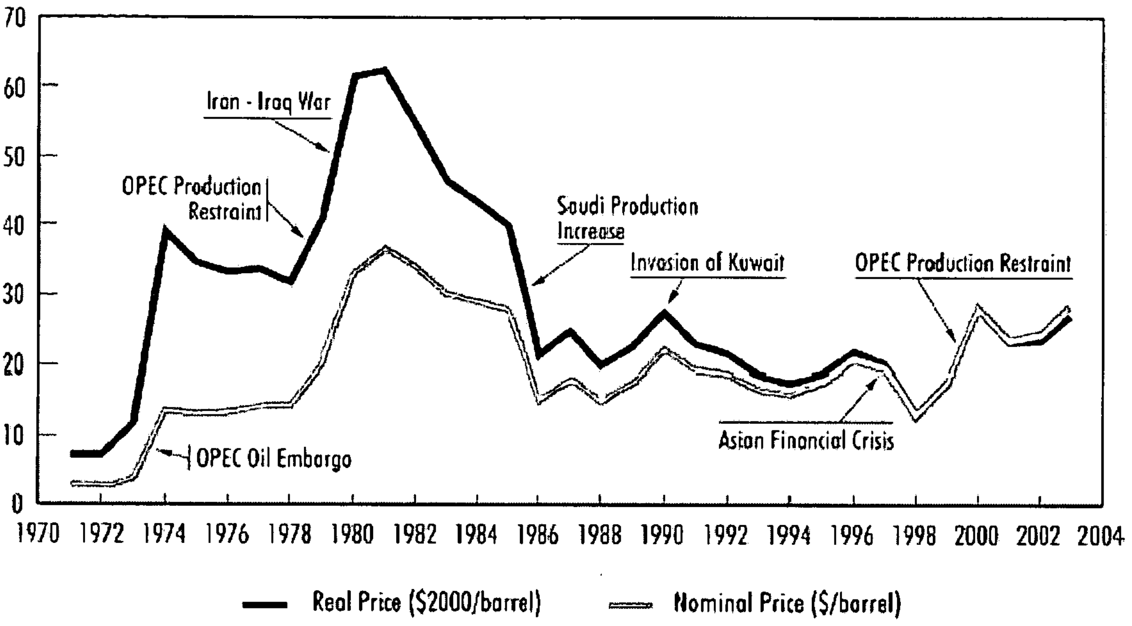
1.2 Problem statement

In today's current technology and process, world's methanol is produced by a process using natural gas or synthesis gas as the feedstock. The conventional route depleted the fossil sources, requires extreme operating condition, involves multiple-step reaction, presence of catalyst and offer only 10% single pass conversion. Besides, the price of crude oil is fluctuating along the years. Figure 1.1 shows the trending of the crude oil price from 1970 to 2004 (IEA, 2004).

Methanol has been commercially produced in gas phase worldwide. Most of the reactions require the presence of synthesis gas which contains H_2, CO and CO_2. Methanol is produced by the hydrogenation of carbon oxides over a suitable catalyst, according to the following reactions:

$$CO + 2H_2 \Leftrightarrow CH_3OH \qquad \text{(Eq. 1.1)}$$

$$CO_2 + 3H_2O \Leftrightarrow CH_3OH + H_2O \qquad \text{(Eq. 1.2)}$$



(Ref: IEA, 2004)

Figure 1.1: Average Crude Oil Import Price

Even via alternative routes, such as Biomass process and Liquid-Slurry process, the presence of synthesis gas is still very vital in order to produce methanol. This technology requires stages of process at very high operating pressure and temperature. The typical reaction conditions are at a temperature of 225-270°C and a pressure of 50-100 bar.

Gas phase methanol synthesis, which relies on hydrogen-rich synthesis gas, results in crude methanol product with 4 to 20% water by weight. The liquid phase methanol process typically contains only 1% water. The fuel-grade methanol is suitable for many applications without purification cost savings.

Therefore, ability to produce methanol from other type of feedstock, such as coal or biomass, or any other natural resources is of interest to reduce the high demand on petroleum. It is very essential to explore the alternative route to produce methanol. The milder and homogeneous route using chemicals that may be extracted from renewable resources which require milder operating condition that involves only a single-step reaction need to be developed.

In searching for alternative route, it is necessary to conduct the experiment in efficient and cost effective approach. Conventional design of experiment involves investigation of one variable at a time which consumes more time for experimental set-up and cost for materials and power. Thus, a statistical experimental design method, i.e. Taguchi method with L_{16} array robust design, was implemented to optimize experimental conditions for the production of methanol via milder route, know as saponification process. Reactor type, reactor volume, flow rate, concentration of reactants, and temperature were chosen as significant factors to obtain the best experimental conditions that give the highest yield of methanol and conversion of methyl acetate.

1.3 Objectives of project

The objectives of the project are:

a. To synthesize liquid methanol in a one-pot reaction via saponification process at atmospheric pressure and low operating temperature of less than 64°C.
b. To find optimum experimental condition using the Taguchi Technique for the best yield of methanol and conversion of methyl acetate under the influence of significant variables.

1.4 Scope of study

Synthesis of methanol is investigated by comparing the effect of variables such as concentrations of reactants, temperature, reactor type, and flow rate of reactants that result in highest methanol yield. The experiment was conducted by reacting methyl acetate and calcium hydroxide at atmospheric pressure and operating temperature in the range of 30 to 50 °C, in liquid form. The reaction is depicted as:

$$Ca(OH)_2 + 2CH_3COOCH_3 \Leftrightarrow 2CH_3OH + (CH_3COO)_2Ca \qquad \text{(Eq. 1.3)}$$

Calcium hydroxide + Methyl Acetate $\Leftrightarrow$ *Methanol + Calcium acetate*

Instead of using traditional approach to design the experiment which requires additional experimental runs to complete the trials, Taguchi Technique is applied where Orthogonal Array is used to design the experiment. Taguchi method is a combination of mathematical and statistical techniques used in an empirical study. it uses fewer experiments required in order to study all levels input parameters, and filters out some effects due to statistical variation. Taguchi method can also determine the experimental condition having the least variability as the optimum condition. (Kim *et al.*, 2004)

This technique allows the data analysis in a systematic manner. The data is analyzed by analysis of variance (ANOVA) method. Result from ANOVA is used to determine the optimum condition that allows the operation of saponification process of methyl acetate and calcium hydroxide that gives the highest yield and conversion. Besides manual calculation of the ANOVA, an engineering software, Qualitek-4, is also used to analyze the Taguchi Experiments.

The reaction order and rate constant for the new route is evaluated using least squares method. Comparison of cost and time saving between Taguchi approach as opposed to traditional method is also conducted.

CHAPTER 2: LITERATURE REVIEW

This chapter discusses the importance of methanol and also the work done by other researchers related to methanol synthesis and the study of Taguchi approach. There have been several approaches done by other researchers on methanol technology developments for the new age.

2.1 Methanol History

The ancient Egyptians used a mixture of substances in their embalming process, including methanol, which they obtained from the pyrolysis of wood. Pure methanol, however, was first isolated in 1661 by Robert Boyle, who called it 'spirit of box' since he found a way of doing it via the distillation of boxwood. It later became known as *pyroxylic spirit*. French chemists Jean-Baptiste Dumas and Eugene Peligot determined its elemental composition in the year 1834. They also introduced the word *methylene* to organic chemistry, forming it from Greek *methy* = 'wine' + *hŷlē* = wood (patch of trees). The term 'methyl' was derived in about 1840 by back-formation from *methylene*, and was then applied to describe 'methyl alcohol'. In 1892, this was shortened to 'methanol' by the International Conference on Chemical Nomenclature.

In 1923, a German chemist, Matthias Pier, developed a way to convert *synthesis gas* (a mixture of carbon oxides and hydrogen) into methanol. This process used a zinc chromate catalyst, and required extremely vigorous conditions—pressures ranging from 30–100 MPa (300–1000 atm), and temperatures of about 400 °C. The development of methanol synthesis process was started by Pier in 1922 using BASF equipment for ammonia synthesis and in 1923 the first tank car of crude methanol oil was produced.

The process stayed the principal technology for over 45 years. Modern methanol production has been made more efficient through use of catalysts (commonly copper) capable of operating at lower pressures. The method and process was then slowly developed by using different type of catalysts, i.e. copper oxide and zinc oxide (Tijm, 2001).

2.2 Methanol World Demand and Usage

Methanol is of high demand during the mid 1990s. This demand was primary driven by the growing acceptance of a major methanol derivative in reformulated gasoline and methyl tertiary-butyl ether (MTBE) (Sri Consulting, 2000).

Producers of methanol announced plans for major new production facilities in regions containing large reserves of low cost natural gas. Advances in oxygen blown natural gas reforming technologies are not only resulting in the more efficient utilization of natural gas feed stock for 'stand-alone' methanol production in remote locations but are also permitting extraordinary increases in single train production capacities. This improved production efficiency coupled with 'mega' plant economies of scale and the relative ease of transport may reduce the delivered cost of methanol sufficiently to be competitive with conventional fuels in certain applications. A vast new market for low cost fuel grade methanol appears to be imminent, possibly along with new markets as a feedstock for olefins and gasoline production.

Methanol has become a commodity product, which in many cases is only produced at 'cash-cost' recovery. Existing excess production capacity, the pressure on the use of MTBE and on the elimination of flaring associated gas, a case where the oil may subsidize the gas price, only underscore this commodity aspect. However, on the bright side, this could open the door for methanol as a cost competitive alternative fuel, e.g. as under-boiler fuel in the power industry, in direct competition with liquefied natural gas in Japan, or as hydrogen carrier for fuel cells. Additionally, the route to chemicals or acetyl precursors from methanol would be favored.

Methanol is commonly produced as chemical grade or AA, according to specifications shown in Table 2.1 (Tijm *et al.*, 2001).The market for this grade AA type of methanol is mainly found in chemical and solvent applications. It can be roughly divided into the usage as shown in the pie chart shown in Figure 2 (Tijm *et al.*, 2001).

Table 2.1: Methanol grade AA specifications (Tijm *et. al.*, 2001)

Test	**Specification**
Methanol (wt.%, min.)	99.9
Water (ppm, max.)	500
Ethanol (ppm, max.)	20
Acetone (ppm, max.)	30
Acidity (acetic acid) (ppm, max.)	30
Alkalinity (ammonia) (ppm, max.)	30
Specific gravity at 25°C, max.	0.7893
Initial boiling point (.C)	64.7 ± 0.2
Distillation range (.C, max)	1.0
Dry point (.C)	63.7–65.7
Odor	Characteristic
Appearances	Clear

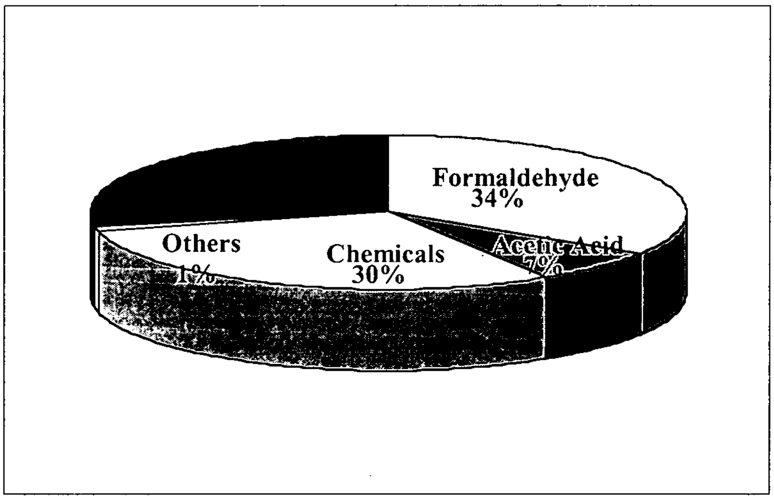


Figure 2.1: Methanol Industrial Usage and World Demand

Methanol is also in a great demand of producing dimethyl ether (DME) that is suggested to be an alternative fuel (Semelsberger *et al.,* 2006). Compared to some of other leading alternative fuels, including methanol itself, DME appears to have the largest potential impact on society, and should be considered as the fuel of choice for eliminating the dependency on petroleum.

Methanol can be used a petrol additive to improve combustion, and work is currently being done on its use as a fuel in its own right. It is also being widely used as an industrial feedstock. Figure 2.2 shows products that can be formed by using methanol as raw material.

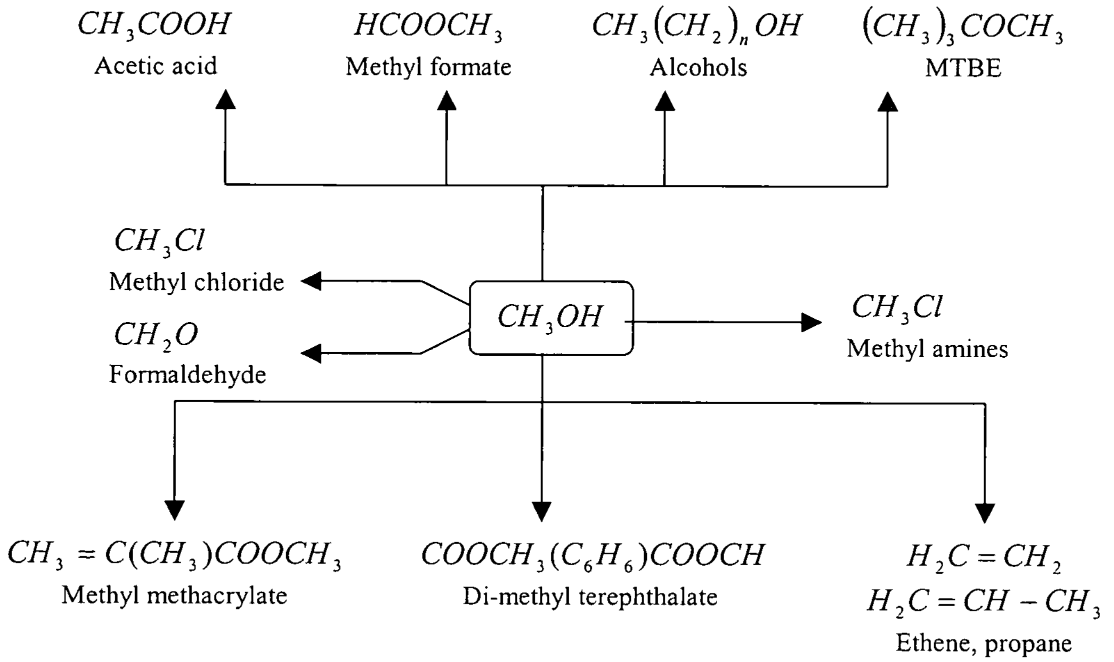


Figure 2.2: Products of methanol

2.3 Methanol Process Technology

Hugill *et al.* (2001) declared that there are about 95 methanol plants worldwide with a total capacity of 34 tonnes/year. About 80% of methanol is produced from natural gas as the feedstock, and methanol production is concentrated in regions where natural gas is cheap and available, e.g. Asia and Europe.

Conventional methanol synthesis consists of several main steps: feed gas purification, steam reforming, heat recovery, synthesis, and distillation, as illustrated in Figure 2.3 (Hugill *et al.*, 2001).

Methanol is produced by the hydrogenation of carbon oxides over a suitable catalyst, according to the following reactions:

$$\begin{aligned} CO + 2H_2 &\Leftrightarrow CH_3OH \\ CO_2 + 3H_2 &\Leftrightarrow CH_3OH + H_2O \end{aligned} \qquad \text{(Eq. 2.1)}$$

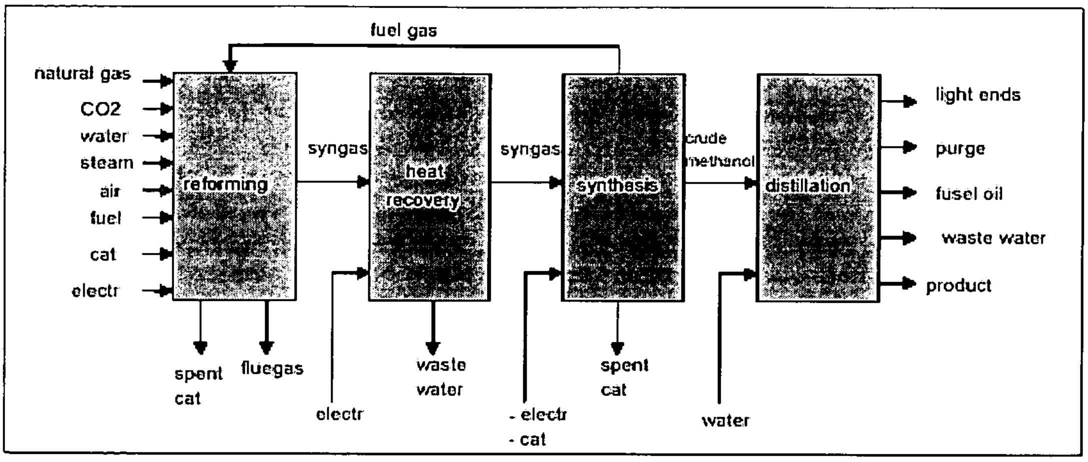


Figure 2.3 Methanol conventional process technology

The typical reaction conditions are at a temperature of 225-270°C and a pressure of 50-100 bar. Higher pressure favor higher conversion, as according to Le Chatelier's rule, the volume of the products is less than the volume of the reactants. Both reactions are isothermic. The first reaction gives 21.7 kcal of heat per gram mole of carbon monoxide while the later gives 12.8 kcal per gram mole of carbon dioxide. However, high temperature reduces catalyst life seriously. This is the most difficult part in designing methanol synthesis, where precise temperature had to be controlled to achieve optimum catalyst life and reaction rate (Hugill *et al.*, 2001).

A technology commercially used by Coogee Chemicals involves similar processes. The gas is first compressed and then purified by removing sulfur compounds. The purified natural gas is saturated with heated and recycled process waste water. The mixed natural gas and water vapor then goes to the gas heated reformer to be partially converted to synthesis gas, a mixture of carbon dioxide, carbon monoxide and hydrogen. This partially converted gas is then completely converted to synthesis gas by reaction with oxygen in the secondary reformer. The synthesis gas is then converted to crude methanol in the catalytic synthesis converter. The crude methanol is purified to standard quality specifications by removing water and organic impurities through distillation. The water and organic impurities are recycled (Coogee, 2003).

On the other hand, there have been several researches done on alternative methanol technology for the new age. For example, direct conversion from methane, production of methanol from biomass, hydrolysis of methyl acetate with water, and methanol synthesis from synthesis gas with presence of catalyst in liquid phase. Some of the routes are reviewed in the following paragraphs.

2.3.1 Hydrolysis of Methyl Acetate

Esters are derived from carboxylic acids. A carboxylic acid contains the -COOH group, and in an ester the hydrogen in this group is replaced by a hydrocarbon group of some kind (Clark, 2003).

Hydrolysis is a reaction involving water. It occurs when esters are hydrolyzed by water or by dilute acids such as dilute hydrochloric acid. The alkaline hydrolysis of esters actually involves reaction with hydroxide ions. The reaction with pure water is so slow that it is never used. Hence, hydrolysis is done either in acidic or alkaline condition. For an acidic condition of hydrolysis, the reaction is catalyzed by dilute acid, and so the ester is heated under reflux with a dilute acid such as dilute hydrochloric acid or dilute sulphuric acid.

An example of hydrolysis using an acid catalyst is shown in the hydrolysis of ethyl ethanoate:

$$CH_3CH_2COOCH_3 + H_2O \xleftrightarrow{H^+(aq)} CH_3CH_2COOH + CH_3OH \qquad \text{(Eq.2.2)}$$

The reaction is reversible. To make the hydrolysis as complete as possible, an excess of water is desired. The water comes from the dilute acid, and so the ester is mixed with an excess of dilute acid.

On the other hand, hydrolysis using dilute alkali is the usual way of hydrolyzing esters. The ester is heated under reflux with a dilute alkali like sodium hydroxide solution. There are two advantages of doing this rather than using a dilute acid. Firstly, the reactions are one-way rather than reversible, and secondly, the products are easier to be separated. Taking the same ester, i.e. ethyl ethanoate, but using sodium hydroxide solution rather than a dilute acid, hydrolyzing methyl propanoate using sodium hydroxide solution gives:

$$CH_3CH_2COOCH_3 + NaOH \rightarrow CH_3CH_2COONa + CH_3OH \qquad \text{(Eq. 2.3)}$$

Sodium salt is now formed rather than the carboxylic acid itself. This mixture is relatively easy to be separated. An excess of sodium hydroxide solution is used for complete reaction that leave no esters. The alcohol formed can be distilled off at the end of the reaction.

Complicated esters can be hydrolyzed to make soap. This following paragraphs describe the alkaline hydrolysis (using sodium hydroxide solution) of the long-chained esters found in animal and vegetable fats and oils. If the large esters present in animal or vegetable fats and oils are heated with concentrated sodium hydroxide solution exactly the same reaction happens as with the simple esters. A salt of a carboxylic acid is formed, in this case, the sodium salt of a large acid such as octadecanoic acid (stearic acid). These salts are the important ingredients of soap used for cleaning (Clark, 2003). A longer chain alcohol is produced, such as propane-1,2,3-triol (glycerol). Because of its relationship with soap making, the alkaline hydrolysis of esters is known as saponification. Carboxylic esters hydrolyze to the parent carboxylic acid and an alcohol. This reaction is known as saponification because it is the basis of making soap from glycerol trimesters in fats.

In this research the saponification reaction is further studied by reacting methyl acetate and calcium hydroxide, producing methanol and calcium acetate as an alternative route due to the potential to synthesize both raw materials from abundant supply of neutral resources.

Methyl acetate hydrolyzes to form acetic acid and methanol, according to the following reaction:

$$2CH_3COOCH_3 + Ca(OH)_2 \rightarrow 2CH_3OH + (CH_3COO)_2Ca \qquad \text{(Eq. 2.4)}$$

The reaction is extremely slow in pure water, but is catalyzed by both hydronium and hydroxide ions (Williams, 2004).

Yu *et al.* (2005) states in order to obtain more valuable compound, it is very necessary to hydrolyzed large amount of by-product, methyl acetate (MeOAc), to methanol (MeOH) and acetic acid (HOAc) in the industrial polyvinyl alcohol plant, which are recycled to the methanolysis reaction of polyvinyl acetate and the synthesis of vinyl acetate, respectively. However, the conversion of methyl acetate is low in the traditional process that consists of a packed bed reactor followed by a series of distillation columns for the separation of components, due to the equilibrium limitation. Yu *et al.* suggested a system to improve the performance by using simulated moving bed reactor (SMBR) called Varicol process for hydrolysis of methyl acetate. SMB systems are used in industry for separations that are either impossible or difficult using traditional separation techniques. In this article, a comprehensive multi-objective optimization study of SMBR and Varicol systems for the hydrolysis of methyl acetate is reported. The non-dominated sorting algorithm was used in obtaining Pareto optimal solutions. The multi-objective optimization problems were formulated aiming at simultaneous maximization of purity and yield of both raffinate and extract stream. Effect of column length, raffinate flow rate, effluent flow rate, and distributed feed flow were studied.

2.3.2 Liquid Phase Methanol Synthesis

A process proposed by Chem. Systems Inc. called LPMeOH™ (Liquid Phase Methanol) offers considerable advantages over the conventional vapor phase synthesis of methanol in the areas of heat transfer, exothermicity, and selectivity toward methanol. However, this process suffers from the drawback that the methanol synthesis reaction is a thermodynamically governed equilibrium reaction (Frank, 1982). Methanol concentration in the liquid phase in the vicinity of the catalyst sites is quite high due to its low solubility. Thus the productivity of the liquid phase methanol synthesis as well as the conversion of syngas could be limited by the chemical equilibrium barrier caused by the high local methanol concentration in the liquid phase. One of the routes to alleviate this limitation is the in-situ dehydration of methanol with dimethyl ether (DME). Co-production of DME along with methanol significantly improves the methanol reactor productivity. This single step liquid phase synthesis of DME from coal or natural gas based syngas is extremely significant from both key advantages of this process over methanol synthesis include higher methanol reactor productivity, higher syngas conversion, and lesser dual catalyst deactivation and crystal growth (Frank, 1982).

2.3.3 Methanol Production from Biomass

In the near future, the economy of methanol production through coal and biomass gasifications can be achieved by their linking with modern gas-steam power systems (Tomasz & Mareck, 2003). Specht *et al.* (1998) investigates methanol generation concepts via synthesis gas production from biomass and a subsequent CO/CO_2 hydrogenation. Figure 2.4 shows flow diagram for a methanol synthesis plant via biomass utilization.

According to them, the utilization of biomass for methanol production via gasification faces the problem of a large excess carbon in the produced synthesis gas. The stoichiometric adjustment can be accomplished either by adding hydrogen or by removing carbon in form of carbon dioxide. The addition of hydrogen allows a nearly complete utilisation of the carbon contained in the biomass, with a high methanol production rate. But hydrogen admixture to the synthesis gas requires supplementary investments for an electrolysis unit. The removal of carbon dioxide is less investment intensive, but due to the extremely low carbon conversion efficiency of about 20 % of the biomass carbon content, the methanol production costs become very high. An acceptable way is a partial compensation of the carbon excess by adding electrolytic hydrogen (using the oxygen for the gasifying process), saving about half of the carbon from the biomass and avoiding extremely high investment and electricity costs.

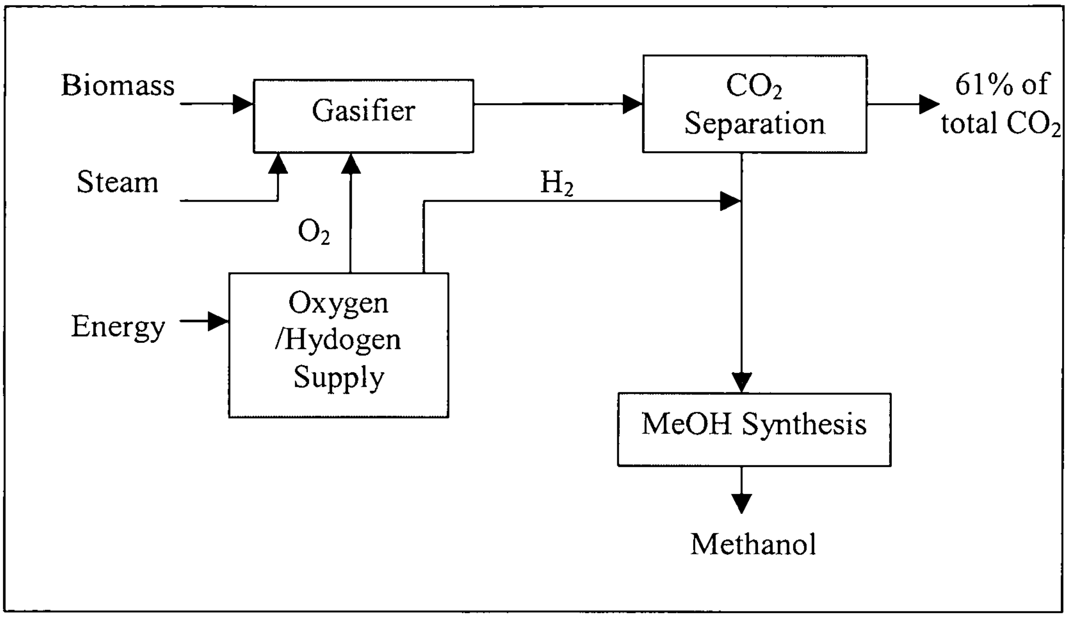


Figure 2.4: Flow diagram for a methanol synthesis plant with oxygen/hydrogen supply and CO_2 removal unit

Table 2.2: Comparison of techniques to produce methanol

Process	**Operating**	**Reference**	**Year**
Steam/methane reforming to methanol	High Pressure Heat Exchange	DOE	1992
Oxidation of methane to methanol	Methyl bisulfate	Horsely *et al.*	1995
Co-current production of methanol and DME	Carbon dioxide hydrogenation	Jun *et al.*	1999
Direct methanol synthesis from methane	Nonthermal plasma approach	Okumoto & Mizuno.	2001

Table 2.2 gives the summary of techniques to produce methanol. All of the techniques operate at pressure of between and temperature of range. Thus, this research work provides another alternative route to produce methanol from methyl acetate at milder operating condition.

2.4 Study of stoichiometric equation

Rahman & Somalu (2003) reported that the reaction rate constant for the hydrolysis of ethyl acetate can be determined conductometrically, since the stoichiometry of the reaction can be expressed as

$$CH_3COOC_2H_5 + OH^- \Leftrightarrow CH_3COO^- + C_2H_5OH \qquad \text{(Eq. 2.5)}$$

As the reaction proceeds, hydroxyl ion is consumed and acetate ion is produced. Hydroxyl ion has a very much larger specific conductivity than acetate ion. Since the conductivities of ethanol and ethyl acetate are negligibly small in comparison with those of the ions, the conductance of a solution containing all four species is dominated by the hydroxyl ion concentration, and the rate of disappearance of hydroxyl ion from the reacting mixture can be determined by measuring and extrapolating the conductance of the solution.

Theoretically, the rate of a second order reaction is proportional to the concentrations of the two species. If C_A and C_B are the concentrations of acetate and base, respectively, then the second order specific reaction rate constant k is defined by the reaction

$$-\frac{dC_A}{dt} = -\frac{dC_B}{dt} = kC_A C_B \qquad \text{(Eq. 2.6)}$$

As a is the initial concentration of ethyl acetate and b is the initial concentration of base, while x represents the number of moles per liter of either OH^- or $CH_3COOC_2H_5$ that have reacted at time t, then at time t the concentrations are $C_A = a - x$ and $C_B = b - x$. The rates $\frac{-dC_A}{dt}$ and $\frac{-dC_B}{dt}$ are then $+\frac{dx}{dt}$ and Eq. 3.4 may be written as

$$\frac{dx}{dt} = k(a - x)(b - x) \qquad \text{(Eq. 2.7)}$$

Equation 2.7 is a first order ordinary differential equation, which can be solved by integrating between limits of zero time (concentrations are the initial concentrations a and b) and time t later (when the concentrations are $(a - x)$ and $(b - x)$. Two cases must be treated separately. If the initial concentrations are equal ($a = b$), the rate constant is given as

$$k = \frac{1}{t}\frac{x}{a - x} \qquad \text{(Eq. 2.8)}$$

If the initial concentrations are different ($a \neq b$), the integration proceeds differently and the result is as given in Equation 2.9.

$$k = \frac{1}{t(a-b)} \ln\left[\frac{b(a-x)}{a(b-x)}\right] \qquad \text{(Eq. 2.9)}$$

For this work, since the reaction involves methyl acetate, same concept applies but the corresponding stoichiometric equation is given as follows:

$$CH_3COOCH_3 + OH^- \Leftrightarrow CH_3COO^- + CH_3OH \qquad \text{(Eq. 2.10)}$$

2.4.1 Reaction order

Foggler (1999) wrote that the dependence of the reaction rate $-r_A$ on the concentrations of the species present, fn(C_j), is determined by experimental observation. Although the functional dependence may be postulated from theory, experiments are necessary to verify the proposed form. One of the most general forms of this dependence is the product of concentrations of the individual reacting species, each of which is raised to a power, for example,

$$-r_A = k_A^{'} C_A^{\alpha} C_B^{\beta} \qquad \text{(Eq. 2.11)}$$

The exponents of the concentrations in Equation 2.10 lead to the concept of reaction order. The 'order of a reaction' refers to the powers to which the concentrations are raised in the kinetic rate law. In equation 3.9, the reaction is α order with respect to reactant A, and β order with respect to reactant B. The overall order of the reaction, n, is

$$n = \alpha + \beta \qquad \text{(Eq. 2.12)}$$

2.4.2 Rate of reaction

Foggler (1999) also wrote that if a rate law depends on the concentration of more than one species, it is necessary to choose a linearized least-squares method to solve for the rate law and kinetic order. This method of analysis is also useful to determine the best values of the rate law parameters from a series of measurements when three or more parameters are involved, for example, the reaction order (α) and the activation energy (E_a).

As stated in Equation 2.12, the rate law of the saponification reaction in this study is postulated as:

$$-r_A = k_A C_A^{\alpha} C_B^{\beta} \qquad \text{(Eq. 2.13)}$$

The rate law depends on the concentration of more than one species and it is not possible to use the method of excess due to the solubility limitation of $Ca(OH)_2$. Therefore the linearized least-squares method is used to determine the rate law of this reaction. This method of data analysis is also useful to determine the best valued of the rate law parameters from a series of measurements when three or more parameters are involved (e.g., reaction order, α; frequency factor, A; and activation energy, E).

Linearized least-squares method

A mole balance on a constant-volume semi-batch reactor gives

$$-\frac{dC_A}{dt} = -r_A = kC_A^{\alpha} C_B^{\beta} \qquad \text{(Eq. 2.14)}$$

If the method of initial rates is used, then

$$\left(-\frac{dC_A}{dt}\right)_0 = -r_{A0} = kC_{A0}^{\alpha} C_{B0}^{\beta} \qquad \text{(Eq. 2.15)}$$

Taking the log of both sides, it will give

$$\ln\left(-\frac{dC_A}{dt}\right)_0 = \ln k + \alpha \ln C_{A0} + \beta \ln C_{B0} \qquad \text{(Eq. 2.16)}$$

Letting $Y = \ln(-dC_A/dt)_0$, $X_1 = \ln C_{A0}$, $X_2 = \ln C_{B0}$, $a_0 = \ln k$, $a_1 = \alpha$, and $a_2 = \beta$.

Then,

$$Y_j = a_0 + a_1 X_{1j} + a_2 X_{2j} \qquad \text{(Eq. 2.17)}$$

where $X_{1j} = \ln C_{A0j}$, with C_{A0j} being the initial concentration of the jth run. The best values of the parameters a_0, a_1, and a_2 are found by solving Equations 2.15 through 2.17 simultaneously. There are now three linear equations and three unknowns which can solve for: a_0, a_1, and a_2. Consequently k, α, β can be found.

2.4.3 Activation Energy

The reaction rate constant k is not truly a constant, but merely independent of the concentrations of the species involved in the reaction. The quantity 1 is also referred to as the specific reaction rate (constant). It is almost always strongly dependent on temperature.

$$k_A(T) = Ae^{-E/RT} \qquad \text{(Eq. 2.18)}$$

The activation energy is determined experimentally by carrying out the reaction at several different temperatures. After taking the natural logarithm of Equation 2.17

$$\ln k_A = \ln A - \frac{E}{R}\left(\frac{1}{T}\right) \qquad \text{(Eq. 2.19)}$$

It can be seen that a plot of ln k_A versus $\frac{1}{T}$ should be a straight line whose slope is proportional to the activation energy.

2.5 Semi-batch Reactor vs. Continuous Stirred Tank Reactor

2.5.1 Semi-Batch Reactor

According to Foggler (1999), in a case of semi-batch system, it is necessary to predict the concentration and conversion as a function of time. Closed-form analytical solutions to the differential equations arising from the mole balance of these reaction types can be obtained only for zero- and first-order reactions.

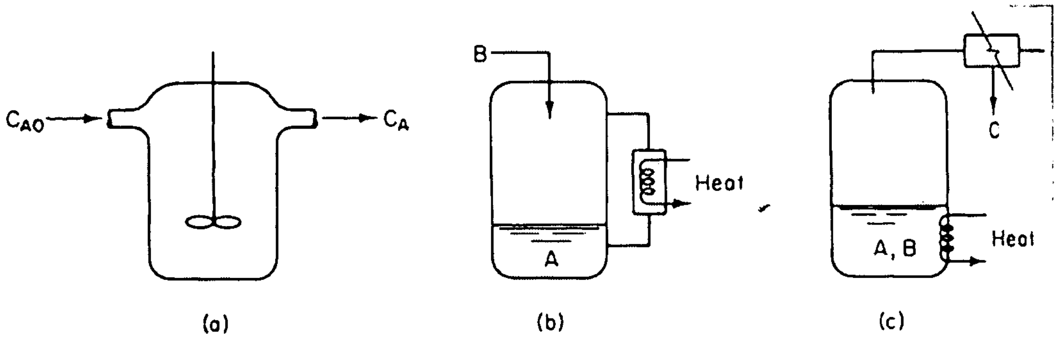


Figure 2.5 Semi-batch reactors

There are two basic types of semi-batch operations. In one type, as in Eq. 2.20, one of the reactants in the reaction

$$A + B \rightarrow C + D \qquad \text{(Eq.2.20)}$$

(e.g., B) is slowly fed to a reactor containing the other reactant (e.g., A), which has already been charged to a reactor such as that shown in Figure 2.5(b). This type of reactor is generally used when unwanted side reactions occur at high concentrations of B, or the reaction is highly exothermic. In some reactions, the reactant B is a gas and is bubbled continuously through liquid reactant A. Examples of reactions used in this type of semi-batch reactor operation include ammonolysis, chlorination and hydrolysis. The other type of semi-batch reactor is shown schematically in Figure 2.5(c). Here reactants A and B are charged simultaneously and one of the products is vaporized or withdrawn continuously. Removal of one of the products in this manner (e.g., C) shifts the equilibrium towards the right, increasing the final conversion above that which would be achieved had C not been removed. In addition, removal of one of the products further concentrates the reactant, thereby producing an increased rate of reaction and decreased processing time. This type of reaction operation is called reactive distillation. Examples of reactions carried out in this type of reactor include acetylation reactions and esterification reactions in which water is removed.

A schematic diagram of this semi-batch reactor is shown in Figure 2.6. In this study, the elementary liquid-phase reaction with constant molar feed is considered,

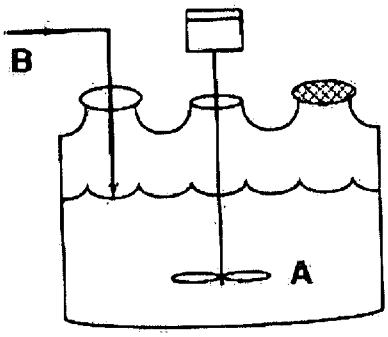


Figure 2.6: Schematic of Semi-batch reactor

in which reactant B is slowly added to a vessel containing reactant A. A mole balance on species A yields

$$\begin{bmatrix}\text{rate}\\ \text{in}\end{bmatrix}-\begin{bmatrix}\text{rate}\\ \text{out}\end{bmatrix}+\begin{bmatrix}\text{rate of}\\ \text{generation}\end{bmatrix}=\begin{bmatrix}\text{rate of}\\ \text{accumulation}\end{bmatrix} \qquad \text{(Eq. 2.21)}$$

$$0 \;-\; 0 \;+\; r_A V(t) \;=\; \frac{dN_A}{dt} \qquad \text{(Eq. 2.22)}$$

There are three variables that can be used to formulate and solve semi-batch reactor problems: the concentration, C_j, the number of moles, N_j, and the conversion, X.

2.5.2 Semi-Batch Reactor Equations in Terms of Concentrations

For the reaction of saponification process, the reaction is written as in Eq. 2.4

$$2CH_3COOCH_3 + Ca(OH)_2 \rightarrow 2CH_3OH + (CH_3COO)_2Ca \qquad \text{(Eq. 2.4)}$$

$$(2A) \quad + \quad (B) \quad \rightarrow \quad (2C) \quad + \quad (D)$$

Writing the mole balance of A, recalling that the number of moles of A is just the product of concentration of *A*, C_A, and the volume *V*, Equation (4-51) can be rewritten as

$$r_A V = \frac{d(C_A V)}{dt} = \frac{V dC_A}{dt} + C_A \frac{dV}{dt} \qquad \text{(Eq. 2.23)}$$

Since the reactor is being filled, the volume, *V*, varies with time. The reactor volume at any time *t* can be found from an overall mass balance of all species:

$$[\text{rate in}] - [\text{rate out}] + [\text{rate of generation}] = [\text{rate of accumulation}]$$

$$\rho_o v_o \quad - \quad 0 \quad + \quad 0 \quad = \quad \frac{d(\rho V)}{dt} \qquad \text{(Eq.2.24)}$$

For a constant-density system, $\rho_0 = \rho$, and

$$\frac{dV}{dt} = v_o \qquad \text{(Eq. 2.25)}$$

with the initial condition $V = V_0$ at $t = 0$,integrating for the case of constant Volumetric flow rate v_o yields

$$V = V_o + v_o t \qquad \text{(Eq. 2.26)}$$

Substituting Equation (2.24) into the right hand side of Equation (2.25) and rearranging gives us

$$-v_o C_A + V r_A = \frac{V dC_A}{dt} \qquad \text{(Eq.2.27)}$$

The balance of A [i.e. Equation (2.23)] can be rewritten as

$$\frac{dC_A}{dt} = r_A - \frac{v_o}{V} C_A \qquad \text{(Eq. 2.28)}$$

From the rate law,

$$-r_A = k_A' C_A^{\alpha} C_B^{\beta} \qquad \text{(Eq. 2.9)}$$

Eq. 2.27 can be rewritten as

$$\frac{dC_A}{dt} = -k C_A C_B^{\ 2} - \frac{v_o}{V} C_A \qquad \text{(Eq. 2.29)}$$

A mole balance of B, in this case, that is fed to the reactor at a rate F_{Bo} is

In – Out + Regeneration = Accumulation

$$F_{Bo} - 0 + r_B V = \frac{dN_B}{dt} \qquad \text{(Eq. 2.30)}$$

Rearranging

$$\frac{dN_B}{dt} = r_B V + F_{Bo} \qquad \text{(Eq. 2.31)}$$

Differentiating N_B ($N_B = C_B V$),

$$\frac{dVC_B}{dt} = \frac{dV}{dt}C_B + \frac{VdC_B}{dt} = r_B V + F_{Bo} = r_B V + v_o C_{Bo} \qquad \text{(Eq. 2.32)}$$

Substituting Equation (2.25) in terms of V and differentiating, the mole balance on B becomes

$$\frac{dC_B}{dt} = r_B + \frac{v_o(C_{Bo} - C_B)}{V} \qquad \text{(Eq. 2.33)}$$

From the rate law,

$$-r_B = 2r_A \qquad \text{(Eq. 2.34)}$$

Eq. 2.31 can be rewritten as

$$\frac{dC_B}{dt} = -2kC_A C_B{}^2 - \frac{v_o(C_{B_o} - C_B)}{V} \qquad \text{(Eq. 2.35)}$$

Writing the mole balance of C and D,

$$[\text{rate in}] - [\text{rate out}] + [\text{rate of generation}] = [\text{rate of accumulation}]$$

$$0 \quad - \quad 0 \quad + \quad r_C V \quad = \quad \frac{dN_C}{dt} \qquad \text{(Eq. 2.36)}$$

$$\frac{dN_C}{dt} = \frac{dC_C}{dt} = V\frac{dC_C}{dt} + C_C\frac{dV}{dt} \qquad \text{(Eq. 3.37)}$$

Therefore,

$$r_C V = V\frac{dC_C}{dt} + v_o C_C \qquad \text{(Eq. 2.38)}$$

$$\frac{dC_C}{dt} = r_C - \frac{v_o}{V}C_C \qquad \text{(Eq. 2.39)}$$

From the rate law,

$$r_C = 2r_A \tag{Eq. 2.40}$$

$$r_D = r_A \tag{Eq. 2.41}$$

Eq. 2.35 can be rewritten as

$$\frac{dC_C}{dt} = 2kC_A C_B^{\ 2} - \frac{v_o}{V} C_C \tag{Eq. 2.42}$$

and

$$\frac{dC_D}{dt} = kC_A C_B^{\ 2} - \frac{v_o}{V} C_D \tag{Eq. 2.43}$$

2.5.3 Continuous Stirred Tank Reactors

A stirred tank operated continuously is a type of reactor used very commonly in industrial processing. It is referred to as the continuous-stirred tank reactor (CSTR) or backmix reactor. The reactor is usually run at steady state by feeding the reactants into the reactor and continuously withdrawing the products. It is perfectly well-mixed and has no spatial variation in concentration or temperature. As a result of the second quality, the CSTR is generally modeled as having no spatial variations in concentration, temperature, or reaction are throughout the vessel. Since the temperature and the concentration are identical everywhere within the reactor vessel, they are the same at the exit point as they are elsewhere in the tank. Thus the temperature and concentration in the exit stream are modeled as being the same as those inside the reactor. In systems where mixing is highly non-ideal, the well-mixed model is inadequate, hence other techniques, such as residence-time distributions, to obtain meaningful results is resorted.

When a general mole balance equation

$$F_{j0} - F_j + \int^{V} r_j dV = \frac{dN_j}{dt} \tag{Eq. 2.44}$$

is applied to a CSTR operated at steady state (i.e., conditions do not change with time),

$$\frac{dN_j}{dt} = 0 \qquad \text{(Eq. 2.45)}$$

in which there are no spatial variations in the rate of reaction,

$$\int^{V} r_j dV = Vr_j \qquad \text{(Eq. 2.46)}$$

it takes the familiar form known as the design equation for a CSTR:

$$V = \frac{F_{j0} - F_j}{-r_j} \qquad \text{(Eq. 2.47)}$$

The CSTR design equation gives the reactor volume necessary to reduce the entering flow rate of species, *j*, F_{jo}, to the exit flow rate F_j. A CSTR is modeled such that the conditions in the exit stream (e.g. concentration, temperature) are identical to those in the tank. The molar flow rate F_j is just the product of the concentration of species *j* and the volumetric flow rate *v*:

$$F_j = C_j \cdot v \qquad \text{(Eq. 2.48)}$$

2.5.4 Yield and Conversions

Yield is defined as the fraction of the limiting reactant that is converted to the specific product. The yield may be based on the total amount of the limiting reactant fed, or the amount of the limiting reactant that is consumed by all the reactions.

Hence, it is necessary to calculate the yield of the methanol produced to obtain a more significant figure of methanol produced from the reaction by using the equation:

$$Yield = \frac{moles\ of\ methanol\ produced}{moles\ of\ methyl\ acetate\ fed} \times 100\% \qquad \text{(Eq. 2.49)}$$

Conversion is defined as:

$$Conversion = \frac{initial\ mole\ of\ methyl\ actate - final\ mole\ of\ methyl\ acetate}{initial\ mole\ of\ methyl\ acetate} \times 100\% \qquad \text{(Eq. 2.50)}$$

2.6 Taguchi Techniques in Engineering Application

Taguchi method has been widely used in the engineering application in order to optimize a process or product. Several papers are reviewed as evidences to support the usage of this method in optimizing engineering process related to reaction engineering.

Optimization methodology adopted by Prasad *et al.* (2005) in their study was divided into four phases (with various steps), i.e. planning, conducting, analysis and validation. The schematic representation of the designed methodology was depicted in Figure 2.5. Taguchi method of DOE involves establishment of large number of experimental situation described as OAs to reduce experimental errors and to enhance their efficiency and reproducibility of the laboratory experiments. Each phase has separate objective, inter connected in sequence wise to achieve the overall optimization process.

Ali *et al.* (2004) employed Taguchi method to optimize a newly developed time-modulated chemical vapor deposition process. The implementation of the Taguchi method to optimize the TMCVD process can effectively save valuable time, considerable effort and money since the Taguchi method significantly reduces the number of experiments required to optimize a fabrication process. In the study, they investigated the effect of five TMCVD process parameters on five key factors of the as-frown samples. Each parameter was varied at four different values (experimental levels). After considering the experimental levels, the five parameters were optimized after performing only 16 experiments. The as-grown films were characterized for hardness, quality, surface roughness, and microstructure using SEM, Raman spectroscopy, surface profilometry and Vickers hardness testing.

Wu *et al.* (2004) applies the Taguchi method to optimize the process parameters for the die casting on thin-walled magnesium alloy parts in computer, communications, and consumer electronics (3C) industries. The study investigated the effects of various die casting control parameters, including the die temperature, injection velocity, and cooling time upon the surface warping of magnesium alloy die cast components. The Taguchi robust design method had revealed that the outlet temperature of the temperature controller and the use of natural cooling play important roles in determining the warping of the personal data assistant (PDA) cover surface. The ANOVA results indicate that the die temperature, the injection delay time, and the die temperature distribution have a less significant effect on the surface warping of the die cast product.

Kim *et al.* (2004) uses Taguchi robust design method with L9 orthogonal array to optimize experimental conditions for the preparation of nano-sized silver particles using chemical reduction method. Particle size and the particle size distribution of silver nano-particles were considered as the properties. Molar concentration ratio of *R* value, concentration of dispersant, and feed rate of reactant were chosen as main parameters. As a result of Taguchi analysis in this study, the concentration of dispersant was the most influencing parameter on the particle size and the size distribution. The feed rate of reactant had also principal effect on particle size distribution. The optimal conditions were determined by using Taguchi robust design method.

Nihal *et al.* (2006) performed a study to determine the effective operating parameters and the optimum conditions of a batch saponification process in the frame of the process improvement. Full-two level factorial and face-centered composite (FCCC) Statistical Experimental Design Methods were used successively. Parameters were examined by investigating interaction effects of temperature, agitation rate, and initial sodium hydroxide and ethyl acetate concentrations. Selected process response was the fractional conversion rate of sodium hydroxide. Temperature and agitation rate were found to have no effect on the response at the 10% selected significance level. Examination of the residuals served as a diagnostic check of the model and it was found that the model was good enough to fit the experimental data. Optimum operating conditions at which maximum conversion rate of sodium hydroxide was obtained about 100% were found to be 0.01 mol/L sodium hydroxide and 0.1 ml/L ethyl acetate by applying Response Surface Method (RSM). With the use of the residual analysis and statistical techniques, more reliable and proper results were obtained at the process improvement stage of the saponification process.

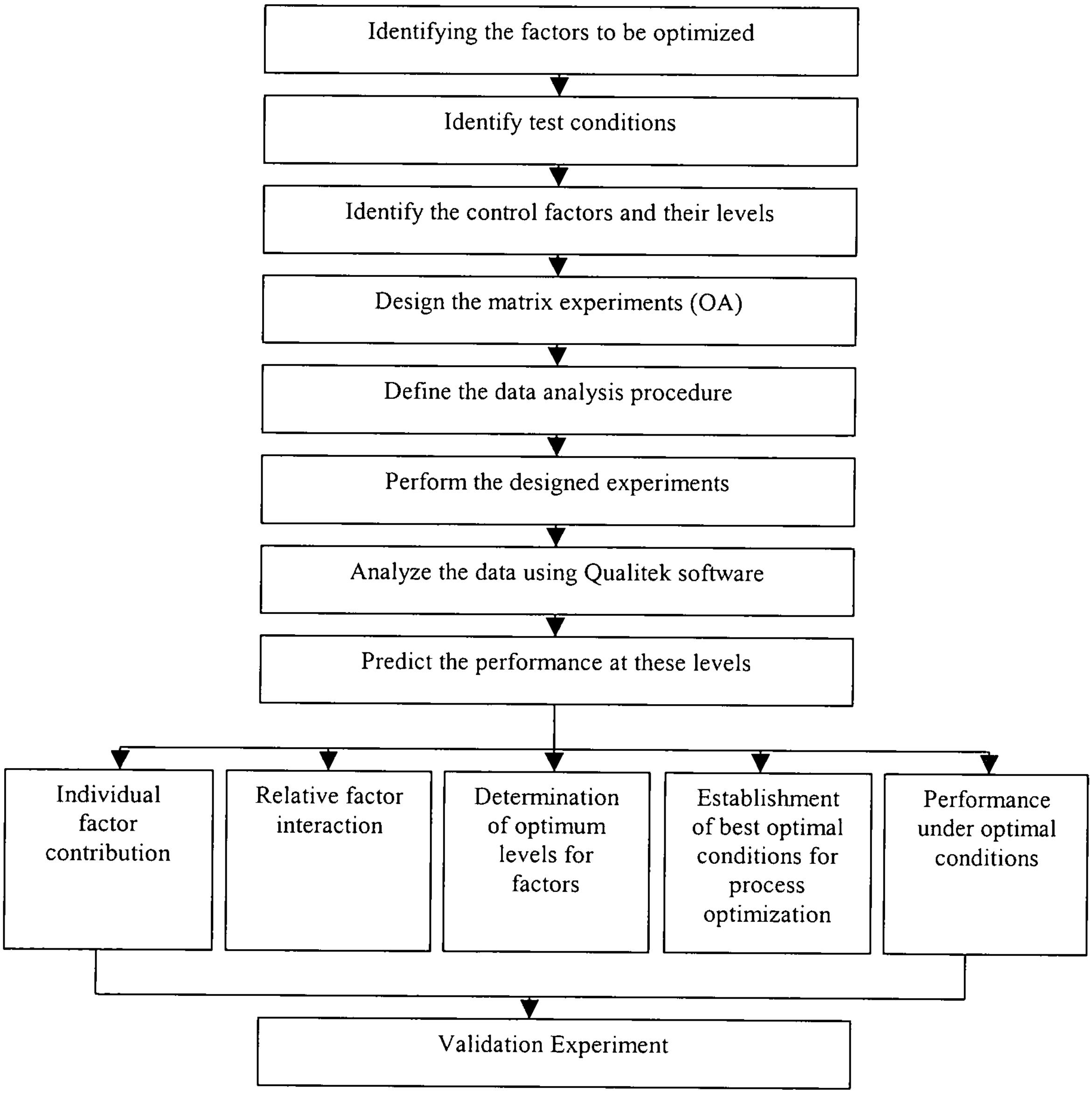


Figure 2.7: Schematic representation of the steps involved in the Taguchi DOE methodology designed for optimization (Ross, 1996)

In this work, further application of Taguchi technique to screen significant variables affecting the yield of methanol is explored.

2.7 Comparison of reactors configuration

Rahman & Somalu (2003) compared plug-flow reactor (PFR) and continuous stirred tank reactor (CSTR) for the saponification process. The research was done to investigate the second order chemical reaction between 0.05 M sodium hydroxide and 0.05 M ethyl acetate in both reactors. The performance of these reactors with different temperature, range from 30 to 50°C, was investigated. The flow rate was set to 60mL/min. The analysis of the parameters such as conversion of the reactant, rate constant, and activation energy were used to determine the performance of the reactors. The overall results showed that the performance of the PFR is 10 to 20% better than CSTR with respect to temperature variation.

Grau *et al.* (2002), investigated two chemical reactions with different behavior in batch and semibatch reactors, states that for the ethyl acetate saponification reaction. They found possible to operate the reactor in both modes of operation (batch and semibatch). For the saponification process the concentration evolution with time for different components were obtained by measuring the pH value. The work focuses in the interest to obtain the concentrations of the species in the reactor, by measuring experimentally with different sensors (pH, temperature, etc.) the needed values to get the concentration profiles.

Since reactor configuration influences a process performance, current work explored the performance of Continuous Stirred Tank Reactor (CSTR) and Semi-batch reactor for the saponification reaction involving methyl acetate and calcium hydroxide.

CHAPTER 3: DESIGN OF EXPERIMENT

This chapter discusses the importance of designing experiment and the options available for methods of designing the experiment. Details on the principle of Taguchi Technique are also discussed to strengthen the reasons of selecting the technique.

3.1 Introduction to Design of Experiment (DOE)

Lazic (2004) stated that an experiment takes a central place in science, particularly nowadays, due to the complexity of problems science deals with. The question of efficiency of using an experiment is therefore imposed.

A designed experiment is the simultaneous evaluation of two or more factors (parameters) for their ability to affect the resultant average or variability of particular product or process characteristics. To accomplish this in an effective and statistically proper fashion, the levels and the factors are varied in a strategic manner. The results of the particular test combinations are then observed, and the complete set of results is analyzed to determine the influential factors and preferred levels. We can also then determine whether increases or decreases of those levels will potentially lead to further development and improvement.

3.2 The Design of Experiments Process

The purpose of process development is to improve the performance characteristics of the process relative to customer needs and expectations. The purpose of experimentation should be to understand how to reduce and control variation of a product or process; subsequently, decisions must be made concerning which parameters affect the performance of the process. The loss function quantifies the need to understand which design factors influence the average and variation of a performance characteristic of a process. By properly adjusting the average and reducing variation, the process losses can be minimized.

To design the experiment is to develop a scheme or layout of the different conditions to be studied. The Taguchi design of experiment can be used to optimize many designs. An experiment must satisfy two objectives. First, the number of trials must be determined. Second, the conditions for each trial must be specified.

For this particular process or chemical reaction, it is crucial to identify the parameters that might be influencing the final product, which is the yield of methanol. The parameters will determine the number of trials and the orthogonal array suitable for the experimental design. The use of orthogonal arrays is just one methodology to design an experiment, but is the most flexible in accommodating a variety of situations and yet easy for non-statistical oriented individuals to execute on a practical basis.

3.3 Selection of experimental design

NIST (2003) said that the choice of an experimental design depends on the objectives of the experiment and the number of factors to be investigated. There are several types of design, according to the experimental objective they meet. They include comparative objective, screening objective, response surface objective, optimizing responses when factors are proportion of a mixture objective and optimal fitting of a regression model objective. Table 3.1 shows the summary of selection of designs.

Table 3.1: Summary of selection of design

Number of Factors	Comparative Objective	Screening Objective	Response Surface Objective
1	1-factor completely randomized design	–	–
2 - 4	Randomized block design	Full or fractional factorial	Central composite or Box-Behnken
5 or more	Randomized block design	Fractional factorial or Plackett-Burman	Screen first to reduce number of factors

Choice of a design from within these various types depends on the amount of resources available and the degree of control over making wrong decisions (Type I and Type II errors for testing hypotheses) that the experimenter desires. It is a good idea to choose a design that requires somewhat fewer runs than the budget permits, so that center point runs can be added to check for curvature in a 2-level screening design and backup resources are available to redo runs that have processing mishaps.

3.4 Traditional Scientific Approach of experimental design

Ross (1996) suggested that the traditional scientific approach of experimental design is used to either evaluate one variable at a time, several variables at a time (i.e. changing levels or values of variables, one at a time while holding all other constant) or to evaluate several variables, all at the same time. The interaction effect between the variables studied the percentage contribution of each variable and the uncontrollable errors can also be investigated by these techniques.

3.5 Experimental design based on full factorial method

The technique of laying out the conditions of experiments involving multiple factors was first proposed by the Englishman, Sir R.A. Fisher. The method is popularly known as the factorial design of experiments. In a full factorial design method, all possible combinations of variables' levels are investigated in each complete trial (run) or repetition of the experiment. For example, if there are 'x' levels of variable X and 'y' levels of variable Y, then each trial (run) or repetition, involves a combined treatment of 'xy'. To see clearly a full factorial experiment layout, Table 3.2 below is referred:

Table 3.2: Example of Array for 2 factor at 2 levels

Trial number	**X**	**Y**
1	1	1
2	1	2
3	2	1
4	2	2

where:

X and Y denote the variables

1 and 2 in the X and Y columns denote the values or levels of the variables under investigation (1: lower value, 2: higher value)

For this full factorial method, in order to find the number of trials required, the equation used is:

$$N = L^f \qquad \text{(Eq. 3. 1)}$$

where:

N = total number of trials

f = number of variables

L = total number of levels or values of the variables under investigation

According to the Table 3.2 above, the number of variable is two, which are X and Y, and the total number of levels of the variables under investigation (L) are two as well. Then by using equation 3.51, total number of trials is four.

This factorial design also allows interaction between the variables to be investigated. This determines whether the effect of one variable, say (X) depends on the level or value chosen for variable Y. If the effect of variable X does not depend on the level chosen for variable Y, there is no interaction between the variables X and Y. Since most industrial experiments usually involve a significant number of factors, a full factorial design results in a large number of experiments. Hence, a full factorial experiment is applicable only when there are a few variables to be investigated (Yusup, 1998), otherwise, it is not an economical option from both the time and the financial perspective since there are too many trials required. To reduce the number of experiments to a practical level, only a small set from all the possibilities is selected. The method of selecting a limited number of experiments which produces the most information is known as a partial fraction experiment. Although this method is well known, there are no general guidelines for its application or the analysis of the results obtained by performing the experiments. Taguchi constructed a special set of general design guidelines for factorial experiments that cover many applications and the strategies are outlined in the following section.

3.6 Experimental design based on orthogonal arrays

The design of experiment is a systematic procedure to put down the variables and conditions of an experiment in order to reduce experimental attempts (Yusup, 1998). The concept of experimental design based on orthogonal arrays was initiated by Jacques Hadamand, a French mathematician in 1897. The concept was explored further by two British statisticians, Plackett and Burman. They used a saturated design approach which involves assigning all variables and interactions between variables to the columns in an orthogonal array. An orthogonal array is a set of tables used to determine the least number of experiments and their conditions.

Orthogonal mean balanced. To maintain orthogonality within an experiment array, equal numbers of tests under each level of each variable are carried out and any two variables are tested against each other twice at all the settings. Taguchi has developed an especially efficient set of orthogonal arrays to lay out his experiments, based on a family of fractional factorial experiments (FFEs) to determine an optimum quality of a product or a process. The collection and analysis of data are made simpler by following the set of orthogonal arrays. FFEs use only a portion of the total possible combinations to estimate the main effects of the variables and some of the interactions.

Each trial was repeated for the same experimental settings before moving to the next trial. Any variation in the results due to unknown or uncontrollable variables would be spread equally throughout the experiment (Ross, 1996). This procedure reduces the set-up time for the experiment throughout and the effect of external variables may not be captured during the successive repetitions if the repetitions are short in duration (Roy, 1990).

Various sets of standard orthogonal array matrices and modified standard orthogonal matrices, prepared by Taguchi considering two-levels, three-levels and multi-levels of variables is well explained by Ross (1996).

3.7 Comparison between a full factorial and orthogonal arrays of Taguchi experimental design

Table 3.3 shows a comparison between the fully factorial design and an orthogonal array of Taguchi experimental design. It shows that the experimental design by orthogonal array is more attractive because of the higher experimental efficiency. Several variables can be evaluated in a minimum number of tests. Hence, much more information about the variables can be obtained from fewer conducted trials without loss of confidence. Additionally, optimum operating conditions of significant variables or interactions as well as the estimates of the results at the optimum can be obtained accurately within the calculated confidence interval.

Table 3.3: Comparison between a full factorial and orthogonal arrays of Taguchi experimental design (Ross, 1996)

Total number of variables	Total number of levels or values (L)	Total number of trials (N) (Factorial design)	Total number of trials (N) (Taguchi Design)
2	2	$2^2=4$	4
3	2	$2^3=8$	4
4	2	$2^4=16$	8
7	2	$2^7=128$	8
15	2	$2^{15}=32768$	16

Table 3.3 clearly shows that the Taguchi's experimental design is very useful when there are more than two variables to be investigated as it reduces the number of experimental trial. This is very economical compared to the full factorial design number of trials which is based on the formula given in Equation 3.1. The factorial design is not economical in terms of cost and time due to the very large number of experiments needed. For research and development work or for product or process design as well as in actual production and in the field, it is crucial to develop a high quality product at a minimum cost and time, i.e. through performing the least number of tests.

3.8 Steps in designing experiments

According to Ross (1996), when designing the experiments process, there are three main phases are very important to follow. It encompasses all experimentation approaches. The three phases are:

a. the planning phase
b. the conducting phase
c. the analysis phase

The most important and crucial phase for the experiment to provide the expected information is the planning phase. The planning phase is when factors and levels are selected. The correct selection of factors and levels is non-statistical in nature and is more dependent upon product and process expertise.

The design of an experiment involves the following steps:

a. Selection of independent variables
b. Selection of number of level settings for each independent variable
c. Selection of orthogonal array
d. Assigning the independent variables to each column
e. Conducting the experiments
f. Analyzing the data
g. Inference

3.8.1 Selection of the independent variables

Before conducting the experiment, the knowledge of the product/process under investigation is of prime importance for identifying the factors likely to influence the outcome. Studies are done regarding the area involved and factors most likely to influence the process and the products are identified and short listed.

3.8.2 Deciding the number of levels

Once the independent variables are decided, the number of levels for each variable is decided. The selection of number of levels depends on how the performance parameter is affected due to different level settings. If the performance parameter is a linear function of the independent variable, then the number of level setting shall be 2. However, if the independent variable is not linearly related, then one could go for 3, 4 or higher levels depending on whether the relationship is quadratic, cubic or higher order.

In the absence of exact nature of relationship between the independent variable and the performance parameter, one could choose 2 level settings. After analyzing the experimental data, one can decide whether the assumption of level setting is right or not based on the percent contribution and the error calculations.

3.8.3 Selection of an orthogonal array (OA)

The selection of which OA to use predominantly depends on the following items in order of priority, as suggested by Ross (1996):

a. The number of factors and interactions of interest
b. The number of levels for the factors of interest
c. The desired experimental resolution or cost limitations

The first two items determine the smallest orthogonal array that it is possible to use, but this will automatically be the lowest-resolution, lowest-cost experiment. The experimenter may choose to run a larger experiment (larger orthogonal array) which will have higher resolution potential but will also be more expensive to complete.

Before selecting the orthogonal array, the minimum number of experiments to be conducted shall be fixed based on the total number of degrees of freedom present in the study. The minimum number of experiments that must be run to study the factors shall be more than the total degrees of freedom available. In counting the total degrees of freedom the investigator commits 1 degree of freedom to the overall mean of the response under study. The number of degrees of freedom associated with each factor under study equals one less than the number of levels available for that factor. Hence the total degrees of freedom without interaction effect is 1 +. For example, in case of 11 independent variables, each having 2 levels, the total degrees of freedom is 12. Hence the selected orthogonal array shall have at least 12 experiments. An L12 orthogonal satisfies this requirement.

Once the minimum number of experiments is decided, the further selection of orthogonal array is based on the number of independent variables and number of factor levels for each independent variable.

3.8.4 Assigning the independent variables to columns

The order in which the independent variables are assigned to the vertical column is very essential. In case of mixed level variables and interaction between variables, the variables are to be assigned at right columns as stipulated by the orthogonal array.

Finally, before conducting the experiment, the actual level values of each design variable shall be decided. It shall be noted that the significance and the percent contribution of the independent variables changes depending on the level values assigned. It is the designers' responsibility to set proper level values.

Table below shows guide of assigning factors in a two-level orthogonal arrays (Source: Ross, 1996):

Table 3.4: Two-Level Orthogonal Array Factor Assignment

OA	Numbers of factors	Use column nos.
L4	1-2	1,2
	1-3	1-3
L8	1-3	1,2,4
	4	1,2,4,7
	5-7	1,2,4,7,(3,5,6)
L12	1-11	1-11
L16	1-4	1,2,4,8
	5	1,2,4,8,15
	6-8	1,2,4,7,8,(11,13,14)
	9-15	1,2,4,7,8,11,13,14,(3,5,6,9,10,12,15)
	1-5	1,2,4,8,16
	6	1,2,3,8,16,31
	7-16	1,2,4,8,16,31,(7,11,13,14,19,21,22,25,26,28)
	17-31	1,2,4,7,8,11,13,16,19,21,22,25,26,28,31,(3,5,6, 9,10,12,15,17,18,20,23,24,27,29,30)

*Column numbers in parentheses may be assigned in any order; column numbers not in parentheses must be used first.

3.8.5 Designs with interaction

The term 'interaction', expressed by inserting '×' mark between the two interacting factors is used to describe a condition in which the influence of one factor upon the result is dependent on the condition of the other. Two factors A and B are to interact ($A \times B$) when the effect of changes in the level of A, determines the influence of B and vice versa. The graphical method reveals if interaction exists. It is calculated from the experimental data. However, Taguchi methods do not specify any general guidelines for predicting interactions. It is by some other means, perhaps from experience or a previous Taguchi experiment.

Experimental design using Taguchi OA requires a little more care to design an experiment where interactions are to be included. Taguchi's research on interacting columns is well explained and presented in a table called the 'Triangular Table of Interaction' which suits to different levels of OA. A large triangular table as shown in Table A-1 in Appendix A made for 2 level columns will satisfy most commonly 2 level orthogonal arrays.

3.8.6 Conducting the experiment

Once the orthogonal array is selected, the experiments are conducted as per the level combinations. It is necessary that all the experiments be conducted. The interaction columns and dummy variable columns shall not be considered for conducting the experiment, but are needed while analyzing the data to understand the interaction effect. The performance parameter under study is noted down for each experiment to conduct the sensitivity analysis.

Whenever possible, the trial conditions; the individual combinations in a designed experiment; should be run in a random order to avoid the influence of experiment setup. If only one run for each of the above conditions is planned, they could be run as experiment number 2, 4, 3, and 1, or any other random order. If on the other hand, multiple repetitions are planned, say runs 3 for each of the 4 conditions, then there are two ways to proceed; Replication and Repetition.

Replication approach means that all the trial conditions will be run in a random order. One way to decide the order is to randomly pull one trial number at a time from a set of trial numbers including repetitions. Often a new setup will be required for each run. This increases the cost of the experiment. While in Repetition approach, each trial is repeated as planned before proceeding to the next trial run. The trial run sequence is selected in a random order.

3.8.7 Analysis of the data

The final phase of the design of experiment process is to analyze and interpret the experimental results to improve the performance characteristics of the process relative to the needs and expectations. After all tests are conducted, decisions must be made concerning which parameters affect the performance of a process. These decisions are made with the assistance of various analytical techniques such as the

a. Observation method
b. Ranking methods
c. Column effects method
d. Plotting methods
e. Analysis of variance

Some of these methods for determining influential factors are subjective and others are objective decision-making tools. Analysis of Variance (ANOVA) will be the predominant statistical method used to interpret experimental data and make the necessary decisions since this method is the most objective.

ANOVA was developed by Sir Ronald Fisher in the 1930s as a way to interpret the results from agricultural experiments. ANOVA is not a complicated method and has a lot of mathematical beauty associated with it.

Analysis of results follows either paths of repetitions or no repetitions. Generally, for single observation of each trial condition, the standard analysis approach is followed. Where there are repetitions of the trial runs, whether by outer array designed noise condition, or under random noise condition, S/N analysis should be performed. The final analysis for the optimum condition is based on one of three characteristics greatest, smallest, or nominal value of quality.

Since each experiment is the combination of different factor levels, it is essential to segregate the individual effect of independent variables. This can be done by summing up the performance parameter values for the corresponding level settings. For example, in order to find out the main effect of level 1 setting of the independent variable 2, sum the performance parameter values of the experiments

1, 4 and 7. Similarly for level 2, sum the experimental results of 2, 5 and 7 and so on.

Once the mean value of each level of a particular independent variable is calculated, the sum of square of deviation of each of the mean value from the grand mean value is calculated. This sum of square deviation of a particular variable indicates whether the performance parameter is sensitive to the change in level setting. If the sum of square deviation is close to zero or insignificant, one may conclude that the design variables are not influencing the performance of the process. In other words, by conducting the sensitivity analysis, and performing analysis of variance (ANOVA), one can decide which independent factor dominates over other and the percentage contribution of that particular independent variable.

CHAPTER 4: MATERIALS AND METHOD

This chapter discusses on the methodology adopted to synthesize methanol. The chapter also describes the equipment and the procedures used in synthesizing methanol from methyl acetate and calcium hydroxide. The product analysis, i.e. of methanol, is conducted using gas chromatography. To ensure consistencies of the results and systematic experimental approach, Taguchi design of experiment is adopted and is discussed in the following sections.

4.1 Materials

The raw materials for the saponification reaction are methyl acetate, (CH_3COOCH_3, 99.9%), (Merck) and calcium hydroxide, ($Ca(OH)_2$), (Merck). Concentrations of 0.01 M and 0.05 M for both reactants were used in the experiments.

4.1.1 Preparation of methyl acetate

The methyl acetate obtained from Merck is of 99.9% purity of methyl acetate. The pure methyl acetate was diluted with distilled water to prepare the solutions at the desired concentration, of 0.01 M and 0.05 M.

4.1.2 Preparation of calcium hydroxide

Calcium hydroxide was obtained in powder form from Merck. It was dissolved in distilled water to prepare the solution at the desired concentrations, of 0.01 M and 0.05 M.

4.1.3 Preparation of standard solutions

For the gas chromatography to be able to detect the presence and thus analyze the quantity of methanol in the product of the experiment, standard solutions of methanol need to be prepared. These standards will be referred in order to know the amount of methanol in the product. The preparation of the methanol standard is based on the calibration curve. Since the value of methanol to be produced is unknown, preparation of the calibration curve is crucial. The calibration curve is referred to obtain the expected methanol produces from the experiment. The methanol, with 99.7% purity obtained from Merck was diluted with distilled water to prepare the solutions at the desired concentrations to generate the calibration curve.

From the reaction done, the maximum amount of methyl acetate and calcium hydroxide used as reactants are 0.05 M. As for methyl the initial percentage based on the volume ratio is postulated as below:

$$\%\ of\ methyl\ acetate = \frac{Amount\ of\ methyl\ acetate}{Amount\ of\ water} = \frac{3.983mL}{1000mL} \times 100 = 0.3983\%$$

Hence, the amount of methanol produced will also be expected to be around the figure, which is less than 1% of volume ratio (with respect to low concentration of methyl acetate used). The standards of methanol were prepared at five (5) different concentrations, in volume percentage against water, i.e. 1%, 0.8%, 0.6%, 0.4%, and 0.2%. The standards are analyzed with the gas chromatography and a standard curve was developed as a reference for sample analysis.

The standard curve for methanol is shown in the Figure 4.1. This curve is referred to calculate the area under the peak of methanol when it is detected. The area is converted into concentration terms to obtain the amount of methanol synthesize from the saponification process.

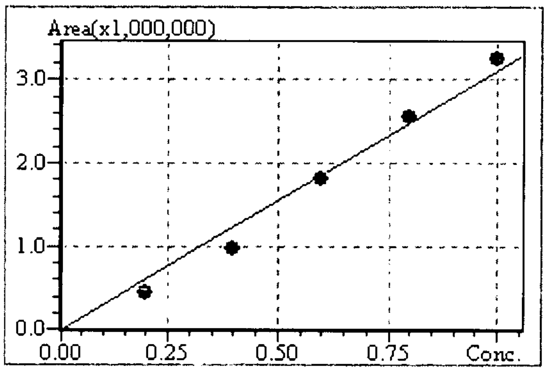


Figure 4.1: Standard Curve for methanol in GC

4.2 Equipment

The equipment used in the experiment are Continuous Stirred Tank Reactor (CSTR) with hot water circulator from Armfield, where the same unit is used and converted to operate as semi-batch reactor, and also Gas Chromatography from Shimadzu.

4.2.1 CSTR with hot water circulator

The experimental work was performed using the CSTR with hot water circulator, model CEM MK II by Armfield. The experimental procedure is discussed in the following section. The schematic diagram of the equipment is shown in Figure 4.2.

The CSTR is equipped with one reactor consist of a stirrer and internal heater and a temperature probe, and two storage tanks for reactants. The storage tanks are connected to the reactor with separate pumps.

4.2.2 Gas Chromatography

Gas Chromatography of Model Shimadzu (GC 2010) was used to analyze the samples of products that contain methanol. The schematic diagram is shown in Figure 4.3. Table 4.1 shows the properties of the gas chromatography. The column used is of type BP-X5, which is a water-resistant column.

Table 4.1: Gas Chromatography Properties

GC Type	Shimadzu GC-2010
Column	HP GS-Q
Oven profile	110°C ramp to 200°C at 10°C/min
Mobile phase	Gaseous
Column Flow	3.36 mL/min
Detection	Flame Ionization Detector (FID) @ 200°C
Injection	1 μL
Column Length/ID	25 meter/0.32mm

4.2.2.1 Instrumentation component of a gas chromatography

Carrier gas

The carrier gas must be chemically inert. Commonly used gases include nitrogen, helium, argon, and carbon dioxide. The choice of carrier gas is often dependant upon the type of detector which is used. The carrier gas system also contains a molecular sieve to remove water and other impurities. In this experiment, the carrier gas used was hydrogen.

Sample injection port

For optimum column efficiency, the sample should not be too large, and should be introduced onto the column as a 'plug' of vapor. Slow injection of large samples causes band broadening and loss of resolution. The most common injection method is where a microsyringe is used to inject sample through a rubber septum into a flash vaporizer port at the head of the column. In this analytical study, an auto-injector of model AOC20i and an auto-sampler of model AOC 20s are used. The temperature of the sample is set at 110°C. The sample size is of one microliter (1 µL). The sample vaporizes to form a mixture of carrier gas, vaporized solvent and vaporized solutes. A proportion of this mixture passes onto the column, but most exits through the split outlet

Columns

And as for this analysis, a column of type HP GS-Q^{TM} was used, which is suitable in the presence of water. Most of the columns are not suitable to be used with the presence of water in a sample since water may corrode the column and in a long term, damage the column completely.

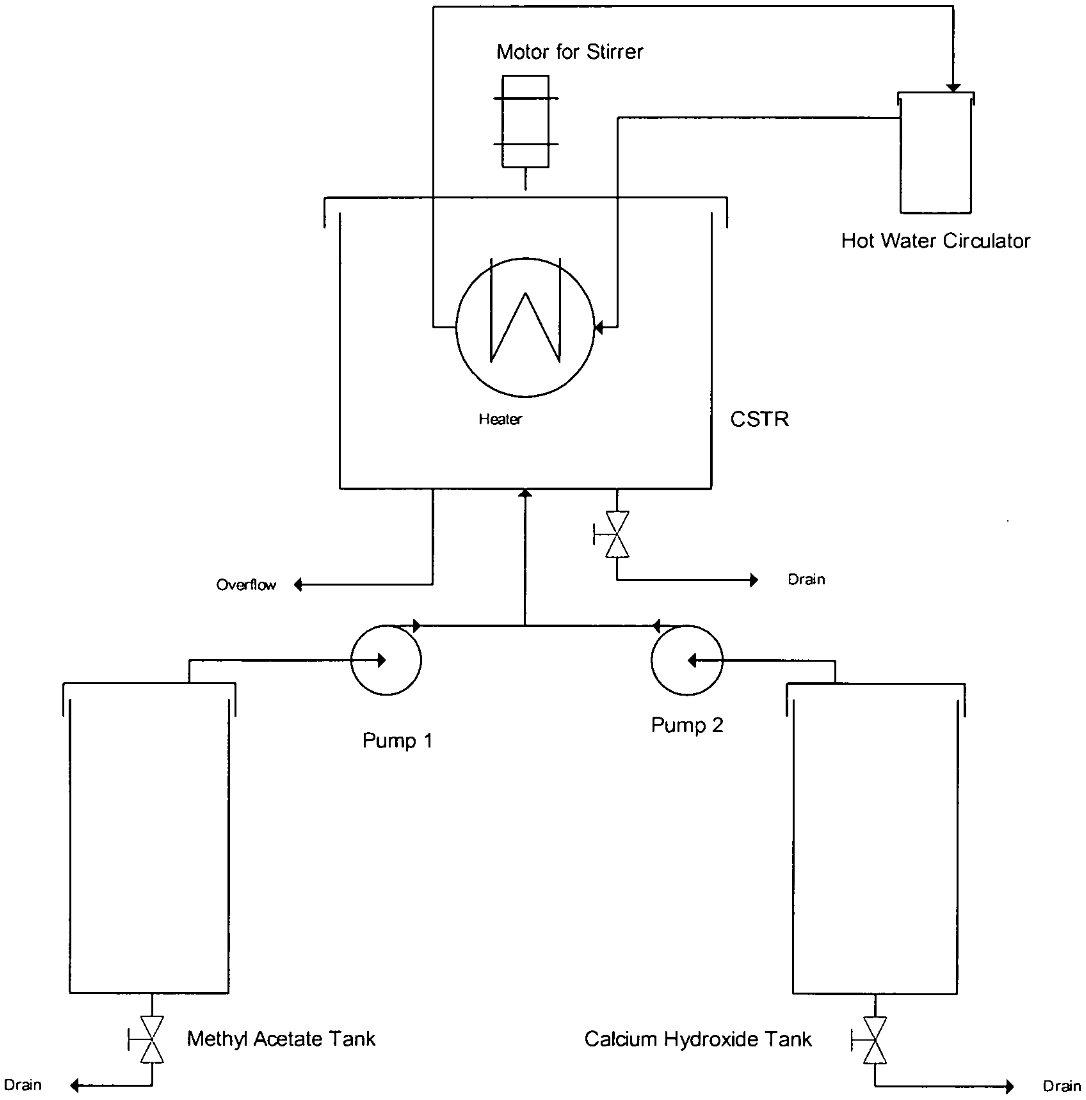


Figure 4.2: Schematic diagram of CSTR equipment

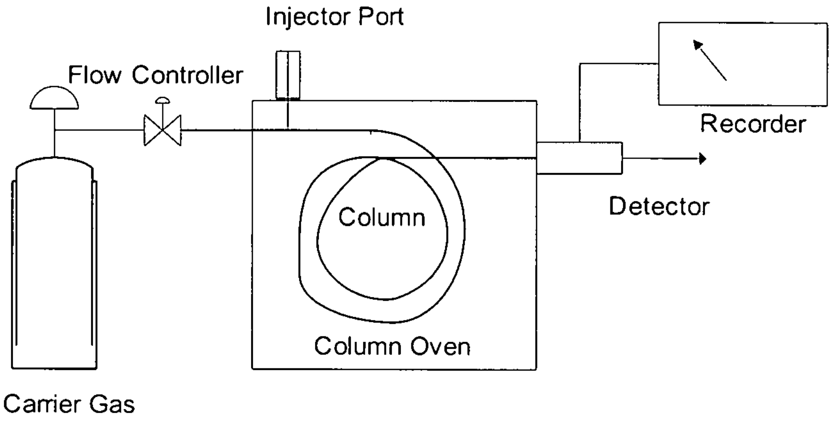


Figure 4.3: Gas chromatograph schematic diagram

4.2.3 Gas Chromatography / Mass Spectrometer

Samples are injected in the GCMS for analysis. The method used is purge and trap. Below are the steps in handling the GCMS for the purge and trap method. The steps shown is applied in the interface of the GCMS application in the computer attached to the GCMS:

STATUS	
Purge Ready	Introduce sample (using syringe – 1mL)
	Press "START" on "TEKLINK" window
Purge (Duration: 11 minutes)	Key in data sample in "Real Time Analysis" Window
	Select "Single sample"
	Fill the name of data
	Press "OK"
	Press "Send Parameter" button
Desorb Ready	Press "STEP" on "TEKLINK"
Desorb Preheat (Duration: 30 seconds)	
Desorb (Duration: 4 minutes)	
Bake (Duration: 10 minutes)	
Standby (Duration: 4 minutes)	Reset to standby parameter
Purge Ready	Ready for introduction of the next sample

4.3 Saponification of methyl acetate for methanol synthesis

The synthesis of liquid methanol (CH_3OH) via saponification of methyl acetate (CH_3COOCH_3) with calcium hydroxide is given by Equation 4.1:

$$Ca(OH)_2 + 2CH_3COOCH_3 \Leftrightarrow 2CH_3OH + (CH_3COO)_2Ca \qquad \text{(Eq. 4.1)}$$

$$\Delta H^o_{298K} = -50.26\frac{kJ}{mol}$$

The reaction is exothermic and reversible. Occurrence of other reactions besides the main reaction is avoided. In addition, the process is operated below the boiling point of both reactants and products to ensure the reaction is in liquid phase.

4.4 Design of Experiment using Taguchi Technique

4.4.1 Selections of main variables and level

The main variables were selected based on the reaction engineering principles and taking into the consideration the chemistry of the reaction. The following paragraphs discuss the characteristics and levels of the selected variables. This research involves a study on a new one-pot route to synthesize methanol. By bounding the effect of the selected variables at two levels, it is assumed that the performance of the parameters are linearly related. Hence, each variable are set to low (1) and high (2) values.

4.4.1.1 Reactor Type

The performance of a process depends on mode of operation, which is, either batch, continuous or semi-batch. Thus this is largely influence by the type of reactor used and reactor type is a significant variable to be considered. Different types of reactors are suitable for specific reactions. Since the process under study involves liquid phase and homogeneous system, a comparison between a continuous stirred tank reactor (CSTR) and semi-batch reactor performance is considered.

4.4.1.2 Reactor Volume

This variable is important since it gives direct correlation to the residence time of the reactants in the reactor. Sufficient and exact time of residence of reactants will result in the best conversion and yield obtained. The volume is chosen to be 1L and 2L based on capacity of the equipment.

4.4.1.3 Flow rate

For a CSTR system, the flow rate gives direct correlation to the residence time of the reactants in the reactor. Improper controls of flow rate of the reactants will results in incomplete mixing and thus lower the formation of the desired products. For the semi-batch system, the flow rate of the limiting reactant will give effects on the rate of reaction. The minimum flow rate is at 25 cm^3/min and the highest is at 80 cm^3/min. Both flow rates give laminar flow of the reactants to the reactor.

4.4.1.4 Concentration of reactants

The rate of reaction for this particular saponification of methyl acetate and calcium hydroxide is correlated to the concentration of both reactants, as shown in the Equation 2.6.

$$-r_A = k_A' C_A^{\alpha} C_B^{\beta} \qquad \text{(Eq. 2.6)}$$

Hence, it is vital to evaluate the concentration variation on the highest value of methanol yield. The concentration is selected to be at 0.01 M and 0.05 M. A restraint by the ability of calcium hydroxide to dissolve in water when the reactant is prepared. Solubility expresses the maximum amount of solute that will be dissolved in a given amount of solvent at a given temperature. When a soluble salt is dissolved in water, the dissolution is up to a certain extent at a certain temperature. The solution produced is known as a saturated solution at that temperature. For instance, equilibrium exists between the solid form of $Ca(OH)_2$ with the ionic form of the $Ca(OH)_2$. The solubility of the calcium hydroxide is determined to be at a maximum of 0.05 M. The calculation is shown in APPENDIX A.

4.4.1.5 Temperature

Temperature is one of the important variable that influence the yield of methanol and conversion of the reactants. Operating temperature affected the rate of reaction. In this design of experiment, the low end of the temperature setting is at room temperature, which is 25°C and the high end is at 50°C, the maximum temperature limited by the equipment and to ensure the product, which is methanol, is in liquid form and not reaching its boiling temperature.

Table 4.2: Variables and Levels for Saponification Process Experiment

	Factor	**Level 1**	**Level 2**
A	Reactor Type	Continuous-Flow	Semi-Batch System
B	Reactor Volume (Liter)	1	2
C	Flow rate (cm^3/min)	25	80
D	Concentration of Methyl Acetate (M)	0.01	0.05
E	Concentration of Calcium Hydroxide (M)	0.01	0.05
F	Temperature	25	50

Once the factors are assigned, the 16 trial runs are described by the rows of the orthogonal arrays (OA).

4.4.2 Selection of orthogonal array

In this case, there are six (6) variables with two (2) levels each. There is also evaluation on the interaction between the variables, i.e. reactor type and reactor volume, reactor type and temperature, concentrations of reactants, and reactor volume and flow rate. The degree of freedom is calculated as seven (7). Choosing an array of L_8 is not sufficient because the experiment will be of resolution two (2). Thus, an orthogonal array of L_{16} was chosen so that the experiment to be of resolution four (4). This array is chosen so that all main effects and all interactions can be estimated in a high-resolution experiment. In addition, by selecting the appropriate array, systematic experiment can be conducted at a minimum cost.

4.4.3 Assignments of variables

In designing experiments with interactions, the columns for interactions are first identified. L_{16} array consist of 15 columns. Each of the variables is labeled alphabetically to simplify the presentation. Referring to the guide given by Ross (1996), the variables and the interaction between variables are assigned to the respective columns. Table 4.3 shows assignment of variables for the assigned column in the selected L_{16} orthogonal array.

Table 4.3: Assignments of variables at column

Column	Factors
1	A (Reactor Type)
2	B (Reactor Volume)
3	A x B (Interaction between A and B)
4	C (Flow Rate)
5	A x C (Interaction between A and C)
6	B x C (Interaction between B and C) A x D (Interaction between B and C)
7	D (Concentration of methyl acetate)
8	E (Concentration of calcium hydroxide)
9	Unused column
10	A x F (Interaction between A and F)
11	F (Temperature)
12	Unused column
13	Unused column
14	Unused column
15	D x E (Interaction between D and E) C x F (Interaction between C and F)

4.4.4 The experimental set-up

From the design of experiment, the sets of experimental set-up to be used for the saponification process of methanol are shown in Table 4.4. The array being used for the experimental work is:

Table 4.4: Orthogonal Array

Trial	A	B	C	D	E	F
1	1	1	1	1	1	1
2	1	1	1	1	2	2
3	1	1	2	2	1	1
4	1	1	2	2	2	2
5	1	2	1	2	1	2
6	1	2	1	2	2	1
7	1	2	2	1	1	2
8	1	2	2	1	2	1
9	2	1	1	2	1	2
10	2	1	1	2	2	1
11	2	1	2	1	1	2
12	2	1	2	1	2	1
13	2	2	1	1	1	1
14	2	2	1	1	2	2
15	2	2	2	2	1	1
16	2	2	2	2	2	2

The variables and their levels are substituted into the orthogonal array and gave a set of experimental set-up, as shown in Table 4.5.

Table 4.5: Experimental Set-up

Factor / Trial	Reactor Type	Reactor Volume (L)	Flow rate (cm^3/min)	Conc. of methyl acetate (M)	Conc. of calcium hydroxide (M)	Temperature (°C)
1	CSTR	1	25	0.01	0.01	25
2	CSTR	1	25	0.01	0.05	50
3	CSTR	1	80	0.05	0.01	25
4	CSTR	1	80	0.05	0.05	50
5	CSTR	2	25	0.05	0.01	50
6	CSTR	2	25	0.05	0.05	25
7	CSTR	2	80	0.01	0.01	50
8	CSTR	2	80	0.01	0.05	25
9	Semi-batch	1	25	0.05	0.01	50
10	Semi-batch	1	25	0.05	0.05	25
11	Semi-batch	1	80	0.01	0.01	50
12	Semi-batch	1	80	0.01	0.05	25
13	Semi-batch	2	25	0.01	0.01	25
14	Semi-batch	2	25	0.01	0.05	50
15	Semi-batch	2	80	0.05	0.01	25
16	Semi-batch	2	80	0.05	0.05	50

For each trials of the experiment, replication is carried out to capture the effect of random variables. A complete run of all 16 trials is conducted before moving to the duplicate run. The data was then averaged.

4.5 Procedures

4.5.1 Continuous flow versus semi-batch system

The experimental investigation was carried out in either a CSTR or Semi-Batch reactor system. The temperatures are set at two different values, which are at room temperature of 25°C and 50°C under atmospheric pressure following the designated experimental trials conditions being set by the orthogonal array. The reactor used in this work is a Stirred Tank Reactor with Hot Water Circulation (Model CEM MK II by Armfield) as shown in Figure 4.2 in page 47. The reactants are stored in separate feed tanks connected to the reactor with a pump each for both feed tanks.

The equipment is equipped with a conductivity probe and a temperature probe to give readings of conductivity and temperature respectively. Figure 4.2 in page 47 shows the schematic diagram of the corresponding reactor.

4.5.1.1 Continuous-Flow System

For an experiment using a continuous-flow system, the reactants are fed simultaneously and continuously into the reactor.

The reactor volume was set either to be at 1L or 2L. Then, both reactants were fed into the reactor with pump speed of 25cm^3/min or 80cm^3/min. The stirrer was switched on at a speed of 200 rpm. The heater was switched on to heat the solution to the desired operating temperature, i.e. 25°C or 50°C. The reactor temperature was maintained at the set point value through out the experiment. The conductivity is recorded as the reaction proceeds. The experiment is stopped when the conductivity reading reaches a stable value (steady state). A milliliter (mL) of the product is drawn from the overflow to be tested using gas chromatography.

4.5.2.2 A Semi-Batch System

For an experiment using a semi-batch system, the reactor volume was set by adjusting the overflow line.

The excess reactant, calcium hydroxide, is initially fed into the reactor. Then, the limiting reactant, methyl acetate, is pumped into the reactor with pump speed of 25cm^3/min or 80cm^3/min. The stirrer was set at a speed of 200 rpm. The heater was switched on to heat the solution to 25°C or 50°C. The reactor temperature was maintained at the set point value through out the experiment. The pumps were stopped when the solution reaches the volume required. The conductivity was recorded. The experiment was stopped when the conductivity reading reaches a stable value (steady state). One milliliter of the product from the overflow was drawn to be analyzed using gas chromatography.

4.5.2 Sample Analysis using Gas Chromatography

The sample drawn from the experimental run; via overflow or sampling point; was then brought to the analytical laboratory to be analyzed using a Gas Chromatography of Model Shimadzu (GC 2010). This is to verify and calculate the amount of methanol produced for each trials. Standard analytical techniques are followed.

Gas chromatography involves a sample in liquid form being vaporized and injected onto the head of the chromatographic column. The sample is transported through the column by the flow of inert, gaseous mobile phase. The column itself contains a liquid stationary phase which is adsorbed onto the surface of an inert solid. The methanol peak is detected and the amount produced is calculated by comparing the peak with standard calibration curve.

4.5.3 Purification of Methanol

In this saponification reaction, liquid methanol is synthesized from methyl acetate and calcium hydroxide with formation of another product, which is calcium acetate. The methanol produced at this stage is in its crude form. In order to purify the crude methanol, the sample is distilled at a temperature of 76°C using a rotational vaporizer.

An amount of 375 mL of crude methanol sample is drawn from the reactor outlet and is heated up to 76°C. The temperature is set higher than methanol boiling point, which is 65°C, thus ensure only the pure liquid methanol is to be vaporized. The melting point of calcium acetate is 160°C. The amount of pure liquid methanol is collected from the vaporization process and tested using a gas chromatography to obtain the purity of the methanol produced.

4.5.4 Determination of reaction kinetics

The reaction under investigated is new. Thus it is essential to particularly determine the reaction order, rate of reaction and the activation energy of the reaction for better understanding of reaction kinetics. Series of further experiment is carried out, based on the optimum condition. The experiment is aimed to find the optimum ratio of reactants. The rate of conversion of the reaction at different ratio of reactants to calcium acetate and methanol is monitored. The experiment is repeated for five (5) times at different initial concentration of calcium hydroxide and methyl acetate.

The chemicals are prepared as shown in Table 4.6. Five (5) experiments are conducted to complete the series with two replication at each trial.

Table 4.6: Set-Up for Reaction Kinetic Study

Experiment No	Reactant ratio	Concentration of $Ca(OH)_2$ (M)	Concentration of $(CH_3COO)_2Ca$ (M)	Weight of $Ca(OH)_2$ (g)	Volume of $(CH_3COO)_2Ca$ (mL)
1	1 : 4	0.002	0.008	0.148	0.6373
2	2 : 3	0.004	0.006	0.297	0.478
3	3 : 2	0.006	0.004	0.445	0.319
4	4 : 1	0.008	0.002	0.593	0.1593
5	1 : 1	0.010	0.010	0.741	0.7966

One (1) Liter of Calcium hydroxide solution is prepared for each concentration. The Calcium hydroxide is poured inside the semi-batch reactor carefully avoiding any spillage. The stirrer is switched on at the speed of 200rpm. The heater is switched on to heat up the solution to 50°C. When the Calcium hydroxide solution reaches 50°C, the changes in the conductivity are recorded and at the same time 0.6373 mL (0.008 mol) of methyl acetate is injected inside the reactor immediately. The experiment is stopped when the conductivity becomes stable, after 60 minutes. One (1) mL of the final solution is drawn from the reactor for GC analysis.

The steps are repeated with other experiments (2 to 5) for different ratio of concentrations of Calcium hydroxide to Methyl acetate.

4.6 Statistical data analysis by Analysis of Variance (ANOVA)

ANOVA is a short of Analysis of Variance. According to Roy (1990), ANOVA establishes the relative significance of the individual factors and the interaction effects. The data obtained are analyzed by using this method. The calculation and formulated steps adapted are shown in the following sections:

Step 1: Total of All Results

Each and all of the results are summed up to give a value of T.

Step 2: Correction factor

Correction factor ($C.F.$) is calculated for the particular experiment. The formula is

$C.F. = \frac{T^2}{n}$, where n is the total number of experiments (trials)

Step 3: Total Sum of Squares

The sum of squares is a measure of the deviation of the experimental data from the mean value of the data. Summing each squared deviation emphasizes the total deviation. Thus

$$S_T = \sum_{i=1}^{n} y_i^2 - C.F.$$

Step 4: Factor sum of squares

Squared deviations of each factor, including the interactions, are calculated using the equation shown below. Taking a two level array with factor A as example,

$$S_A = \frac{A_1^2}{N_{A1}} + \frac{A_2^2}{N_{A2}} - C.F.,$$

where

A_1 is sum of results where factor A at level 1 is present

A_2 is sum of results where factor A at level 2 is present

N_{A1} is the number of experiments in which factor A at level 1 is present

N_{A2} is the number of experiments in which factor A at level 2 is present

For a case of 2 level factors, there is also an alternative formula:

$$S_A = \frac{(A_1 - A_2)^2}{(N_{A1} + N_{A2})}$$

The same formula is used for all factors and interactions involved in the experiment. Finally, the error for the factor sum of squares is also calculated using the formula below:

$$S_e = S_T - \left(S_{all\ factors\ and\ interactions}\right)$$

Step 5: Total and factor degree of freedom (DOF)

DOF is a measure of the amount of information that can be uniquely determined from a given set of data.

DOF total = number of test runs minus 1

$$f_T = n - 1$$

DOF of each factor is also calculated:

For factor A,

f_A = (Number of levels of factor A) – 1

And the same formula is used for all factors and interactions.

The DOF of error term is calculated as

$$f_e = f_T - (f_{\text{of all factors and interactions}})$$

Step 6: Mean Square (Variance)

Variance measures the distribution of the data about the mean of the data. Since the data is representative of only a part of all possible data, DOF rather than the number of observation is used in the calculations.

Variance for factor A, $V_A = \dfrac{S_A}{f_A}$

For the error term, $V_e = \dfrac{S_e}{f_e}$

Step 7: Percentage Contribution

Percentage contribution represents the contribution of a factor or interaction to the overall results of the experiment. For factor *A*,

$$P_A = \frac{S_A}{S_T}$$

The same formula is used for other factors and interactions.

The analysis is verified via a software named QUALITEK-4. QUALITEK-4 (QT4) Version 4.75 is the WINDOWS version of software for Automatic Design and Analysis of Taguchi Experiments. The software was originally introduced in 1987 as Qualitek-3, and later enhanced and released in 1991 as Qualitek-4. Results from the analysis are discussed in the following chapter.

CHAPTER 5: RESULTS AND DISCUSSIONS

This chapter discusses the results of the experimental work on milder route to synthesize methanol from methyl acetate and calcium hydroxide at lower temperature of 50°C and atmospheric pressure. Since the proposed route is new, thus, the determination of physical constant such as reaction rate constant, activation energy and frequency variable of the proposed route is crucial. Taguchi L_{16} array has been adapted to assist in systematic analysis of the results. Yield of methanol produced from the reaction is calculated for all trials and analyzed using the Analysis of Variance (ANOVA).

5.1 Production of methanol via saponification process

5.1.1 Yield of methanol

The route tested, which is saponification of methyl acetate and calcium hydroxide, is a novel route that has not being tested before. Hence, the initial part of the work is to study on the feasibility and the ability of the route in producing liquid methanol. From the gas chromatography analysis of the sample, as shown in Figure 5.1 and APPENDIX B, it is proven that methanol is sufficiently produced via the proposed milder route. Thus the feasibility of the route is proven. Figure 5.1 shows the yield of methanol at each of the 16 trials.

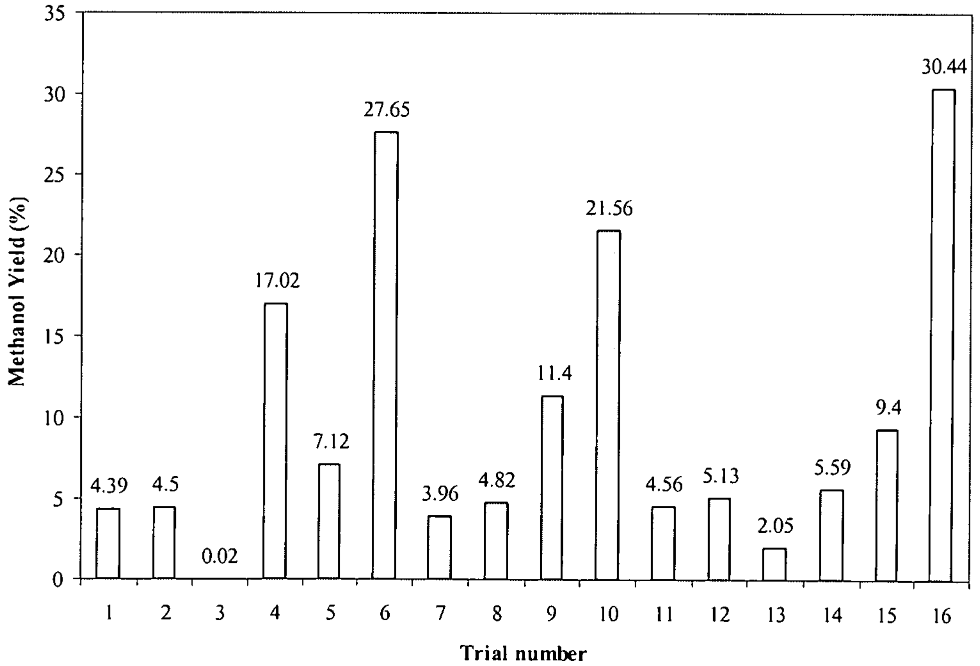


Figure 5.1: Methanol yield (%) at each trial

From Figure 5.1, it is clearly shown that trial 16 gave the highest yield of methanol, i.e. 30.44%.

Standard deviation of a random variable is a measure of the spread of its value. It is defined as the square root of the variance. In other words, the standard deviation is the root mean square (RMS) deviation of values from the mean. Variance of a random variable is a measure of its statistical dispersion, indicating how its possible values are spread around the expected value, where the expected values shows the location of the distribution, the variance indicates the scale of the values.

For all the 16 trials, the maximum value of standard deviation and variance obtained are1.35E-02 and 9.05E-05, respectively, which are acceptable. Details for all the standard deviations and variances are shown in Table C1 in APPENDIX C.

At trial 16, both concentration of reactants and the operating temperature were at the higher level, i.e. 0.05M and 50°C respectively. Furthermore at this condition, a semi-batch reactor was used. For a semi-batch process, the reactant in excess was fed initially into the reactor. Then, the limiting reactant, methyl acetate, was pumped at a rate of 80cm^3/min. This had allowed the limiting reactant to react with the reactant in excess to produce more methanol. In semi-batch system, the rate of consumption of the limiting reactant was higher and the reaction was completed faster as compared to CSTR system to achieve the same conversion values and yield required.

Comparing trial 1 and trial 16, all of the experimental conditions are at lower level. The reactor being used was a CSTR and the concentrations of both reactants were 0.01M. The operating temperature was at 25°C. So, this lower value of the variables has led to lower yield of methanol produced.

At trial 6, the yield of methanol produced at this condition is found to be the second highest, i.e. 27.65%. This observation is due to significant influence of concentrations on the rate of reaction. Higher concentration of both reactants, 0.05M, will result in higher rate of consumption, thus, higher methanol yield.

Trial 10 gave lower yield than trial 16 because at this trial, even though semi-batch reactor is used, the process condition was at lower temperature of 25°C and lower flow rate of 25cm^3/min. At higher temperature, molecules can collide with greater energy and frequency. Thus, lower temperature restricts the rate of collision and reduces the rate of reaction, hence producing fewer methanols. As for the flow rate influence, the higher flow rate is expected to give higher yield but in this trial, the effect of the flow rate is influenced by temperature. The interaction effect is shown by the severity index percentage, i.e. 86.33%. Severity index through the ANOVA indicates the extend of interaction between the variables. 90^0 angles between the lines indicate 100% of interaction. This profile can be seen in Figure 5.2. The summary of the severity index for the identified interaction between variables in this work is summarized in Figure 5.3. The interaction shown is between flow rate (variable C) and temperature (variable F).

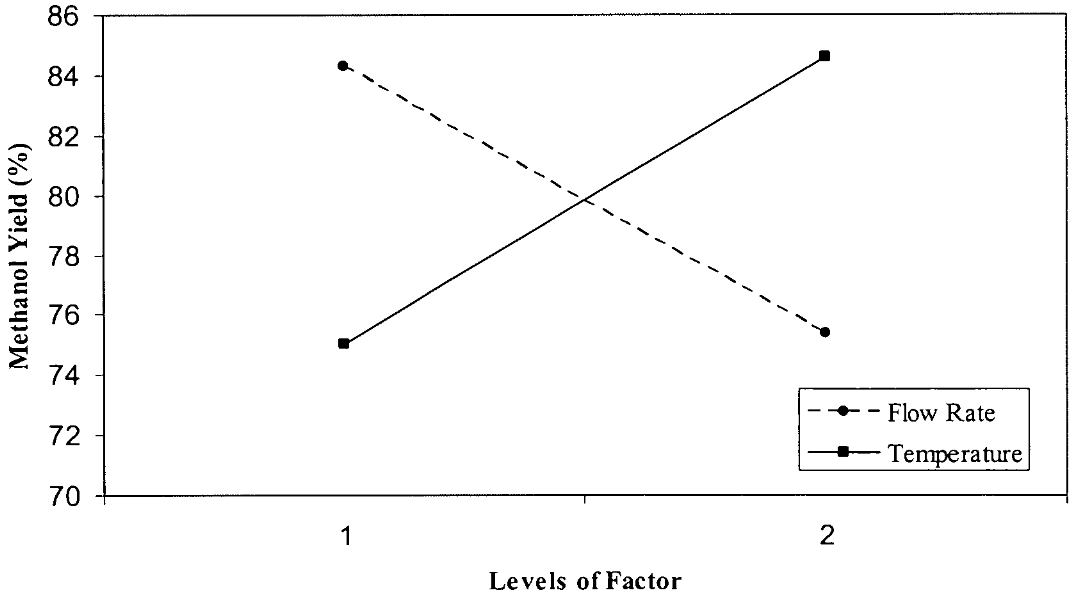


Figure 5.2: Interaction between Flow Rate (C) and Temperature (F)

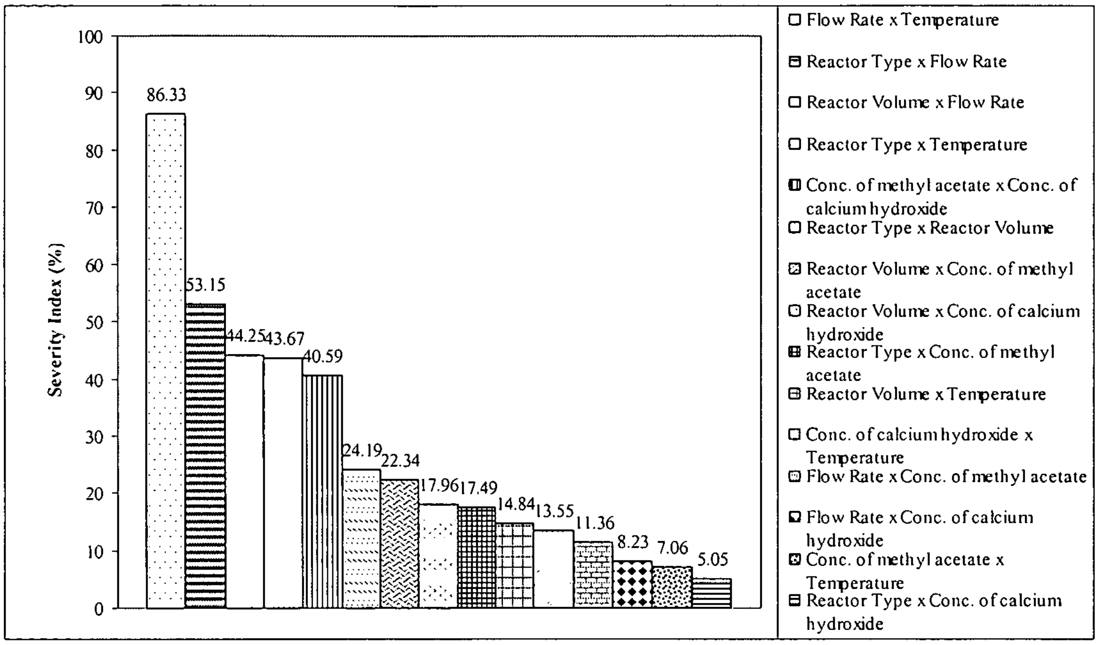


Figure 5.3: Severity index of interaction between variables

Methanol yield of 17.02% was detected at trial 4. Compared to trial 16, the conditions at this trial were at the same level except for the reactor type used. A CSTR was used instead of a semi-batch system. By using CSTR, the mode of contacting differs from a semi-batch system because both reactants were simultaneously fed into the reactor. Semi-batch system allowed mixing to occur at the earliest possible moment and the mixing is complete at the moment of the injection of the limiting reactant into the reactor. As for CSTR, since both reactants were fed continuously into the reactor, a complete mixing of the reactants is necessary before the reaction can proceed. This incurred additional time for the reaction to proceed.

At trial 9 and 15, the yield of methanol was suddenly dropped to 11.4% and 9.4%, respectively, even though a semi-batch reactor was used. This is due to the difference in the concentration of calcium hydroxide fed, i.e. 0.01M, as opposed to trial 16, where the concentration of calcium hydroxide was at 0.05M. At trial 16, the ratio of both reactants concentrations was one to one. On the other hand, at trial 9 and 15, different ratio of concentration of methyl acetate to calcium hydroxide was set to 5 to 1. Hence, this violate the stoichiometry equation whereby the methyl acetate should be the limiting reactant, instead, at these trials, methyl acetate had become the reactant in excess. Thus, lower production of methanol was obtained. The effect of the concentration ratio is also true for trial 5, which gave the yield of methanol of 7.12%. However, at trial 3, the yield is much lower, which is 0.02%, because of the additional influence of reactor type and temperature. A CSTR was used and it was operating at the lower temperature of 25°C.

As for trial 12 and 14, the yield of methanol was given as 5.13%, and 5.59%. At these trials the concentration of methyl acetate was at 0.01M and concentration of calcium hydroxide was at 0.05M. Since the ratio of methyl acetate to calcium hydroxide was at 1 to 5, it is expected for the yield to be high, since the methyl acetate was the limiting reactant and the calcium hydroxide was the reactant in excess. However, there were other influences that cause it to be lower. One of the influences was the concentration of methyl acetate itself. The methyl acetate was at the lower level of concentration, i.e. 0.01M. Hence, the number of moles participating in the reaction is less, thus, producing lower yield of methanol. Besides, it is also influenced by the interaction between temperature and flow rate, which has the severity index of 86.33% as shown in Figure 5.3.

Methanol yield of 4.82% and 4.50% were obtained at trial 8 and 2 respectively. At these trials, the conditions were differing to that of trial 16 in several variables. The concentration of methyl acetate was 0.01M while concentration of calcium hydroxide was of 0.05M. The reactor used was a CSTR. Hence, the yield of methanol was lower due to the system, whereby, both of the reactants were fed continuously into the reactor. This system contributed smaller space time for the reactant to react with each other.

Trial 11 and 13 gave yield of 4.56 and 2.05% respectively. As compared to trial 16, the concentration of both reactants at trial 11 and 13 are at the lower level, i.e. 0.01M. Although both of the are at the same level, it produces lower yield of methanol since the number of moles of methyl acetate and calcium hydroxide in the reactor are less as compared to trial 16.

The yield of methanol at Trial 1 and 7 are also low, i.e. 4.39 and 3.96% respectively. This is due to the type of reactor used, i.e. CSTR. This reactor, as discussed before, gave smaller space time for the reactant to react with each other. Besides, the concentrations of both reactants were at the lower level, hence number of moles of methyl acetate and calcium hydroxide available is not enough to produce high yield of methanol.

To conclude, from the chromatograph analysis of all the samples, the highest concentration of methanol was to be found in the sample from Trial 16, as shown in the chromatogram in Figure 5.4. The process conditions are as shown in Table 5.1.

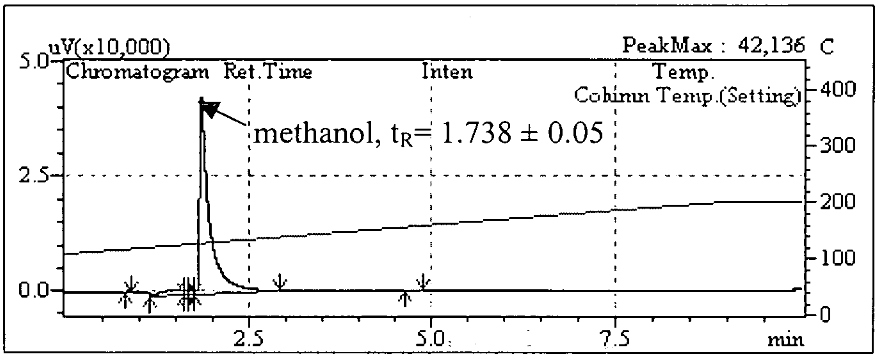


Figure 5.4: Gas chromatogram for methanol at trial 16

Table 5.1: Process condition for highest concentration of methanol produced

Parameters	Condition
(A) Type of Reactor	Semi-batch
(B) Volume of Reactor (L)	2
(C) Flow rate (cm^3/min)	80
(D) Concentration of Methyl Acetate (M)	0.05
(E) Concentration of Calcium Hydroxide (M)	0.05
(F) Temperature (°C)	50

Figure 5.2 shows the gas chromatogram for the highest methanol yield which is at Trial 16. The retention time to detect presence of methanol is at 1.738 ± 0.05 minute, which is comparable to the standard methanol being prepared prior to testing. Chromatograms for the other trials are shown in APPENDIX B. Trial 16 gave highest yield of methanol, i.e. 30.4%, since it has the largest area under the curve, which is of 600257.8 μV/min, as compared to the other trials.

Based on the GC analysis and experimental approach, using trial 16, the process conditions that will produce the highest yield, as per listed in Table 5.1. According to Table 5.1, it is shown that all of the variables, i.e. reactor type, reactor volume, flow rate, concentration of methyl acetate, concentration of calcium hydroxide and temperature, are all at Level 2.

From the analysis of the product that gave the maximum concentration of methanol, the corresponding yield is 30.4%. Using other routes and approaches to produce methanol, the yield of methanol obtained is between 2% to 47% per pass as shown in Table 5.2. The table summarizes the route that had been studied to produce methanol considering the yield of methanol per pass.

Table 5.2: Comparison studies of methanol yield

Researcher	**Scope**	**Methodology**	**Yield of methanol (%)**
Proposed work	Production of methanol via one-pot reaction at milder condition	Saponification of methyl acetate and calcium hydroxide	32.95
Takemoto T. *et al.* (2002)	Optimization of methanol yield in direct selective oxidation of methane	Presence of Cu-ZnO/Al_2O_3 at 0.4 MPa	2.3
Tsubaki N. *et al.* (2001)	Continuous synthesis process of methanol at low temperature from synthesis gas	Presence of alcohol promoter at 443K and 50 bar	47
Dong Y. *et al.* (1997)	HYNOL Process for methanol production from biomass	Recycle of H_2-rich gas through hydrogasifier	2.32
Lui Q. *et al.* (1996)	Partial oxidation of methane to methanol in a non-isothermal reactor	Homogeneously at 55MPa and 80K with non-perm selective membrane	3.8

Thus, the proposed new route is able to regenerate methanol with acceptable value at milder operating condition, i.e. 50°C temperature and 1 bar pressure, without usage of any solid catalyst.

The yield is calculated based on the average value of the methanol produced from the reaction using Equation 5.1. In this case, methyl acetate is taken as the limiting reactant. As for example, for the reaction using 0.01M of methyl acetate, the concentration of methyl acetate reacted is calculated in percentage as 0.07965 vol% while for the reaction using 0.05M of methyl acetate, the percent concentration is 0.39830 vol%. Calculation shown is for the yield at trial 16, where 0.12124 vol% of methanol is detected in the GC. The value are shown in Equation 5.1.

$$Yield, Y_{methanol} = \frac{0.12124}{0.39830} \times 100\% = 30.44\% \qquad \text{(Eq. 5.1)}$$

Other values of the methanol yield are shown in APPENDIX C.

5.1.2 Conversion of methyl acetate

The conversion of methyl acetate is calculated in the excess of calcium hydroxide and is shown in Figure 5.3. To analyze the unreacted methyl acetate in the sample, the experiment is stopped after one hour when the conductivity reached steady state. The sample is drawn from the reactor and analyzed using the gas chromatograph. From the analysis, the amount of unreacted methyl acetate was detected and represented by the area under the curve.

Example of calculation for conversion, taking the initial concentration of methyl acetate of 0.01M, for trial 1, which is equivalent to 0.07965 vol%, is

$$Conversion, X_{methyl\,acetate} = \frac{0.07965 - 0.000367}{0.07965} \times 100\% = 99.77\%$$

Conversion of methyl acetate for all the trials is shown in Figure 5.5. Most of the trials, i.e. trial 2, 4, 6, 8, 10, 11, 12, 13, 14, and 16, gave 100% of methyl acetate conversion. At this condition, methyl acetate is the limiting reactant for the saponification process.

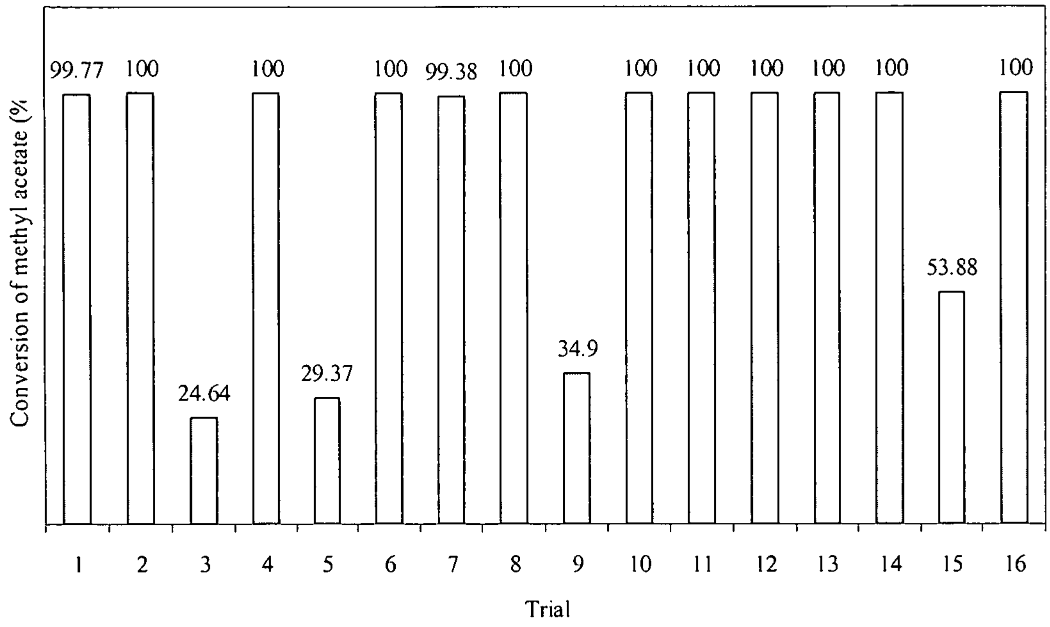


Figure 5.5: Conversion of methyl acetate

Trial 1 and 7 gave almost a 100% of methyl acetate conversion, i.e. 99.77% and 99.38%, respectively. The concentration of reactants used in these trials is at 0.01M for both methyl acetate and calcium hydroxide. Even though it has the same reactants' concentrations as in trial 11 and 14, which gave 100% of methyl acetate conversion, these trials used CSTR system that allowed smaller space time for the reactants to react with each other. Hence, percentage of unreacted methyl acetate was detected in these trials.

Trial 15 gave conversion of methyl acetate of 53.88%. The concentration of methyl acetate and calcium hydroxide were at 0.05M and 0.01M respectively. From the stoichiometry equation, methyl acetate is the limiting reactant for the reaction,

$$Ca(OH)_2 + 2CH_3COOCH_3 \Leftrightarrow 2CH_3OH + (CH_3COO)_2Ca \qquad \text{(Eq. 3.1)}$$

Hence, having 0.05M of methyl acetate and 0.01M calcium hydroxide is violating the reaction stoichiometry. Methyl acetate in excess produces lower yield of methanol since all of the calcium hydroxide have been used.

The same case is detected at trial 9. The conversion was given as 34.90%. The concentration of methyl acetate and calcium hydroxide were also at 0.05M and 0.01M, respectively. Both of trial 15 and 9 were operating on a semi-batch system.

Trial 5 gave conversion of methyl acetate of 29.37%. The concentration of methyl acetate and calcium hydroxide were at 0.05M and 0.01M respectively, similar to trial 15 and 9. However, at this trial, a CSTR system was used and hence, it had allowed smaller space time for the methyl acetate to react with the calcium hydroxide in producing methanol.

The lowest conversion of methyl acetate is given at trial 3, which is at 24.64%. The concentration of methyl acetate and calcium hydroxide were of 0.05M and 0.01M, similar to trial 5, and the system used was also a CSTR system. However, at this trial, the flow rate of the limiting reactant was at lower level, i.e. 25cm^3/min, thus, it has allowed smaller space time for the reaction to occur.

5.2 Statistical data analysis

The amount of methanol yield and conversion of methyl acetate represents the actual composition of reacted reactants and amount of products formed. The final phase of the design of experiment (DOE) process is to analyze and interpret the experimental results to improve the performance characteristics of the product or process relative to customer needs and expectations (Ross, 1996).

ANOVA is conducted to decide on which independent variable dominates over other variables and to calculate the percentage contribution of that particular independent variable.

The main objective of this work is to find the optimum condition to produce the highest product of methanol through this saponification process between methyl acetate and calcium hydroxide. The analysis is done based on 'the bigger the better' factor since high yield of methanol is desired.

5.2.1 Contribution of variables

From the tabulated calculation shown in Table C1 of Appendix C, for the determination of the optimal operating condition for the saponification process using ANOVA, there are a total of seven overall steps involved. These includes calculation the total of all results in vol%, calculation of the correction factor, calculation of the total and factor of sum of squares, the total and factor degree of freedom (DOF), calculation of mean squares or variance, and the calculation of the percentage contribution. The results of the calculations are represented in an ANOVA table as shown in Table E1 in APPENDIX E.

The portion of the total variation observed in an experiment attributed to each significant variable and interaction is reflected in the percent contribution, as shown in Figure 5.6. The percent contribution is a function of the sums of squares for each significant item. The percent contribution indicates the relative power of a variable and interaction to reduce variation. If the variable and interaction levels were controlled precisely, then the total variation could be reduced by the amount indicated by the percent contribution.

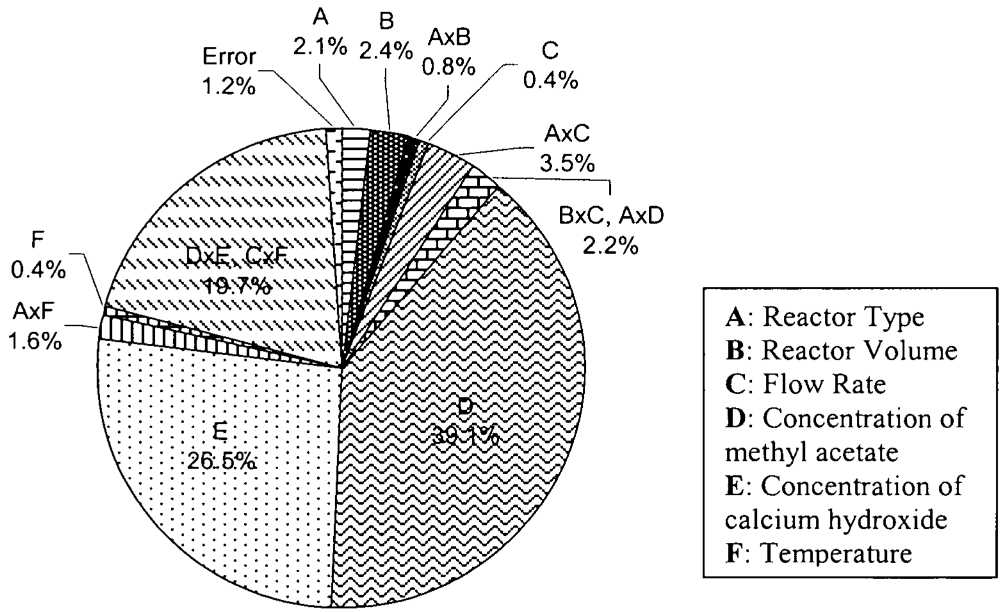


Figure 5.6: Percentage Contribution of the Variables

Figure 5.6 summarizes the contribution of the selected variables in graphical form. The finding agrees with that of those researchers work on saponification reaction using sodium hydroxide and ethyl acetate. The effect of concentration on the rate of reaction and conversion of hydroxide ions reacted agrees with the study carried out by Nihal *et al.* (2006). In their study, at 10% significance level, they found that initial concentration of the reactants has effects on the process response, which is the conversion rate of the hydroxide ions.

From Figure 5.6, it is shown that the concentration of methyl acetate (D) contributes 39.13% concentration of calcium hydroxide (E) of 26.49%. So, these variables have the largest influence on the percentage of methanol produced via this saponification process. A slight variation in these variables within the selected levels, i.e. 0.01M and 0.05M, will results in significant change the amount of methanol yield. So, proper control of concentration of methyl acetate and calcium hydroxide is crucial when conducting the experiment of saponification process.

Both reactants are the most influencing variable in producing methanol via saponification process. The reaction is written as

$$Ca(OH)_2 + 2CH_3COOCH_3 \Leftrightarrow 2CH_3OH + (CH_3COO)_2Ca \qquad \text{(Eq. 3.1)}$$

From the equation, it can be seen that two moles of methyl acetate is needed to react with one mole of calcium hydroxide to produce two moles of methanol and one of calcium acetate. In this reaction, methyl acetate is the limiting reactant. Hence the initial concentrations of both reactants are crucial to determine the production of methanol. In the experimental trials with excess of methyl acetate, it is shown that the production of methanol is suppressed. The initial concentrations however are chosen after taking into consideration the solubility of the calcium hydroxide. Hence, it is essential to conclude that the production of methanol is higher at higher concentrations of limiting reactants.

As for the interaction effect, according to Figure 5.6, the interaction between the concentration of both reactants (D x E) and interaction between flow rate and temperature (C x F) gave 19.74% contribution. So, it shows that for certain trials, interaction effect is also significant in influencing the amount of methanol produced. For an example, referring to Figure 5.1 in section 5.1, trial 10 gave lower yield than trial 16 because at this trial, interaction effect was found to influence the result. The process condition was at lower temperature of 25°C and lower flow rate of 25cm^3/min. in this trial, flow rate is not the sole variable that influence the result. The result is also influenced by the interaction between the flow rate and temperature.

Reactor type (A) and volume of reactor (B) have the similar magnitude of percentage contribution, which is about 2%. For example, even though trial 16 and 6 have the same condition for concentrations of reactants, i.e. 0.05M., but different reactors has been used, which gave 30.44% and 27.65%, respectively.

At trial 16 a semi-batch system was used. For a semi-batch process, the reactant in excess was fed initially into the reactor. Then, the limiting reactant, methyl acetate, was pumped at a rate of 80 cm^3/min. This had allowed the limiting reactant to react with the reactant in excess to produce more methanol. In a semi-batch system, the rate of consumption of the limiting reactant was higher and the reaction was completed faster as compared to CSTR system to achieve the same conversion values and yield required. Thus, reactor type does influence the amount of methanol produced.

Comparing continuous and semi-batch system for this saponification process, it can be seen that the semi-batch system is favorable. Theoretically, both continuous and semi-batch system is very suitable for this homogeneous liquid system. However, for this particular saponification of methyl acetate and calcium hydroxide to produce methanol, semi-batch gives higher production compared to continuous system.

Semi-batch system is a system with which the excess reactant, i.e. calcium hydroxide, is fed originally to the reactor to its desired volume. Then only the limiting reactant, i.e. methyl acetate, is injected into the reactor at the desired flow rate. This allows the limiting reactant to be fully reacted until the system reaches equilibrium; hence, the production of methanol is optimized.

In addition for the reactor volume (B) effect, comparing for trial 16 and trial 10, the yield given was 30.44% and 21.56% respectively. Although the reactor type used was similar, the volume is however differing for these trials. Trial 16 operated at a volume of 2L and trial 10 operated at a volume of 1L. Hence, it has influenced the yield of methanol produced.

The interaction between reactor type and flow rate effect gave a contribution of 3.5%. For example, in comparing the yield of methanol produced at trial 6 and trial 4, the yield is 27.65 and 17.02% respectively. Both of the trials operate on a CSTR system. However the flow rate is given as 25cm^3/min for trial 6 and 80cm^3/min for trial 4. Another example is between trial 1 and 7 which also operate on a CSTR system. Trial 1 operate at 25cm^3/min while trial 7 at 80cm^3/min of flow rate. The yield is given as 4.39% and 3.83% respectively. Hence, it can be seen that interaction between reactor type and flow rate does have influence on the yield of methanol.

Flow rate of the reactants is significant for the continuous flow system. Analysis shows that lower flow rate, i.e. 25 cm^3/min is favorable against the higher flow rate. More methyl acetate was converted into methanol via saponification process.

Flow rate is directly related to the retention time, τ, of a reaction. Lower flow rate indicate longer time of residence of reactants in a reactor. It allows longer time for the reactants to reacts hence producing more desired product. Though some reactions are unfavored to longer retention time, this saponification reaction does in favor of longer residence time.

The overall contact time allowed was 1 hour. Once the conductivity of the reactants in the reactor reached equilibrium, the experiment was ceased.

Temperature effect has the least influence on the reaction of producing methanol. Figure 5.6 shows that it has only 0.4% contribution to the yield of methanol.

Looking at the effects of temperature variation on the production of methanol from the saponification reaction, the reaction rate, *k*, is postulated as 0.074 $(mol/L)^{-0.6}s^{-1}$ at 25 °C, and 0.097 ± 0.05 $(mol/L)^{-0.6}s^{-1}$ at 50°C. From the equation 2.9,

$$-\frac{dC_A}{dt} = -r_A = kC_A^{\alpha}C_B^{\beta} \qquad \text{(Eq. 2.9)}$$

k has effects on the rate of the reaction, conversion of reactants and the production of methanol. Higher *k* gives higher rate of reaction. This means that higher temperature, i.e. 50°C is favorable in producing methanol via this proposed route.

5.2.2 Effect of variables

The experimental analysis is done based on the higher the better characteristics. Table 5.3 shows the average values of yield of methanol based on the contribution of each of the variables, excluding the interaction effect.

From Table 5.3(a) and (b), the most influencing variable is the concentration of methyl acetate, with a difference of 11.20% of methanol yield between the low and high level. By operating the system at a high level, i.e. 0.05M, of methyl acetate concentration, the average methanol yield is given as 15.58%. On the other hand, when operating the system at a lower level of methyl acetate concentration, i.e. 0.01M, the average yield of methanol is given as only 4.38%. This is due to the availability of moles of methyl acetate to react in producing methanol. The large difference in the average yield at low and high level indicates that this is the most influencing variable towards the reaction. Thus, proper control of this variable to ensure that the highest methanol yield is produced is crucial.

Table 5.3: Comparison of variables influence

Level	Variable					
	A (Reactor Type)	Average % methanol yield	B (Reactor Volume)	Average % methanol yield	C (Flow rate)	Average % methanol yield
1 (Low)	CSTR	8.69	1	8.57	25	10.53
2 (High)	Semi-batch	11.27	2	11.38	80	9.42
Difference (%methanol yield)		2.58		2.81		1.11
Order	4		3		6	
Level	Variable					
	D (Concentration of methyl acetate)	Average % methanol yield	E (Concentration of calcium hydroxide)	Average % methanol yield	F (Temperature)	Average % methanol yield
1 (Low)	0.01M	4.38	0.01M	5.36	25°C	9.38
2 (High)	0.05M	15.58	0.05M	14.59	50°C	10.57
Difference (%methanol yield)		11.20		9.23		1.20
Order	1		2		5	

The concentration of calcium hydroxide is the second most influencing variable to the yield of methanol produced. Average value of 14.59% methanol yield is obtained when the concentration of calcium hydroxide is at 0.05M and 5.36% of methanol yield is gained at the concentration of calcium hydroxide is at 0.01M. This is also due to the number of moles of calcium hydroxide available to react with the methyl acetate to produce methanol. The difference between the low and high level is given as 9.23% of methanol yield.

Reactor volume effect is the third variable that has the most influence on the yield of methanol. By operating the system at a high level of reactor volume, i.e. 2 L, the average methanol yield is given as 11.38%. In the contrary, an average value of methanol yield of 8.57% is given when the system is operated at a low level, i.e. 1L. The difference between the high and low level is only 2.81%, which has only a small affects on the amount of methanol produced. Slight change of the variable within the selected levels will not give any changes in the results.

This is similar with the fourth variables influencing the results if methanol yield. The reactor type has an average value of methanol yield of 11.27% when operating at the high level, i.e. semi-batch system, and 8.69% when operating at the low level, i.e. CSTR system. The difference of average methanol yield at low and high level is also low, i.e. 2.58%

The next variable is the operating temperature. High level of temperature, i.e. 50°C, gave 10.57% of average yield of methanol, while low level of temperature, i.e. 25°C, gave a value of 9.38% A small difference of 1.20% indicates that this variable has insignificant effect on the results. Slight change of this particular variable within the range of the selected levels may have no influence on the yield of methanol.

The last variable to be having influence on the results of yield of methanol is the flow rate. Flow rate has and average value of methanol yield of 10.53% by operating it at a low level, i.e. 25cm^3/min, and 9.42% by operating it at the high level, i.e. 80cm^3/min. The difference between this two levels is only 1.11% and this also indicates that by changing slightly the values of the flow rate within the range of the selected levels, it will not affect the production of methanol.

Table 5.3 is represented in graphical form as shown in Figure 5.7. From Figure 5.7, the values of average yields for each variable and level are shown by the numerical values within the graph. As stated before, the concentration of methyl acetate has the pronounce effects on the methanol yield, followed by the concentration of calcium hydroxide, reactor volume, reactor type, temperature and flow rate. It can also be seen that for variables A, B, D, E, and F, by operating at higher level, i.e. level 2, for each variable, results in higher methanol yield. While for variable C, i.e. flow rate effect, operating at lower level, i.e. 25 cm^3/min, results in higher yield of methanol.

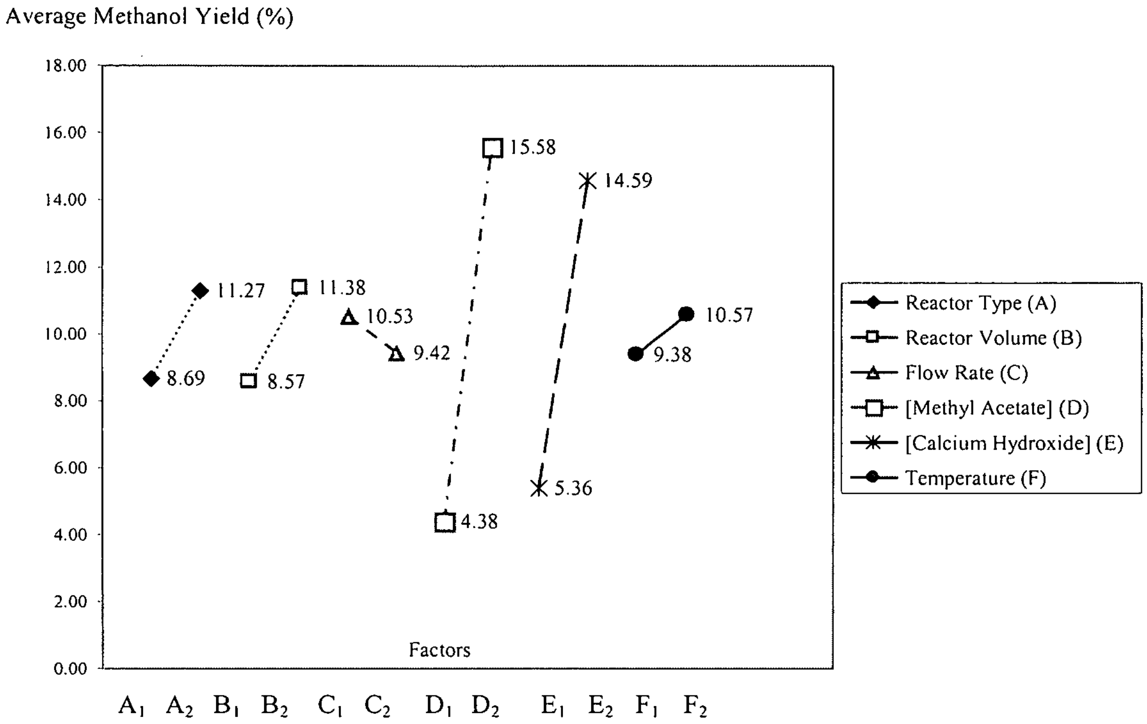


Figure 5.7: Main effects of variables

The variables' influence on the amount of methanol produced in the experiments is listed in order in Table 5.4, where variables A (reactor type), B (reactor volume), C (flow rate) and E (temperature) have less influence. Only two variables, i.e. D (concentration of methyl acetate) and E (concentration of calcium hydroxide), have pronounced effect on the production of methanol. Nevertheless, the effects of each variable are discussed in detail in the following paragraphs, from the most significant to less significant variable.

5.3 Optimum conditions using Taguchi design of experiment

The optimum condition depicted by the analysis is shown in Table 5.4:

Table 5.4: Optimum Condition from ANOVA

Variables	Level Description	Level
Reactor Type	Semi-batch	2
Reactor Volume	2L	2
Flow Rate	25cm^3/min	1
Concentration of Methyl Acetate	0.05M	2
Concentration of Calcium Hydroxide	0.05M	2
Temperature	50°C	2

Since Taguchi approach involves fractional factorial method, the optimum condition settings is found to be exclusive of the sixteen trials within the L_{16} array. The orthogonal array (OA) represents only a small fraction of all the combinations of operating condition possibilities.

5.3.1 Confirmation of Optimum Condition for Experimental Settings

A confirmation run of the experiment at the optimum condition was done to prove that the Taguchi Technique is reliable. The experiment was set to be at the given optimum conditions stated in Table 5.4.

The methanol yield obtained at the optimum condition is 32.95% and is proven by the gas chromatogram as in Figure 5.8.

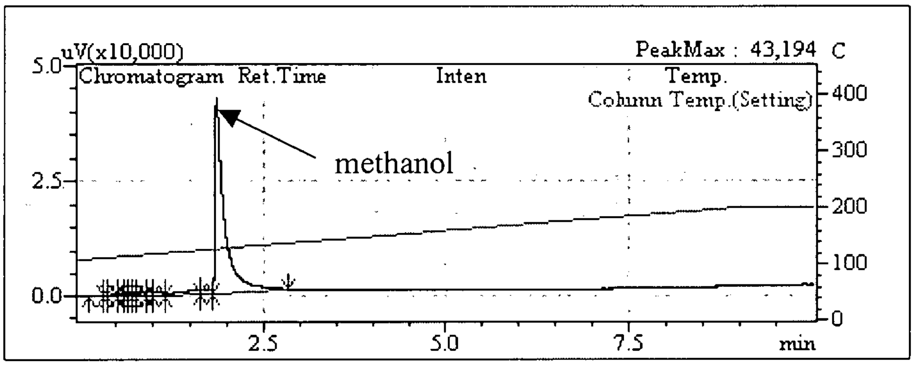


Figure 5.8: Chromatogram at optimum condition

For the confirmation run, through ANOVA analysis using Qualitek-4 software, a value of 30.91% for the yield of methanol was obtained. By running the experiment at depicted optimum condition, the yield of methanol produced is 32.95%, which is 2.04% more than the expected value calculated through Qualitek-4 software. The standard error calculated was 0.72%. Thus, this shows good agreement between predicted and actual values for the yield of methanol obtained through the proposed new route of saponification process.

5.3.2 Purity of methanol

The purity of methanol produced at the optimum condition is analyzed. Referring to Table 5.5, that shows the composition of purified methanol obtained through the saponification reaction, it shows that the methanol produced has the purity of

96.92%. The purity is obtained through the analysis by using GCMS. The balance composition consists of traces of impurities element which contributes to 3.08%. The purity value of the synthesize methanol is comparable to the commercial analytical grade of methanol, which is 99.8%, obtained from Merck.

Table 5.5: Composition of product from saponification process

Component	**Percentage (%)**
Methanol	96.92
Impurities	3.08
Total	**100.0**

5.4 Kinetics Rate Law

Kinetic study of the rate law is significant. Kinetic studies involving determination of reaction order, reaction rate and activation energy were focused in this work. By knowing these values, rate of reaction for a particular process can be determined, and sizing of reactor can be made since reactor size is largely influenced by the value of reaction rate. Thus, for upscaling of the developed route, the kinetic study is crucial.

5.4.1 Determination of the Reaction Order

By applying the linearized least squares method, the order of reaction is calculated. Table 5.6 shows the order of reaction for calcium hydroxide, α, and methyl acetate, β. The steps taken in determining the reaction order is shown in Table F1 to F9 in Appendix F.

Table 5.6: The Reaction Order

	Run 1	Run 2	Average	Std Error
α	0.662	0.724	0.69	0.03
β	0.861	1.014	0.94	0.08

The order of reaction with respect to calcium hydroxide, α, is estimated as 0.69 ± 0.03, while with respect to methyl acetate,β, is 0.94 ± 0.08. This findings show that for the new route, the reaction is a non-elementary reaction since the order of reaction is not represented by the stoichiometric coefficient of the reaction.

5.4.2 Reaction rate

In order to determine the rate of reaction, Linearized least square method is also applied. Steps taken in arriving to the results are shown in Table F1 to F9 of Appendix F.

The average value of the rate constant obtained through the linearized least squares approach is 0.097 ± 0.05.

From the mole balance of a constant-volume semi-batch reactor, and assuming power law model, the rate law is considered as the product of concentrations of the individual reacting species, each of which is raised to a power as shown in Equation 2.9.

$$-\frac{dC_A}{dt} = -r_A = kC_A^{\alpha}C_B^{\beta} \qquad \text{(Eq.2.9)}$$

with a value of 0.097 and the value of the rate constants, α and β, are given as 0.69 ± 0.03 and 0.94 ± 0.08, respectively, at 50°C of experimental condition.

The developed rate law for the developed route is thus, $-r_A = 0.097kC_A^{0.69}C_B^{0.94}$. Theoretically, the reaction was assumed as elementary reaction but through experimental approach, the reaction was found to be non-elementary. This indicates occurrence of side reactions which was unidentified, as results of pathway involving active intermediates or series reactions. However, it could be claimed that the reaction is a pseudo-first-order reaction with respect to the limiting reactant, methyl acetate.

5.4.3 Activation Energy

Activation energy, E_a, is the minimum amount of energy required to initiate a reaction. For this reaction to proceed, the reactants molecules must posses a minimum amount of energy equivalent to 8.47 kJ/mol and react at a process temperature of 50°C. The kinetic energy of the reactant molecules is transferred through molecular collision to internal energy to increase the stretching and bending of bonds that causing them to reach an activated stage, vulnerable to bond breaking and reaction.

From the rate of reaction,

$$-\frac{dC_A}{dt} = -r_A = kC_A^{\alpha} C_B^{\beta} \qquad \text{(Eq.2.9)}$$

where the values of the unknown variables are calculated previously,

$\alpha = 0.69 \pm 0.03$

$\beta = 0.94 \pm 0.08$

k = 0.097 $\pm$ 0.05 (mol/L)$^{-0.6}$s^{-1} at 50°C

k = 0.074 (mol/L)$^{-0.6}$s^{-1} at 25 °C

From the Eq. 2.18,

$$k_A(T) = Ae^{-E/RT} \qquad \text{(Eq. 2.18)}$$

Hence, the Activation Energy, E_a is calculated to be 8.47 kJ/mol at the temperature of 50°C.

5.5 Economic Study on Full Factorial and Fractional Factorial Design of Experiment

Ganeshan *et al.* (2001) in their studies asserted that most of the studies done on the interaction between economics of production and process quality have been viewed from a very traditional perspective. However, recent views on quality have shown that such a definition greatly underestimates the costs of poor quality leads to sub-optimal decisions.

An economic analysis is carried out to compare between the traditional scientific and of Taguchi orthogonal array approach.

If traditional full factorial approach is applied in completing this type of experiment, whereby six variables are studied at two levels, the total of experiments required is 64 runs. On the other hand, by applying Taguchi approach, only 16 runs are required in order to complete the study.

The analysis is carried out to compare costs of reactants and experimental run time as shown in the Table 5.7. The basis of calculation is the cost of reactants used and the time consumed in one experiment. The cost of methyl acetate and calcium hydroxide were given as RM 90/L and RM 60/kg, respectively. The amount of chemicals used in each experiment is as shown and calculated in Chapter 4. The time consumed to complete one run was 60 minutes.

Table 5.7: Comparison between Traditional and Taguchi approach for economic review

	Reactant cost	**Operating time**
Full Factorial (64 runs)	RM 280.88	15360 minutes
Taguchi Approach / Partial Fractional Method (16 runs)	RM 70.22	3840 minutes
Saved cost/time	RM 210.66	11520 minutes
Percentage saving	75%	

Referring to Table 5.7, it is clearly shown that if the experiment of saponification process was run using the fully factorial method, considering the six variables to be studied at two levels, the total cost for the reactant used is RM 280.88. Compared to the Taguchi approach, the cost of the reactant needed to complete the 16 runs was only RM 70.22.

This is also observed for the operating time. Comparing the total operating time to run the experiments, full factorial method will require 15360 minutes while Taguchi only required 3840 minutes.

The calculation shows that by applying Taguchi approach, saving of costs and time could be up to 75%. This conclude that Taguchi approach can be applied in the saponification process in order to improve the quality levels by producing smaller batches and also at a very low costs of operation and time consumption.

CHAPTER 6: CONCLUSIONS AND RECOMMENDATIONS

6.1 Conclusions

Synthesis of methanol via saponification process of methyl acetate and calcium hydroxide was investigated by comparing the effect of variables such as concentrations of reactants, temperature, reactor type, reactor volume, and flow rate of reactants that result in the highest methanol yield. The experiment was conducted by reacting methyl acetate and calcium hydroxide at atmospheric pressure and maximum operating temperature of 50°C in a reactor at two reactor conditions, continuous stirred and semi-batch.

Instead of using traditional approach to design the experiment which requires additional experimental runs to complete the trials, Taguchi technique was applied where orthogonal array (OA) is used to design the experiment. This technique allowed the data analysis in a systematic manner. The data was analyzed by analysis of variance (ANOVA) method. Result from ANOVA was used to determine the optimum condition that allowed the operation of saponification process of methyl acetate and calcium hydroxide that gave the highest yield and conversion. Besides manual calculation of the ANOVA, an engineering software, Qualitek-4, was also used to analyze the Taguchi experiments.

Taguchi robust design method with L_{16} orthogonal array was implemented to optimize experimental conditions for the production of liquid methanol. Reactor type, reactor volume, flow rate of reactants, reactants' concentrations and temperature were chosen as significant parameters in designing the experiment. Taguchi approach of design of experiment allowed evaluation of both the main and interaction effects of the experimental variables. This methodology facilitated analysis of the experimental data to establish the optimum conditions for the process, understand the contribution of individual factors and to evaluate the response under optimal conditions.

The product of the reaction that consists of methanol was analyzed using a gas chromatogram. Analysis of the gas chromatogram shows that methanol was produced via this saponification process at a retention time of 1.783 ± 0.05 minute.

Results showed that the optimum conditions for the saponification process of methyl acetate and calcium hydroxide in producing methanol was at a semi-batch system, at 2L volume, 25 cm^3/min of flow rate, 0.05M concentration of both methyl acetate and calcium hydroxide, and temperature of 50°C. Results also indicated that concentrations of reactants strongly influence the yield of methanol. It is found that reactants' concentrations were the most influencing parameters that affect the production of methanol, with 38.15% contribution from methyl acetate and 25.39% from calcium hydroxide.

The rate law of the saponification reaction was determined using the linearized least-squared method. It was found that the order of reaction with respect to calcium hydroxide and methyl acetate are not first order; 0.69 ± 0.03 and 0.94 ± 0.08 respectively. The rate constant, *k* is postulated as 0.097±0.05 $(mol/L)^{-0.6}$ s^{-1} at 50°C. The reaction is said to be a pseudo-first-order reaction with respect to the limiting reactant, methyl acetate. At these optimum conditions, the yield of methanol obtained was 32.95% with error of 0.72% compared to the expected value from the Qualitek-4 software.

This new experimental route proved that methanol can be produced via this saponification of methyl acetate and calcium hydroxide. Taguchi method was successfully applied to design the experiment for the process and it showed that of could save time and costs of reactants by 75% as compared to traditianal statistical apporach.

The objective of the project, to synthesize liquid methanol in a one-pot reaction via saponification process at atmospheric pressure and lower operating temperature of less than 64°C, was successfully done. Also, the second objective, which is to find an optimum experimental condition using the Taguchi Technique for the best yield of methanol and conversion of methyl acetate under the influence of significant variables, was achieved.

6.2 Recommendations for Future Work

This project has proved that it is possible to produce methanol via the saponification process of methyl acetate and calcium hydroxide. Hence it is necessary to extent the study of this reaction to improve the yield and economy of the process.

It is recommended that further studies to be done for the same reaction but by utilizing the natural resources, for example, the limestone that could be converted into calcium hydroxide. This will show a more significant result for the production of methanol with utilization of natural resources. Further study may also be done to find the natural resources that will give ample amount of methyl acetate when extracted. This methyl acetate can be later used as the reactant for the saponification process.

Since the rate law and reaction order of the reaction has been developed via this study, it is also recommended for a study on the optimization of the production of methanol to be done by upscaling the reactor size. This could be very essential in producing a more significant amount of methanol in a bigger reactor.

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APPENDIX A: Solubility of Calcium hydroxide

Solubility product of calcium hydroxide is calculated prior to the preparation of the reactant. The maximum concentration that can be achieved by dissolving the calcium hydroxide powder in distilled water will be used as the higher level for the reactants' concentrations.

$$Ca(OH)_2(s) \xleftrightarrow{\text{room temprature}} Ca^{2+}(aq) + 2OH^-(aq) \qquad \text{Eq. A1}$$

where

$$K = \frac{[Ca^{2+}][OH^-]^2}{[Ca(OH)_2]} \qquad \text{Eq. A2}$$

$$K[Ca(OH)_2] = [Ca^{2+}][OH^-] \qquad \text{Eq. A3}$$

At equilibrium, the value of $[Ca(OH)_2]$ is constant. [Ca^{2+}] and [OH^-] are the concentrations of Ca^{2+} and OH^- in the saturated solution of $Ca(OH)_2$ respectively.

The concentration of OH^- is determined by titration using an acid solution with known concentration while the concentration of Ca^{2+} is obtained from the equation.

Titration equation;

$$Ca(OH)_2(aq) + 2HCl(aq) \rightarrow CaCl_2(aq) + 2H_2O(l)$$

Solution A is a calcium hydroxide solution that has been prepared earlier and left overnight to ensure that the solution is at equilibrium and all the solute are dissolved in the water. Concentration of OH^- in solution A is calculated. The volume of hydrochloric acid used in the titration is 10 mL. The volume of unknown concentration of calcium hydroxide is 2.02 in average.

$$\frac{M_1V_1}{M_2V_2}=\frac{a}{b}\rightarrow\frac{(0.02)(10)}{M_{Ca(OH)_2}(2.02)}=\frac{2}{1}$$

$$M_{Ca(OH)_2}=0.05\ mol/L$$
$$\therefore[OH^-]=2\times M_{Ca(OH)_2}=2\times 0.05=0.10mol/L$$

Concentration of Ca^{2+} in solution A

$$[Ca^{2+}]=[Ca(OH)_2]=0.05mol/L$$

∴ maximum concentration of $Ca(OH)_2$ at 27°C (room temperature) is 0.05 M.

Hence, the maximum concentration of reactants to be used in the study is 0.05M.

APPENDIX B: Chromatograms of experimental samples

The chromatograms of the 16 trials are shown in Figure B1 to B16.

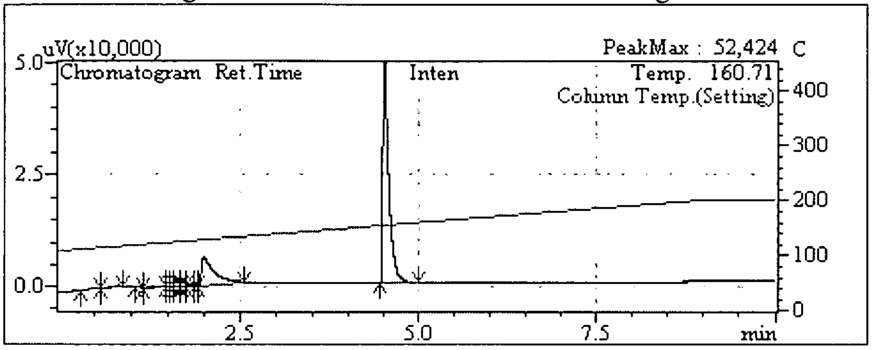

Figure B1: Chromatogram for Trial 1

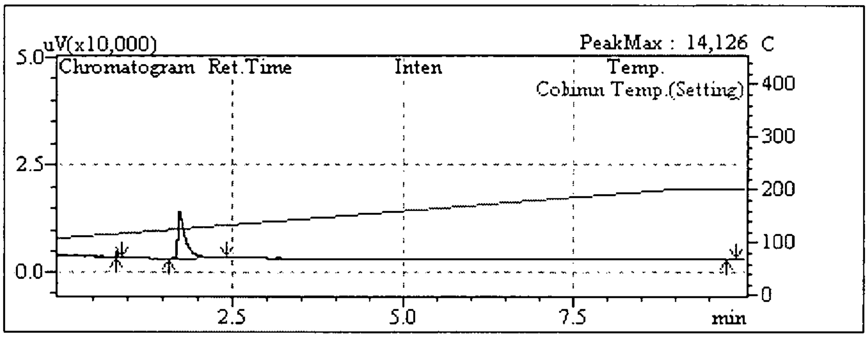

Figure B2: Chromatogram for Trial 2

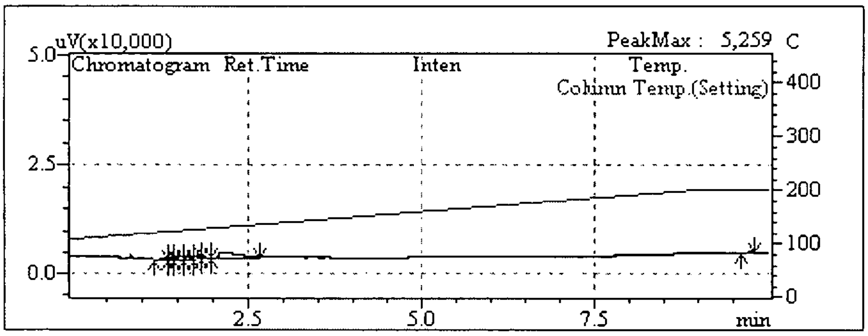

Figure B3: Chromatogram for Trial 3

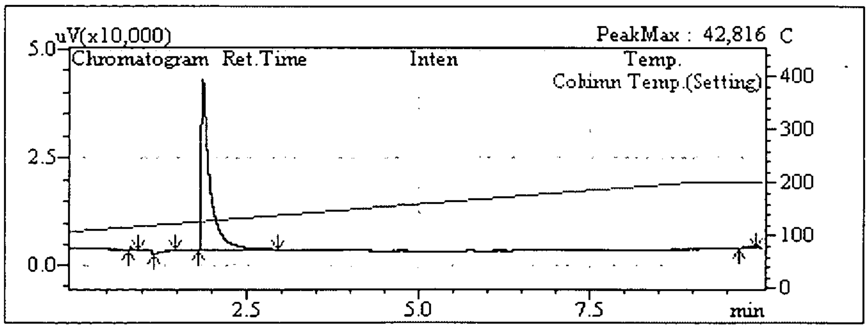

Figure B4: Chromatogram for Trial 4

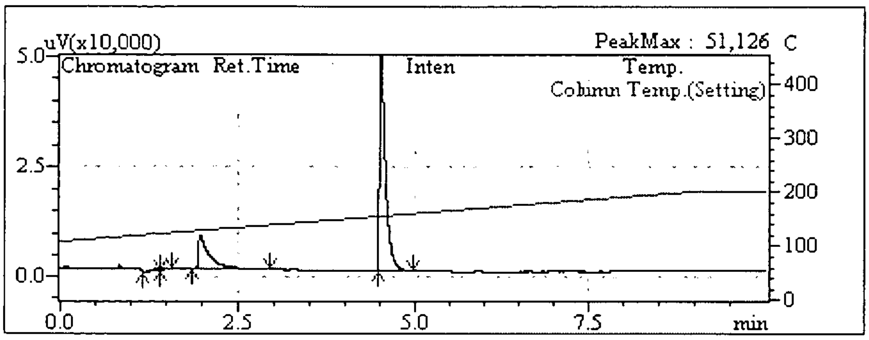

Figure B5: Chromatogram for Trial 5

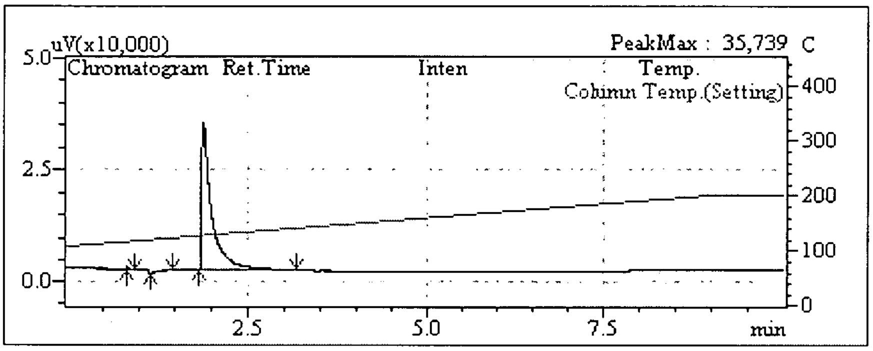

Figure B6: Chromatogram for Trial 6

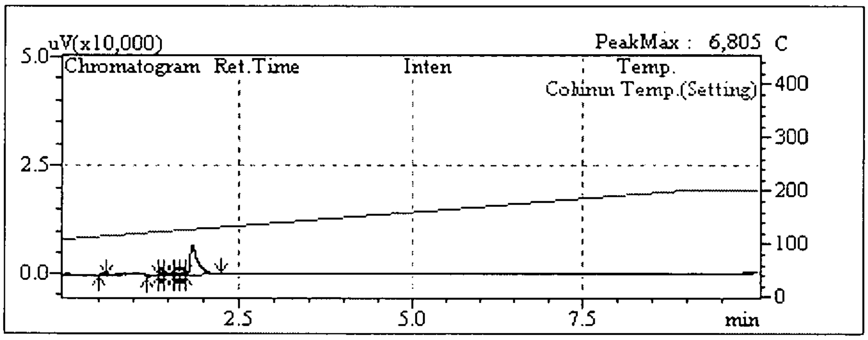

Figure B7: Chromatogram for Trial 7

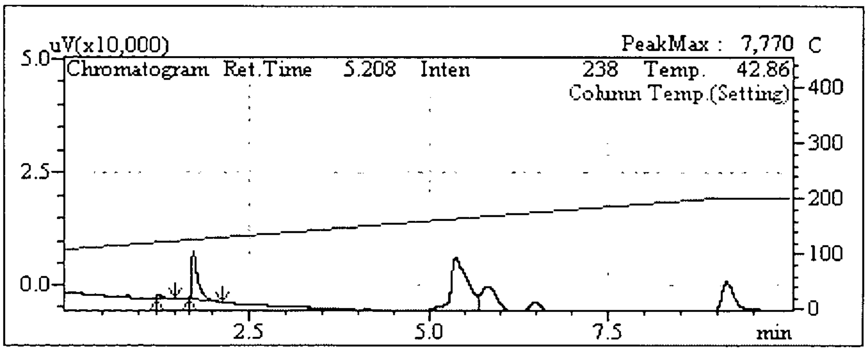

Figure B8: Chromatogram for Trial 8

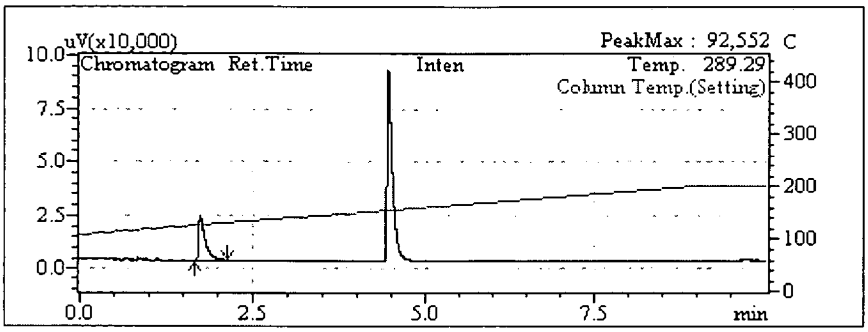

Figure B9: Chromatogram for Trial 9

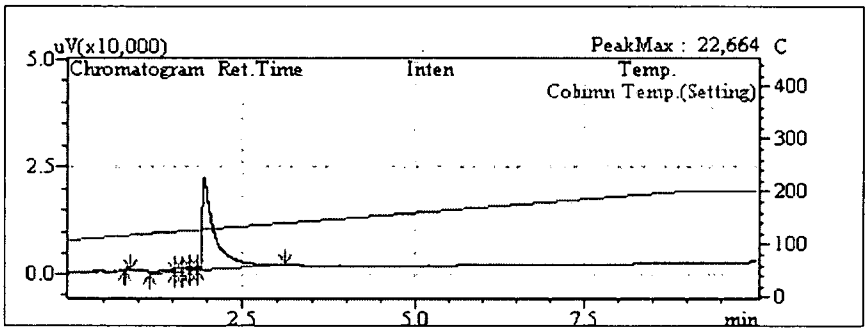

Figure B10: Chromatogram for Trial 10

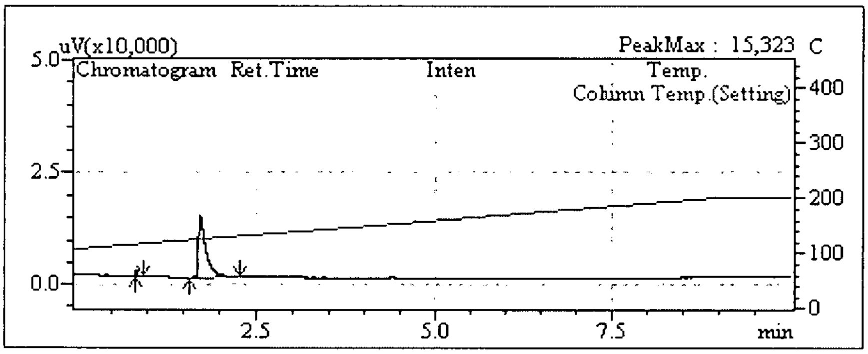

Figure B11: Chromatogram for Trial 11

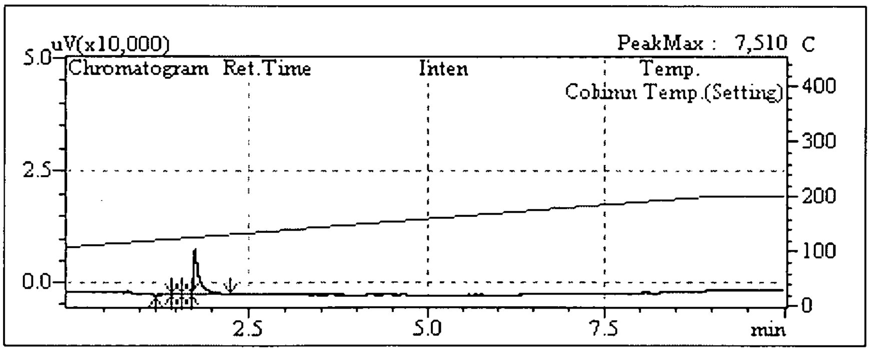

Figure B12: Chromatogram for Trial 12

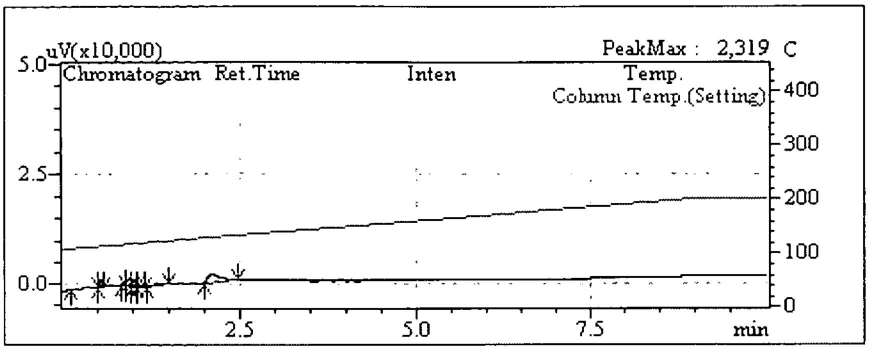

Figure B13: Chromatogram for Trial 13

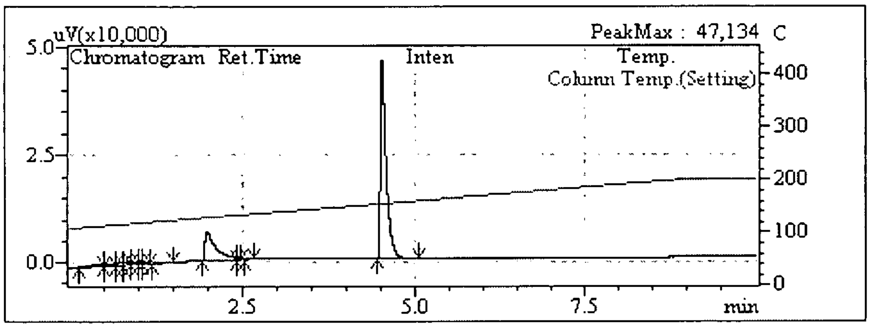

Figure B14: Chromatogram for Trial 14

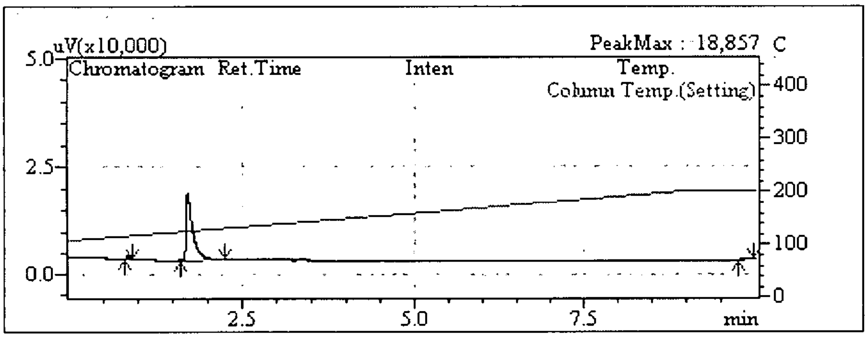

Figure B15: Chromatogram for Trial 15

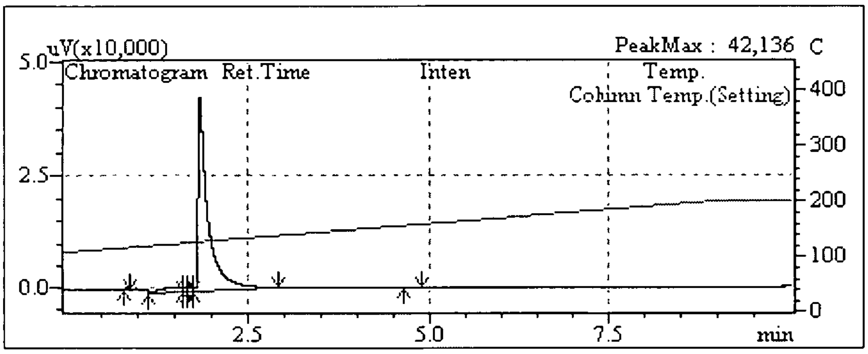

Figure B16: Chromatogram for Trial 16

APPENDIX C: Yield of Methanol

The average yield of methanol was calculated for each trial and the results are tabulated in Table C1.

Table C1: Yield of methanol at all trials

Trial	YIELD (%)	Standard deviation	Standard Error	Variance
1	4.39	5.10E-04	3.60E-04	1.30E-07
2	4.5	1.78E-03	1.25E-03	1.58E-06
3	0.02	7.00E-05	4.00E-05	0.00E+00
4	17.02	1.37E-03	9.60E-04	9.30E-07
5	7.12	8.26E-03	5.84E-03	3.41E-05
6	27.65	6.92E-03	4.89E-03	2.39E-05
7	3.96	8.30E-04	5.00E-04	3.40E-07
8	4.82	1.13E-03	7.90E-04	6.30E-07
9	11.4	1.35E-02	9.51E-03	9.05E-05
10	21.56	6.56E-03	4.63E-03	2.15E-05
11	4.56	2.06E-03	1.45E-03	2.12E-06
12	5.13	2.90E-03	2.04E-03	4.19E-06
13	2.05	8.16E-03	5.77E-03	3.33E-05
14	5.59	1.53E-03	1.08E-03	1.17E-06
15	9.4	2.45E-03	1.73E-03	3.00E-06
16	30.44	1.03E-02	7.29E-03	5.32E-05

APPENDIX D: Determination of optimal condition

The optimum condition is determined by using ANOVA. Steps taken in calculating the contribution of each variables are shown in Step 1 to Step 7. The tabulated result is shown in Table E1 of APPENDIX E.

Step 1: Calculation of the Total of All Results

Table D1: Total of all results

	R1	R2	Raverage
1	0.01800	0.01698	0.01749
2	0.01616	0.01971	0.01794
3	0.00000	0.00013	0.00007
4	0.06642	0.06915	0.06779
5	0.03663	0.02011	0.02837
6	0.11704	0.10320	0.11012
7	0.01659	0.01493	0.01576
8	0.02033	0.01808	0.01921
9	0.05888	0.03198	0.04543
10	0.07932	0.09243	0.08588
11	0.02023	0.01611	0.01817
12	0.01753	0.02332	0.02043
13	0.00000	0.01632	0.00816
14	0.02057	0.02363	0.02210
15	0.03991	0.03501	0.03746
16	0.13155	0.11093	0.12124
		T	0.63559
		n	16

Step 2: Correction factor

$$C.F. = \frac{T^2}{n} = \frac{0.63559^2}{16} = 0.02525$$

Step 3: Total Sum of Squares

$$S_T = \sum_{i=1}^{n} y_i^2 - C.F. = \begin{pmatrix} 0.01749^2 + 0.01794^2 + 0.0007^2 + 0.06779^2 + \\ 0.02837^2 + 0.11012^2 + 0.01576^2 + 0.01921^2 + \\ 0.04543^2 + 0.08588^2 + 0.01817^2 + 0.02043^2 + \\ 0.00816^2 + 0.02210^2 + 0.03746^2 + 0.12124^2 \end{pmatrix} - 0.02525$$

$$S_T = 0.02037$$

Step 4: Factor sum of squares

Table D2: Calculation of Factor Sum of Squares

(a)

Trial	**A1**	**A2**	**B1**	**B2**	**C1**	**C2**	**D1**	**D2**	**E1**	**E2**	**F1**	**F2**
1	0.01749		0.01749		0.01749		0.01749		0.01749		0.01749	
2	0.01794		0.01794		0.01794		0.01794			0.01794		0.01794
3	0.00007		0.00007			0.00007		0.00007	0.00007		0.00007	
4	0.06779		0.06779			0.06779		0.06779		0.06779		0.06779
5	0.02837			0.02837	0.02837			0.02837	0.02837			0.02837
6	0.11012			0.11012	0.11012			0.11012		0.11012	0.11012	
7	0.01576			0.01576		0.01576	0.01576		0.01576			0.01576
8	0.01921			0.01921		0.01921	0.01921			0.01921	0.01921	
9		0.04543	0.04543		0.04543			0.04543	0.04543			0.04543
10		0.08588	0.08588		0.08588			0.08588		0.08588	0.08588	
11		0.01817	0.01817			0.01817	0.01817		0.01817			0.01817
12		0.02043	0.02043			0.02043	0.02043			0.02043	0.02043	
13		0.00816		0.00816	0.00816		0.00816		0.00816		0.00816	
14		0.02210		0.02210	0.02210		0.02210			0.02210		0.02210
15		0.03746		0.03746		0.03746		0.03746	0.03746		0.03746	
16		0.12124		0.12124		0.12124		0.12124		0.12124		0.12124
Total	**0.27673**	**0.35886**	**0.27318**	**0.36242**	**0.33548**	**0.30011**	**0.13925**	**0.49635**	**0.17091**	**0.46469**	**0.29880**	**0.33679**

continued…

…continued for sum of squares of the interactions

(b)

Trial	**(AxB)1**	**(AxB)2**	**(AxC)1**	**(AxC)2**	**(AxF)1**	**(AxF)2**	**(DxE)1**	**(DxE)2**	**(BxC)1**	**(BxC)2**
1	0.01749		0.01749		0.01749		0.01749		0.01749	
2	0.01794		0.01794			0.01794		0.01794	0.01794	
3	0.00007			0.00007	0.00007			0.00007		0.00007
4	0.06779			0.06779		0.06779	0.06779			0.06779
5		0.02837	0.02837			0.02837		0.02837		0.02837
6		0.11012	0.11012		0.11012		0.11012			0.11012
7		0.01576		0.01576		0.01576	0.01576		0.01576	
8		0.01921		0.01921	0.01921			0.01921	0.01921	
9		0.04543		0.04543	0.04543			0.04543	0.04543	
10		0.08588		0.08588		0.08588	0.08588		0.08588	
11		0.01817	0.01817		0.01817		0.01817			0.01817
12		0.02043	0.02043			0.02043		0.02043		0.02043
13	0.00816			0.00816		0.00816	0.00816			0.00816
14	0.02210			0.02210	0.02210			0.02210		0.02210
15	0.03746		0.03746			0.03746		0.03746	0.03746	
16	0.12124		0.12124		0.12124		0.12124		0.12124	
Total	**0.29224**	**0.34336**	**0.37121**	**0.26438**	**0.35382**	**0.28177**	**0.44460**	**0.19099**	**0.36040**	**0.27520**

Table D3: Simplified table for factor sum of squares

Factor Sum of Squares	
S_A	4.22E-04
S_B	4.98E-04
S_C	7.82E-05
S_D	7.97E-03
S_E	5.39E-03
S_F	9.02E-05
S_{AxB}	1.63E-04
S_{AxC}	7.13E-04
S_{BxC}	4.54E-04
S_{AxF}	3.24E-04
S_{DxE}	4.02E-03
S_{total}	2.01E-02
S_{error}	4.22E-04

Hence the total sum of square is **0.0201265**

Step 5: Total and factor degree of freedom (DOF)

Table D3: Degree of freedom (DOF)

DOF,f_T	15
f_A	1
f_B	1
f_C	1
f_D	1
f_E	1
f_F	1
f_{AxB}	1
f_{AxC}	1
f_{BxC}	1
f_{AxF}	1
f_{DxE}	1
Total	11
DOFerror	4

Step 6: Calculation of Mean Square (Variance)

Table D4: Mean Square (Variance)

Mean Square (Variance)	
V_A	4.22E-04
V_B	4.98E-04
V_C	7.82E-05
V_D	7.97E-03
V_E	5.39E-03
V_F	9.02E-05
V_{AxB}	1.63E-04
V_{AxC}	7.13E-04
V_{BxC}	4.54E-04
V_{AxF}	3.24E-04
V_{DxE}	4.02E-03
V_{error}	5.98E-05

Step 7: Calculation of Percentage Contribution

Table D5: Percentage Contribution

Percentage Contribution	
P_A	2.07E+00
P_B	2.44E+00
P_C	3.84E-01
P_D	3.91E+01
P_E	2.65E+01
P_F	4.43E-01
P_{AxB}	8.02E-01
P_{AxC}	3.50E+00
P_{BxC}	2.23E+00
P_{AxF}	1.59E+00
P_{DxE}	1.97E+01
P_{error}	1.17E+00
Total	2.07E+00

APPENDIX E: Analysis of Variance (ANOVA)

Appendix E shows the ANOVA Table for the calculation of yield. The data were analyzed based on the bigger the better characteristic.

Table E1: ANOVA Table

Column	Variables	f	s	v	F	P
1	Reactor Type (A)	1	0.00042	0.00042	7.05540	2.07008
2	Reactor Volume (B)	1	0.00050	0.00050	8.32985	2.44401
3	AxB	1	0.00016	0.00016	2.73338	0.80198
4	Flow Rate (C)	1	0.00008	0.00008	1.30854	0.38393
5	AxC	1	0.00071	0.00071	11.93725	3.50244
6	BxC, AxD	1	0.00045	0.00045	7.59272	2.22773
7	Concentration of Methyl Acetate (D)	1	0.00797	0.00797	133.38212	39.13483
8	Concentration of Calcium Hydroxide (E)	1	0.00539	0.00539	90.27394	26.48672
10	AxF	1	0.00032	0.00032	5.42983	1.59313
11	Temperature (F)	1	0.00009	0.00009	1.50958	0.44292
15	DxE, CxF	1	0.00402	0.00402	67.27453	19.73861
Error		4	0.00024	0.00006		1.17362
Total		15	0.02013			100

APPENDIX F: Determination of reaction kinetics

The kinetics of the reaction is determined since the reaction being developed is a novel route. The reaction order, reaction rate, and rate constant are determined.

Table F1: Conductivity versus time for 0.01M $Ca(OH)_2$ reacts with 0.01M CH_3COOCH_3 at 50°C.

	Conductivity,mS	
Time (min)	Run 1	Run 2
0	5.13	5.15
1	4.24	4.19
2	3.87	3.85
3	3.66	3.72
4	3.6	3.6
5	3.54	3.59
6	3.53	3.55
7	3.5	3.54
8	3.48	3.52
9	3.48	3.52
10	3.48	3.52
11	3.48	3.52
12	3.48	
13	3.48	
14	3.48	

Table F2: Conductivity versus time for 0.008M $Ca(OH)_2$ reacts with 0.002M CH_3COOCH_3 at 50°C.

	Conductivity,mS	
Time (min)	Run 1	Run 2
0	4.24	4.16
1	4.01	4
2	3.95	3.9
3	3.92	3.86
4	3.87	3.85
5	3.88	3.82
6	3.87	3.81
7	3.86	3.81
8	3.86	3.82
9	3.86	3.82
10	3.86	3.82
11	3.86	

Table F3: Conductivity versus time for 0.006M $Ca(OH)_2$ reacts with 0.004M CH_3COOCH_3 at 50°C.

	Conductivity (mS)	
Time (min)	Run 1	Run 2
0	3.18	3.2
1	2.90	2.91
2	2.75	2.74
3	2.65	2.66
4	2.57	2.6
5	2.54	2.57
6	2.53	2.55
7	2.51	2.54
8	2.49	2.53
9	2.48	2.52
10	2.48	2.53
11	2.48	2.53
12	2.47	2.53
13	2.48	2.52

Table F4: Conductivity versus time for 0.004M $Ca(OH)_2$ reacts with 0.006M CH_3COOCH_3 at 50°C.

	Conductivity (mS)	
Time (min)	Run 1	Run 2
0	2.22	2.25
1	1.9	1.91
2	1.73	1.72
3	1.59	1.61
4	1.51	1.51
5	1.47	1.46
6	1.43	1.43
7	1.4	1.39
8	1.37	1.35
9	1.34	1.32
10	1.32	1.31
11	1.32	1.3
12	1.3	1.29
13	1.28	1.28
14	1.27	1.25
15	1.27	1.26
16	1.25	1.24
17	1.24	1.24
18	1.23	1.24
19	1.24	1.22
20	1.24	1.22
21	1.22	1.22
22	1.22	1.2
23	1.22	1.2
24		1.2

Table F5: Conductivity versus time for 0.002M $Ca(OH)_2$ reacts with 0.008M CH_3COOCH_3 at 50°C.

	Conductivity (mS)	
Time (min)	Run 1	Run 2
0	1.36	1.24
1	1.08	0.98
2	0.93	0.84
3	0.83	0.76
4	0.77	0.68
5	0.72	0.66
6	0.68	0.62
7	0.65	0.61
8	0.64	0.57
9	0.63	0.56
10	0.63	0.56
11		0.56
12		0.54
13		0.54
14		0.54

Table F6: Conductivity versus time for 0.006M $Ca(OH)_2$ reacts with 0.004M CH_3COOCH_3 at 25°C.

Time (min)	Conductivity (mS)
0	2.29
1	2.23
2	2.18
3	2.13
4	2.09
5	2.05
6	2.02
7	1.99
8	1.97

Table F7: Conductivity table of mixture of $Ca(OH)_2$ and $(CH3COO)_2Ca$ at 50°C.

Concentration $Ca(OH)_2$	Concentration Calcium acetate	Conductivity (mS)
0.01	0	5.11
0.009	0.001	4.76
0.008	0.002	4.42
0.007	0.003	4.11
0.006	0.004	3.79
0.005	0.005	3.42
0.008	0	4.19
0.007	0.001	3.87
0.006	0	3.26
0.005	0.001	2.91
0.004	0.002	2.58
0.004	0	2.23
0.003	0.001	1.87
0.002	0.002	1.52
0.001	0.003	1.17
0.002	0	1.36
0.001	0.001	0.99
0	0.002	0.63

Table F8: Conductivity table of mixture of $Ca(OH)_2$ and (CH3COO)2Ca at 25°C.

Concentration $Ca(OH)_2$	Concentration Calcium acetate	Conductivity (mS)
0.006	0	2.29
0.005	0.001	2.03
0.004	0.002	1.77

Table F9: Concentration of $Ca(OH)_2$ versus time for different initial concentration of reactants at 50°C.

	0.01 : 0.01		0.008 : 0.002		0.006 : 0.004		0.004 : 0.006		0.002 : 0.008	
Time (min)	Run 1	Run 2	Run 1	Run 2	Run 1	Run 2	Run 1	Run 2	Run 1	Run 2
0	0.01	0.01	0.008	0.008	0.006	0.006	0.004	0.004	0.002	0.002
1	0.00735	0.00713	0.007395	0.007529	0.00523	0.00517	0.00311	0.00306	0.001243	0.001297

Table F10: Result of calculation using Linear-least-square method for first run.

	CA_o	CB_o	Initial rate	Y	X1	X2	X1Y	X2Y	SQRT(X1)	SQRT(X2)	X1X2
1	0.01	0.01	4.42E-05	-10.0275	-4.60517	-4.60517	46.17853	46.17853	21.20759	21.20759	21.20759
2	0.008	0.002	1.01E-05	-11.5046	-4.82831	-6.21461	55.54795	71.49675	23.31261	38.62135	30.00608
3	0.006	0.004	1.28E-05	-11.2635	-5.116	-5.52146	57.62384	62.19078	26.17341	30.48653	28.24777
4	0.004	0.006	1.48E-05	-11.1186	-5.52146	-5.116	61.3911	56.88288	30.48653	26.17341	28.24777
5	0.002	0.008	1.26E-05	-11.2805	-6.21461	-4.82831	70.10384	54.46575	38.62135	23.31261	30.00608
Sum				-55.1948	-26.2855	-26.2855	290.8453	291.2147	139.8015	139.8015	137.7153

Table F11: Result of calculation using Linear-least-square method for second run.

	CA_o	CB_o	Initial rate	Y	X1	X2	X1Y	X2Y	SQRT(X1)	SQRT(X2)	X1X2
1	0.01	0.01	4.78333E-05	-9.94779	-4.60517	-4.60517	45.81126	45.81126	21.20759	21.20759	21.20759
2	0.008	0.002	0.00000785	-11.755	-4.82831	-6.21461	56.75681	73.0527	23.31261	38.62135	30.00608
3	0.006	0.004	1.38333E-05	-11.1884	-5.116	-5.52146	57.23996	61.77648	26.17341	30.48653	28.24777
4	0.004	0.006	1.56667E-05	-11.064	-5.52146	-5.116	61.08931	56.60325	30.48653	26.17341	28.24777
5	0.002	0.008	1.17167E-05	-11.3545	-6.21461	-4.82831	70.56376	54.82308	38.62135	23.31261	30.00608
Sum				-55.3097	-26.2855	-26.2855	291.4611	292.0668	139.8015	139.8015	137.7153

Table F12: Result of calculation using Linear-least-square method for second run.

	Run 1	Run 2	Average	Std Error
a0	-3.053	-1.925		
a1	0.662	0.724	0.69	0.03
a2	0.861	1.014	0.94	0.08
k	0.047	0.146	0.097	0.05

Table F13: Activation energy.

rate constant at 25°C	0.0741
rate constant at 50°C	0.096
T1, K	298
T2, K	323
E, J/mol	8290.884