Production of Ester by Reactive Distillation of Acid and Alcohol

by

Nuur Syafyka Bt Shafie

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CERTIFICATION OF APPROVAL

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A project dissertation submitted to the
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Approved by,

(Ap Dr. Ye Lwin) 6/1/12

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CERTIFICATION OF ORIGINALITY

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

NUUR SYAFYKA SHAFIE

ABSTRACT

Reaction of an acid with a hydroxyl compound forms ester and water as products. Ester is separated from other products by distillation. Reactive distillation is an improvement of conventional distillation by combining the reactive and separation section in one unit. The problems associated with conventional distillation are limited conversion due to equilibrium limitation, formation of azeotropes as well as high cost and energy consumption. The advantages of reactive distillation are cost saving, breaking equilibrium limitation and favor the elimination of azeotropes in the mixture. The aim of this project is to study the feasibility of esterification of acetic acid with ethanol by reactive distillation as well as to study the effect of alcohol to acid ratio and catalyst loading to the purity of ester. In this project, the product ester is continuously separated from the alcohol in volatile phase by fractional distillation while alcohol is recycled back to the reaction flask, thereby shifting the equilibrium to the direction of higher equilibrium conversion of acetic acid. The experiment is conducted both in the presence and absence of sulfuric acid catalyst. The ethanol to acetic acid molar ratio of 2:1 with 1 (% w/w) catalyst loading gives the highest ester purity of 77%.

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CHAPTER 1
INTRODUCTION

1.1 Background

Esters are chemical compounds that are formed as products, together with water, from reaction of a carboxylic acid with a hydroxyl compound such as alcohol or phenol. Esters are normally separated from the products by distillation. Esters are widely used in the cosmetic, perfume, food additives, plastic and molding industries.

Reactive distillation (RD) is an improvement of conventional distillation process by having combination of reactor and separation steps in only one unit. The main purpose of a RD column is to separate products from the reactants to boost the conversion and to improve selectivity by breaking the reaction equilibrium restrictions (Estrada-Villagrana, Quiroz-Sosa, M.L. Jiménez-Alarcón, & Cano-Dominguez, 2006). Reducing capital cost, higher conversion, improving selectivity, lower energy consumption and avoidances of azeotropes are a few of the potential advantages offered by RD (Mueanmas, Prasertsit, & Tongurai, 2010). Esterification, alkylation and hydrolysis processes are some of the applications of RD in the industry.

1.2 Problem Statement

Conventional processes of reaction followed by distillation or other separation approaches have several disadvantages. These processes consume high capital costs due to complex processes involving many units. It needs at least one to two reactants and several units for separations to produce pure products (Mueanmas, Prasertsit, & Tongurai, 2010). Higher operating cost is also needed due to excess of reactant which is normally used to minimize side reactions and to overcome limitations caused by chemical equilibrium. The energy consumption of conventional process is also high due to energy needed for separation (Kaymak, Yilmaz, Yilmaz, & Hosgor, 2010). Azeotropes in the mixture is also another problem of conventional distillation (Malone & Doherty, 2000).

1.3 Objectives

The aims of this project are:

- To study the feasibility of esterification by RD.
- To study the effect of alcohol to acid ratio and catalyst loading on the purity of ester.

1.4 Scope of Study

Experiments done in this project applies RD related concepts, and not the real RD column, due to limited resources and apparatus. All researches and literatures used for this project aims to study the effect of catalyst loading and initial ethanol to acetic acid molar ratio on the purity of ester as well as the feasibility of esterification by RD. The range of catalyst loading amount studied is from 0-1 (% w/w). The molar ratios of alcohol to acid used are the stoichiometric (1:1) and excess alcohol of (1.5:1) and (2:1). The effect of reaction temperature is not studied in the experiment due to narrow range of reactants and products boiling points. The analysis is done by using a gas chromatograph.

1.5 Feasibility of the Project

This project is feasible to be conducted within two semesters considering that the apparatus and chemicals needed are not complicated and literatures available are sufficient to help in understanding and analyzing the data.

CHAPTER 2

LITERATURE REVIEW

The concept of RD is very well demonstrated by R. Taylor & R. Krishna, (2000). A reversible reaction of $A + B \rightleftharpoons C + D$ is considered. The conventional flow sheet of this process consists of a reactor followed by a sequence of distillation columns as shown in Fig. 1. The mixture of A and B is fed to the reactor, where the reaction takes place in the presence of a catalyst until it reaches equilibrium. A sequence of distillation columns is needed to produce pure products of C and D. The unreacted components, A and B are recycled back to the reactor (Taylor & Krishna, 2000). The sequence of distillation column can be more complex than Fig. 1 if one or more azeotropes are formed in the mixture.

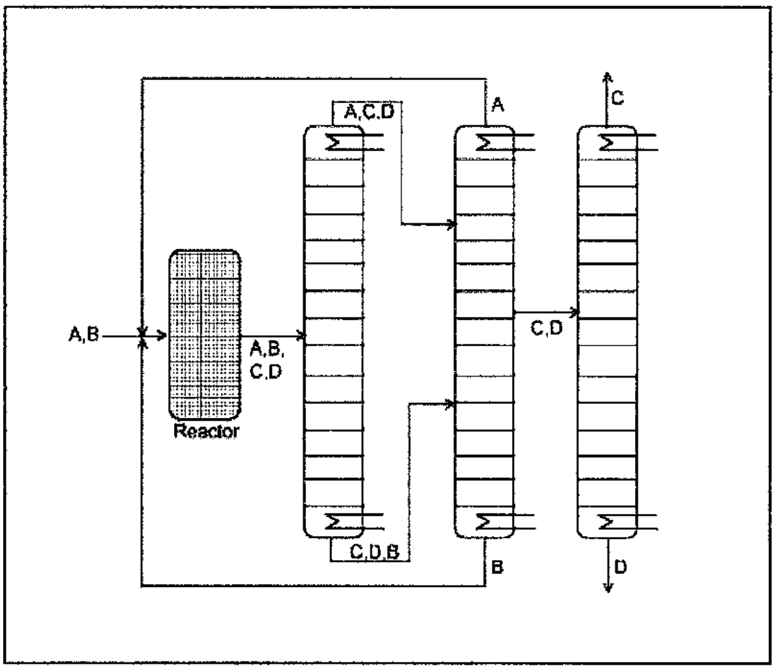


Fig. 1. Typical configuration of conventional distillation process.
(Source : R. Taylor & R. Krishna, 2000)

Fig. 2 shows the RD column which consists of a reactive section in the middle with separation (rectifying and stripping) section at the top and bottom respectively. In rectifying section, reactant B is covered from the product stream C. Reactant A is stripped from the product stream D in the stripping section. The products are separated in situ, driving the equilibrium to the right and preventing any undesired side reactions to occur. 100 % conversion can be achieved virtually for a properly designed RD column.

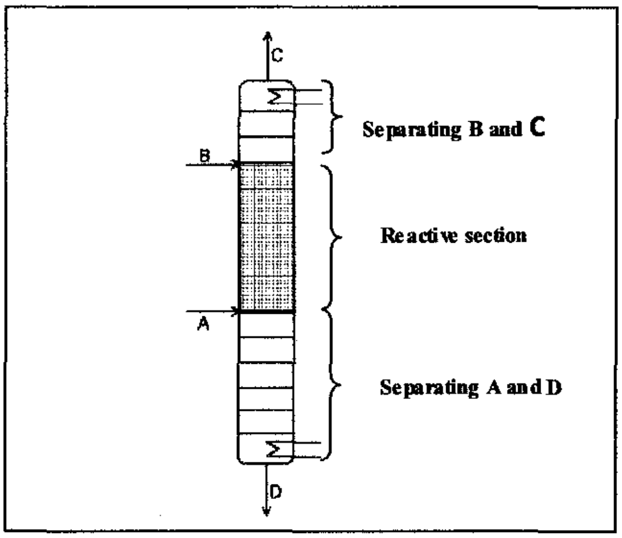


Fig. 2. Typical configuration of a RD column.
(Source : R. Taylor & R. Krishna, 2000)

According to Malone & Doherty, (2000), reactive distillation is not a feasible alternative for all chemical processes. The features for ideal and azeotropic mixtures must be taken into account when doing the feasibility analysis. The main reason the old technology to make methyl acetate expensive and complicated is the existence of azeotropes in the reactor effluent mixture, consisting of acetic acid and methanol (both unreacted reactants due to reaction equilibrium limitation) and methyl acetate and water (both products). The azeotropes between methyl acetate and water is very important to be broken in order to obtain pure products. However in RD these azeotropes disappear because it reacts into four components mixture, and "destroy" the azeotropes (Malone & Doherty, 2000).

The RD process for transesterification of palm oils was done by Mueanmas, Prasertsit & Tongurai, (2010). The experiment was done by using palm oil and methanol as reactants. The palm oil contained free fatty acid about 0.3 to 0.6 %. The effect of methanol to oil ratio on methyl esters content is presented in Fig. 3. The methyl ester content increases with molar ratio justify the need for excess alcohol to drive the reaction to a higher yield. A higher methanol to palm oil ratio increases the reaction rate and consequently decreases the processing time. A higher concentration of alcohol increases the raeaction rate because the reaction is a second-order reaction with respect to methanol as described by the rate law and explained by the collision theory. As reactant concentration increases, the frequency of collision increases. It also displaces the equilibrium towards the products. The methyl ester content in the product increases from 84.9 % to 92.37 % as the methanol to oil ratio increases from 3:1 to 5:1.

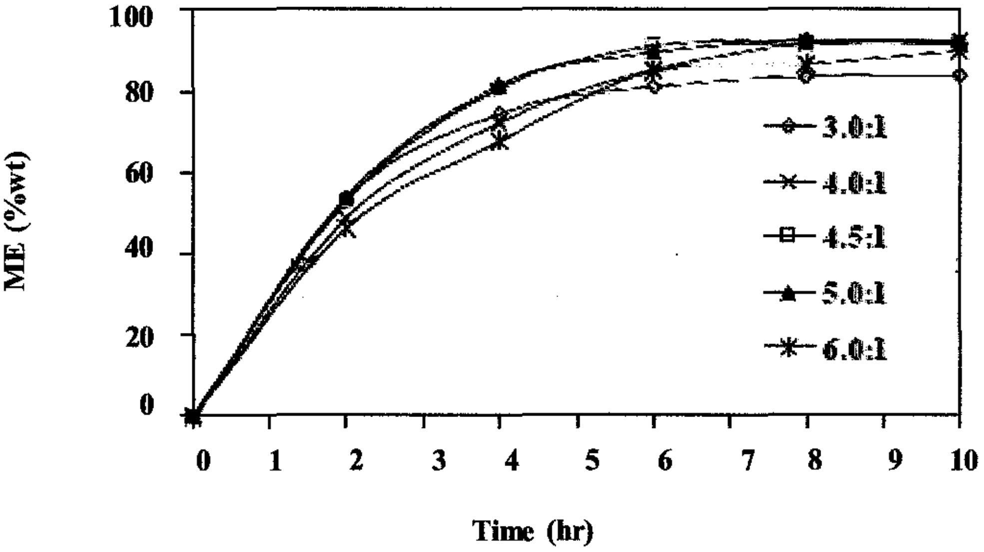
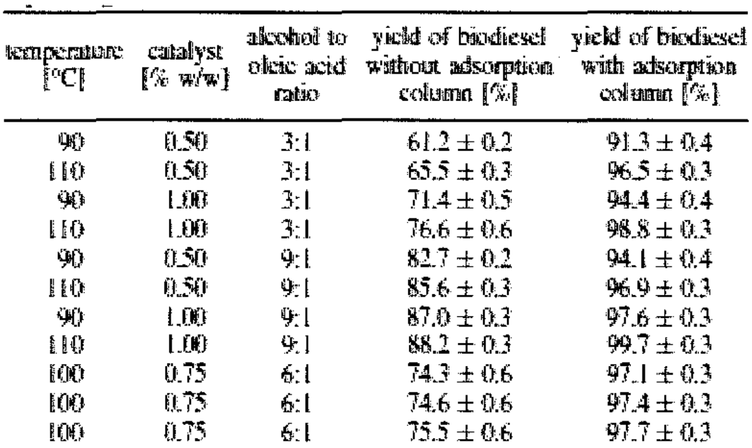


Fig. 3. Effect of time on methyl esters content at varying methanol to oil ratio.
(Source : Muenmas, Prasertsit, & Tongurai, 2010)

Normally, the conventional process requires 100 percent excess methanol to drive the reaction close to completion and break the chemical equilibrium limitation. The excess methanol that remains has to be separated from the products to be reused. The use of lower alcohol to acid molar ratio in RD application has several economic and ecological advantages. Smaller process equipment needs to be designed, reducing capital costs. Less mass needs to be heated, reducing energy costs. Less volume of alcohol needs to be processed, reducing the operating cost. Less methanol needs to be washed to remove catalyst, reducing the impacts of wastewater on the environment (Lucena, Silva, & Fernandes, 2008).

Biodiesel production by esterification of oleic acid with methanol was done by Lucena, Silva & Fernandes, (2008) using a water adsorption method. The esterification reaction was carried out above the boiling points of methanol and water to evaporate the water produced from the reaction. A condenser is placed above the adsorption column to condense the water and methanol vapor. The water-free methanol will be returned to the reactor after passing through the adsorption column. The adsorption system aims to remove the water produced during the reaction to shift the equilibrium towards methyl ester production. In the experiment, the removal of water is achieved using adsorbents selective for water adsorption, such as zeolite 3A. The experimental result, as tabulated in Table 1 shows that when the water adsorption column was employed, the yield of biodiesl increased. Therefore, the water adsorption system was effective in shifting the equilibrium towards the products.

Table 1. Yield of Biodiesel, After 80 min of Reaction, at Different Operating Condition.
(Source : Lucena, Silva & Fernandes, 2008)



temperature [°C]	catalyst [% w/w]	alcohol to oleic acid ratio	yield of biodiesel without adsorption column [%]	yield of biodiesel with adsorption column [%]
90	0.50	3:1	61.2 ± 0.2	91.3 ± 0.4
110	0.50	3:1	65.5 ± 0.3	96.5 ± 0.3
90	1.00	3:1	71.4 ± 0.5	94.4 ± 0.4
110	1.00	3:1	76.6 ± 0.6	98.8 ± 0.3
90	0.50	9:1	82.7 ± 0.2	94.1 ± 0.4
110	0.50	9:1	85.6 ± 0.3	96.9 ± 0.3
90	1.00	9:1	87.0 ± 0.3	97.6 ± 0.3
110	1.00	9:1	88.2 ± 0.3	99.7 ± 0.3
100	0.75	6:1	74.3 ± 0.6	97.1 ± 0.3
100	0.75	6:1	74.6 ± 0.6	97.4 ± 0.3
100	0.75	6:1	75.5 ± 0.6	97.7 ± 0.3

The two levels, three-factor full factorial design of experiments was applied in the study done by Rattanaphanee, (2010) to see the relationship between the operating variables and lactic acid conversion in esterification with ethanol and n-butanol. The variables are reaction temperature, initial alcohol to acid molar ratio and catalyst loading. The effect of agitation speed is not being studied in this paper because it has previously been observed in several studies that agitation speed does not affect the reaction rate due to absence of external mass transfer resistance in the operation and the external mass transfer does not control the overall reaction rate unless the agitation speed is very low or the viscosity of reactant mixture is very high (Yadav & Kulkarni, 2000).

Table 2 tabulates the experimental data for the effect of catalyst loading to the conversion of lactic acid. Run 1-4 are the experiments data for the effect of catalyst loading, while Run 5-8 are those with high catalyst loading. It can be concluded from the table that larger catalyst loading leads to higher lactic acid conversion with the exception in the processes with high reaction temperature and low initial molar ratio. An increase in catalyst loading increases the conversion of lactic acid in consonance with the proportional increase in the active sites. In the absence of mass transfer resistance, the initial rate of reaction is directly proportional to the catalyst loading based on the entire liquid phase volume. This further supports that the controlling mechanism is the surface reaction on the pore wall. At higher catalyst loading, the rate of mass transfer is excessively high and therefore there is no significant increase in the rate (Yadav & Thathagar, 2002).

Table 2. Conversion of Lactic Acid in Esterification After 480 minutes of Reaction (Source : Rattanaphanee, 2010)

Group	Run	Temperature (°C)	Initial Reactant Molar Ratio (mole$_{Alcohol}$:mole$_{Lactic}$)	Catalyst Loading %(w/v)	Coding			% Conversion of Lactic Acid at 480 min	
								Ethanol	n-Butanol
A	1	65	1:1	1	-1	-1	-1	42.26	40.67
	2	85	1:1	1	+1	-1	-1	49.27	50.69
B	3	65	5:1	1	-1	+1	-1	57.67	59.14
	4	85	5:1	1	+1	+1	-1	72.75	77.93
C	5	65	1:1	5	-1	-1	+1	48.47	50.78
	6	85	1:1	5	+1	-1	+1	46.59	50.89
D	7	65	5:1	5	-1	+1	+1	73.33	80.11
	8	85	5:1	5	+1	+1	+1	78.52	82.12

According to KIRBAŞLAR, BAYKAL, & DRAMUR, (2000), combination of an esterification reaction with distillation in a reactive distillation column either in batch or continous mode leads to a larger increase in the purity of esthyl acetate in the distillate. A continous reactive distillation column gave the highest ethyl acetate concentration achieved, which is far better than corresponding thermodynamic equilibrium concentrations. The effects of variables such as refulx ratio, vapor rate and feed flow rate on ethyl acetate production were studied experimentally. Fig. 4 shows the schematic diagram of reactive distillation column used in the experiment setup.

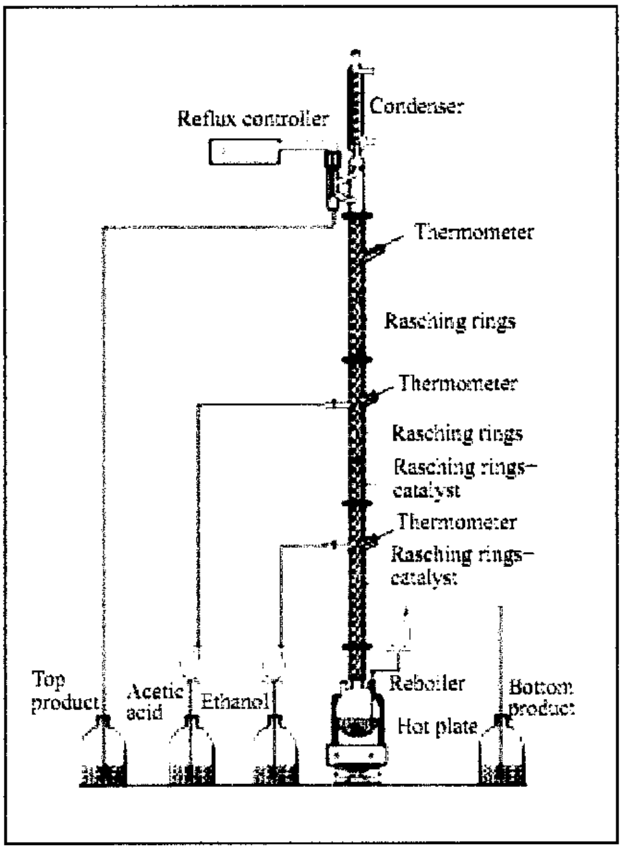
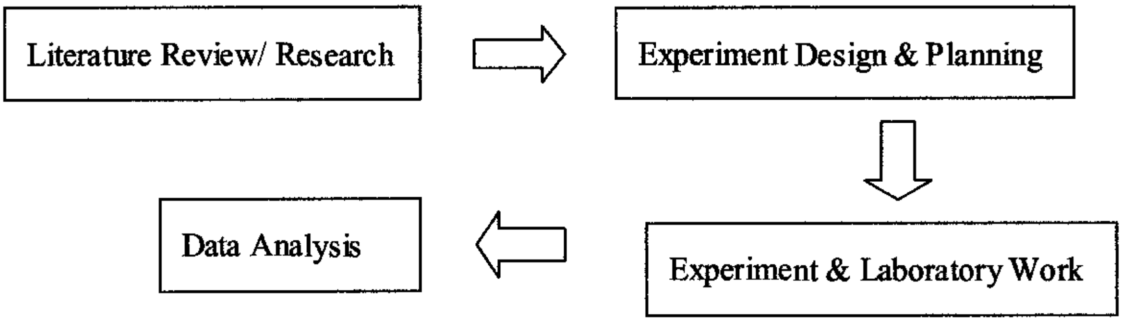


Fig. 4. Schematic diagram of reactive distillation column.
(Source : KIRBAŞLAR, BAYKAL, & DRAMUR, 2000)

CHAPTER 3

METHODOLOGY

3.1 Project Activities



3.2 Materials and Methods

3.2.1 Chemicals

Acetic acid and ethyl acohol were used as reactants with concetrated sulfuric acid catalyst. The purity of ethanol and acetic acid is 96 % and 99.98 % (w/w), respectively.

3.2.2 Experimental Apparatus

The experimental apparatus consisted of a 500 mL round bottom flask with three necks. A thermometer was inserted in the first neck. A magnetic stirrer was inserted in the flask. A distillation column was connected to the second neck. The third neck is used to take sample while experiment is running. A heating mantle with stirer was used to control the temperature of reaction mixture.

The distillation column was filled with gravel packing to increase the separation efficiency of ethanol and ethyl acetate. Ethyl acetate which has lower boiling point went to the top of the column and ethanol condensed at the bottom of the column. The vapor at the top of the column went into the condeser while the bottom condensate returned to the round bottom flask. The distillation column was insulated with layers of wool and aluminum foil to increase the efficiency of heat supplied from the reaction flask to the distillation column. The distillation column was 17 cm high.

A water condenser was placed at the top of the distillation column to condense the top vapor from the distillation column. The condensate was collected in a 250 mL two neck flask. One neck is connected to the condensate and the other neck is used to take sample while experiment is running. Fig. 5 shows the experimental appratus used in this project.

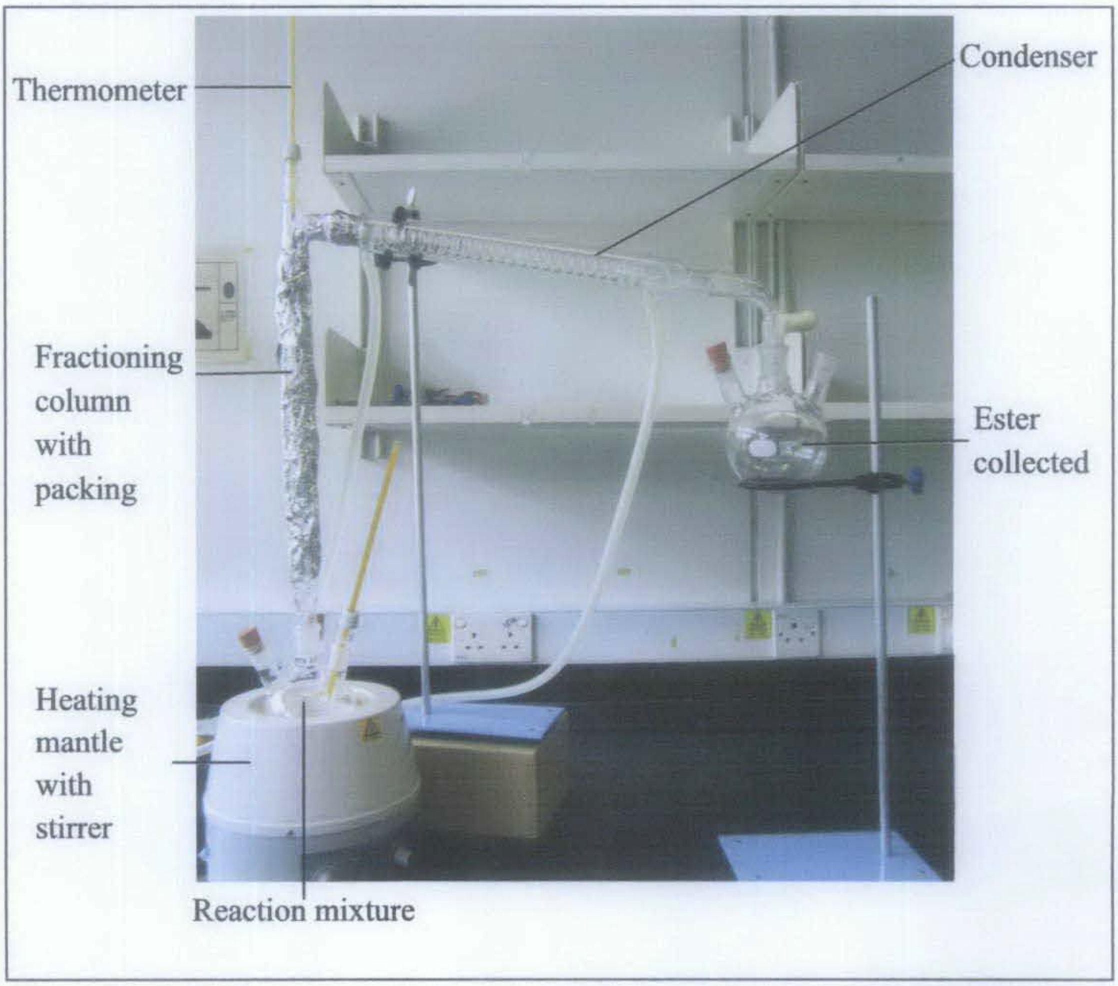


Fig. 5. Experiment setup.

3.2.3 Esterification Reaction

The esterification reaction was carried out in the experimental apparatus described previously (Fig. 5). Acetic acid (100 mL) was added to the round bottom flask. Ethanol and catalyst (sulfuric acid) were added according to the 3^2 experimental design where alcohol to acid molar ratio and catalyst loading were studied. Temperature was kept constant at 85°C by manually controlling the heating supplied by heating mantle based on temperature shown by the themomerter. The reaction was carried out for 70 minutes, and samples of 2 mL were collected from reaction flask and end flask for analysis every 10 min.

Temperature of 85°C was used throughout the experiment as it is higher than boiling point of ethyl acetate (77 °C) and ethanol (78 °C) but below the boilion point of water (100 °C). Catalyst concentration ranging from 0 to 1% w/w were studied. Ethanol to acetic acid ratios of 1:1, 1.5 : 1 and 2:1 were studied. The ranges studied for catalyst concentration is within the industrial ranges used in esterification (Unnithan & Tiwari, 1987). The initial ratios used are relatively low from the industrial ranges as the purpose of reactive distillation is to minimize the excess of alcohol used.

3.2.4 Analyses

Samples were analyzed by a Shimadzu (Model GC2010) gas chromatograph equipped with a flame ionisation detector (FID) for the quantitive determination of ethyl acetate, acetic acid, water and ethanol. A SGE-BP20 column (Polyethylene glycol with dimension of 30m x 0.25 mm i.d x 0.25 μm film) was used. The temperature of the injector and detector was 250 °C, with nitrogen as carrier gas. The temperature program used was 40 °C hold for 2 min, ramped to 50 °C at 5 °C/min and then ramped to 170°C at 20°C/min.

3.3 Reaction Pressure

The optimum pressure for the experiment to be conducted has been determined by using graph of vapor pressure versus temperature. Fig. 6 shows the plot of vapor pressure versus temperature for water, ethanol and ethyl acetate. For each of the component, at any pressure, the corresponding temperature is the boiling point of that component. For example, the black dashed line in the graph shows the boiling point of water at atmospheric pressure, which is 100 °C. From the graph, the optimum pressure for the experiment to be conducted is between 150 to 250 mmHg as the gap between boiling points of ethanol and ester is the largest. However, the experiment was conducted only at atmospheric pressure as equipment for other pressure was not available.

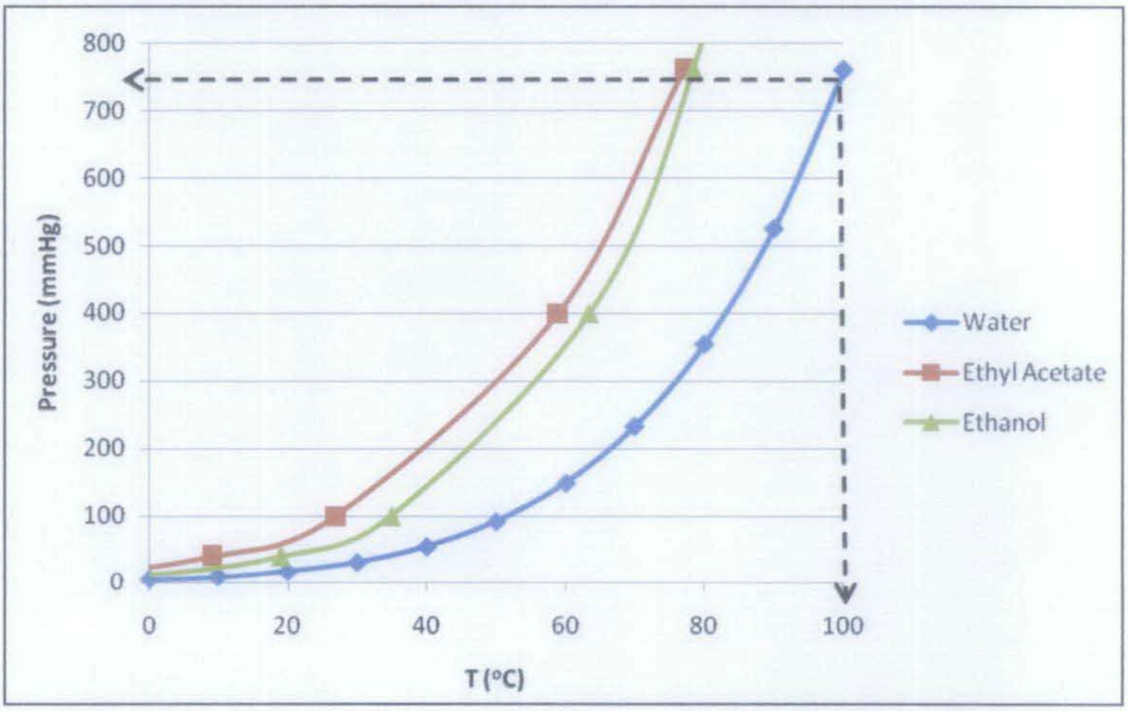


Fig. 6. Plot of vapor pressure versus temperature for ethanol, ethyl acetate and water.

3.4 Key Milestones

Table 3 below summarizes the overall milestones and general flow of this project.

Table 3. Key Milestones

Steps	Activity
Title Selection (Completed)	Selection of the suitable title of project. Production of ester by reactive distillation of acid and alcohol was chosen.
Preliminary Research (Completed)	Papers and researches done related to esterification and reactive distillation were studied.
Experimental Setup (Completed)	Experiment was designed in such a way that is efficient, cost and energy saving as well as safe to be conducted. Variables to be studied were determined.
Experimental Work (Completed)	Experiments were conducted and all samples were collected for analysis.
Analysis (Completed)	Samples were analyzed and results were discussed.

CHAPTER 4

RESULTS & DISCUSSION

Fig. 6 shows the analysis result of the samples withdrawn. It was found that the samples taken from the reaction flask contains acetic acid, ethanol, water and ethyl acetate. Samples taken from the distillate contains mostly ethanol and ethyl acetate.

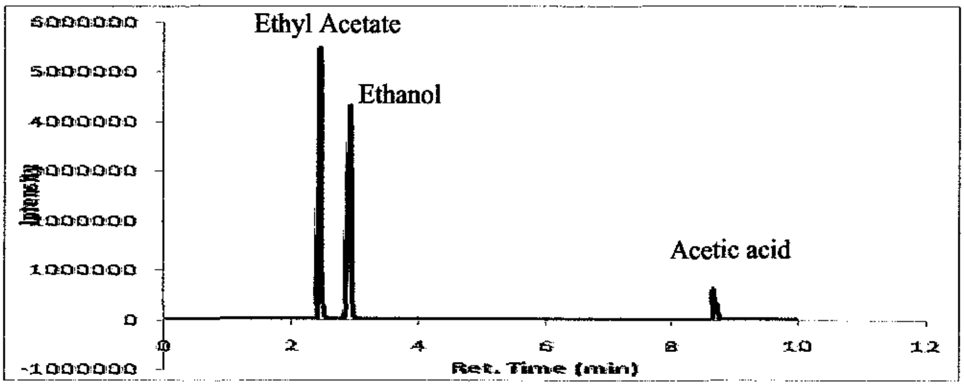


Fig. 7. Chromatogram of samples from reaction flask.

Table 4 summarizes the average composition of distillate for 60 minutes of esterification reaction. Composition of the distillate is analyzed at every 10 minutes interval, and then is averaged for 70 minutes for each run.

Table 4.The Effect of Catalyst Loading and Initial Reactant Molar Ratio on the Ester Purity.

Group	**Run**	**Initial Reactant Molar Ratio ($\mathbf{mole_{Alcohol}:mole_{Acid}}$)**	**Catalyst Loading % (w/w)**	**% Sample Content**	
				Ethyl Acetate	Ethanol
A	1	1:1	0	37.76	62.24
	2	1.5 : 1	0.5	45.58	54.42
	3	2 : 1	1	52.03	47.97
B	4	1:1	0	38.64	61.36
	5	1.5:1	0.5	57.06	42.94
	6	2:1	1	62.14	37.86
C	7	1:1	0	40.98	59.02
	8	1.5 : 1	0.5	61.59	38.41
	9	2:1	1	77.50	22.50

The first experiment in each group, e.g. run 1, run 4 and run 7, are the experiments with 0 % catalyst loading, while the second run and third run represents 0.5 % and 1 % catalyst loading respectively. As seen, ester purity increased with increasing catalyst loading, which clearly stated that ester purity was dependent on the catalyst loading.

Catalyst loading is the amount of catalyst per unit amount of reactant, expressed in mol % of substance. Increasing the catalyst amount increases the rate of reaction (Berrios, J.Siles, Marin, & Martin, 2007). It was observed from conducting the experiment that the time taken for the first distillate to form is shorter when higher catalyst loading is used. The higher the catalyst amount, the higher the catalyst surface site density. The product yield will also increase with higher catalyst surface site density (Stutz, Hotz, & Poulikakos, 2006).

Effect of initial reactant molar ratio on the purity of ester is evaluated by comparing the result of experiment in Group A with experiments with the identical catalyst loading in group B and C. It can be seen that, for reaction with 0 % (w/w) catalyst loading, ester purity increases with increasing initial reactant molar ratio. Similar trend is observed for 0.5 and 1 % catalyst loading.

The etherification is reversible reaction and is an equilibrium limited reaction. Excess alcohol is required to drive the reaction close to completion by shifting the equilibrium to the product (Rattanaphanee, 2010). This explains the reason why higher amount of alcohol used speeds up the reaction.

The effect of catalyst loading and initial molar ratio on the ester purity is shown in Fig. 8. The maximum purity of approximately 77 % was obtained for alcohol to acid molar ratio of 2:1 with a catalyst loading of 1% and at a temperature of 90°C.

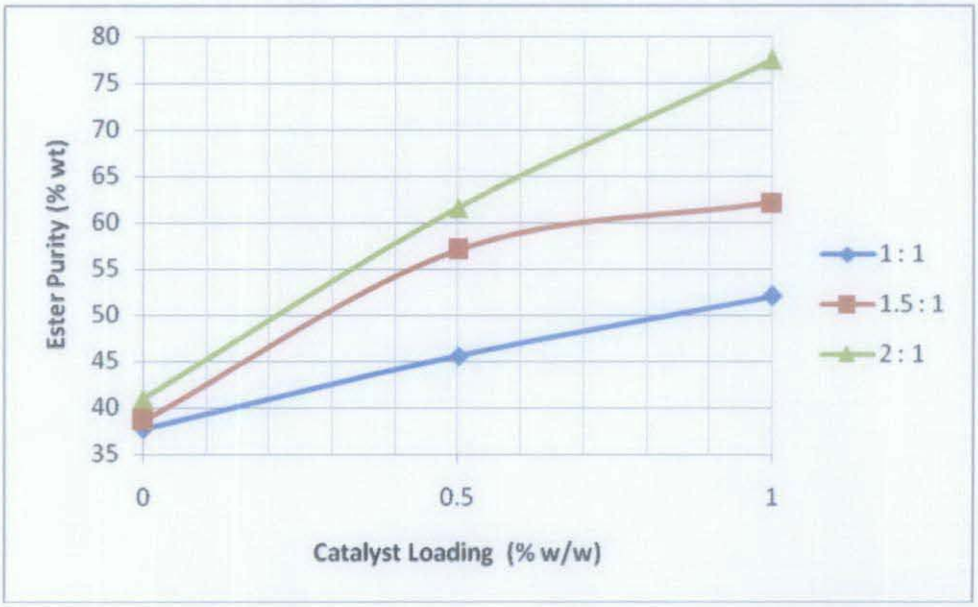


Fig. 8. Effect of catalyst loading on the ester purity at various initial molar ratios of ethanol to acetic acid.

Ester purity depends on the rate of ester production and the efficiency of separation. As observed in the graph, when catalyst loading of 0.5 % is used, increasing the initial molar ratio from 1.5:1 to 2:1 does not gives significant improvement in the ester purity. Therefore, it can be said that the high purity of ester is due to high catalyst loading which leads to increasing reaction rate, and not the high initial molar ratio. The purity improves significantly from 40 % to 77% when catalyst loading is varied from 0 to 1 %, respectively.

Increasing the initial molar ratio of alcohol to acid increases the conversion, and not the rate of reaction. However, it reduces separation efficiency as it is more difficult to separate ester from alcohol when high amount of alcohol is present.

CHAPTER 5

CONCLUSION & RECOMMENDATION

5.1 Conclusion

In this project, the feasibility of esterification of acetic acid with ethanol by reactive distillation has been studied. Several experiments have been conducted whereby different amount of catalyst loading, 0, 0.5 and 1 (% w/w) has been used for each of the initial alcohol to acid molar ratio, 1:1, 1.5 : 1, 2:1. Concentrated sulfuric acid was used as catalyst. The results show that ester purity increases with increasing catalyst loading and initial alcohol to acetic acid molar ratio. The maximum purity of 77 % was obtained when using 1% catalyst loading with 2:1 alcohol to acetic acid molar ratio. This is mainly caused by the high catalyst loading which increased the reaction rate.

However, some practical aspects of the experiments should be modified to get a higher purity of ester. Higher distillation column with a more efficient packing should be used to replace the 17 cm distillation column with gravel packing. A more efficient temperature control system should be installed in place of manual system used to control the reaction flask temperature in this project. The distillation column should also be properly insulated to make sure that no heat loss to the surrounding from the bottom of the column to the top of the column.

5.2 Recommendation

Higher ester purity can be achieved if there are some modifications done to the experiment. A higher distillation column should be used to increase the separation efficiency to replace the 17 cm distillation column used in this project. As the distance from the reaction flask increases, a heat gradient is formed in the column where it is coolest at top and hottest at the bottom. As the mixed vapor ascends the temperature gradient, some of the vapor condenses and revaporizes along the temperature gradient. Each time the vapor condenses and vaporizes, the composition of the more volatile liquid in the vapor increases. This distills the vapor along the length of the column, and eventually the vapor is composed solely of the more volatile liquid. A higher distillation column will result in a higher purity product.

Packing is used to improve the separation in the distillation column. It increases the contact time between the vapor and the liquids in the column and helps to collect liquids that form at various height in the column. A more efficient packing should be used to replace the gravel packing used. A proper packing height should be calculated to determine the optimum packing height needed to achieve desired purity.

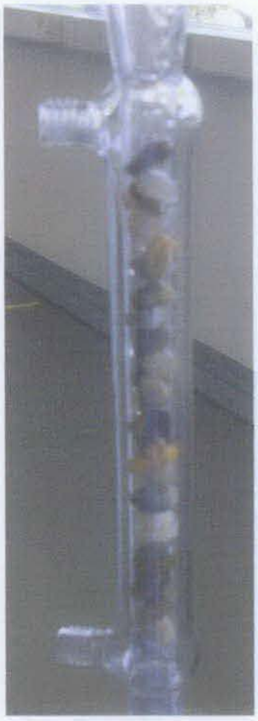


Fig. 9. Distillation column with gravel packing.

Better column insulation should also be employed to achieve high efficiency in terms of the amount of heating and time required to get fractionation. Properly manufactured distillation column with insulation might also be used to replace column with wool and aluminum foil insulator. A vacuum jacket can also be a better option.

The temperature of the reaction flask should be kept constant since temperature is not a variable to be studied in this project. A more efficient temperature control system should be employed to keep the temperature variation at minimum as compared to variation of ± 5°C in this project. A small variation in temperature would affect the studies as temperature increases the reaction rate rapidly.

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APPENDIX

Appendix 1 : Gantt Chart

No	Activities / Weeks	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15
1	Conducting experiments															
2	Submission of progress report															
3	Experimental work continues															
4	Pre-EDX															
5	Submission of draft report															
6	Submission of dissertation															
7	Submission of technical paper															
8	Oral presentation															
9	Submission of dissertation (hard bond)															

Appendix 2 : Vapor Pressure Data

Table 1. *Vapor pressure data for water.*

(Source : http://www. S-ohe.com/vp_data.html)

Temperature (degrees C)	Pressure (mmHg)
0	4.6
10	9.2
20	17.5
30	31.8
40	55.3
50	92.5
60	149.4
70	233.7
80	355.1
90	525.8
100	760

Table 2. *Vapor pressure data for ethanol.*

(Source : http://en.wikipedia.org/wiki/Ethanol_(data_page)

Temperature (degrees C)	Pressure (mmHg)
-31.3	1
2.3	10
19	40
34.9	100
63.5	400
97.5	1520
126	3800

Table 3. *Vapor pressure data for ethyl acetate.*

(Source : http://en.wikipedia.org/wiki/Ethyl acetate_(data_page)

Temperature (degrees C)	Pressure (mmHg)
-43.4	1
-13.5	10
9.1	40
27	100
59	400
77.1	760