

PERPUSTAKAAN UMP



0000086968

CHEMICAL **STUDY OF THE**
ESTERIFICATION OF PURE AND DILUTED ACRYLIC ACID WITH 2
ETHYL HEXANOL CATALYSED BY AMBERLYST 15

MOHD AMIRUL ASYRAF BIN AHMAD

Thesis submitted in fulfilment of the requirements
for the award of the degree of
Master of Engineering in Chemical

Faculty of Chemical and Natural Resources Engineering
UNIVERSITI MALAYSIA PAHANG

MARCH 2014

ABSTRACT

In a typical acrylic manufacturing unit, waste water contains acrylic acid (AA) in a range of 4–15 wt% contributes to the high value of chemical oxygen demand. Due to the toxicity of AA to the aquatic organism, this wastewater should be treated before it is discharged. Recovery of AA from the waste water via esterification reaction in a reactive distillation column (RDC) could be a promising method to treat this waste water. Activity and kinetic studies using a batch system are important to examine the practicability of this method. In the present work, the activity and kinetic studies of the esterification of AA and 2-ethyl hexanol (2EH) were carried out in a batch system. Ion exchange resin, Amberlyst 15 was employed as a catalyst. The effect of various variables that affecting conversion and yield such as agitation speed, catalyst particle size, temperature, catalyst loading and initial reactant molar ratio were studied. The effect of the initial water content was studied using both the batch systems with total reflux (TR) and dean stark for continuously water removal (CWR). The increase of equilibrium conversion with the temperature indicated the endothermicity of the reaction. Temperature was the most significant variable that affected the conversion and yield. The highest conversion and yield were obtained at the temperature of 388 K, initial reactant molar ratio of AA to 2EH of 1:3 and catalyst loading of 10 wt%. The yield for the reactions of the AA solutions with different AA concentrations except the AA concentrations of 10-20 wt%, was enhanced significantly when the reactions were carried out using the CWR setup. Catalyst poisoning occurred during the reactions of the very dilute AA solutions (10-20%) due to the water inhibition and poly-acrylic acid deposition on the catalyst surface as validated by the catalyst characterisation studies. The pseudo-homogeneous (PH), Eley-Rideal (ER) and Langmuir-Hinshelwood-Hougen-Watson (LHHW) kinetic models were used to interpret the kinetic data. The best fit kinetic model for the main esterification reaction was shown by the non-ideal ER model while the side reaction, AA polymerisation was best interpreted by PH model. The kinetic data for the esterification of dilute AA was well described by the inclusion of the correction factor to the kinetic model of the esterification.

ABSTRAK

Kebiasaannya, unit penghasilan asid akrilik menghasilkan air sisa yang mengandungi asid akrilik (AA) dalam komposisi 4-15% nisbah berat. Air sisa ini menyumbang kepada nilai permintaan oksigen kimia (COD) yang tinggi. Air sisa ini perlu dirawat sebelum dilepaskan disebabkan oleh sifat toksiknya kepada organisma akuatik. Perawatan air sisa menggunakan kaedah pengesteran dalam turus penyulingan reaktif (RDC) menunjukkan potensi yang tinggi. Kajian tentang aktiviti dan kinetik menggunakan sistem reaktor berkelompok penting untuk mengkaji kesesuaian kaedah ini. Dalam kajian ini, kajian aktiviti dan kinetik pengesteran AA dan alkohol 2-ethylhexyl (2EH) telah dijalankan dalam sistem reaktor berkelompok. Ion bertukar resin komersial, 'Amberlyst 15' telah dipilih sebagai bahan pemangkin. Kesan pelbagai pemboleh ubah yang mempengaruhi kadar tindak balas kimia seperti kelajuan adukan reaktor, saiz zarah pemangkin, suhu tindak balas, kadar muatan pemangkin dan nisbah awal mol bahan tindak balas telah dikaji. Kesan kandungan awal air diuji menggunakan kedua-dua sistem reaktor berkelompok pada keadaan refluks keseluruhan (TR) dan penyingkiran air berterusan (CWR). Peningkatan penukaran pada keseimbangan dengan peningkatan suhu membuktikan sifat endotermik tindak balas ini. Suhu ialah pemboleh ubah yang paling memberi kesan kepada penukaran dan hasil tindak balas. Penukaran dan hasil tindak balas tertinggi diperolehi pada suhu 388 K, nisbah molar awal bahan tindak balas, AA kepada 2EH pada 1:3 dan kuantiti bahan pemangkin 10% nisbah berat. Hasil bagi tindak balas AA dengan kepekatan berbeza (melainkan kepekatan AA 10-20% berat), telah dipertingkatkan dengan ketara apabila tindak balas dijalankan dengan menggunakan set radas CWR. Keracunan pada pemangkin dilihat berlaku semasa tindak balas pada kepekatan AA yang sangat rendah (10-20 %) disebabkan oleh perencatan oleh air dan pempadapan polimer akrilik pada permukaan mangkin sepertimana yang disahkan oleh kajian pencirian pemangkin. Model kinetik Pseudo-homogen (PH), Eley-Rideal (ER) dan Langmuir-Hinshelwood-Hougen-Watson (LHHW) telah diguna pakai untuk mentafsir data kinetik. Model kinetik terbaik bagi aktiviti tindak balas pengesteran utama ialah model ER tidak ideal manakala bagi tindak balas sampingan, pempolimeran AA, ditafsirkan dengan baik oleh model PH. Data kinetik untuk pengesteran cecair AA boleh ditafsirkan dengan pertambahan faktor pembetulan kepada model kinetik pengesteran.

TABLE OF CONTENTS

	Page	
SUPERVISOR'S DECLARATION	ii	
STUDENT'S DECLARATION	iii	
DEDICATION	iv	
ACKNOWLEDGEMENTS	v	
ABSTRACT	vii	
ABSTRAK	viii	
TABLE OF CONTENTS	ix	
LIST OF TABLES	xiii	
LIST OF FIGURES	xvii	
LIST OF SYMBOLS	xxii	
LIST OF ABBREVIATIONS	xxiv	
CHAPTER 1 INTRODUCTION		
1.0	Introduction	1
1.1	Problem Statement	2
1.2	Objectives	4
1.3	Scope of Study	4
1.4	Significant of Study	4
1.5	Organisation of This Thesis	5
CHAPTER 2 LITERATURE REVIEW		
2.0	Introduction	7
2.1	Wastewater Containing Acrylic Acid	7
2.2	Treatment Methods for Wastewater Containing Carboxylic Acid	9
2.3	Reactive Distillation Column (RDC)	12
	2.3.1 Esterification in Reactive Distillation Column (RDC)	13

	<i>Esterification of Pure Carboxylic Acids in RDC</i>	14
	<i>Esterification of Diluted Carboxylic Acids in RDC</i>	15
2.4	Catalyst for the Esterification	17
	2.4.1 Homogeneous Catalyst	18
	<i>Homogeneous catalyst for the esterification of other carboxylic acids</i>	18
	<i>Homogeneous catalyst for the esterification of AA</i>	20
	2.4.2 Heterogeneous Catalyst	21
	<i>Heterogeneous catalysts for the esterification of other carboxylic acid</i>	21
	<i>Heterogeneous catalysts for the esterification of AA</i>	25
	2.4.3 Biocatalyst	29
	<i>Bio catalysts for the esterification of other carboxylic acid</i>	29
	<i>Bio catalysts for the esterification of AA</i>	32
2.5	Reaction Kinetics for the Heterogeneously Catalysed Esterification Reaction	32
	2.5.1 Reaction kinetics for the esterification of other carboxylic acid	34
	2.5.2 Reaction kinetics for the esterification of AA	35
CHAPTER 3 RESEARCH METHODOLOGY		
3.1	Materials	38
3.2	Apparatus and Equipment	39
	3.2.1 Catalyst Characterization	39
	3.2.2 Esterification Reaction Studies	39
	3.2.3 Sample Analysis	42
3.3	Experimental Procedures	42
	3.3.1 Catalyst Characterisation	42

	<i>Particle Size Analyzer</i>	42
	<i>Nitrogen Physisorption Measurement</i>	42
	<i>Scanning Electron Microscope (SEM)</i>	43
	<i>X-Ray Fluorescence (XRF)</i>	43
	<i>Fourier Transmitter Infrared (FTIR)</i>	43
3.3.2	Esterification Reaction Studies	44
	<i>Effect of Mass Transfer</i>	44
	<i>Effect of Important Operating Variables</i>	45
	<i>Reaction Water Tolerance Study</i>	45
3.4	Analysis	47
3.5	Kinetic Modelling	48
CHAPTER 4 RESULT AND DISCUSSION		
4.1	Fresh Catalyst Characterisation	52
	4.1.1 Particle Size Analyser	52
	4.1.2 Nitrogen Physisorption Measurement	53
	4.1.3 Scanning Electron Microscope (SEM)	55
	4.1.4 X-Ray Fluorescence (XRF) analysis	57
	4.1.5 Fourier Transform Infrared Spectroscopy (FTIR) analysis	57
4.2	Chemical Equilibrium Study for The Esterification of Pure AA with 2EH	58
4.3	Study of The Mass Transfer Effect on The Esterification of Pure AA With 2EH	65
	4.3.1 Effect of External Mass Transfer	65
	4.3.2 Effect of Internal Mass Transfer	68
4.4	Study of The Effect of Different Operating Variables on The Esterification of Pure AA With 2EH	71
	4.4.1 Effect of Temperature	71
	4.4.2 Effect of Initial Reactant Molar Ratio	73
	4.4.3 Effect of Catalyst Loading	74
	4.4.4 Recyclability	76

4.5	Study of The Effect of Different Initial Water Content To The Esterification Reaction	79
	4.5.1 Comparison Study Using Different Experimental Setup	79
	4.5.2 Used Catalyst Characterisation	81
4.6	Kinetic Study	87
	4.6.1 Main Reaction (Esterification)	87
	4.6.2 Side Reaction (Dimerization)	93
	4.6.3 Water Inhibition	99
CHAPTER 5 CONCLUSIONS		
5.1	Conclusion	104
5.2	Recommendation for Future Work	104
REFERENCES		105
APPENDICES		
A	Standard Calibration Curve of Acrylic Acid	121
B	Standard Calibration Curve of 2 Ethyl Hexyl Acrylate	126
C	UNIFAC (VLE) for Esterification System	132
D	Chromatogram for Yield-Time Data for Acrylic Acid with 2 Ethyl Hexanol Esterification	133
E	The Concentration-Time Data for The Reaction Studies Using Different Catalyst Loading	137
F	The Concentration-Time Data for The Reaction Study at Different Initial Reactant Molar Ratio (AA:2EH)	139
G	The Comparison of The Predicted and Experimental Concentration-Time Data	143
H	The Predicted and Experimental Concentration-Time Data for The Reaction Study with Different AA Concentration	162

LIST OF TABLES

Table No.	Title	Page
2.1	Physico-chemical properties of AA	8
2.2	List of literature studies using extraction as method of recovery	12
2.3	Applications of RDC for esterification of pure carboxylic acid.	15
2.4	The recovery of diluted carboxylic acid via esterification in RDC	17
2.5	Operating condition of the heterogeneously catalysed esterification of carboxylic acids other than AA	23
2.6	Operating condition of the heterogeneously catalysed esterification of carboxylic acids other than AA	28
2.7	Advantages and disadvantages of biocatalyst in comparison with chemical catalyst	29
2.8	Operating condition of the biocatalyst catalysed esterification of carboxylic acids other than AA with alcohol.	31
2.9	Kinetic studies for the esterification reaction of acrylic acid and other carboxylic acids with different type of alcohols.	36
3.1	List of chemicals	38
3.2	Properties of Amberlyst 15	39
3.3	List of main components in the experimental setup for the esterification reaction studies	41
3.4	Important operating variable study and the range	45
4.1	Particle size distribution of Amberlyst 15	53
4.2	Comparison of the nitrogen physisorption result of the fresh Amberlyst with the data obtained from the Rohm & Haas technical sheet	54
4.3	Results of the elemental analysis using XRF analyser	57
4.4	Mole fractions and the evaluated activity coefficients of components in the equilibrium state of the reaction at various temperatures	60

4.5	The apparent and activity based equilibrium constants (K_x and K_a respectively), the corresponding enthalpy of reaction and the equilibrium conversion of AA (X_c).	61
4.6	The b_i variables and their standard errors, $\sigma(b_i)$	63
4.7	Enthalpy of formation of the selected components.	64
4.8	The Mears parameter for external diffusion	68
4.9	The Weisz–Prater parameter for internal diffusion.	70
4.10	Percentage of water removed from the CWR system	81
4.11	The BET surface area and pore size data for used and unused catalyst	85
4.12	Result of elemental analysis using XRF analyser	87
4.13	Kinetic variables for the model used to fit the experimental data.	90
A1	Concentration versus ABS for standard calibration curve plot of AA.	122
B1	Concentration versus ABS for standard calibration curve plot of 2EHA	128
D1	Yield time data for recyclability experimental (1 st run)	134
E1	The concentration-time data for the reaction at 1 wt% of catalyst loading	135
E2	The concentration-time data for the reaction at 5 wt% of catalyst loading	135
E3	The concentration-time data for the reaction at 10 wt% of catalyst loading	135
E4	The concentration-time data for the reaction at 15 wt% of catalyst loading	136
F1	The concentration-time data for the reaction at 1:7 of initial reactant molar ratio (AA:2EH)	137
F2	The concentration-time data for the reaction at 1:5 of initial reactant molar ratio (AA:2EH)	138
F3	The concentration-time data for the reaction at 1:3 of initial reactant molar ratio (AA:2EH)	138

F4	The concentration-time data for the reaction at 1:1 of initial reactant molar ratio (AA:2EH)	139
F5	The concentration-time data for the reaction at 3:1 of initial reactant molar ratio (AA:2EH)	139
F6	The concentration-time data for the reaction at 5:1 of initial reactant molar ratio (AA:2EH)	140
F7	The concentration-time data for the reaction at 7:1 of initial reactant molar ratio (AA:2EH)	140
G1	Experimental concentration-time data for reaction temperature at 388 K, $m_{aa/2eh}$ is 1:6, , catalyst loading is 10% w/w and stirring speed at 400 rpm.	141
G2	Predicted concentration-time data for reaction temperature at 388 K, $m_{aa/2eh}$ is 1:6, , catalyst loading is 10% w/w and stirring speed at 400 rpm	142
G3	Experimental concentration-time data for reaction temperature at 378 K, $m_{aa/2eh}$ is 1:6, , catalyst loading is 10% w/w and stirring speed at 400 rpm.	145
G4	Predicted concentration-time data for reaction temperature at 378 K, $m_{aa/2eh}$ is 1:6, , catalyst loading is 10% w/w and stirring speed at 400 rpm	146
G5	Experimental concentration-time data for reaction temperature at 368 K, $m_{aa/2eh}$ is 1:6, , catalyst loading is 10% w/w and stirring speed at 400 rpm	150
G6	Predicted concentration-time data for reaction temperature at 368 K, $m_{aa/2eh}$ is 1:6, , catalyst loading is 10% w/w and stirring speed at 400 rpm	150
G7	Experimental concentration-time data for reaction temperature at 358 K, $m_{aa/2eh}$ is 1:6, , catalyst loading is 10% w/w and stirring speed at 400 rpm	155
G8	Predicted concentration-time data for reaction temperature at 358 K, $m_{aa/2eh}$ is 1:6, , catalyst loading is 10% w/w and stirring speed at 400 rpm	155
H1	The predicted and experimental concentration-time data for the reaction study with 10% w/w AA concentration	160
H2	The predicted and experimental concentration-time data for the	160

	reaction study with 20% w/w AA concentration	
H3	The predicted and experimental concentration-time data for the reaction study with 30% w/w AA concentration	160
H4	The predicted and experimental concentration-time data for the reaction study with 40% w/w AA concentration	161
H5	The predicted and experimental concentration-time data for the reaction study with 50% w/w AA concentration	161
H6	The predicted and experimental concentration-time data for the reaction study with 60% w/w AA concentration	161
H7	The predicted and experimental concentration-time data for the reaction study with 70% w/w AA concentration	162
H8	The predicted and experimental concentration-time data for the reaction study with 80% w/w AA concentration	162
H9	The predicted and experimental concentration-time data for the reaction study with 90% w/w AA concentration	162

LIST OF FIGURES

Figure No.	Title	Page
2.1	(a) RDC and (b) traditional process for methyl acetate	14
3.1	The experimental setup for esterification reaction studies	40
3.2	The experimental setup with dean stark	46
3.3	Chromatogram obtained from the GC-FID analysis	47
3.4	The procedure involved throughout the research studies	51
4.1	Nitrogen adsorption/desorption isotherm at -195 °C for the fresh Amberlyst 15. Inset shows the pore size distribution	54
4.2	Micrographs of fresh Amberlyst 15 outer surface under magnification , a) 15x, b) 2000x, and inner surface under magnification c) 8000x	56
4.3	FTIR spectra of fresh Amberlyst 15	58
4.4	The temperature dependence of the apparent (K_x) and thermodynamic (K_a) equilibrium constant of the esterification of AA with 2EH at 1:1 molar ratio of AA to 2EH, catalyst loading of 10 % w/w, at 600 rpm stirring speed	62
4.5	The yield of 2-ethylhexyl acrylate at stirring effect of 0 – 600 rpm (\diamond 0 rpm \square 200 rpm Δ 400 rpm \circ 600 rpm) temperature of 388 K and catalyst loading of 10 wt% with the initial molar ratio acid to alcohol of 1:3.	66
4.6	Effect of stirring speed on the initial rate of reaction at temperature 388 K and catalyst loading of 10 wt% with the initial molar ratio acid to alcohol of 1:3.	67
4.7	The yield of 2-ethylhexyl acrylate at different catalyst particle sizes (\diamond <0.68mm \square between 0.68mm and 0.80mm Δ >0.80mm) stirring speed of 400 rpm, temperature of 388 K and catalyst loading of 5 wt% with the initial molar ratio acid to alcohol of 1:3	69
4.8	Effect of different size distribution on the initial rate of reaction at temperature 388 K and catalyst loading of 10 wt% with the initial molar ratio acid to alcohol of 1:3	70

4.9	a) The AA conversion b) The yield of 2EHA at the temperatures of 358–388 K (□ 358 K ○ 368 K Δ 378 K ◇ 388 K), stirring speed of 400 rpm, initial molar ratio acid to alcohol of 1:6 and catalyst loading of 10 wt%.	72
4.10	Effect of reaction temperature on the initial rate of reaction at stirring speed of 400 rpm, initial molar ratio acid to alcohol of 1:6 and catalyst loading of 10 wt%	73
4.11	The AA conversion and yield of 2EHA for different initial molar ratio of AA to 2EH at 6 hrs. Operating condition: stirring speed of 400 rpm, temperature of 388 K and catalyst loading of 15 wt%.	74
4.12	The 2EHA yield for the catalyst loading of 1 – 15 wt% (○ 1 wt% Δ 5 wt% □ 10 wt% ◇ 15 wt%) at stirring speed of 400 rpm, temperature of 388 K and $M_{AA/2EH}$ of 1:3.	75
4.13	Effect of reaction catalyst loading on the initial rate of reaction at stirring speed of 400 rpm, initial molar ratio acid to alcohol of 1:3 and temperature of 388 K.	76
4.14	The recyclability study of Amberlyst 15 for the reaction of AA with 2EH under 388 K, molar ratio of AA:2EH, 1:3, catalyst loading of 10% w/w, with 400 rpm stirring speed	77
4.15	The activity behaviour of the catalyst for the 5 time cycles usage.	78
4.16	$1/a$ as a function of \sqrt{t}	78
4.17	Yield for the esterification of AA with 2EH after 6 hours reaction at catalyst loading of 10% w/w of acid; temperature of 373 K; initial molar ratio acid to alcohol of 1:3 for different concentrations of AA (10- 100% AA)	80
4.18	SEM micrographs (magnification: 15x) of outer surface of Amberlyst 15 under condition; a) unused catalyst, b) 50% AA in TR setup, c) 10% AA in TR setup, d) 50% AA in CWR setup, and e) 10% AA in CWR setup	82
4.19	SEM micrographs (magnification: 500x) of outer surface of Amberlyst 15 under condition; a) unused catalyst, b) 50% AA in TR setup, c) 10% AA in TR setup, d) 50% AA in CWR setup, and e) 10% AA in CWR setup	83

4.20	Conversion for the esterification of AA with 2EH after 6 hours reaction at catalyst loading of 15% w/w of acid; temperature of 373 K; initial molar ratio acid to alcohol of 1:3 for different concentrations of AA (10- 50% AA)	85
4.21	FTIR spectra of fresh and used Amberlyst 15.	86
4.22	Parity plot for the experimental and predicted rate of reaction of a) LHHW; b) ER and c) PH (\diamond 358 K \square 368 K Δ 378 K \circ 388 K; dotted line stand for \pm 5% error)	91
4.23	Energy profile for reaction pathway of AA with 2EH	93
4.24	Parity plot for the experimental and predicted rate of reaction of LHHW; a) without considering polymerization of AA, b) considering polymerization of AA (\circ 358 K Δ 368 K \square 378 K \diamond 388 K; dotted line stand for \pm 5% error)	95
4.25	Comparison between experimental and calculated (with LHHW model considering polymerization of AA) concentration profiles. Molar ratio of AA to 2EH is 1:6, temperature at 388 K, catalyst loading is 10% w/w and stirring speed at 400 rpm.	96
4.26	Effect of different molar ratio on the main esterification reaction rate constant. The reaction was carried out at the temperature of 388 K, catalyst loading of 10% w/w and stirring speed of 400 rpm.	97
4.27	Effect of different molar ratio on the polymerisation reaction rate constant. The reaction was carried out at the temperature of 388 K, catalyst loading of 10% w/w and stirring speed of 400 rpm.	98
4.28	Comparison between experimental and calculated (for ER model considering polymerization of AA) C_{AA} profiles for different molar ratio of AA to 2EH at temperature at 388 K, catalyst loading is 10% w/w and stirring speed at 400 rpm.	98
4.29	Comparison between experimental and calculated (for ER model considering polymerization of AA) C_{2EHA} profiles for different molar ratio of AA to 2EH at temperature at 388 K, catalyst loading is 10% w/w and stirring speed at 400 rpm.	99
4.30	Water inhibition correction factor at different initial water content in the reaction mixture under 373 K, molar ratio of AA:2EH, 1:3, catalyst loading of 10% w/w, with 400 rpm stirring speed.	101

4.31	Water inhibition correction factor at different initial water content in the reaction mixture under 373 K, molar ratio of AA:2EH, 1:3, catalyst loading of 10% w/w, with 400 rpm stirring speed.	101
4.32	Parity plot of predicted vs experimental 2EHA concentration, a) 10 – 50 % AA; b) 60 – 90 % AA, under 373 K, molar ratio of AA:2EH, 1:3, catalyst loading of 10% w/w, with 400 rpm stirring speed.	102
A1	GC-FID spectrometry of 6,393.27 ppm AA	119
A2	GC-FID spectrometry of 12,786.55 ppm AA	119
A3	GC-FID spectrometry of 25,573.10 ppm AA	120
A4	GC-FID spectrometry of 38,359.64 ppm AA	120
A5	GC-FID spectrometry of 51,146.19 ppm AA	121
A6	GC-FID spectrometry of 63,932.74 ppm AA	121
A7	Calibration curve for AA using GC-FID	122
B1	GC-FID spectrometry of 2,000 ppm 2EHA	124
B2	GC-FID spectrometry of 4,000 ppm 2EHA	124
B3	GC-FID spectrometry of 6,000 ppm 2EHA	125
B4	GC-FID spectrometry of 8,000 ppm 2EHA	125
B5	GC-FID spectrometry of 10,000 ppm 2EHA	126
B6	GC-FID spectrometry of 12,000 ppm 2EHA	126
B7	GC-FID spectrometry of 14,000 ppm 2EHA	127
B8	GC-FID spectrometry of 16,000 ppm 2EHA	127
B9	Calibration curve for 2EHA using GC-FID	128
D1	GC-FID chromatogram of sample from recyclability experimental (1 st run) at 30 min.	131
D2	GC-FID chromatogram of sample from recyclability experimental (1 st run) at 60 min.	132

D3	GC-FID chromatogram of sample from recyclability experimental (1 st run) at 120 min.	133
D4	GC-FID chromatogram of sample from recyclability experimental (1 st run) at 180 min.	134
G1	Comparison between experimental and calculated (with ER model considering polymerization of AA) concentration profiles. Molar ratio of AA to 2EH is 1:6, temperature at 378 K, catalyst loading is 10% w/w and stirring speed at 400 rpm.	149
G2	Comparison between experimental and calculated (with ER model considering polymerization of AA) concentration profiles. Molar ratio of AA to 2EH is 1:6, temperature at 368 K, catalyst loading is 10% w/w and stirring speed at 400 rpm.	154
G3	Comparison between experimental and calculated (with ER model considering polymerization of AA) concentration profiles. Molar ratio of AA to 2EH is 1:6, temperature at 358 K, catalyst loading is 10% w/w and stirring speed at 400 rpm.	159

LIST OF SYMBOLS

$\%$	Percent
C_M	Mears parameter
$r_{A,obs}$	observed reaction rate
R_C	catalyst particle radius
ρ_b	bulk density of catalyst
C_{Ab}	bulk concentration
k_C	mass transfer coefficient
D_{AB}	diffusivity of the solute A in solution
d_p	diameter of the catalyst particle
μ_C	viscosity of the solution
g	gravitational acceleration
ρ_l	density of the solution
C_{WP}	Weisz–Prater parameter
D_{eff}	effective diffusivity
ΔG^0	Gibbs energy
ΔH_r^0	standard enthalpy of reaction
ΔH_{rxn}	Heat of reaction
Å	Armstrong
A_{cs}	adsorbate cross sectional area
a_i	Activity coefficient of component i
b_i	i^{th} adjustable variable
C_{BET}	BET constant
C_i	Concentration of component

d_p	Particle diameter
E_f	Activity energy of reaction
K_a	Thermodynamic equilibrium constant
K_{eq}	Equilibrium constant
k_f	Rate constant
k_f^0	Pre-exponential factor
K_i	Adsorption equilibrium constant for species i
K_x	Apparent equilibrium constant
M	number of adjusted variables
M	Molecular weight of adsorbate
N	number of experimental points
N_{Av}	Avogadro's number
P/P^0	Relative pressure
R	Gas constant
R^2	Coefficient of determination
r_i	Rate of reaction of component
T	Reaction temperature
T	Reaction time
W	Weight of gas adsorbed
W	Catalyst weight
W_m	Weight of adsorbate
X_e	Degree of equilibrium conversion
x_i	Mole fraction of component I
γ_i	Gamma of component I
σ	standard deviations

LIST OF ABBREVIATIONS

2EH	2 ethyl hexanol
2EHA	2 ethyl hexyl acrylate
AA	Acrylic acid
BET	Brunauer, Emmett and Teller
BJH	Barrett-joyner-halenda
COD	Chemical oxygen demand
CWR	Continuous water removal
DBSA	Dodecyl benzene sulfonic acid
EQA	Environment quality act
ER	Eley Rideal
FID	Gas chromatography flame ionization detector
FTIR	Fourier transform infrared
GC	Gas chromatography
IUPAC	International Union of Pure and Applied Chemistry
LHHW	Langmuir Hinshelwood Hougen Watson
PH	Pseudo Homogeneous
PVC	Polyvinyl chloride
RDC	Reactive distillation column
SEM	Scanning electron microscope
SMBR	Simulated-moving-bed reactor
TOC	Total organic content
TR	Total reflux
UNIFAC	Universal functional activity coefficient

W	Water
XRF	X-ray fluorescence

CHAPTER 1

INTRODUCTION

1.0 INTRODUCTION

Acrylic acid (AA) has served for more than 30 years as an essential component in the production of acrylate polymers from acrylate ester such as methyl acrylate, butyl acrylate, ethyl acrylate and 2-ethyl hexyl acrylate, which are applied in the industry of paints, coatings, textiles, adhesives, and plastics (Xu *et al.*, 2006).

Wastewater containing 4-10 wt% AA could be generated after the extraction and distillation process in the AA manufacturing plant. AA is categorized as hazardous chemical compound. Release of AA to the effluent can cause serious damage to the environment due to the high toxicity to the aquatic organism. The prolonged exposure may cause destructive to the mucous membranes and upper respiratory tract, even cause fatal as a result of spasm, inflammation and edema of the larynx and bronchi, chemical pneumonitis and pulmonary edema (Sigma-Aldrich, 2013).

High value of total organic content (TOC) and chemical oxygen demand (COD) of the wastewater from a typical acrylic manufacturing unit were attributed to the high concentration of AA (Li *et al.*, 2008). Wastewater containing AA has been treated with various methods in order to fulfil the standard limit set by the local environmental authority. Most of the AA manufacturers have burned this type of wastewater using incinerator (Alison *et al.*, 2011). However, this method is neither environmental friendly nor economical feasible. High content of COD also has restricted to the application of biological treatment and adsorption to this type of wastewater (Scholz, 2003).

1.1 PROBLEM STATEMENT

In view of the shortcomings of the existing treatment method, esterification of AA with alcohol could be a promising method to recover the AA from the wastewater stream. AA could be recovered as a useful polyester compound while the wastewater is purified

2-ethyl hexyl acrylate is widely known for the use in the polymer industries for the production of different copolymers, such as those with AA and its salts, amides, methacrylates, acrylonitriles, styrene vinyls and butadiene (Klien *et al.*, 2012; Peykova *et al.*, 2012). It is normally produced by the esterification of prop-2-enoic acid or commonly known as AA with 2-ethyl hexanol (2EH). It is a classical reaction system where the conversion achieved is limited by equilibrium. Unfortunately, this method alone shows low performance in diluted compound and has difficulty in product separation.

Reactive distillation column (RDC) is an intensified process in which reaction and separation occur simultaneously in a column. It is used to enhance particularly the reversible reaction by removing product from the system continuously. RDC was used to overcome the equilibrium limitation of the esterification reaction. A typical commercialised example is esterification of methanol with acetic acid and esterification of fatty acid with isopropyl alcohol. Numerous researches were carried out for the esterification of different type of pure/diluted carboxylic acids with alcohols. These acids include formic acid, phthalic acid, succinic acid and lactic acid (Saha and Sharma, 1996; Bock *et al.*, 1997; Choi and Hong, 1999; Sanz *et al.*, 2002). Esterification in a RDC is one of the promising methods to recover AA from wastewater (Saha *et al.*, 2000; Bianchi *et al.*, 2003; Calvar *et al.*, 2007).

Catalyst is used in the esterification process to accelerate the chemical reaction process by lower the activation energy required for the reaction. Homogeneous acid catalyst such as sulphuric acid, hydrofluoric acid, para-toluenesulfonic acid and heteropolyacid are often used in industrial processes for this purpose (Lilja *et al.*, 2002; Jaques and Leisten, 1964; Sejidova *et al.*, 1990; Gonçalves *et al.*, 2012; Santia *et al.*,

2012; Pappu *et al.*, 2013). Nevertheless, these corrosive homogeneous catalysts are difficult to be removed from the reaction medium (Farnetti *et al.*, 2004). Meanwhile, esterification reaction catalysed by biocatalyst/enzymatic catalyst suffers with poor thermal stability (about 323-328 K) and longer reaction time despite the low energy consumption and operating cost (Gómez-Castro *et al.*, 2012; Demirbas, 2008; Gerpen, 2005). Heterogeneous catalysts are claimed to be more relevant and appropriate as it is easy and cheap for recovery purpose, good in thermal stability, besides having better conversion and selectivity (Kiss, 2011). The usage of heterogeneous catalyst in esterification reaction could produce clean reaction product solution and reduce waste water (Sejidov *et al.*, 2005; Cordeiro *et al.*, 2008).

The suitability of commercially available solid acid catalyst such as macroporous sulfonic acid resin (Indion 130 and Amberlyst 15), gelular or microreticular cation-exchange resin (amberlite IR 120), acid-treated montmorillonite clay (Engelhard F 24), Zeolite (ZSM-5 and MCM-41) sulfated zirconia, and heteropolyacids (12-tungstophosphoric acid) were assessed for the esterification of carboxylic acid/ waste water containing carboxylic acid with alcohol (Bianchi *et al.*, 2003; Peters *et al.*, 2006; Fernandes *et al.*, 2012). The organic resin is preferable compared to solid oxides due to higher conversion (Chen *et al.*, 1999; Komoń *et al.*, 2013).

To the best of our knowledge, the study about esterification of AA with 2EH catalysed by Amberlyst 15 Dry (an acidic cation-exchange resin) is yet to be reported in the literature. In the present study, which is a part of a wider project with the aim of designing RDC for the AA recovery from the wastewater stream, diluted AA with different concentration (model wastewater) was reacted with 2EH in a stirred batch reactor. Amberlyst 15 Dry was used as catalyst. Information required for RDC design such as the important operating variables and kinetic model were identified. The practicability of carrying out this reaction in RDC was examined.

1.2 OBJECTIVES

The objectives of the study of esterification of AA with 2EH catalysed by Amberlyst 15 Dry are:

- To study the effect of important operating variables to the reaction kinetics.
- To develop the kinetic model of the reaction.
- To determine the effect of water inhibition toward the reaction.

1.3 SCOPES OF STUDY

The scopes of study include:

- The study on the effect of external and the internal diffusion on the reaction.
- The study on the effect of the operating variables such as initial concentration of AA, reaction time, catalyst loading, temperature and ratio of reactants.
- The equilibrium study.
- The kinetic data correlation with pseudo-homogeneous (PH), Eley Rideal (ER), and Langmuir Hinshelwood Hougen Watson (LHHW) models.

1.4 SIGNIFICANCE OF STUDY

The outcome of the present research serves as a basis for the analysis of the prospect and feasibility of the AA recovery from the waste water stream using RDC. The range of the important operating variables and the kinetic model identified in the present study can be adopted in the modelling and simulation of the RDC for AA recovery. The feasibility can be examined based on the results obtained from the simulation study. The success of the present work would lead to a breakthrough of new treatment method for wastewater containing acrylic acid from the petrochemical industries. Hence, the environmental impact of the wastewater generated by petrochemical industries could be reduced. More revenue would also be generated from the ester produced from the wastewater stream.