

TABLE OF CONTENTS

	Page
TABLE OF CONTENT	i
LIST OF TABLES	iii
LIST OF FIGURES	vi
INTRODUCTION	1
Objectives	2
Scope of the investigation	2
Impact of result	2
LITERATURE REVIEW	
Thermal cracking	3
Catalytic cracking	10
Hydrocracking	14
Polyvinyl chloride (PVC)	16
Design of experiment	24
METHODOLOGY	
Copyrolysis of polyvinyl chloride and cattle manure	32
Kinetics study of copyrolysis of PVC with cattle manure	35
Upgrading of pyrolyzed oil	35
RESULTS AND DISCUSSION	
Design of experiment	40
Investigation of kinetic parameters of copyrolysis reaction between PVC and cattle manure by isothermal and dynamic study	58
Catalytic upgrading of copyrolyzed oil derived from copyrolysis between PVC- containing mixed plastics and cattle manure	68
CONCLUSIONS	96
LITERATURE CITED	99
APPENDICES	105

TABLE OF CONTENTS (cont'd)

	Page
Appendix A	106
Appendix B	110
Appendix C	115
Appendix D	120
Appendix E	122
Appendix F	125
Appendix G	128
Appendix H	155
Appendix I	158
Appendix J	171

LIST OF TABLES

Table		Page
1	Basic model of solid reaction	23
2	The theoretical values of $\alpha_{\max}$ of n^{th} -order reaction at various reaction orders	24
3	The design matrix of 2^4 factorial design	29
4	The design matrix of Box-Behnken design	31
5	Experimental conditions according to factorial design	33
6	Experimental conditions according to Box- Behnken design	34
7	The chemical shift of proton of each hydrocarbon compound	38
8	Experimental results of HCl reduction following 2^4 factorial design	40
9	Fractional factorial fit: %HCl reduction versus ratio of PVC:cattle manure, temperature, heating rate, and holding time.	41
10	Analysis of variance	42
11	Experimental results of HCl reduction following Box-Behnken design conditions.	44
12	Estimated regression coefficients from Minitab program	44
13	The percents of composition in each hydrocarbon group and octane number from NMR results	57
14	α -T data from dynamic degradation of PVC and cattle manure at the ratio of 1:0	59
15	α -T data from dynamic degradation of PVC and cattle manure at the ratio of 1:1	60
16	α -T data from dynamic degradation of PVC and cattle manure at the ratio of 1:3	61
17	α -T data from dynamic degradation of PVC and cattle manure at the ratio of 1:5	62

LIST OF TABLES (cont'd)

Table		Page
18	The activation energies at various ratios of PVC:cattle manure	66
19	The values of $\alpha_{\max}$ observed in the dynamic degradation	66
20	Reaction order derived from isoconversional method	67
21	The pre-exponential factors and reaction orders from isothermal study	68
22	Physical properties of silica alumina-ZnO and silica alumina-Fe ₂ O ₃ composite catalysts	69
23	Isoparaffin index and octane number of upgrading oils with various types of catalyst	75
24	Isoparaffin index and octane number of the upgraded oils when using various ratios of silica alumina:ZnO	83
25	Isoparaffin index and octane number of gasoline products from upgrading of oil at various oil feed rates	91

Appendix Table

C1	α -T data of copyrolysis of PVC and cattle manure mixture at the ratio of 1:0	116
C2	α -T data of copyrolysis of PVC and cattle manure mixture at the ratio of 1:1	117
C3	α -T data of copyrolysis of PVC and cattle manure mixture at the ratio of 1:3	118
C4	α -T data of copyrolysis of PVC and cattle manure mixture at the ratio of 1:5	119
D1	The product yields of pyrolyzed oils from pyrolysis of PVC-containing plastic mixture with and without cattle manure.	121

LIST OF TABLES (cont'd)

Appendix Table	Page
D2 The distillation products of pyrolyzed oils from pyrolysis of PVC-containing plastic mixture with and without cattle manure.	121
D3 The peak areas of NMR and fractions of chlorinated hydrocarbon of pyrolyzed oils from pyrolysis of PVC- containing plastic mixture with and without cattle manure.	121
E1 The product yields from upgrading the copyrolyzed oil	123
E2 The distillation product yields from upgrading the copyrolyzed oil	123
E3 The peak areas from NMR analysis and fractions of chlorinated hydrocarbon in the upgraded oil	124
H1 Electricity rate of Provincial Electricity Authority Thailand	156
I1 Analysis of variance	159
I2 Experimental results of oil yields obtained from upgrading by silica alumina-Fe ₂ O ₃	160

LIST OF FIGURES

Figure		Page
1	Overview of the main forms of feedstock recycling for waste plastics by thermolysis	3
2	Reaction scheme of hydrogen abstraction	6
3	The factorial experiment (a) without interaction, and (b) with interaction	25
4	Copyrolysis process diagram	32
5	Upgrading process diagram	36
6	Nuclear Magnetic Resonance graph of gasoline fraction	38
7	The main effect plot calculated by factorial design using Minitab program	42
7	Interaction plot of factors: ratio of PVC:cattle manure, reaction temperature, heating rate, and holding time.	43
8	Relation between %HCl reduction, reaction temperature, and heating rate at ratio of PVC:cattle manure of 1:1 (a) response surface plot and (b) contour plot.	45
9	Relation between %HCl reduction, reaction temperature, and heating rate at ratio of PVC:cattle manure of 1:3 (a) response surface plot and (b) contour plot.	46
10	Relation between %HCl reduction, reaction temperature, and heating rate at ratio of PVC:cattle manure of 1:5 (a) response surface plot and (b) contour plot.	46
11	Relation between %HCl reduction, reaction temperature, and ratio of PVC:cattle manure at heating rate of 1 °C/min (a) response surface plot and (b) contour plot.	47
12	Relation between %HCl reduction, reaction temperature and ratio of PVC:cattle manure at heating rate of 3 °C/min (a) response surface plot and (b) contour plot.	48

LIST OF FIGURES (cont'd)

Figure		Page
13	Relation between %HCl reduction, reaction temperature, and ratio of PVC:cattle manure at heating rate of 5 °C/min (a) response surface plot and (b) contour plot.	49
14	Relation between %HCl reduction, heating rate, and ratio of PVC:cattle manure at reaction temperature of 250 °C (a) response surface plot and (b) contour plot.	50
15	Relation between %HCl reduction, heating rate and the ratio of PVC:cattle manure at reaction temperature of 350 °C (a) response surface plot and (b) contour plot.	51
16	Relation between %HCl reduction, heating rate, and ratio of PVC:cattle manure at reaction temperature of 450 °C (a) response surface plot and (b) contour plot.	52
17	Weights of copyrolyzed products of mixed plastics with manure, without manure, and pure manure.	54
18	Synergistic effect of copyrolyzed product of mixed plastics with cattle manure	54
19	The yields of distillation product from copyrolysis product of mixed plastics with and without cattle manure.	55
20	Fractions of chlorinated carbon in oil from copyrolysis product of mixed plastics with and without cattle manure	56
21	The concentrations of benzene, toluene and xylene in gasoline from copyrolysis product of mixed plastics with and without cattle manure.	56
22	Thermal decomposition profile of PVC and cattle manure by thermal gravimetric analysis at heating rate of 1 °C/min	58
23	Isoconversional plot from experimental data of dynamic degradation study at PVC:cattle manure ratio of 1:0	60

LIST OF FIGURES (cont'd)

Figure		Page
24	Isoconversional plot from experimental data of dynamic degradation study at PVC:cattle manure ratio of 1:1	61
25	Isoconversional plot from experimental data of dynamic degradation study at PVC:cattle manure ratio of 1:3	62
26	Isoconversional plot from experimental data of dynamic degradation study at PVC:cattle manure ratio of 1:5	63
27	The relation between E/R with conversion at PVC:cattle manure ratio of 1:0.	63
28	The relation between E/R with conversion at PVC:cattle manure ratio of 1:1.	64
29	The relation between E/R with conversion at PVC:cattle manure ratio of 1:3.	64
30	The relation between E/R with conversion at PVC:cattle manure ratio of 1:5	65
31	The XRD patterns of silica alumina-ZnO composite catalysts at the silica alumina:ZnO ratios of 1:1 and 1:2 and silica alumina-Fe ₂ O ₃ (1:1) composite catalyst	69
32	Oil yields from upgrading reaction, using various catalyst types, and at feed rates of 30ml/h and 50ml/h	70
33	The distillation yields of the upgraded oil, using various types of catalyst, and at feed rate of 30ml/h	71
34	The distillation yields of the upgraded oil, using various types of catalyst, and at feed rate of 50ml/h	72
35	Fractions of chlorinated carbon in upgraded oil, using various types of catalyst, at feed rates of 30 and 50 ml/min	73
36	The percents of composition in each hydrocarbon group in gasoline product when using various types of catalyst	74

LIST OF FIGURES (cont'd)

Figure		Page
37	The concentrations of benzene, toluene, and xylene in gasoline from upgrading of oil using various types of catalyst at feed rate of 30ml/min	76
38	The concentrations of benzene, toluene, and xylene in gasoline from upgrading of oil using various types of catalyst at feed rate of 50ml/min	76
39	Oil yields from upgrading reaction, using various silica alumina: ZnO ratios and feed rates of 10, 30, and 50ml/min	78
40	The distillation yields of the upgraded oil, using various ratios of silica alumina to ZnO at feed rate of 10ml/h.	79
41	The distillation yields of the upgraded oil, using various ratios of silica alumina to ZnO at feed rate of 30ml/h.	79
42	The distillation yields of the upgraded oil, using various ratios of silica alumina and ZnO at feed rate 50ml/min	80
43	Fractions of chlorinated hydrocarbon in the upgraded oil when using various silica alumina:ZnO ratios at feed rate of 10, 30, and 50 ml/min	81
44	The percents of composition in each hydrocarbon group in gasoline product with various silica alumina: ZnO ratios at feed rates of 10, 30, and 50ml/min	82
45	The concentrations of benzene, toluene, and xylene in gasoline from upgrading of oil with various ratios of silica alumina: ZnO at feed rate 10ml/min	84
46	The concentrations of benzene, toluene, and xylene in gasoline from upgrading of oil using various ratios of silica alumina: ZnO at feed rate 30ml/min	84

LIST OF FIGURES (cont'd)

Figure		Page
47	The concentrations of benzene, toluene, and xylene in gasoline from upgrading of oil using various ratios of silica alumina: ZnO at feed rate 50ml/min	85
48	Oil yields from upgrading reaction at different oil feed rates using catalysts with silica alumina: ZnO ratios of 1:0, 1:1 and 1:2	86
49	The distillation yields of oil products from upgrading of oil at various oil feed rates using silica alumina catalyst.	87
50	The distillation yields of oil products from upgrading of oil at various oil feed rates using silica alumina-ZnO composite catalyst at the ratio of 1:1	88
51	The distillation yields of oil products from upgrading of oil at various oil feed rates using silica alumina-ZnO composite catalyst at the ratio of 1:2	88
52	Fractions of chlorinated carbon in oil from upgrading at various feed rates using silica alumina:ZnO ratio of 1:0, 1:1 and 1:2 catalysts.	89
53	The percents of composition of each hydrocarbon group in gasoline product from reactions at various feed rates using silica alumina:ZnO ratio of 1:0, 1:1 and 1:2 catalysts.	90
54	The concentrations of benzene, toluene, and xylene in gasoline products from upgrading of oil at various feed rates using silica alumina catalyst.	92
55	The concentrations of benzene, toluene, and xylene in gasoline from upgrading of oil at various feed rates using silica alumina:ZnO (1:1) composite catalyst.	93

LIST OF FIGURES (cont'd)

Figure		Page
56	The concentrations of benzene, toluene, and xylene in gasoline from upgrading of oil at various feed rates using silica alumina:ZnO (1:2) composite catalyst.	94
Appendix Figure		
B1	Thermal decomposition profile of PVC and cattle manure mixture at various heating rate and PVC: cattle manure ratio of 1:1	111
B2	Differential weight of thermal decomposition profile of PVC and cattle manure mixture at various heating rates, and PVC: cattle manure ratio of 1:1	111
B3	Thermal decomposition profile of PVC and cattle manure mixture at various heating rates and PVC: cattle manure ratio of 1:3	112
B4	Differential weight of thermal decomposition profile of PVC and cattle manure mixture at various heating rates, and PVC: cattle manure ratio of 1:3	112
B5	Thermal decomposition profile of PVC and cattle manure mixture at various heating rate and PVC: cattle manure ratio of 1:5	113
B6	Differential weight of thermal decomposition profile of PVC and cattle manure mixture at various heating rates, and PVC: cattle manure ratio of 1:5	113
B7	Thermal decomposition profile of PVC and cattle manure mixture at various heating rate and PVC: cattle manure ratio of 1:0	114

LIST OF FIGURES (cont'd)

Appendix Figure	Page
B8 Differential weight of thermal decomposition profile of PVC and cattle manure mixture at various heating rates, and PVC: cattle manure ratio of 1:0	114
F1 Standard curve of benzene	126
F2 Standard curve of toluene	126
F3 Standard curve of xylene	127
G1 NMR pattern of copyrolyzed oil from copyrolysis PVC-containing plastic mixture (without manure)	129
G2 NMR pattern of copyrolyzed oil from copyrolysis PVC-containing plastic mixture and manure	130
G3 NMR pattern of the oil from upgrading by silica alumina at feed rate of 10 ml/h.	131
G4 NMR pattern of the oil from upgrading by silica alumina at feed rate of 30 ml/h.	132
G5 NMR pattern of the oil from upgrading by silica alumina at feed rate of 50 ml/h.	133
G6 NMR pattern of the oil from upgrading by silica alumina-ZnO catalyst at the ratio of 1:1 and feed rate of 10 ml/h.	134
G7 NMR pattern of the oil from upgrading by silica alumina-ZnO catalyst at the ratio of 1:1 and feed rate of 30 ml/h.	135
G8 NMR pattern of the oil from upgrading by silica alumina-ZnO catalyst at the ratio of 1:1 and feed rate of 50 ml/h.	136
G9 NMR pattern of the oil from upgrading by silica alumina-ZnO catalyst at the ratio of 1:2 and feed rate of 10 ml/h.	137
G10 NMR pattern of the oil from upgrading by silica alumina-ZnO catalyst at the ratio of 1:2 and feed rate of 30 ml/h.	138
G11 NMR pattern of the oil from upgrading by silica alumina-ZnO catalyst at the ratio of 1:2 and feed rate of 50 ml/h.	139

LIST OF FIGURES (cont'd)

Appendix Figure	Page
G12 NMR pattern of the oil from upgrading by silica alumina- Fe ₂ O ₃ catalyst at the ratio of 1:1 and feed rate of 30 ml/h.	140
G13 NMR pattern of the oil from upgrading by silica alumina- Fe ₂ O ₃ catalyst at the ratio of 1:1 and feed rate of 50 ml/h.	141
G14 NMR pattern of gasoline fraction of pyrolyzed oil from pyrolysis of PVC-containing plastic mixture (without manure)	142
G15 NMR pattern of gasoline fraction of copyrolyzed oil from copyrolysis of PVC-containing plastic mixture and manure	143
G16 NMR pattern of gasoline fraction of the oil from upgrading by silica alumina at feed rate of 10 ml/h.	144
G17 NMR pattern of gasoline fraction of the oil from upgrading by silica alumina at feed rate of 30 ml/h.	145
G18 NMR pattern of gasoline fraction of the oil from upgrading by silica alumina at feed rate of 50 ml/h.	146
G19 NMR pattern of gasoline fraction of the oil from upgrading by silica alumina-ZnO catalyst at the ratio of 1:1 and feed rate of 10 ml/h.	147
G20 NMR pattern of gasoline fraction of the oil from upgrading by silica alumina-ZnO catalyst at the ratio of 1:1 and feed rate of 30 ml/h.	148
G21 NMR pattern of gasoline fraction of the oil from upgrading by silica alumina-ZnO at the ratio of 1:1 and feed rate of 50 ml/h.	149
G22 NMR pattern of gasoline fraction of the oil from upgrading by silica alumina-ZnO catalyst at the ratio of 1:2 and feed rate of 10 ml/h.	150

LIST OF FIGURES (cont'd)

Appendix Figure	Page
G23 NMR pattern of gasoline fraction of the oil from upgrading by silica alumina-ZnO catalyst at the ratio of 1:2 and feed rate of 30 ml/h.	151
G24 NMR pattern of gasoline fraction of the oil from upgrading by silica alumina-ZnO catalyst at the ratio of 1:2 and feed rate of 50 ml/h.	152
G25 NMR pattern of gasoline fraction of the oil from upgrading by silica alumina-Fe ₂ O ₃ catalyst at the ratio of 1:1 and feed rate of 30 ml/h.	153
G26 NMR pattern of gasoline fraction of the oil from upgrading by silica alumina-Fe ₂ O ₃ catalyst at the ratio of 1:1 and feed rate of 50 ml/h.	154
J1 Thermal gravimetry profile and differential of thermal gravimetry of PVC and cattle manure mixture, PVC:cattle manure (1:1), heating rate of 10°C/min.	172