RESULTS AND DISCUSSION

The research consists of three parts. The first part is to do the experimental design by screening factor and to find the optimum conditions for PVC-cattle manure copyrolysis reaction using statistical method. The second part is the investigation of kinetic parameters of the copyrolysis reaction by isothermal and dynamic studies. The last part is the upgrading of pyrolyzed oil from the copyrolysis reaction by iron oxide, zinc oxide, and silica alumina composite catalyst.

1. **Design of experiment**

1.1 Factor screening by 2^k factorial method

The experimental results of each condition from factorial design in Table 5 are shown in Table 8. These results are the percentages of HCl reduction when PVC was pyrolyzed with cattle manure compared with those in the absence of manure (a blank condition) as shown in equation 25. The negative value was obtained when the amount of HCl from pyrolysis of PVC with cattle manure was higher than that in the absence of manure.

Table 8 Experimental results of HCl reduction following 2^4 factorial design.

Standard order	Run order	% HCl reduction	Standard order	Run order	%HCl reduction
8	1	2.59	5	9	-32.22
6	2	-33.58	1	10	10.32
14	3	-40.11	10	11	27.52
3	4	11.45	12	12	28.81
16	5	14.32	15	13	1.59
13	6	-5.50	11	14	18.44
4	7	15.98	2	15	17.01
9	8	19.22	7	16	0.58

$$\%HCl\,reduction = \frac{\left(HCl_{purePVC} - HCl_{purePVC+manure}\right)}{HCl_{purePVC}} \times 100 \qquad (25)$$

These results were analyzed by fractional factorial method using Minitab program under hypothesis of average results of two conditions that are not different. Results of experiment from two conditions that are not different significantly will be rejected. From normal distribution curve, P values were area under the curve outside the area of reliability. Since the reliability area of 0.95 was chosen (or 95% of reliability), therefore P value of each factor must be less than 0.05. The statistical results including P value of each factor are shown in Table 9. Heating rate and reaction temperature had significant effects on HCl reduction in 95% reliability where P value was less than 0.05. The other two factors, the ratio of PVC:cattle manure and holding time had P values higher than 0.05 which were 0.87 (23% reliability) and 0.19 (81% reliability), respectively. These factors did not affect HCl reduction in this consideration.

Table 9 Fractional factorial fit: %HCl reduction versus ratio of PVC:cattle manure, temperature, heating rate, and holding time.

Term	Effect	Coefficient	SE Coefficient	T	P
Constant		3.53	3.253	1.08	0.302
Ratio of PVC: cattle manure	1.09	0.54	3.253	0.17	0.871
Reaction temperature	16.39	8.19	3.253	2.52	0.029
Heating rate	-30.13	-15.07	3.253	-4.63	0.001
Holding time	9.02	4.51	3.253	1.39	0.193

Note: SE- standard error

The main effect plots in Figure 7 show the effect of holding time on the percentage of HCl reduction, but the statistical result presented less than 95% reliability. Therefore, only heating rate and reaction temperature affected HCl reduction. The ratio of PVC: cattle manure had a slight effect on HCl reduction. Table

10 is analysis of variance (ANOVA). It shows the P value of 0.004, therefore the model of factorial design has more than 99% reliability.

Table 10 Analysis of variance

Source	DF	Seq SS	Adj SS	Adj MS	F	P
Main effect	4	5036	5036	1259.1	7.44	0.004
Residual	11	1863	1863	169.3		
Error	15	6899				
Total						

Note: SS- sum of square DF- degree of freedom

MS- mean square Seq- sequential

Adj- Adjusted

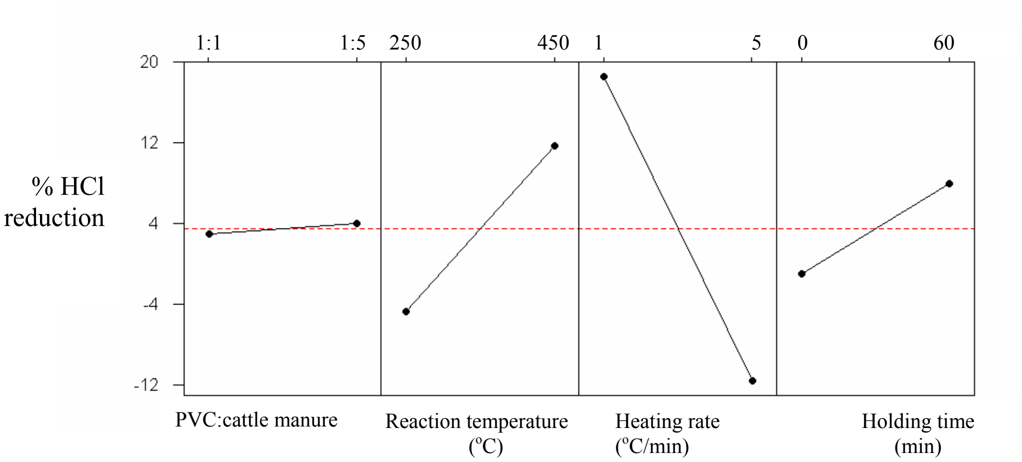


Figure 7 The main effect plot calculated by factorial design using Minitab program.

The interaction plot of each factor is shown in Figure 8. Three factors: ratio of PVC:cattle manure, reaction temperature and heating rate had interaction among them because the lines are crossing in the interaction plot. Holding time did not interact with the other three factors.

From the result of the interaction plot, the ratio of PVC:cattle manure cannot be screened because it interacted with other factors. Holding time had no interaction with any other factors therefore, it was kept constant and among the holding time of 0-60 minutes the holding time of 60 minutes provided the best result.

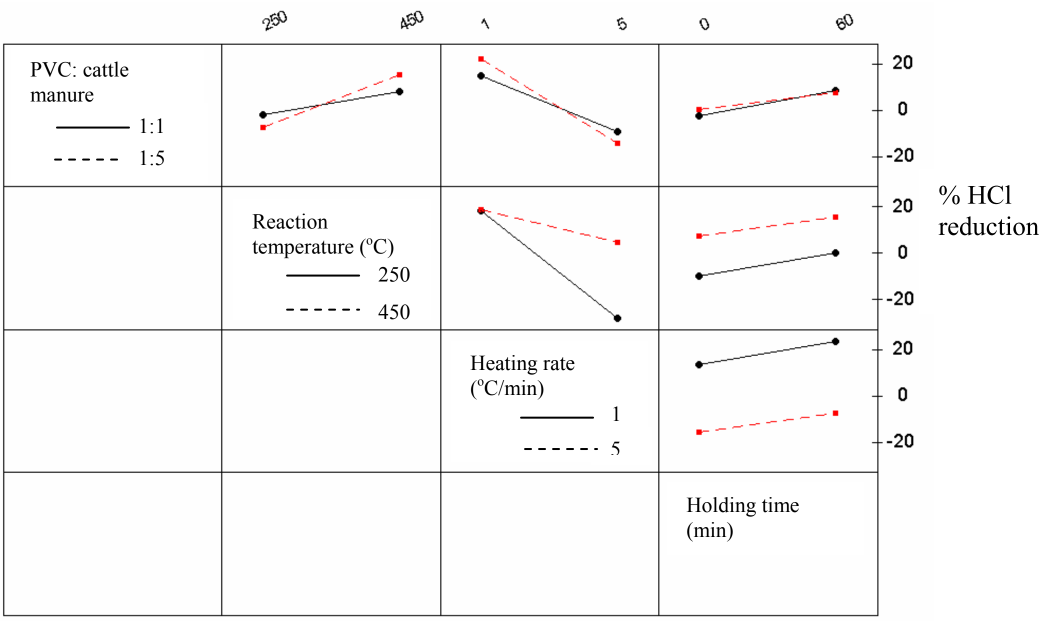


Figure 8 Interaction plot of factors: ratio of PVC:cattle manure, reaction temperature, heating rate, and holding time.

1.2 Optimization of the conditions of copyrolysis reaction between PVC and cattle manure by Box-Behnken model

From the factorial design results, the holding time was kept constant because it did not interact with the other factors and the previous results showed the longest holding time, at 60 min, provided the highest HCl reduction efficiency. Therefore, this study kept the holding time at 60 min and only three factors: heating rate, reaction temperature, and PVC: cattle manure ratio were optimized.

Table 11 Experimental results of HCl reduction following Box-Behnken design conditions.

Standard order	Run order	%HCl reduction	Standard order	Run order	%HCl reduction
6	1	15.04	3.00	9	-2.13
1	2	4.41	14.00	10	8.78
13	3	12.97	12.00	11	3.46
8	4	-1.76	9.00	12	1.06
11	5	23.43	15.00	13	13.58
10	6	1.06	2.00	14	8.76
7	7	8.50	4.00	15	-7.49
5	8	-23.48			

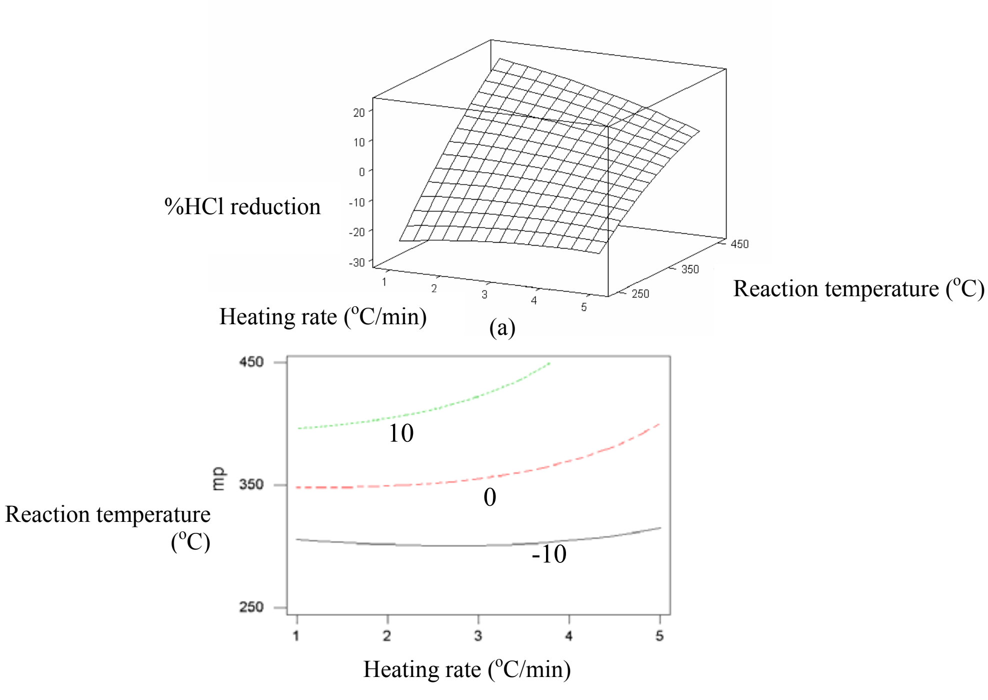
Table12 Estimated regression coefficients from Minitab program.

Term	Coefficient	SE Coefficient	T	P
Constant	-778.8	136.591	-5.702	0.002
Ratio of PVC: cattle manure (X_1)	85.2	18.156	4.694	0.005
Heating rate (X_2)	16.4	10.380	1.576	0.176
Reaction temperature (X_3)	1.1	0.256	4.391	0.007
Ratio*Ratio (X_1^2)	-2.3	0.671	-3.458	0.018
Heating rate*Heating rate (X_2^2)	-0.4	0.671	-0.598	0.576
Reaction temperature*Reaction temperature (X_3^2)	-0.0	0.000	-1.087	0.327
Ratio*Heating rate (X_1*X_2)	-0.6	0.645	-0.941	0.390
Ratio*Reaction temperature(X_1*X_3)	-0.1	0.013	-4.727	0.005
Heating rate*Reaction temperature (X_2*X_3)	-0.0	0.013	-1.935	0.111

The experimental results from Box-Behnkhen are shown in Table 11. These results were calculated statistically by Minitab program. Table 12 shows the coefficients of Box-Behnken model that were used to predict the profile of the percentage of HCl reduction at middle point with all three factors as the following equation (26).

$$\% \text{ of HCl reduction} = -778.8+85.2X_1+16.4X_2+1.1X_3-2.3X_1^2-0.4X_2^2-0.6X_1X_2-0.1X_1X_3 \quad (26)$$

Figures 9-11 show the surface plot and contour plot of the relation between HCl reduction efficiency, heating rate and reaction temperature. The values presented in a contour plot were calculated from statistical model equation using the values of %HCl reduction at various reaction temperatures and heating rates with constant ratio of PVC:cattle manure (X_1) (1:1, 1:3, and 1:5). The highest HCl reduction efficiency was obtained at low heating rate of 1°C/min and high reaction temperature of 450°C at 1:1 and 1:3 ratios, but ratio of 1:5 provided the highest HCl reduction at the temperature range of 250-400°C.



(a)

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Figure 9 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.

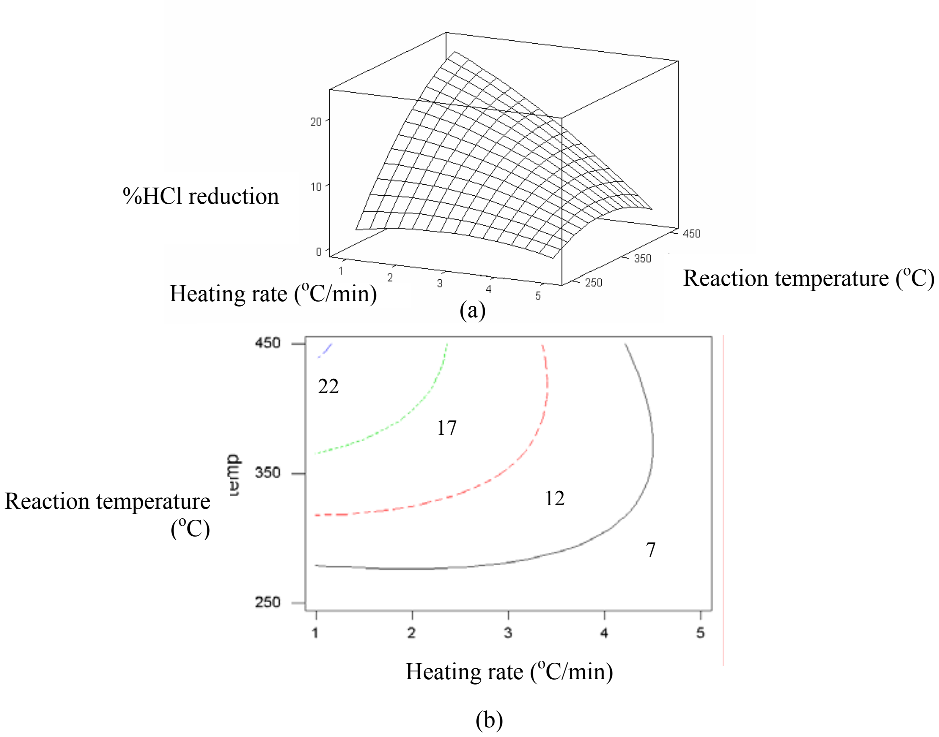


Figure 10 Relation between %HCl reduction, reaction temperature and heating rate at ratio of PVC:cattle manure of 1:3 (a) response surface plot and (b) contour plot.

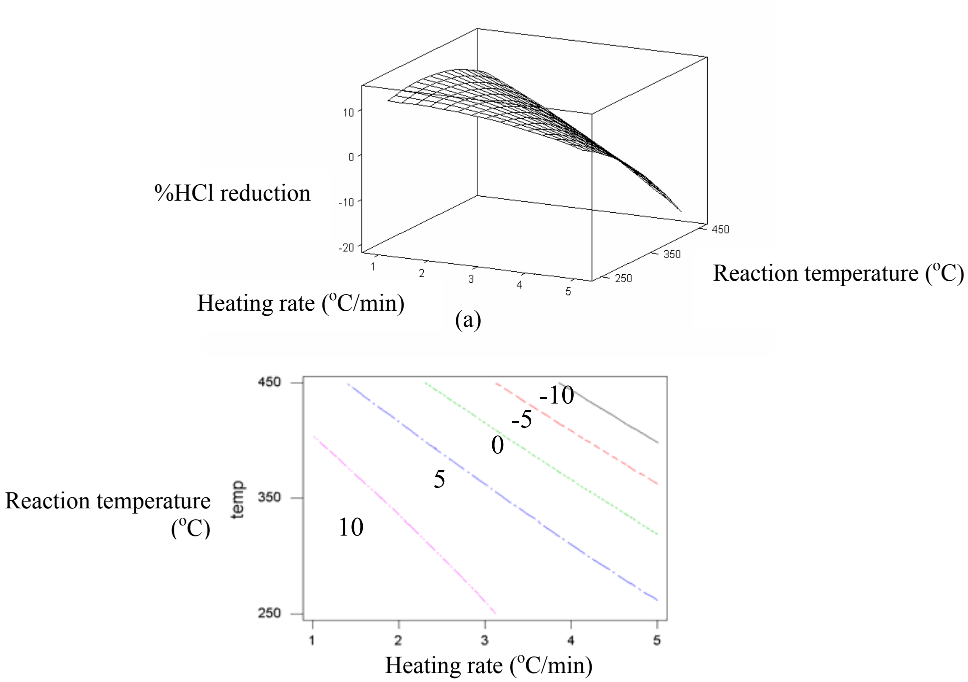


Figure 11 Relation between %HCl reduction, reaction temperature, and heating rate at ratio of PVC:cattle manure of 1:5 (a) response surface plot and (b) contour plot.

The relations among HCl reduction, ratio of PVC:cattle manure and reaction temperature are shown in Figures 12-14. It was calculated from statistical model using the values of HCl reduction at various reaction temperatures and ratios of PVC:cattle manure with constant heating rate of 1°C/min (X_2). At low reaction temperature of 250°C, the PVC:cattle manure ratio of 1:5 gave the highest HCl reduction efficiency but at high reaction temperature of 450°C, the highest HCl reduction efficiency was obtained at the PVC:cattle manure ratios of 1:1-1:3 (Figure 12).

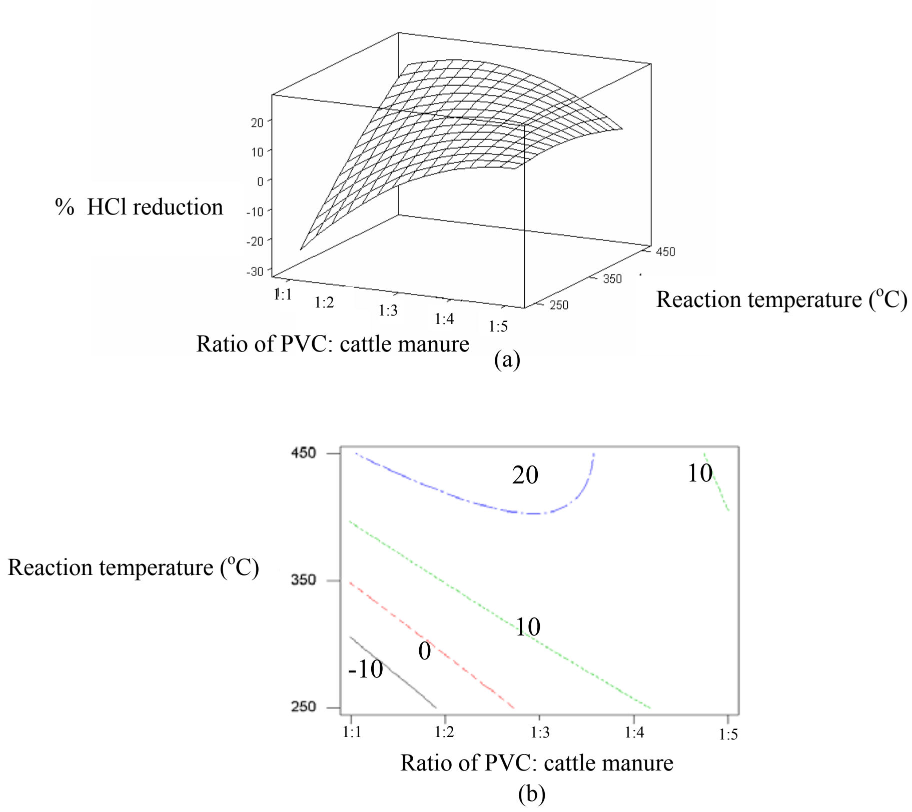


Figure 12 Relation between %HCl reduction, reaction temperature, and ratio of PVC:cattle manure at heating rate of 1°C/min (a) response surface plot and (b) contour plot.

The HCl reduction efficiency at constant heating rate of 3°C/min is shown in Figure 13. At low reaction temperature of 250°C, the PVC:cattle manure ratio of 1:5 gave the highest HCl reduction efficiency but the highest HCl reduction efficiency at high reaction temperature of 450°C was obtained at the PVC:cattle manure ratios in the range of 1:1-1:3.

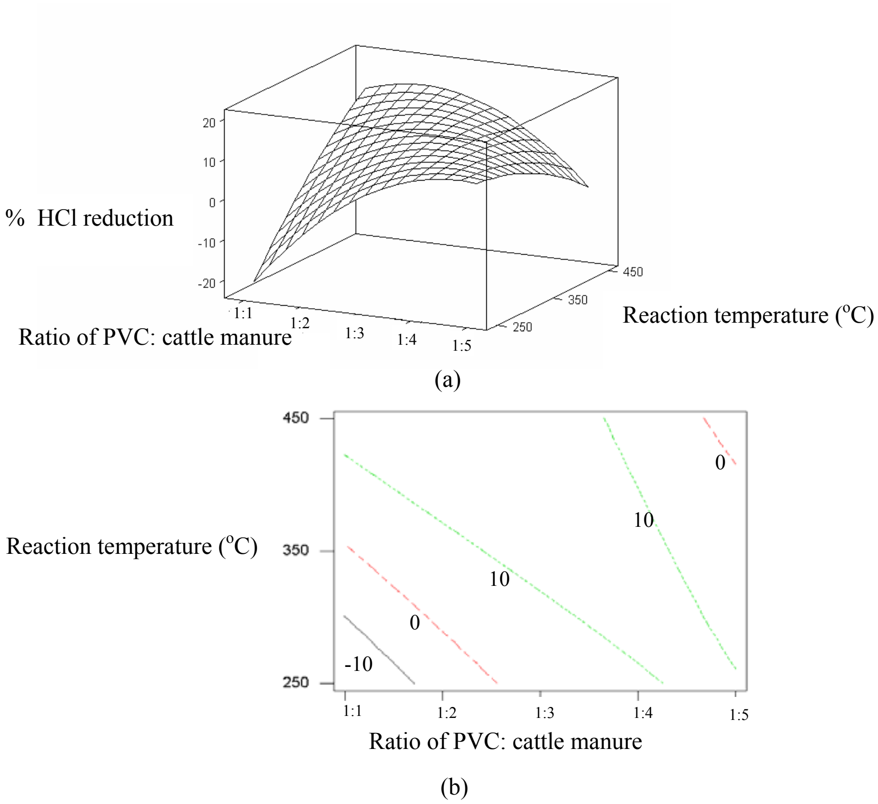
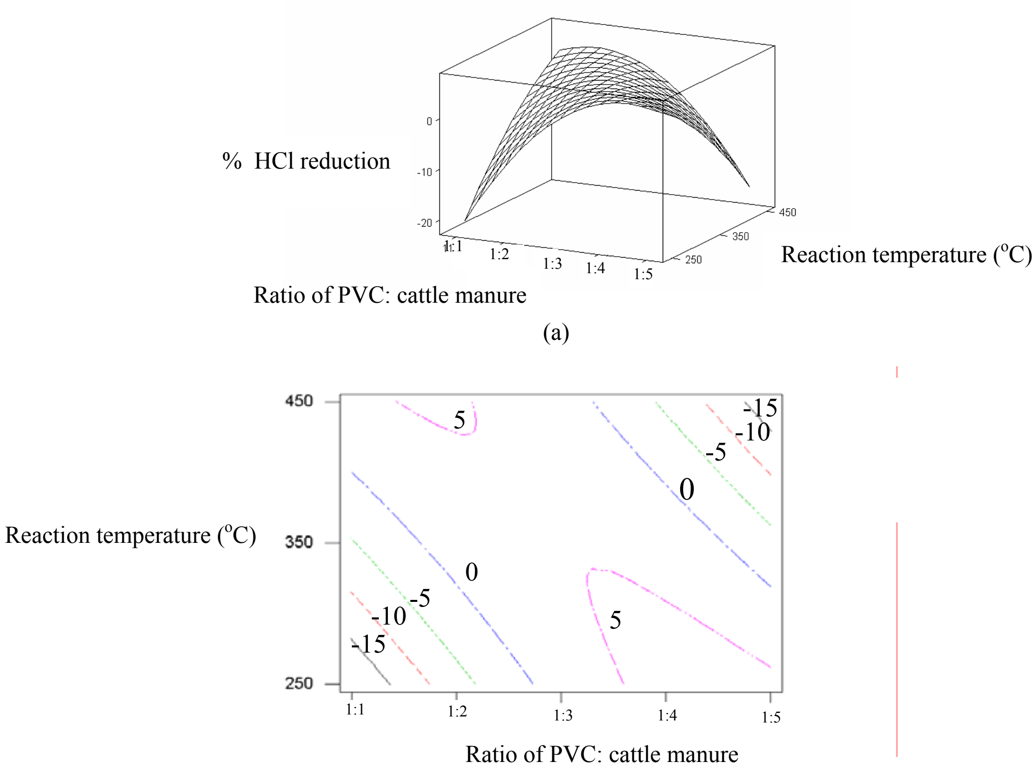


Figure 13 Relation between %HCl reduction, reaction temperature and ratio of PVC:cattle manure at heating rate of 3°C/min (a) response surface plot and (b) contour plot.

The relations among HCl reduction, ratio of PVC:cattle manure and reaction temperature at high constant heating rate of (5°C/min) is shown in Figure 14. At low reaction temperature of 250°C, PVC:cattle manure at 1:4 and 1:5 ratios provided the highest HCl reduction but at high reaction temperature of 450°C the highest HCl reduction was obtained at the ratio of 1:2.



(a)

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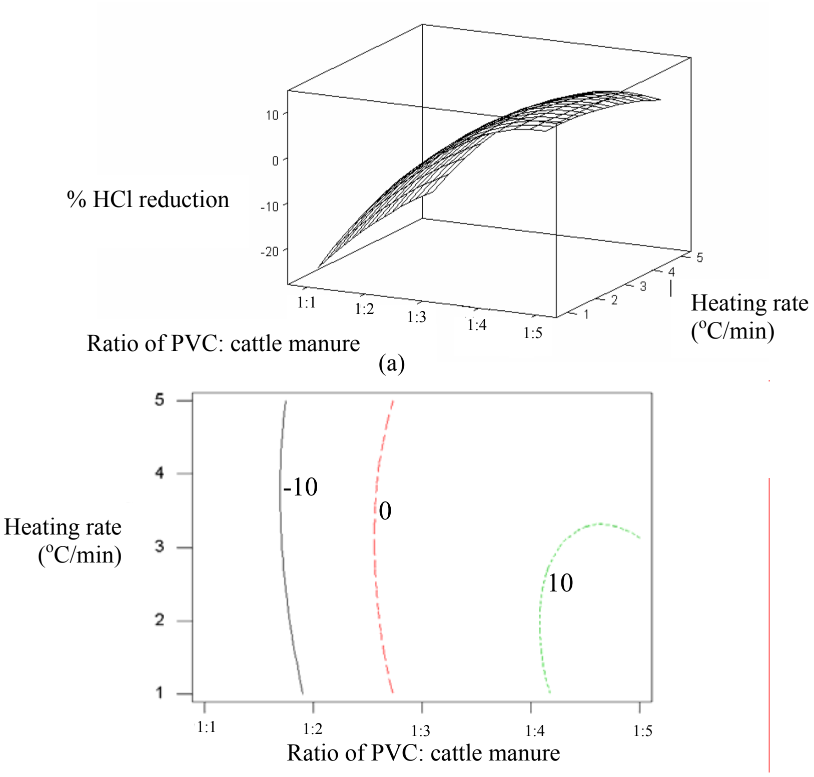
Figure 14 Relation between %HCl reduction, reaction temperature, and ratio of PVC:cattle manure at heating rate of 5°C/min (a) response surface plot and (b) contour plot.

The relation between ratios of PVC to cattle manure, reaction temperature, and % HCl reduction at a constant heating rate shows that the optimum ratio depended on reaction temperature. Various reaction temperatures had different optimum ratios due to the effect of interaction between the ratio of PVC:cattle manure and reaction temperature as shown by factorial design.

The effects of ratio of PVC:cattle manure and heating rate on HCl reduction efficiency are shown in Figures 15-17. The values in this plot were calculated from statistical model using the values of HCl reduction at various heating rates and ratios of PVC:cattle manure with constant reaction temperature (X_3). Figure 15 shows the relation between %HCl reduction, the ratio of PVC to cattle manure, and heating rate at constant reaction temperature of 250°C. Low heating rate of 1°C/min and cattle manure five times that of PVC provided the highest HCl reduction efficiency.



(a)

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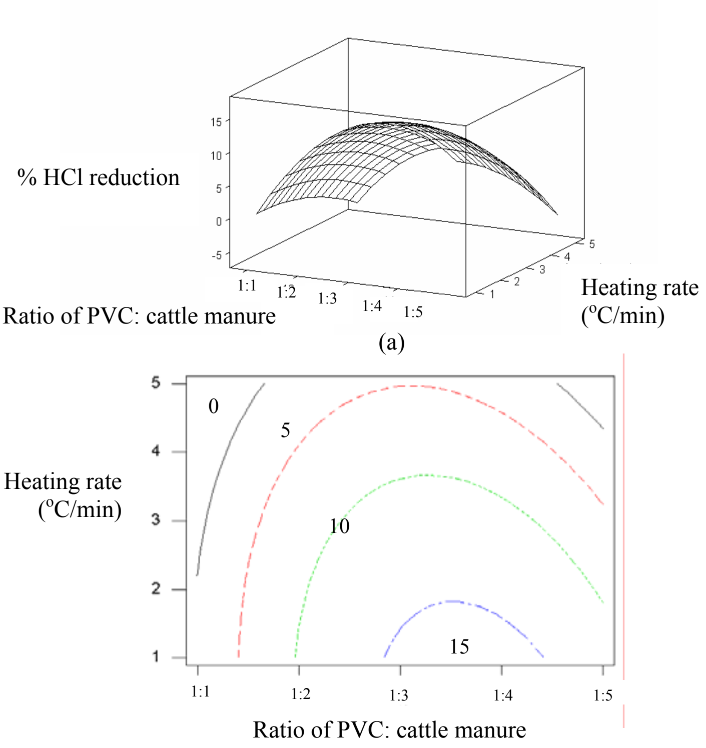
Figure 15 Relation between %HCl reduction, heating rate, and ratio of PVC:cattle manure at reaction temperature of 250°C (a) response surface plot and (b) contour plot.

The effect of PVC:cattle manure ratio and heating rate on %HCl reduction at constant reaction temperature of 350°C is shown in Figure 16. Low heating rate of 1°C/min and at 1:3 and 1:4 ratios gave the highest HCl reduction.



(a)

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Figure 16 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.

Figure 17 shows the relation between %HCl reduction, the ratio of PVC:cattle manure, and heating rate at constant reaction temperature of 450°C. High HCl reduction was obtained by the low heating rate of 1°C/min and the ratio of PVC:cattle manure in the range of 1:1-1:3.

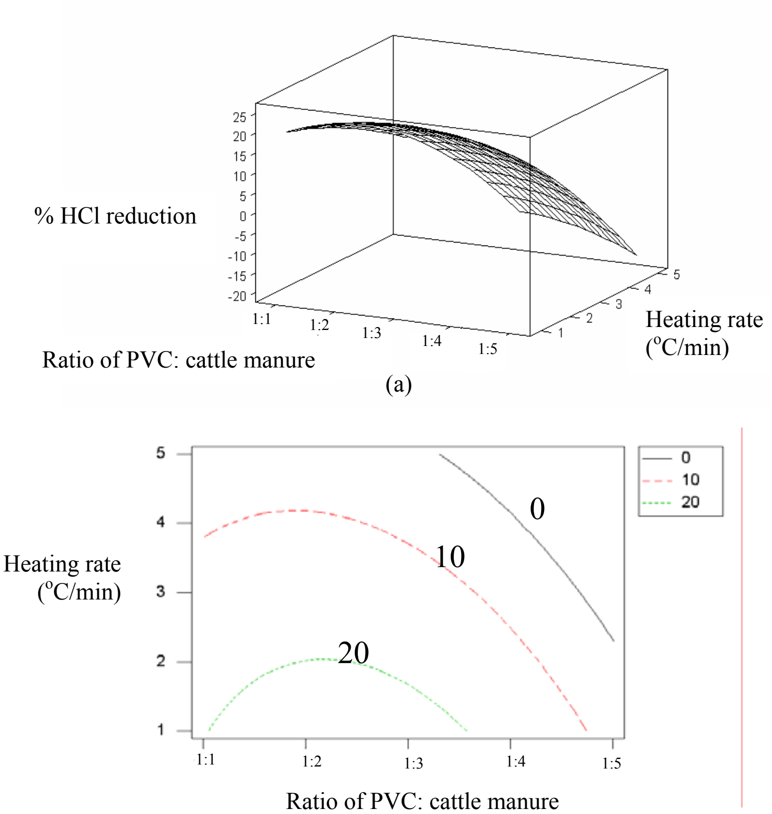

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Figure 17 Relation between %HCl reduction, heating rate, and ratio of PVC:cattle manure at reaction temperature of 450°C (a) response surface plot and (b) contour plot.

The Box-Behnken design showed the best condition of HCl reduction at low heating rate of 1°C/min, high reaction temperature of 450°C, however, the ratio of PVC:cattle manure cannot be optimized because it had interaction with the other two factors. In the statistical method, reliability of our model was R^2=92.2% and lack of fit was 85% reliability, therefore, the optimum ratio of PVC:cattle manure was obtained from experiment at the optimized heating rate and reaction temperature. Among all ratios (1:1 to 1:5) the ratio of 1:5 gave the best result (highest % HCl reduction).

From the results of optimization, it can be explained that at low heating rate of 1°C/min chlorine from PVC and nitrogen compounds from cattle manure were released slowly, therefore, they had more time to complete the reaction. High reaction temperature and high amount of cattle manure gave higher amounts of chlorine and nitrogen compounds than those at low temperature and low amount of cattle manure (see Appendix B).

1.3 Characterization of oil obtained from copyrolysis of mixed plastics and cattle manure at the optimized conditions

The mixed plastics containing PVC were pyrolyzed with cattle manure at the optimized conditions at low heating rate of 1°C/min, high reaction temperature of 450°C, PVC:cattle manure ratio of 1:5 and holding time of 60 min. The oil was distilled to different fractions. The yields of the pyrolyzed oil and each fractions were determined. The amounts of chlorinated compounds, BTX in gasoline fraction, and octane number of the gasoline fraction were compared with the copyrolyzed oil from pyrolysis of mixed plastics without manure.

Figure 18 shows the weights of products from copyrolysis of mixed plastics with manure, pure manure, and without cattle manure. Solid product of the mixture of mixed plastics and manure was increased by the effect of cattle manure because the weight of solid product of the mixture in theory (from each part) was 22.1g but the actual weight of solid was 27.3g. Liquid yield decreased from 42.5g to 35.2g for theory and the real mixture, respectively. Gas yield increased slightly from 15.8g in theory to 18g in real mixture. These results proved that the cattle manure affected the decrease in oil product and the increase in solid and gas products. The percentage of synergistic effect was calculated to show the effect of cattle manure on product yields as shown in Figure 19.

The cattle manure decreased liquid yield by about 17% but increased solid and gas yields by 25% and 14%, respectively. Therefore, cattle manure had an effect on product yields. It increased cracking activity to more gas products and some intermediates which were polymerized to larger molecules.

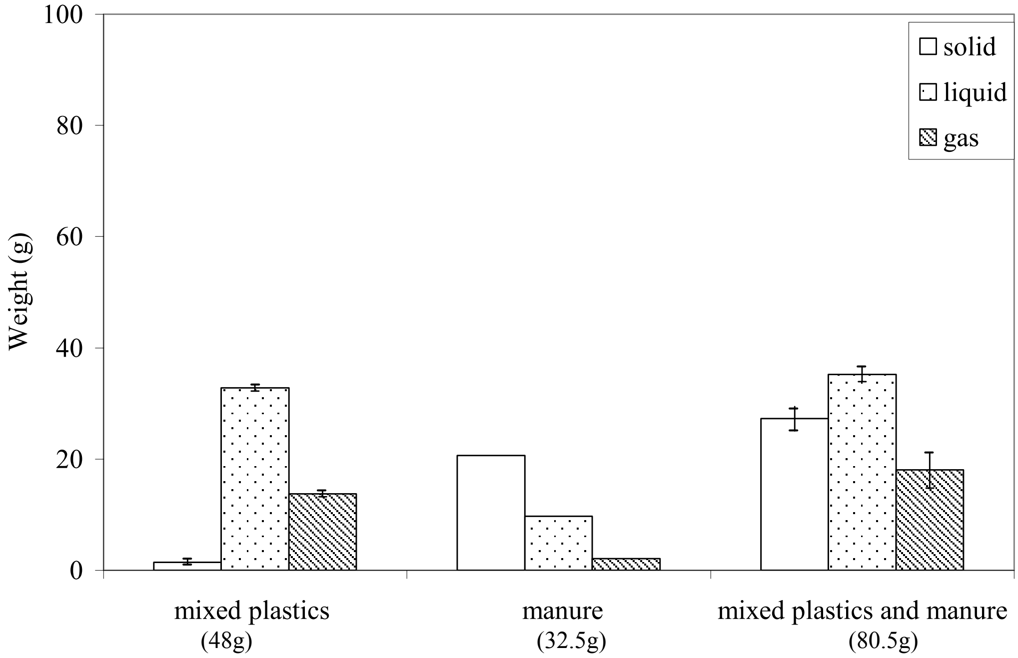


Figure 18 Weights of copyrolyzed products of mixed plastics with manure, without manure, and pure manure.

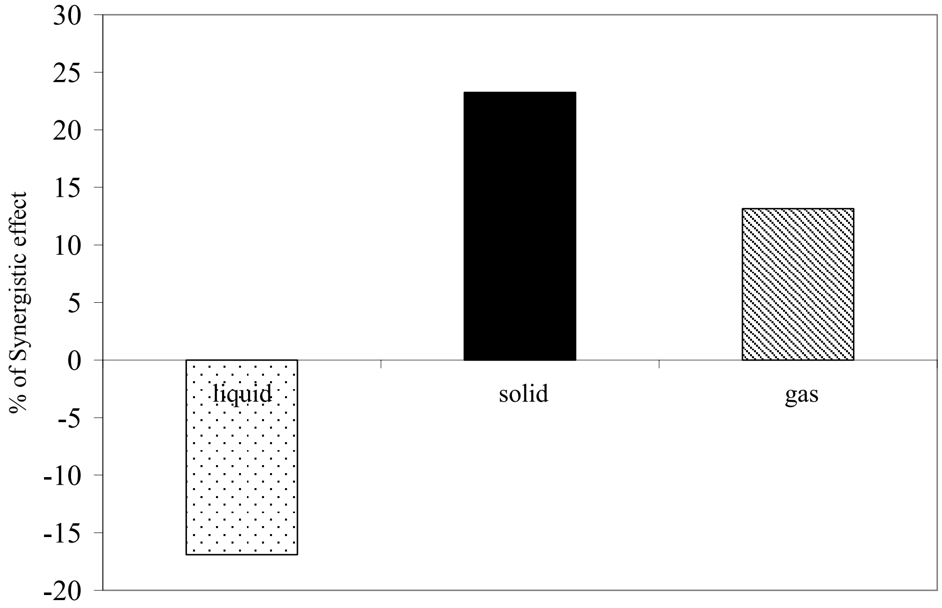


Figure 19 Synergistic effect of copyrolyzed product of mixed plastics with cattle manure.

The liquid products were distilled to four fractions: gasoline (IBP-200°C), kerosene (201°C-250°C), diesel (251°C-370°C) and residue (>370°C). The yields of each fraction from distillation of copyrolyzed oil with and without cattle manure are shown in Figure 20. The copyrolyzed oil obtained from plastics and cattle manure mixture gave higher gasoline (nearly 60%) due to cracking activity from manure.

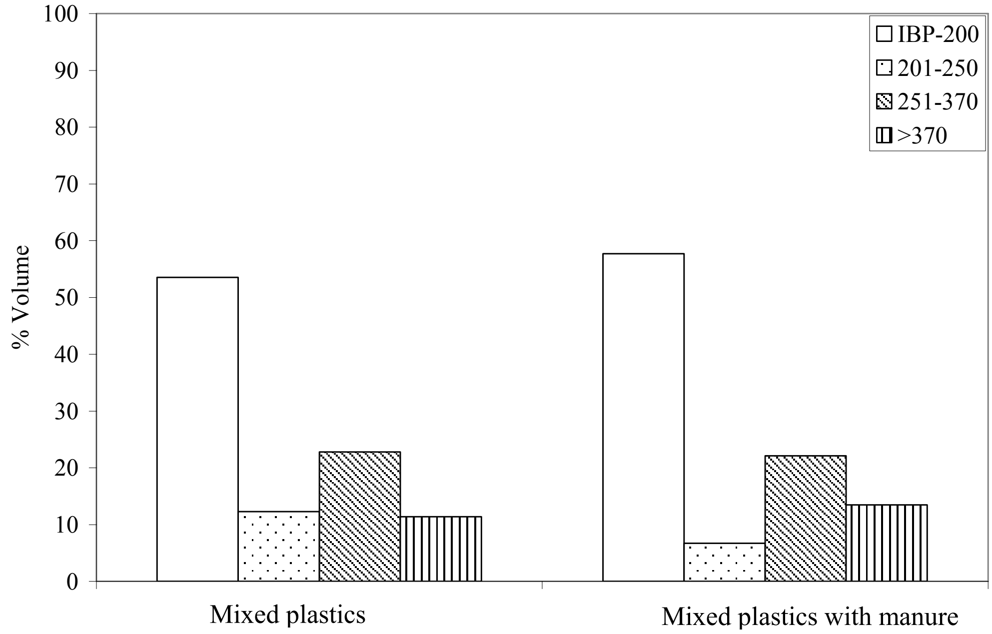


Figure 20 The yields of distillation product from copyrolysis product of mixed plastics with and without cattle manure.

The fraction of chlorinated hydrocarbon in copyrolyzed oil was analyzed by nuclear magnetic resonance. In Figure 21, the cattle manure decreased chlorinated carbon fraction from 0.033 to 0.018 which was a 45% decrease, while Al-Zn composite catalyst decreased chlorine content by 66% (Tang *et al.*, 2003). However, cattle manure has more benefits than metal oxide catalyst because it is a low-value and non-toxic substance.

The amounts of benzene, toluene, and xylene in the gasoline fraction were determined and shown in Figure 22. Cattle manure reduced the total concentration of benzene, toluene, and xylene from 2.46 mol/l to 0.93 mol/l. Especially, xylene disappeared in the presence of manure.

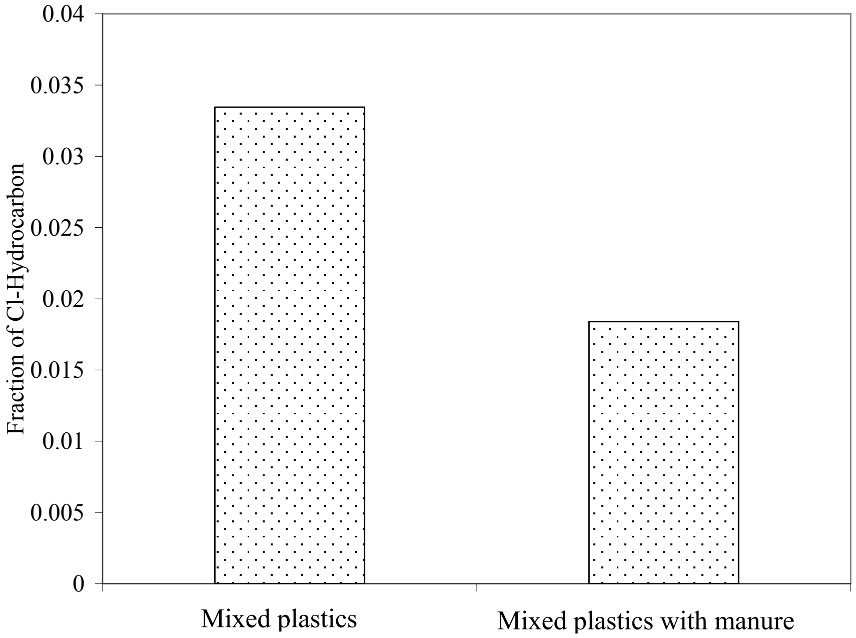


Figure 21 Fractions of chlorinated hydrocarbon in oil from copyrolysis product of mixed plastics with and without cattle manure.

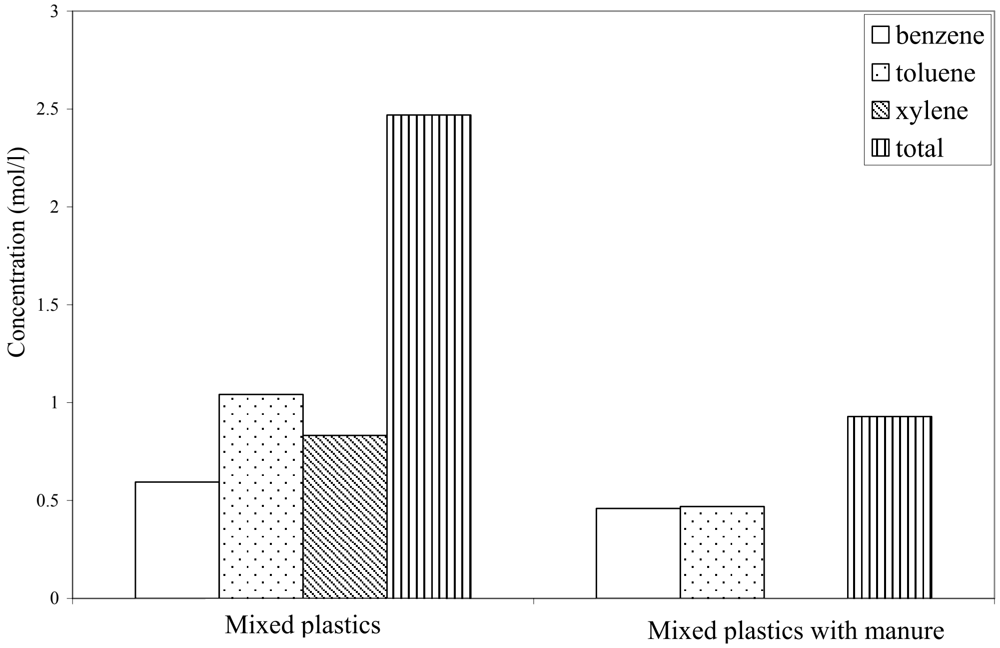


Figure 22 The concentrations of benzene, toluene and xylene in gasoline from copyrolysis of mixed plastics with and without cattle manure.

The percents of paraffin, olefin, and aromatic are shown in Table 13. The cattle manure helped producing more unsaturated hydrocarbons such as olefin and aromatic compounds, they increased from 32.48 and 23.59 to 42.60 and 31.48%vol, respectively. The increase of olefin and aromatics by cattle manure was consistent with the works of Putun (2005) and Dominguez (2006). They reported that pyrolysis of biomass (cattle manure is also biomass), which consists of large molecules of aromatic hydrocarbon, in non-hydrogen atmosphere resulted in aromatic compounds both monoaromatic and polyaromatic. However, the increased aromatic compounds were not benzene, toluene and xylene. The aromatic content in fuel oil, according to the standard from Ministry of Commerce, Thailand, must be not greater than 35%vol. The aromatic content of the oil produced from the copyrolysis was 31.48%vol. Therefore, the fuel oil from copyrolysis of PVC and cattle manure is acceptable. The octane numbers were calculated using NMR results and shown in Table 13. The research octane numbers (RON) of mixed plastics and mixed plastics with cattle manure were 100.3, and 99.35, respectively, which were more than 99. It seems that cattle manure had a slight effect on octane number.

Table 13 The percents of composition in each hydrocarbon group and octane number from NMR results.

Sample	Aromatic (%vol)	Paraffin (%vol)	Olefin (%vol)	Isoparaffin index	RON	MON
Mixed plastics	23.59	43.93	32.48	1.97	100.30	92.93
Mixed plastics with manure	31.48	25.91	42.60	1.77	99.35	91.71

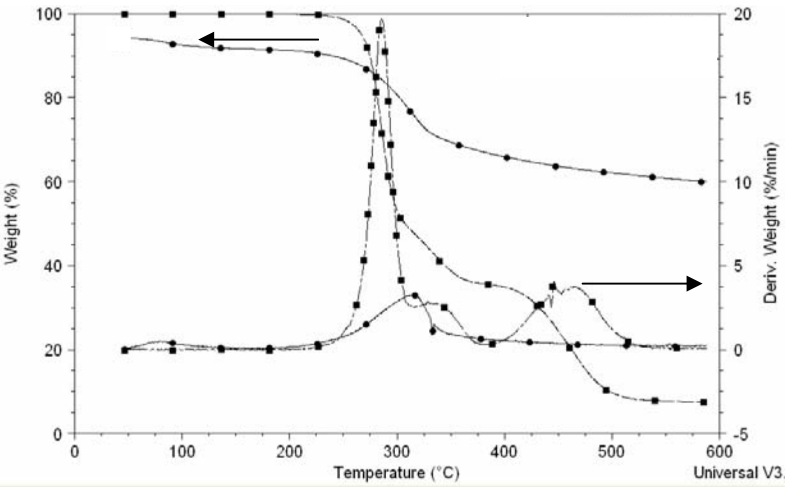
Note: RON = Research octane number

MON = Motor octane number

Cattle manure can reduce HCl and chlorinated hydrocarbon in oil, the aromatic content is within the standard, and the oil has high octane number (>99), therefore, this fuel oil is environmentally friendly and has good quality.

2. **Investigation of kinetic parameters of copyrolysis reaction between PVC and cattle manure by isothermal and dynamic studies.**

Thermal decomposition behavior of PVC and cattle manure was studied by thermal gravimetric analysis as shown in Figure 23. The degradation profile of PVC has two steps. The first step is dechlorination at temperature range of 220-350°C. The chlorine atom in side chain is removed to HCl molecule and PVC structure is converted to polyene structure. The second step is decomposition of polyene molecule at temperature higher than 400°C. The thermal decomposition of cattle manure also has two steps. The first step is when moisture in the manure is evaporated at temperature of 100°C. The second step at temperature greater than 270°C is decomposition of nitrogen compounds in the manure. From these results, nitrogen compounds decompose at a similar temperature range to dechlorination, and interaction between these compounds is possible. However, the derivative weight shows PVC gives more weight loss in the dechlorination step than the decomposition of manure so that the cattle manure cannot react with all HCl from PVC at the same ratio.



Note: -----■----- thermal degradation of PVC.

——●—— thermal degradation of cattle manure

Figure 23 Thermal decomposition profile of PVC and cattle manure by thermal gravimetric analysis at heating rate of 1°C/min

After studying the thermal decomposition behavior, kinetic parameters would be determined for proving this behavior. Isoconversional method was used to estimate activation energy of copyrolysis of PVC and cattle manure mixture at different ratios. The isoconversional plot is a relation between ln(β/T^2) and 1/T at the same conversion in the equation (27). The activation energies which were functions of conversion were determined from the gradient of each graph.

$$\ln\left(\beta/T^2\right) = \left[\ln\left(AR/E\right) - \ln g(\alpha)\right] - E/RT \tag{27}$$

Tables 14-17 show α-T data in dynamic degradation study at the PVC:cattle manure ratios of 1:0, 1:1, 1:3, and 1:5, respectively. They were used for isoconversional plot as shown in Figures 24-27.

Table 14 α-T data from dynamic degradation of PVC and cattle manure at the ratio of 1:0

α	T_5	T_{10}	T_{20}
0.05	255.0	265.9	278.6
0.10	262.7	273.4	287.2
0.15	267.0	277.6	291.8
0.20	270.5	281.1	295.7
0.25	273.5	284.1	298.3
0.30	276.5	287.5	301.6
0.35	280.0	291.2	304.9
0.40	286.0	297.2	309.0
0.45	298.3	308.2	314.5
0.50	311.3	321.4	324.0
0.55	323.8	335.1	340.2
0.60	338.9	351.5	357.5
0.65	404.9	416.7	404.1
0.70	427.9	439.5	440.8
0.75	442.3	455.0	457.4
0.80	454.7	468.6	473.31
0.85	470.3	485.2	487.3

Note: T_1, T_5, T_{10} and T_{20} denote the temperature values measured at 1, 5, 10 and 20°C/min

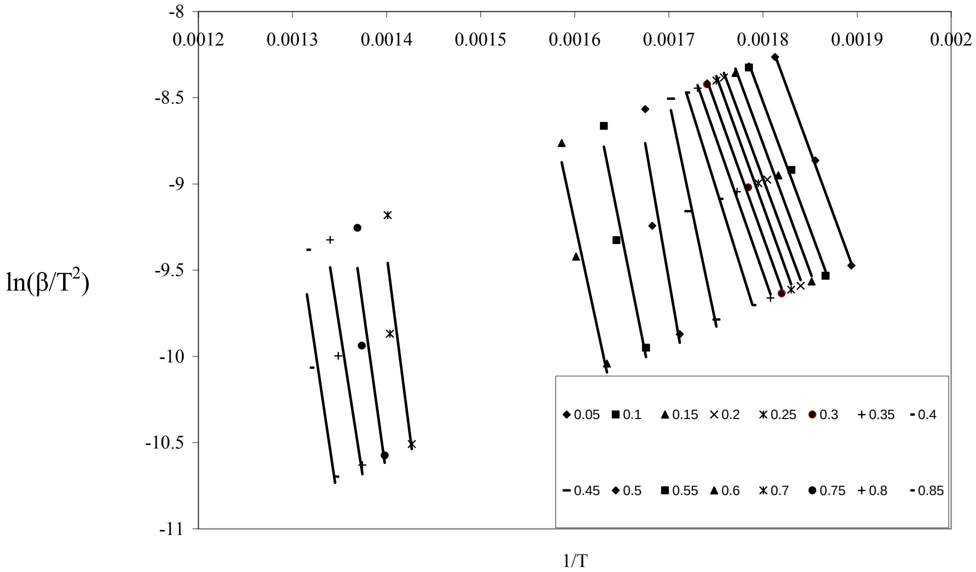


Figure 24 Isoconversional plot from experimental data of dynamic degradation study at PVC:cattle manure ratio of 1:0

Table 15 α-T data from dynamic degradation of PVC and cattle manure at the ratio of 1:1

α	T_1	T_5	T_{10}	T_{20}
0.05	374.0	514.0	423.5	532.5
0.10	495.5	525.0	527.5	547.5
0.15	503.5	530.5	541.0	554.5
0.20	508.0	534.5	547.0	559.0
0.25	511.5	537.5	551.0	562.5
0.30	514.5	540.0	554.0	565.5
0.35	517.5	542.5	557.0	568.5
0.40	522.0	545.5	560.5	571.0
0.45	532.5	549.0	564.0	574.0
0.50	552.0	553.5	569.0	578.0
0.55	569.0	561.5	577.0	583.0
0.60	591.5	576.0	589.5	592.0
0.65	640.0	595.0	605.5	609.5
0.70	679.0	622.0	625.5	633.5
0.75	693.0	676.5	664.0	679.5
0.80	717.0	701.5	702.5	714.5
0.85	755.0	716.5	721.5	732.5
0.90	789.5	731.5	738.0	748.0

Note: T_1, T_5, T_{10} and T_{20} denote the temperature values measured at 1, 5, 10 and 20°C/min

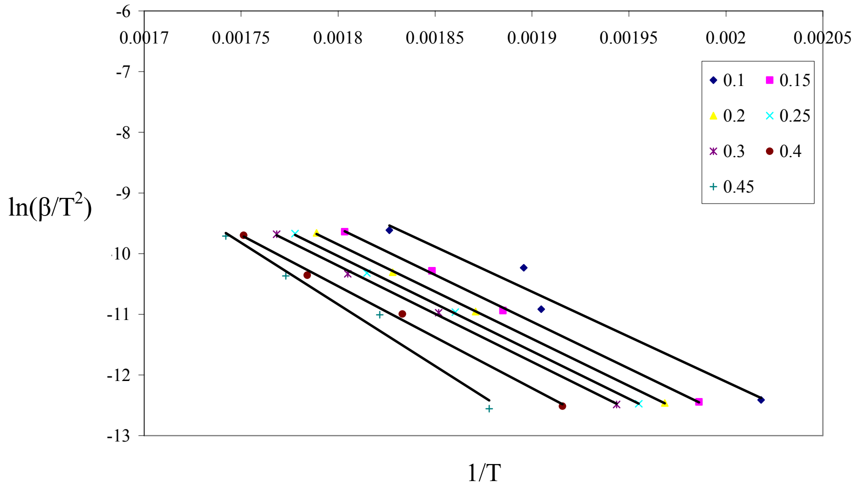


Figure 25 Isoconversional plot from experimental data of dynamic degradation study at PVC:cattle manure ratio of 1:1

Table 16 α-T data from dynamic degradation of PVC and cattle manure at the ratio of 1:3

α	T_1	T_5	T_{10}	T_{20}
0.05	306.5	307.5	323.5	325.5
0.10	329.0	329.0	340.0	362.0
0.15	464.0	456.0	374.5	526.5
0.20	498.0	519.5	515.5	544.0
0.25	504.5	529.0	532.5	550.5
0.30	509.0	534.0	539.5	555.0
0.35	513.0	538.0	544.0	559.0
0.40	518.0	542.0	548.0	562.5
0.45	526.0	547.0	552.0	565.5
0.50	542.0	556.0	556.0	569.0
0.55	559.5	571.5	561.5	573.0
0.60	575.0	586.5	570.5	579.0
0.65	600.5	598.5	585.5	590.5
0.70	641.0	614.0	605.5	611.0
0.75	680.0	652.5	631.0	637.0
0.80	702.0	697.0	667.5	673.5
0.85	742.0	722.0	703.5	712.5
0.90	785.5	763.5	727.0	736.5

Note: T_1, T_5, T_{10} and T_{20} denote the temperature values measured at 1, 5, 10 and 20°C/min

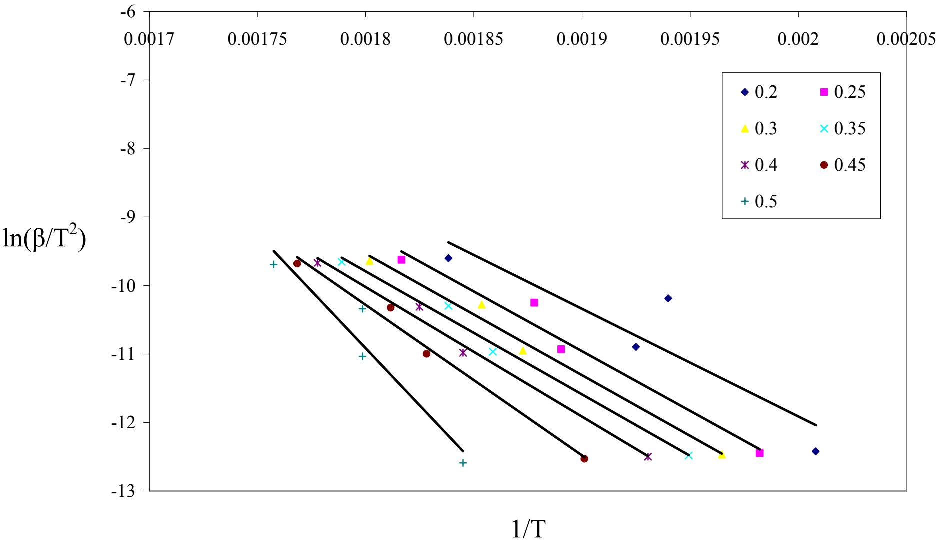


Figure 26 Isoconversional plot from experimental data of dynamic degradation study at PVC:cattle manure ratio of 1:3

Table 17 α-T data from dynamic degradation of PVC and cattle manure at the ratio of 1:5

α	T_1	T_5	T_{10}	T_{20}
0.05	306.0	316.5	319.5	324.5
0.10	319.0	330.0	332.5	350.0
0.15	347.0	360.5	345.0	409.5
0.20	479.5	498.5	371.0	528.0
0.25	498.0	521.0	499.0	546.0
0.30	504.0	527.5	532.0	552.5
0.35	509.5	532.0	543.0	557.0
0.40	514.0	536.0	549.5	561.0
0.45	521.0	540.5	557.5	564.5
0.50	533.5	545.5	569.5	568.0
0.55	550.5	553.5	582.0	572.5
0.60	564.0	566.5	593.5	579.0
0.65	578.5	582.0	602.0	590.5
0.70	602.0	596.5	610.0	613.0
0.75	639.0	616.5	619.0	638.0
0.80	679.0	649.5	639.0	669.5
0.85	707.0	690.0	670.5	706.0
0.90	759.5	719.5	710.5	733.5

Note: T_1, T_5, T_{10} and T_{20} denote the temperature values measured at 1, 5, 10 and 20°C/min

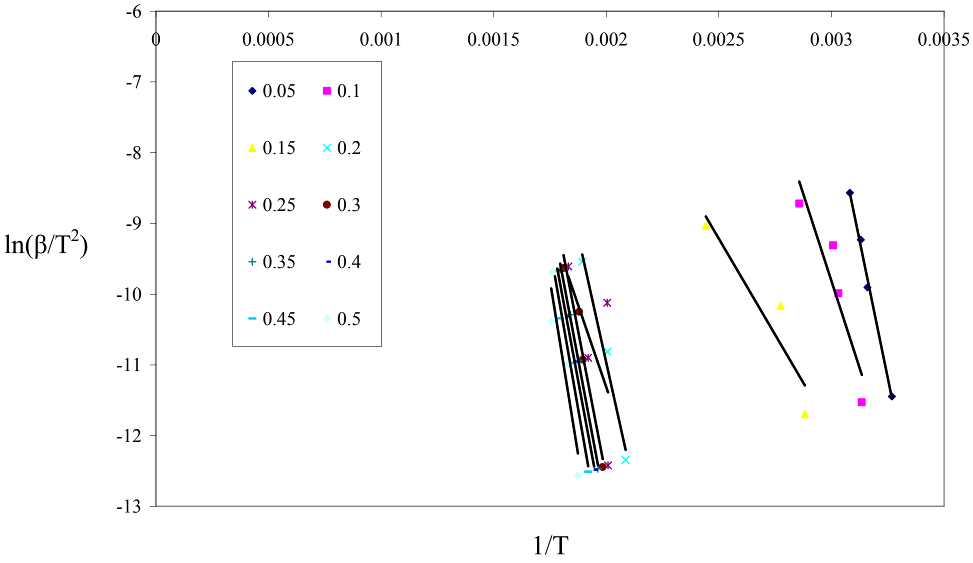


Figure27 Isoconversional plot from experimental data of dynamic degradation study at PVC:cattle manure ratio of 1:5

The activation energies were determined from gradient of isoconversional plot at various conversions. Figures 28-31 show the relation between E/R from isoconversional plot and conversion at different PVC:cattle manure ratios.

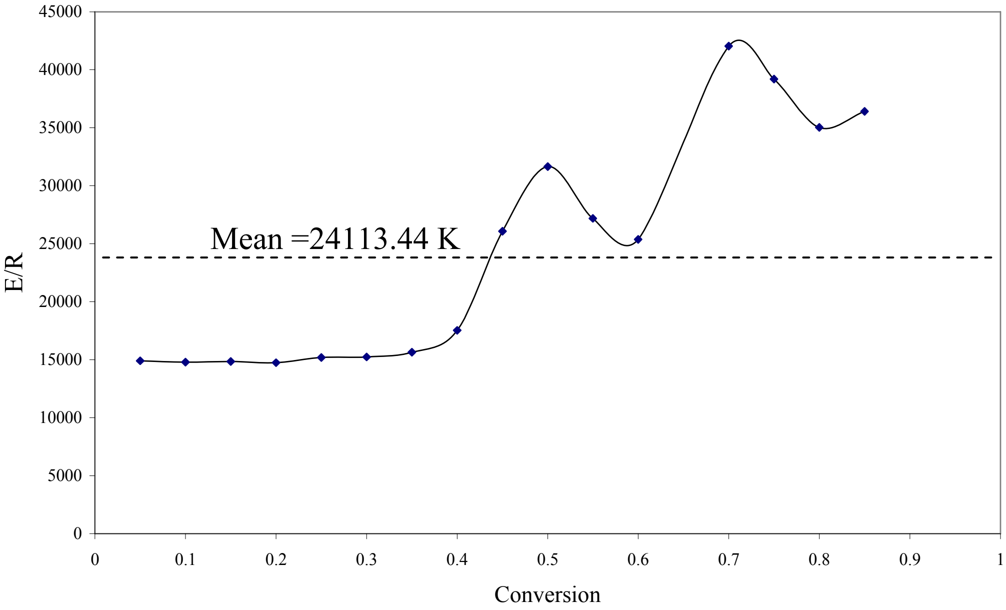


Figure 28 The relation between E/R and conversion at PVC:cattle manure ratio of 1:0

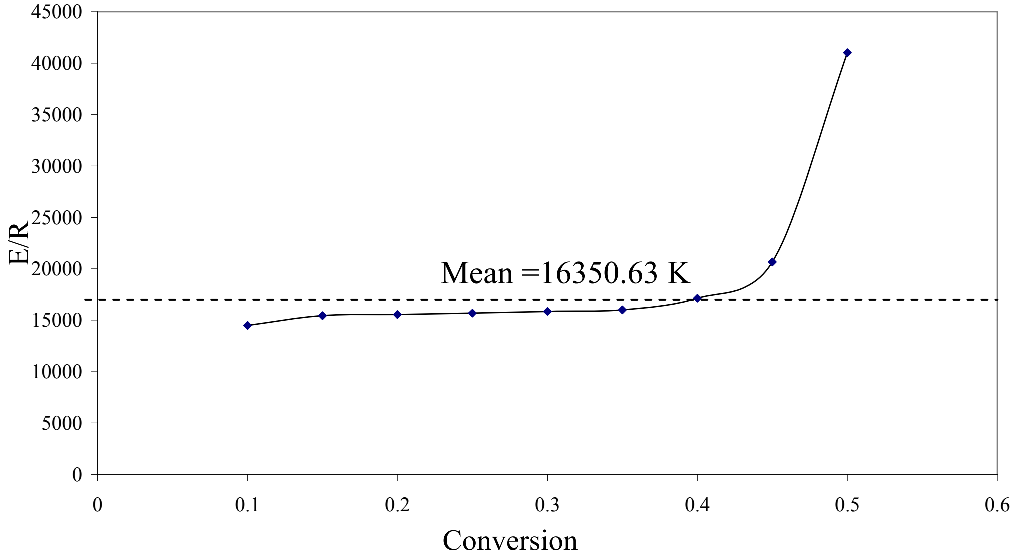


Figure 29 The relation between E/R and conversion at PVC:cattle manure ratio of 1:1

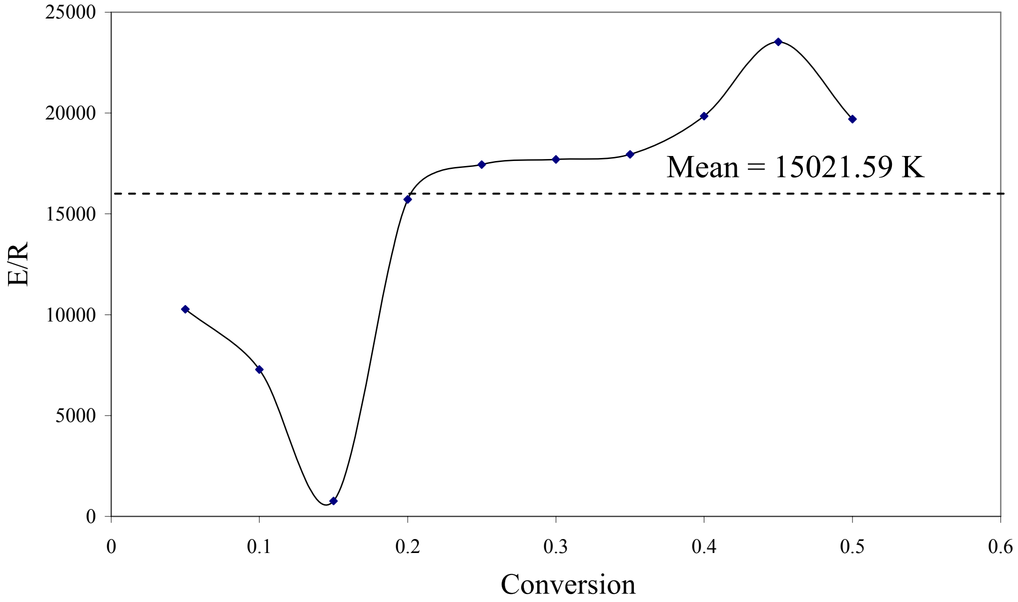


Figure 30 The relation between E/R and conversion at PVC:cattle manure ratio of 1:3

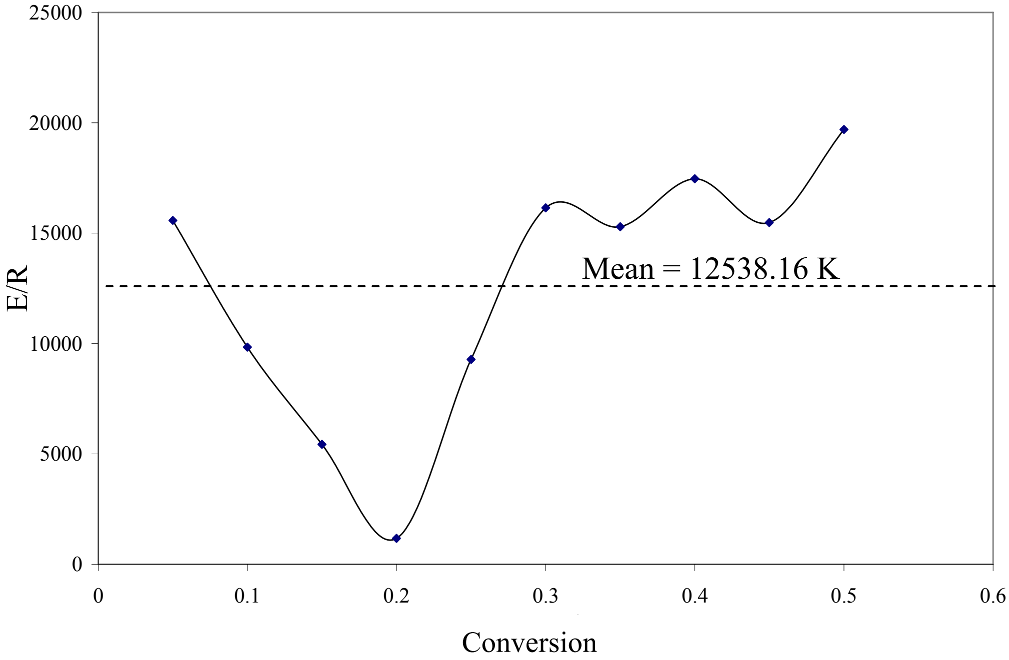


Figure 31 The relation between E/R and conversion at PVC:cattle manure ratio of 1:5

The activation energies at various PVC:cattle manure ratios are shown in Table 7. The activation energy of the pyrolysis of PVC in this work was 200.5 kJ/mol compared with 163 and 135 kJ/mol from the work of Slapak *et al.* (2000) and Vrandecic *et al.* (2005), respectively. Cattle manure reduced the activation energy to 135.9, 124.9, and 104.2 kJ/mol when the ratio of PVC to cattle manure was changed from 1:0 (pure PVC) to 1:1, 1:3, and 1:5, respectively. Similarly, kinetic models of copyrolysis reactions of coal and straw from the study of Vamvuka (2003) and of PVC and chlorinated PE from the study of Vrandecic *et al.* (2005) showed reductions in activation energies. Wong and Broadbelt (2001) suggested that the substance which was copyrolyzed could enhance cracking activity, therefore, cattle manure eased the degradation reaction because it reduced the activation energy of the reaction.

Table 18 The activation energies at various ratios of PVC:cattle manure

Ratio of PVC: cattle manure	Activation energy (kJ/mol)
1:0	200.5
1:1	135.9
1:3	124. 9
1:5	104.2

The maximum conversion rates at various heating rates and PVC:cattle manure ratios are shown in Table 19. The reaction order was determined by comparing experimental conversion at maximum rate in Table 18 and theoretical conversion at maximum rate in Table 2.

Table 19 The values of α_{max} observed in the dynamic degradation

PVC:Manure	1:0	1:1	1:3	1:5
β	α_{max}	α_{max}	α_{max}	α_{max}
1	-	0.28	0.33	0.37
5	0.25	0.30	0.37	0.41
10	0.23	0.28	0.45	0.37
20	0.27	0.35	0.43	0.46
Mean	0.25	0.30	0.40	0.40

The reaction orders of copyrolysis reactions between PVC and cattle manure of different ratios are shown in Table 20. The reaction order of PVC pyrolysis was 4.0 compared with 2.8 from the work of Slapak *et al.* (2000) and decreased to 3.6 (at 1:1) and 2.7 (at1:3) and then leveled off. From the result, the reaction order of the ratio 1:1 was different from the other two ratios. It showed that the reaction behavior of cattle manure at low amount was not similar to that at higher amount. TGA result showed cattle manure provided lower decomposed product than PVC (Figure 23).

Dechlorination had an effect on overall reaction in the lower amount of cattle manure condition. After increasing cattle manure to three and five times the amount of PVC, dechlorination had no effect on reaction.

Table 20 Reaction order derived from isoconversional method

Ratio of PVC: cattle manure	Reaction order (n)
1:0	4.0
1:1	3.6
1:3	2.7
1:5	2.7

Isothermal study is another method to determine reaction order (n) and pre-exponential factor (k_0). From equation 18, the experimental results from TGA were plotted between $\frac{(m-m_{char})^{1-n}}{1-n}$ and time (t). The reaction order was obtained from the graph by trial and error the n value until the straight line had more than 95% reliability. The pre-exponential factor (k_0) was solved from $k=k_0^{(-E/RT)}$ where k was from slope of the graph.

Table 21 shows pre-exponential factor and reaction order of copyrolysis reaction between PVC and cattle manure at various ratios of PVC:cattle manure from isothermal study. Pre-exponential factor was 3.10×10^9 $s^{-1}(mol/l)^{0.5}$ (at 1:1), 6.18×10^8 $s^{-1}(mol/l)^{0.9}$ (at 1:3), and 1.46×10^7 $s^{-1}(mol/l)^{0.9}$ (at1:5). The reaction order decreased from 0.5 to 0.1 and leveled off when cattle manure was increased to three times the amount of PVC.

Table 21 The pre-exponential factors and reaction orders from isothermal study

Ratio of PVC:cattle manure	Pre-exponential factor (k_0)	Reaction order (n)
1:1	$3.11 \times 10^{9}\ s^{-1}(mol/l)^{0.5}$	0.5
1:3	$6.18 \times 10^{8}\ s^{-1}(mol/l)^{0.9}$	0.1
1:5	$1.46 \times 10^{7}\ s^{-1}(mol/l)^{0.9}$	0.1

The kinetic parameters, e.g. activation energy, reaction order and pre-exponential factor were investigated by dynamic and isothermal studies. Cattle manure reduced all kinetic parameters. However, both methods gave different reaction orders but showed similar tendency. The results showed a decrease in reaction order as the amount of manure was increased, therefore, the reaction rates of dechlorination and decomposition were reduced by cattle manure.

3. **Catalytic upgrading of copyrolyzed oil derived from copyrolysis of PVC-containing mixed plastics and cattle manure**

3.1 Catalyst characterization

The crystal structures of composite catalysts were analyzed by x-ray diffraction photometer as shown in Figure 32. The silica alumina-ZnO (1:1) composite catalyst showed peaks of ZnO in XRD pattern but silica alumina-Fe_2O_3 (1:1) composite catalyst did not present any peak but noise in XRD pattern because the particle was very fine. For silica alumina-ZnO composite catalysts, ZnO peak became obvious when the ZnO content was increased twice the amount of silica alumina, the structure showed high crystallinity.

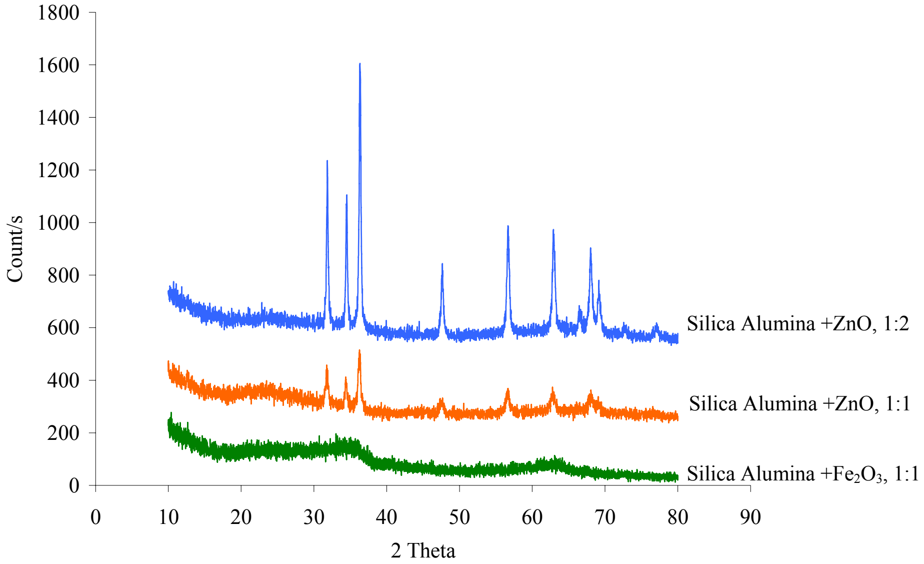


Figure 32 The XRD patterns of silica alumina-ZnO composite catalysts at the silica alumina:ZnO ratios of 1:1 and 1:2 and silica alumina-Fe_2O_3 (1:1) composite catalyst.

The physical properties of composite catalysts were investigated and shown in Table 22. Silica alumina-Fe_2O_3 composite catalyst showed the highest surface area (348.4m^2/g), pore diameter of 537 nm and pore volume of 0.47 ml/g. Silica alumina-ZnO composite catalyst had lower surface area than the Fe_2O_3 composite catalyst but the pore diameter and the pore volume were higher. Silica alumina:ZnO ratio of 1:1 had surface area of 269.2 m^2/g, pore diameter of 750 nm and pore volume of 0.5 ml/g. The increase in ZnO content in the silica alumina-ZnO (1:1) catalyst to the ratio of 1:2 decreased surface area and pore volume to 141.4 m^2/g, and 0.36 ml/g, respectively, but pore diameter was increased to 1023 nm.

Table 22 Physical properties of silica alumina-ZnO and silica alumina-Fe_2O_3 composite catalysts

Catalyst	Surface area $_{BET}$ (m^2/g)	Pore diameter (nm)	Pore volume (ml/g)
Silica Alumina: ZnO 1:1	269.2	750	0.50
Silica Alumina: ZnO 1:2	141.4	1023	0.36
Silica Alumina: Fe_2O_3 1:1	348.4	537	0.47

3.2 Catalytic upgrading

3.2.1 Effect of type of metal oxide

Two types of metal oxide-silica alumina composites, iron oxide-silica alumina and zinc oxide-silica alumina, were studied and compared with pure silica alumina (as a blank). Figure 33 shows the oil yields from various types of composite catalyst at the silica alumina:metal oxide ratio of 1:1 and feed rates of 30 ml/h and 50 ml/h. Metal oxides decreased oil yield. The yields were decreased from 71% (silica alumina) to 60% (silica alumina-ZnO) and 34% (silica alumina-Fe_2O_3) at feed rate of 30ml/h and from 73% (silica alumina) to 72% (silica alumina-ZnO) and 46% (silica alumina-Fe_2O_3) at feed rate of 50ml/h. The decrease in oil yield by iron oxide composite catalyst was from the enhancement of surface area (as shown in Table 21) where the increase cracking activity resulting in more gas product.

From statistical analysis as shown in Appendix J, the oil yields obtained from silica alumina, silica alumina-Fe_2O_3, and silica alumina-ZnO were not different at feed rates of 30 and 50 ml/h.

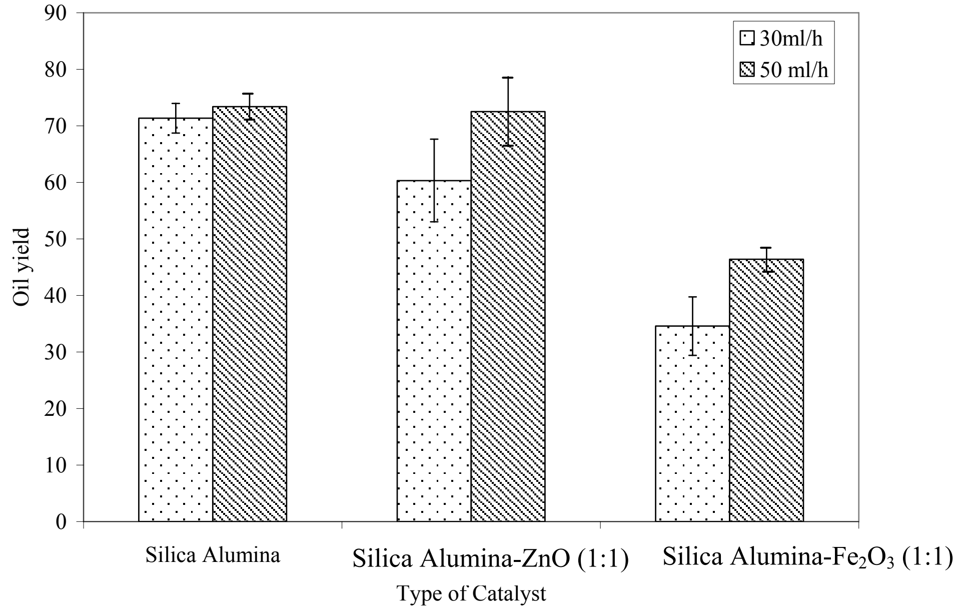


Figure 33 Oil yields from upgrading reaction, using various catalyst types, and at feed rates of 30ml/h and 50ml/h

Metal oxide-silica alumina composites showed increases in gasoline yields. The distillation products of the upgraded oils using various types of catalyst and feed rate of 30 ml/h had gasoline fractions from 50%, 52%, and 65% when catalyst was changed from silica alumina to silica alumina-ZnO, and silica alumina-Fe_2O_3 composite catalysts, respectively, as shown in Figure 34.

When the feed rate was increased to 50 ml/h, the trend is still the same. Gasoline fractions from silica alumina, silica alumina-ZnO, and silica alumina-Fe_2O_3 were 51, 52, and 55%, respectively (Figure 35).

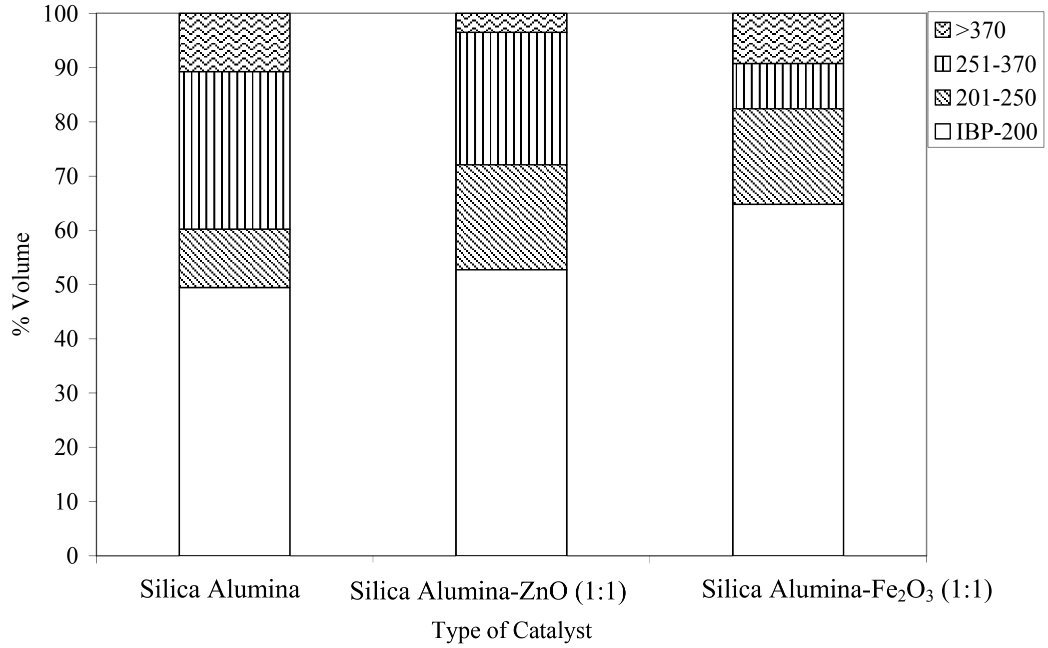


Figure 34 The distillation yields of the upgraded oil, using various types of catalyst, and at feed rate of 30ml/h

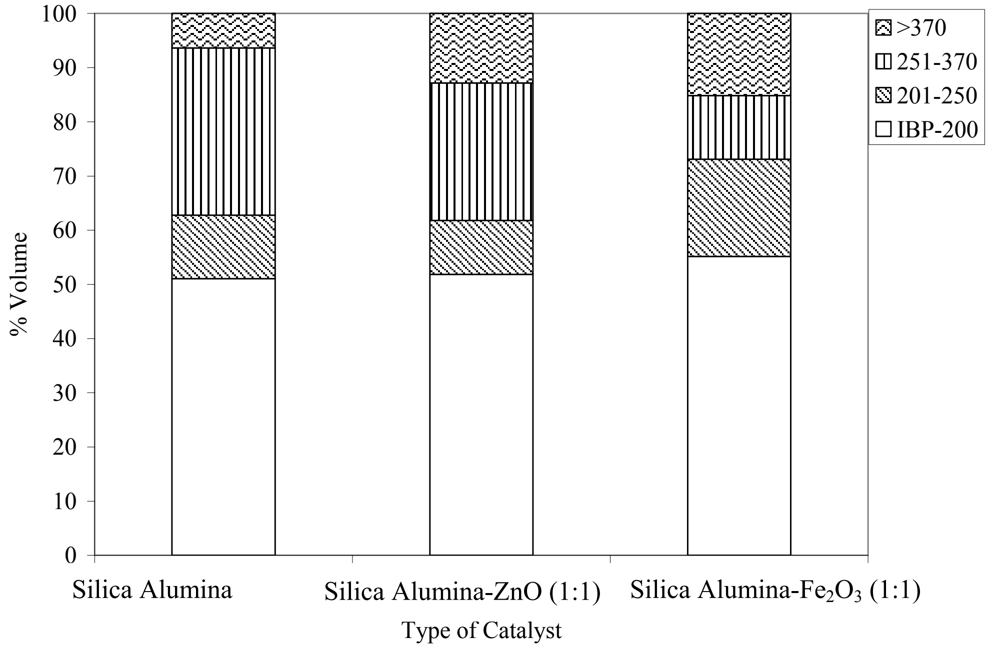


Figure 35 The distillation yields of the upgraded oil, using various types of catalyst, and at feed rate of 50ml/h

From this study, metal oxide showed an increase in cracking activity because it decreased oil yield due to higher cracking activity. However, slow feed rate of 30 ml/h showed lower oil yield than high feed rate of 50 ml/h due to more cracking at longer contact time. In summary, metal oxide-silica alumina composite catalysts showed higher cracking activity than pure silica alumina.

Fraction of chlorinated hydrocarbon was measured by NMR. The results showed that all catalysts reduced chlorinated hydrocarbon at both feed rates and reduced better at the lower rate. Silica alumina-ZnO composite catalyst gave the lowest fraction of chlorinated hydrocarbon at both feed rates as shown in Figure 36. The chlorinated hydrocarbon fraction was reduced from 0.018 to 0.009 ±0.002 by using silica alumina-ZnO catalyst at feed rate of 30ml/h. silica alumina-ZnO showed better dechlorination activity than silica alumina-Fe$_2$O$_3$, and silica alumina. The dechlorination activities of catalysts decreased in the order:
silica alumina-ZnO> silica alumina-Fe$_2$O$_3$> silica alumina.

The statistical analysis was used to prove the level of difference of chlorinated hydrocarbon fraction in each types of catalyst at different feed rates (Appendix J). Only silica alumina-ZnO showed a difference in fraction of chlorinated hydrocarbon at 90% level of significance, at 50 ml/h > at 30 ml/h, the others were not different.

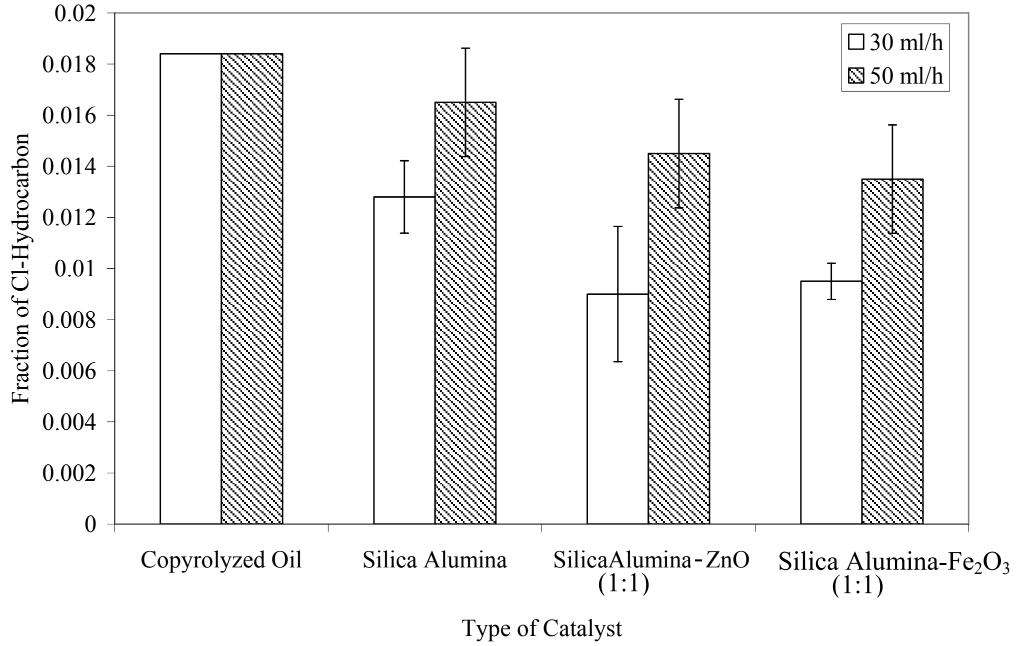


Figure 36 Fractions of chlorinated carbon in the upgraded oil, using various types of catalyst, at feed rates of 30 and 50 ml/h.

The percentages of paraffin, olefin and aromatic compounds in gasoline are shown in Figure 37. The compounds in gasoline were about 40-50% paraffin, 25-30% olefin, and 20-30% aromatic. At both feed rates, paraffin increased when silica alumina was composited with ZnO, and with Fe_2O_3. The percentages of olefin at both feed rates were about the same when ZnO and Fe_2O_3 were composited with silica alumina. Aromatic content was the lowest (19.2%) when silica alumina-Fe_2O_3 composite was used.

From the result, oxides of iron and zinc composite with silica alumina increased paraffin and decreased olefin and aromatic in the gasoline fraction. However, the octane number has to be concerned.

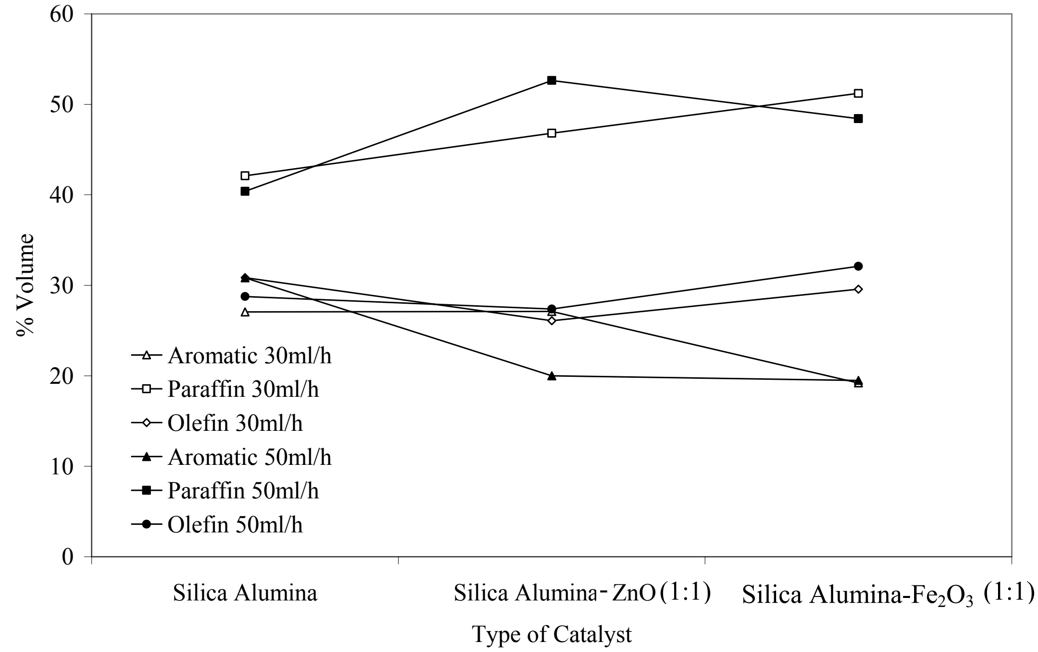


Figure 37 The percents of composition in each hydrocarbon group in gasoline product when using various types of catalyst.

Table 23 shows isoparaffin index and octane number in gasoline fraction of the upgraded oil by using various types of catalyst. Octane number increased from 94.5 to 104.3 and 115.7 and isoparaffin index increased from 1.28 to 2.38 and 3.76 when it was upgraded by silica alumina-ZnO and silica alumina- Fe_2O_3 catalysts, respectively. Although metal oxide decreased unsaturated hydrocarbon but it provided iso-structure (as shown in Table 23), therefore, octane number was increased by using metal oxide composite catalyst.

Table 23 Isoparaffin index and octane number of upgraded oils with various types of catalyst.

Sample	Isoparaffin index	RON	MON
Silica Alumina, 30ml/h	1.28	94.50	86.35
Silica Alumina-ZnO, 30ml/h	2.38	104.31	97.37
Silica Alumina-Fe_2O_3, 30ml/h	3.76	115.74	110.37
Silica Alumina, 50ml/h	1.04	92.77	84.33
Silica Alumina-ZnO, 50ml/h	3.39	112.50	106.71
Silica Alumina-Fe_2O_3, 50ml/h	2.69	106.24	99.69

Note: RON = Research octane number

MON = Motor octane number

Figures 38 and 39 show the concentrations of benzene, toluene, and xylene in gasoline fractions from upgrading oil using various types of composite catalyst. Gasoline upgraded by silica alumina catalyst gave the highest total concentration of benzene, toluene, and xylene of 1.51mol/l and 1.72mol/l at feed rates of 30 and 50 ml/h, respectively. ZnO and Fe_2O_3 silica alumina composites reduced total concentrations of benzene, toluene, and xylene to 1.22mol/l, and nil, respectively, at feed rate of 30 ml/h. However, at feed rate of 50 ml/h. silica alumina-Fe_2O_3 catalyst provided the BTX concentration of 1.22mol/l, slightly higher than that of the silica alumina-ZnO catalyst (1.13mol/l). The composite catalysts gave no xylene content at all feed rates.

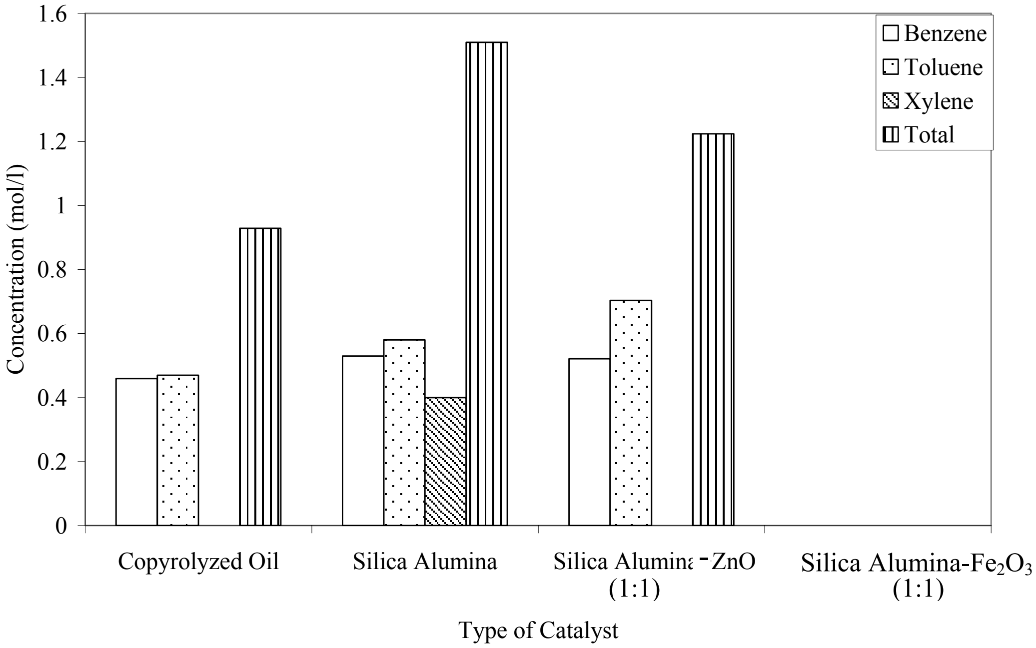


Figure 38 The concentrations of benzene, toluene, and xylene in gasoline from upgrading of oil using various types of catalyst at feed rate of 30ml/h.

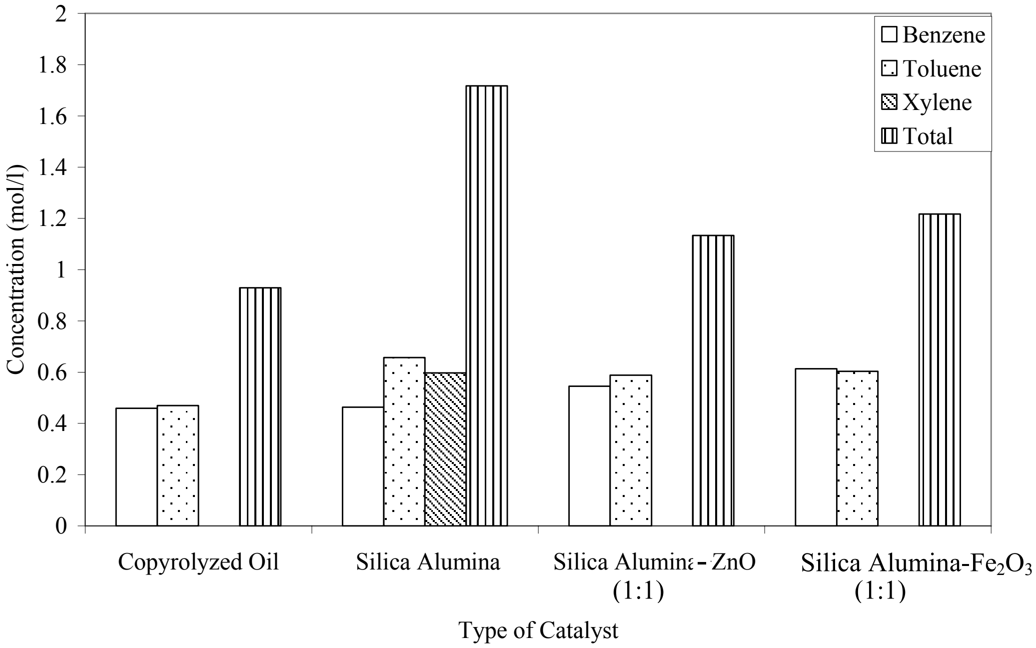


Figure 39 The concentrations of benzene, toluene, and xylene in gasoline from upgrading of oil using various types of catalyst at feed rate of 50ml/h.

Metal oxide composites provided lower the total concentrations of benzene, toluene, and xylene, compared with pure silica alumina. The result agreed with the decrease in aromatic content when using the composite catalysts.

3.2.2 Effect of silica alumina:ZnO ratio.

Silica alumina-ZnO composite catalyst was chosen to study the optimum ratio of ZnO and silica alumina because silica alumina-ZnO composite catalyst showed the highest activity for dechlorination and provided high octane number and low aromatic compounds.

The yields of upgraded oil at three different ratios of silica alumina to ZnO composite catalyst are shown in Figure 40. The oil yield of silica alumina, silica alumina:ZnO (1:1), and silica alumina:ZnO (1:2) at feed rates of 30 and 50 ml/h were 71, 60, and 56% and 73%, 72.5 and 61%, respectively. The oil yields were the highest at the highest feed rate of 50ml/h. At feed rates of 30ml/h and 50ml/h, oil yields decreased in all ratios. The higher amount of ZnO, the lower oil yields. The oil yields decreased in the order:
silica alumina > silica alumina:ZnO (1:1) > silica alumina:ZnO (1:2).

The level of significance of oil yield in each ratio at various feed rates was analyzed as shown in Appendix J. All ratios showed differences in oil yields at various feed rates at 90% level of significance and oil yields were ranked in a decrease order:
at 50 ml/h ≥ at 30 ml/h > at 10ml/h for silica alumina
at 50 ml/h ≥ at 30 ml/h ≥ at 10ml/h for silica alumina:ZnO (1:1)
at 50 ml/h ≥ at 30 ml/h ≥ at 10ml/h for silica alumina:ZnO (1:2)

This result showed metal oxide composite increased cracking activity of silica alumina which caused oil yield to decrease due to cracking to gas product, however, at the 10 ml/h feed rate, polymerization of intermediate compounds from cracking was happened due to longer retention time and more oil yield was obtained.

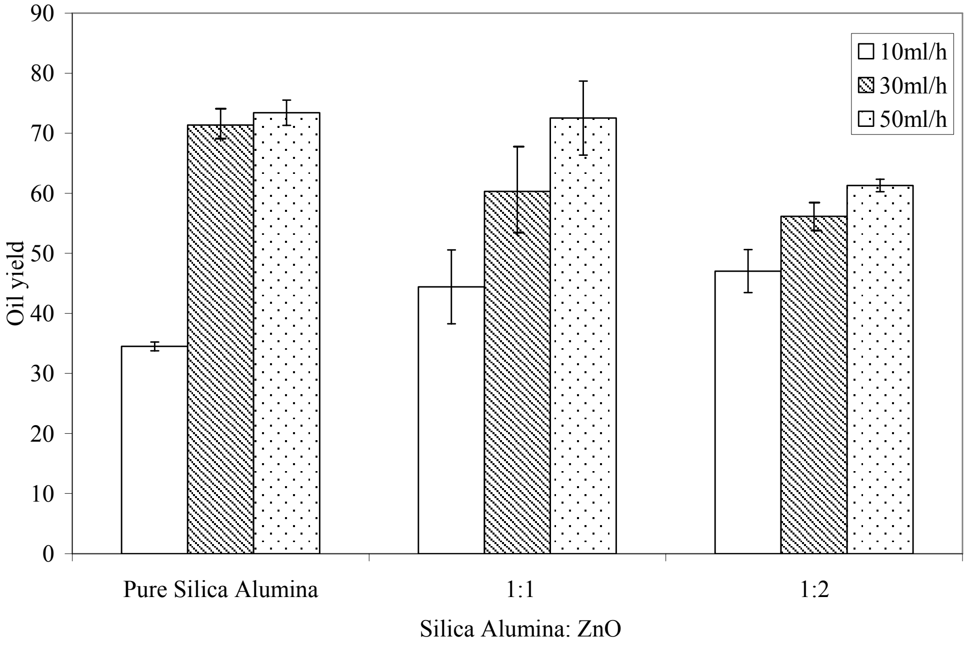


Figure 40 Oil yields from upgrading reaction, using various silica alumina: ZnO ratios and at feed rates of 10, 30, and 50ml/h.

The ratio of silica alumina:ZnO affected gasoline yield at low feed rate as shown in Figure 41. At feed rate of 10 ml/h, gasoline fraction increased from 48.5% to 53.5% when silica alumina was composited with ZnO at the ratio of 1:1 but it was decreased to 38.5% when the amount of ZnO increased twice. However, at feed rates of 30ml/h and 50ml/h, the ratio of silica alumina and ZnO had slightly effect on the gasoline yield. It was nearly constant in the range of 46-51% (Figures 42 and 43).

The effect of silica alumina:ZnO ratio on gasoline yield was obvious at low feed rate because longer retention time allowed more polymerization of intermediates to high boiling fraction. As shown in Figure 41 at the feed rate of 10ml/h, the increase in residue fraction was from 9.8% to 19.2% at the ratios of 1:1 and 1:2, respectively.

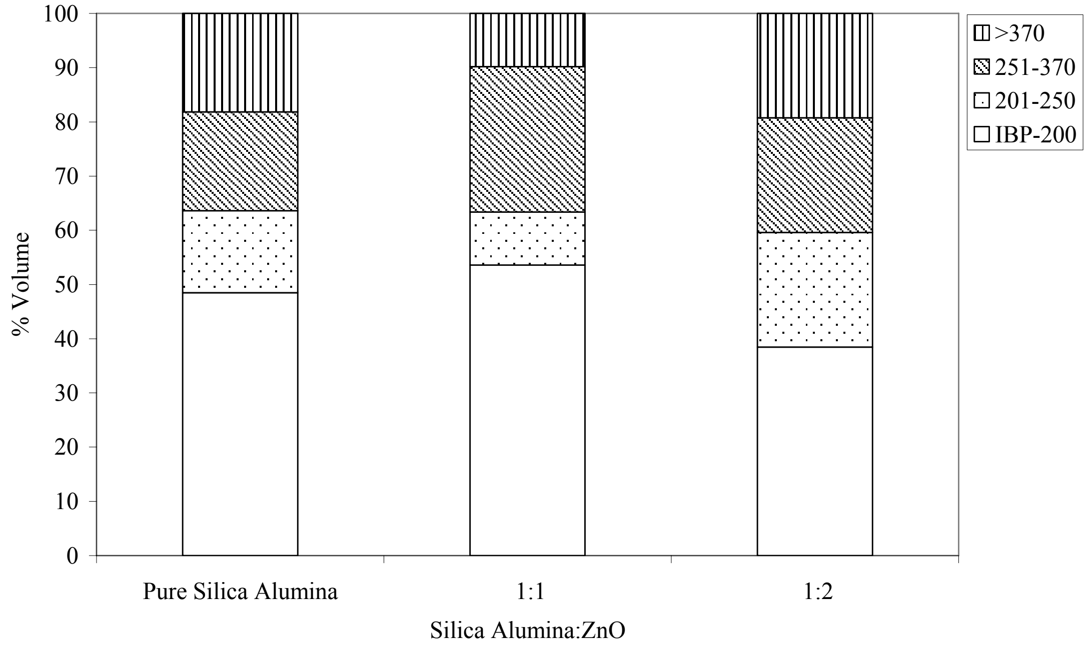


Figure 41 The distillation yields of the upgraded oil, using various ratios of silica alumina to ZnO at feed rate of 10ml/h.

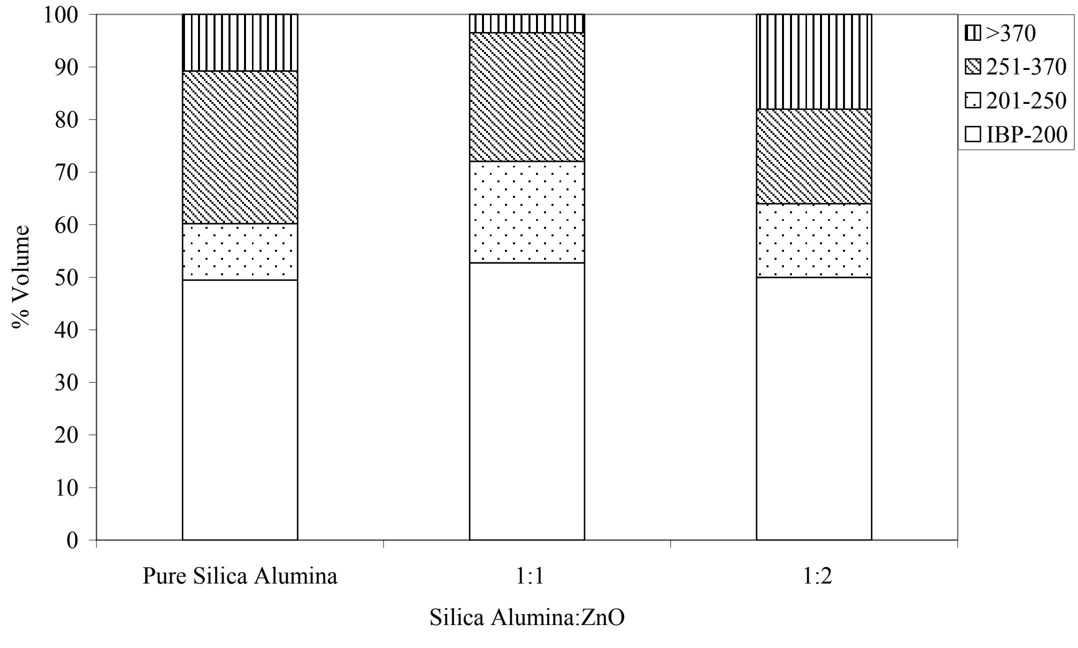


Figure 42 The distillation yields of the upgraded oil, using various ratios of silica alumina to ZnO at feed rate of 30ml/h.

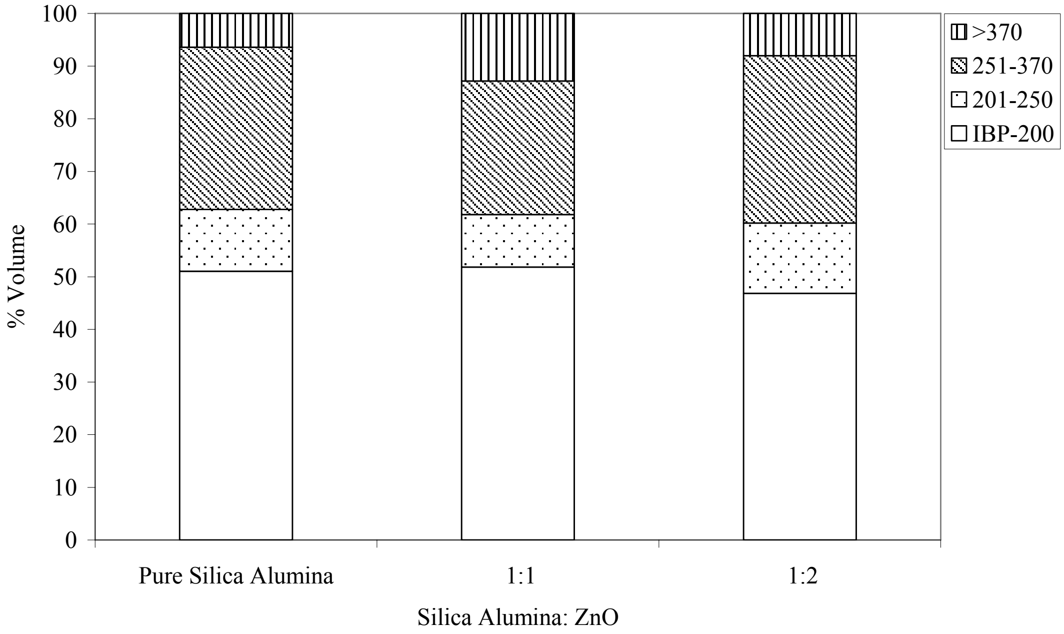


Figure 43 The distillation yields of the upgraded oil, using various ratios of silica alumina and ZnO at feed rate 50ml/min

The effect of silica alumina:ZnO ratio on the amount of chlorinated hydrocarbon is shown in Figure 44. At feed rate of 30ml/h, the fraction of chlorinated hydrocarbon in the copyrolyzed oil decreased from 0.018 to 0.013 ±0.0014 and 0.009 ±0.0026 when it was upgraded by silica alumina and silica alumina-ZnO (1:1) composite catalyst, respectively. However, the fraction of chlorinated hydrocarbon was 0.016 ±0.0021 when the silica alumina: ZnO ratio was 1:2. The higher amount of ZnO reduced the dechlorination activity of the catalyst.

The ratio of silica alumina to ZnO had an effect on the concentration of chlorinated hydrocarbon in the upgraded oil. The optimized ratio of silica alumina: ZnO was 1:1 which provided the lowest fraction of chlorinated hydrocarbon at all feed rates.

The fractions of chlorinated hydrocarbon in each silica alumina:ZnO ratio were analyzed at the 90% level of significance in Appendix J. At ratio of 1:1 the fractions of chlorinated hydrocarbon decreased in the order:

at 50 ml/h > at 10 ml/h > at 30 ml/h

However, at the ratios of 1:0 and 1:2, the feed rates showed no effect on the amounts of chlorinated hydrocarbon at 90% level of significance.

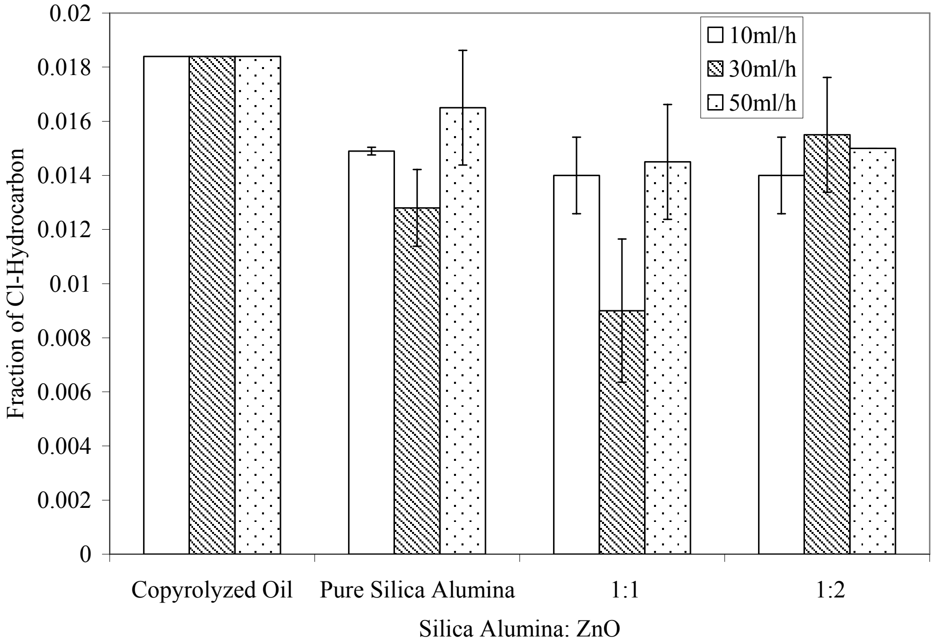


Figure 44 Fractions of chlorinated hydrocarbon in the upgraded oil when using various silica alumina:ZnO ratios at feed rates of 10, 30, and 50 ml/h.

From Figure 45, main hydrocarbon in gasoline fraction was about 40-50% paraffin. Olefin as well as aromatic content was in the range of 20-30%. The percentages of paraffin increased from 42% and 40% to 46.8% and 52.6% when the silica alumina was composited with ZnO at the silica alumina: ZnO ratio of 1:1 at feed rates of 30ml/h and 50ml/h, respectively. However, as ZnO content was twice the amount of silica alumina, paraffin decreased. At low feed rate of 10ml/h, paraffin continuously decreased when the amount of ZnO increased.

The ratio of silica alumina and ZnO in composite catalyst had an effect on the paraffin, olefin, and aromatic content, however, the trends were not the same at different feed rates.

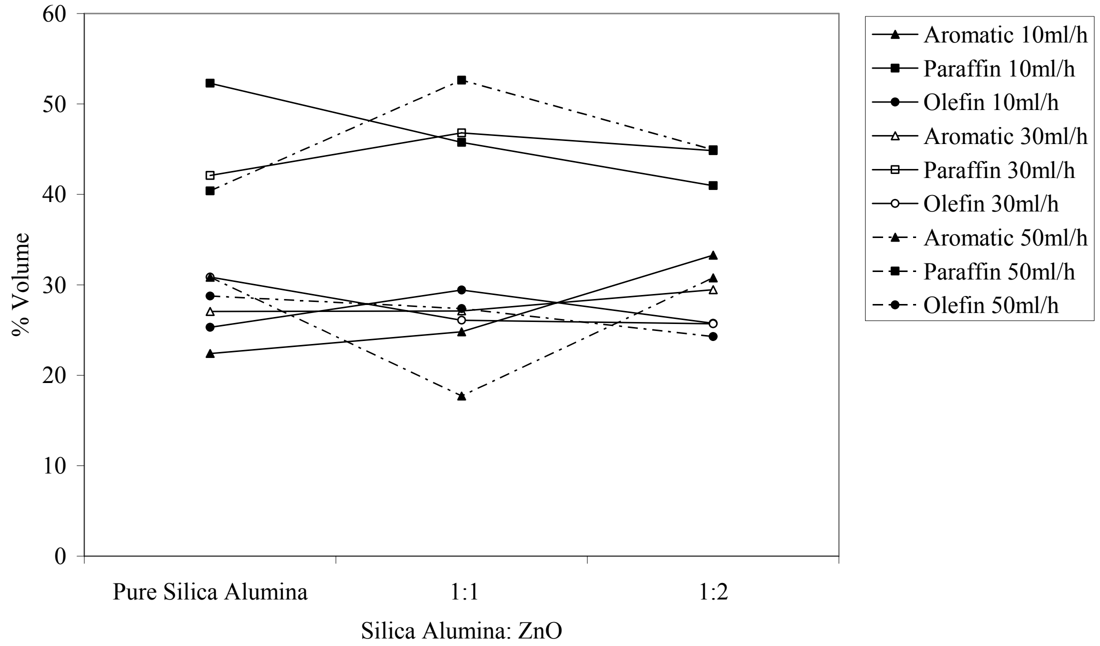


Figure 45 The percents of composition in each hydrocarbon group in gasoline product with various silica alumina: ZnO ratios at feed rate of 10, 30, and 50ml/h.

Table 24 shows the effect of silica alumina: ZnO ratio on isoparaffin index and octane number. The gasoline fraction from the upgraded oil provided high research octane number in the range of 93 to 113. The octane number had a relation to the amounts of isoparaffin and aromatic hydrocarbons. The ratio of 1:1 had high isoparaffin index so that it provided high octane number. As there was more ZnO content, the isoparaffin decreased but aromatic hydrocarbon increased (see Figure 45), therefore, the octane number was decreased slightly.

Table 24 Isoparaffin index and octane number of the upgraded oils when using various ratios of silica alumina:ZnO.

Silica Alumina: ZnO	Isoparaffin index	RON	MON
1:0 (Pure Silica Alumina), 10ml/h	1.44	95.40	87.44
1:1, 10ml/h	1.33	94.73	86.65
1:2, 10ml/h	1.28	95.12	86.92
1:0 (Pure Silica Alumina), 30ml/h	1.28	94.51	86.35
1:1, 30ml/h	2.38	104.31	97.37
1:2, 30ml/h	1.71	98.61	90.92
1:0 (Pure Silica Alumina), 50ml/h	1.04	92.77	84.33
1:1, 50ml/h	3.39	112.50	106.71
1:2, 50ml/h	2.10	102.19	94.92

Note: RON = Research octane number

MON = Motor octane number

The concentrations of benzene, toluene, and xylene at feed rates of 10, 30, and 50 ml/h are shown in Figures 46-48. At all feed rates, silica alumina catalyst increased total concentrations of benzene, toluene, and xylene about 70%-80%. Both ratios of silica alumina-ZnO composite catalyst decreased total concentration of benzene, toluene, and xylene. From this result, it shows that ZnO reduced aromatization activity of silica alumina as seen from the decrease in concentrations of benzene, toluene, and xylene.

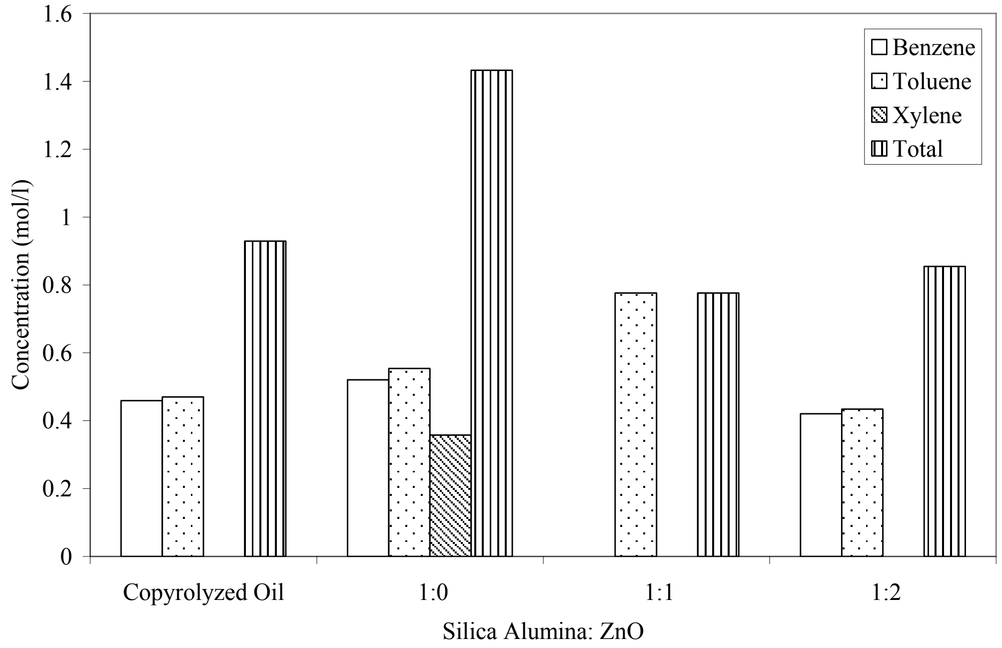


Figure 46 The concentrations of benzene, toluene, and xylene in gasoline from upgrading of oil using various ratios of silica alumina: ZnO at feed rate of 10ml/h.

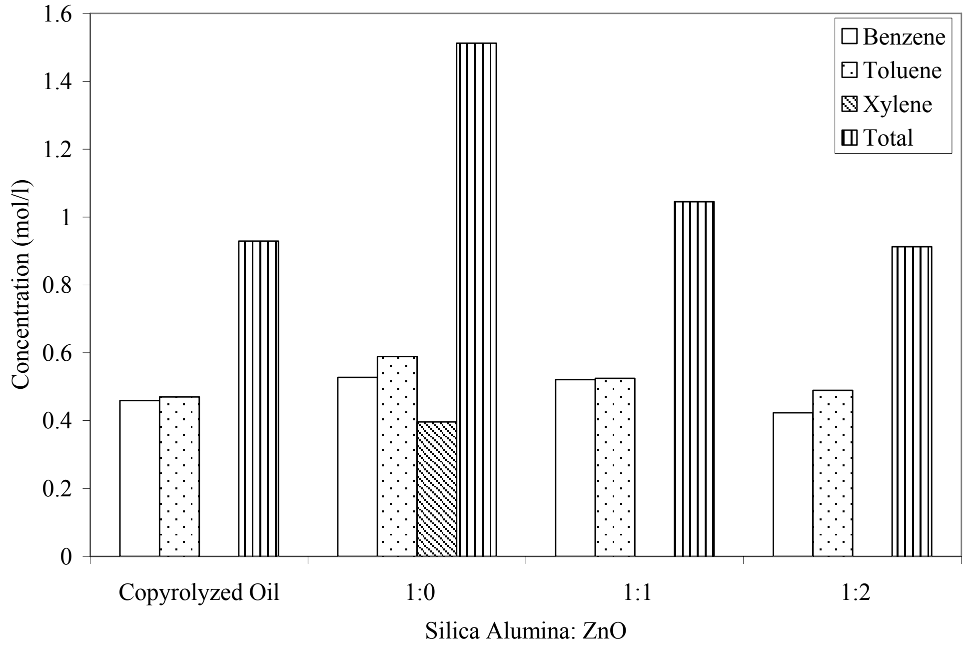


Figure 47 The concentrations of benzene, toluene, and xylene in gasoline from upgrading of oil using various ratios of silica alumina: ZnO at feed rate of 30ml/h.

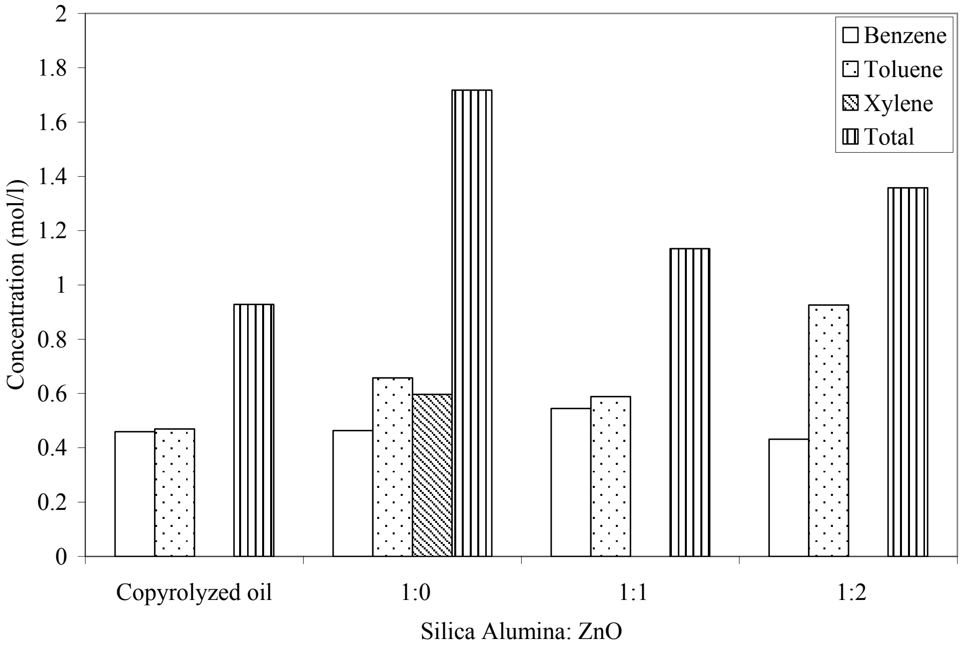


Figure 48 The concentrations of benzene, toluene, and xylene in gasoline from upgrading of oil using various ratios of silica alumina: ZnO at feed rate of 50ml/h.

3.2.3 Effect of oil feed rate

The effect of oil feed rate was studied at three feed rates of 10ml/h, 30ml/h and 50ml/h, and at three ratios of silica alumina to ZnO composite catalyst. Feed rate affected contact time of reactant oil in the reactor, therefore, feed rate was an important factor.

Feed rate of oil had a significant effect on oil product yield as shown in Figure 49. Comparing feed rates of 10 ml/h to 50 ml/h, the silica alumina and the composite catalysts increased oil yield by 100%, and 50%, respectively. The increase in oil yield represented shorter contact time for cracking, resulting in lower oil yield and higher gas product. Therefore, the quality of the oil such as the yield of each distillation fraction was concerned. At feed rate of 30 ml/h, all catalysts but the ratio of 1:2 catalyst showed increases of oil yields. High amount of ZnO up to twice the amount of silica alumina may increase the cracking activity resulting in lower oil yield.

The statistical analysis was applied to determine the level of difference of oil yields in each feed rate at various ratios. Only feed rate of 50ml/h had difference of oil yields in various ratios at level of significance of 90%. The rank of oil yield in various ratios was decreased in order: pure silica alumina ≥ 1:1 ≥ 1:2.

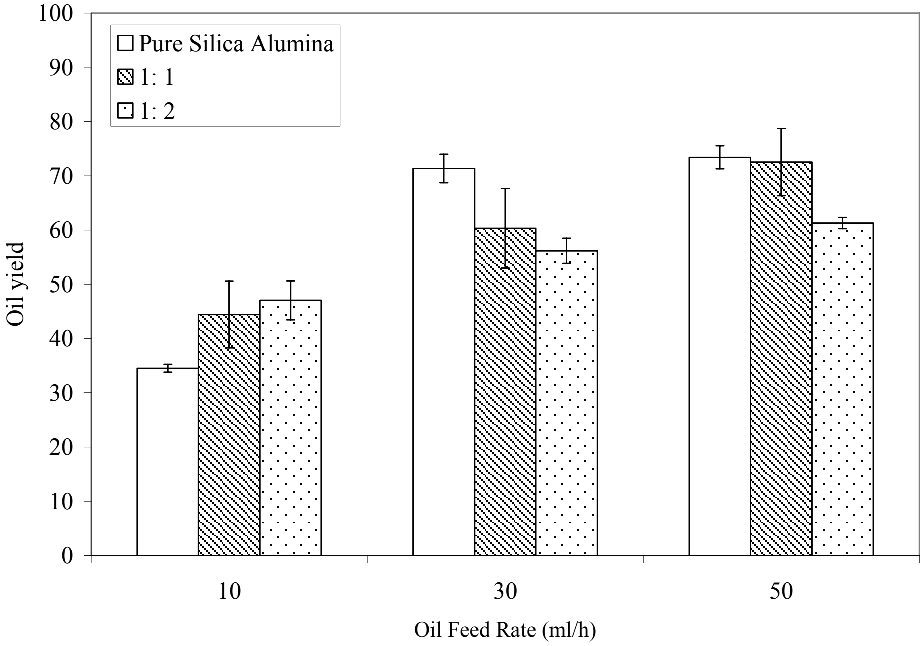


Figure 49 Oil yields from upgrading reaction at different oil feed rates using catalysts with silica alumina: ZnO ratios of 1:0, 1:1 and 1:2.

The yields of distillation products from upgrading oil using silica alumina catalyst are shown in Figure 50. This graph shows an increase in diesel fraction from 18% to 30% and a decrease in residue fraction from 18% to 6% when the feed rate was increased from 10 ml/h to 50 ml/h. Silica alumina catalyst showed cracking activity by cracking the residue fraction to diesel oil, however, low feed rate had more time for cracking but also allowed more time for the intermediate molecules to combine to larger molecules which are in residue fraction. The high feed rate of 50 ml/h allow less time for combining, resulting in lower residue fraction and higher diesel fraction.

Figures 50-52 show the yields of distillation products from upgrading of oil using silica alumina-ZnO composite catalyst at different feed rates. The best feed rate which provided high percent of low boiling fraction and low high boiling fraction was the feed rate of 30ml/h. Using silica alumina: ZnO ratio of 1:1, the gasoline fraction at different feed rates were not different but the feed rate of 30 ml/h gave the lowest residue fraction (3.5%). At the ratio of 1:2, high feed rate of 50ml/h gave the lowest residue (8%) and high amount of gasoline (47%) because ZnO increased cracking activity, therefore, the 1:2 ratio catalyst needs short reaction time to prevent the recombination of the intermediates.

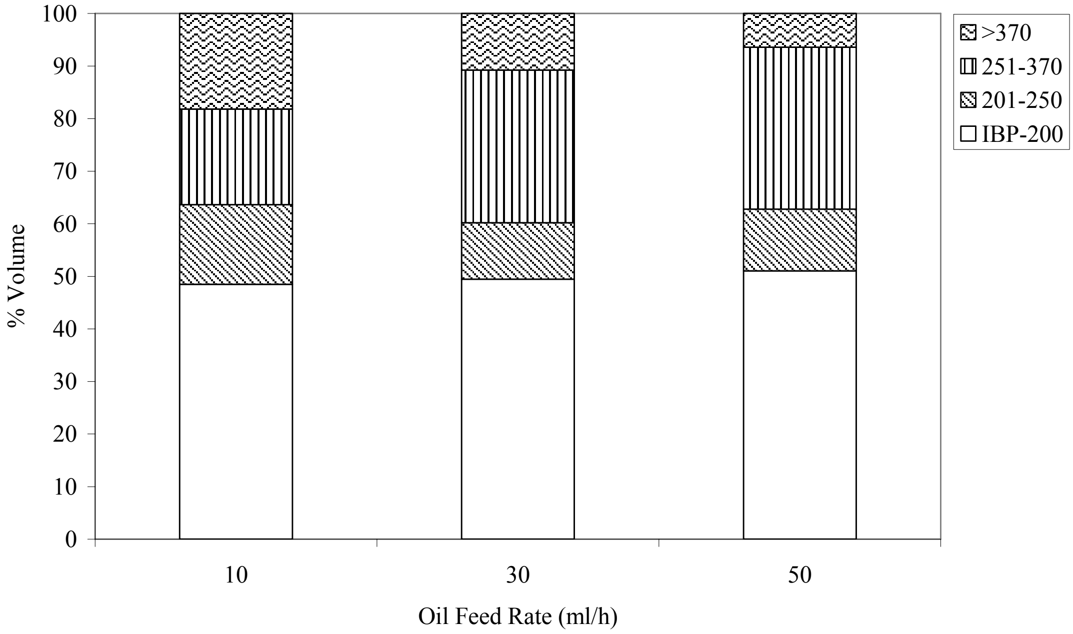


Figure 50 The distillation yields of oil products from upgrading of oil at various oil feed rates using silica alumina catalyst.

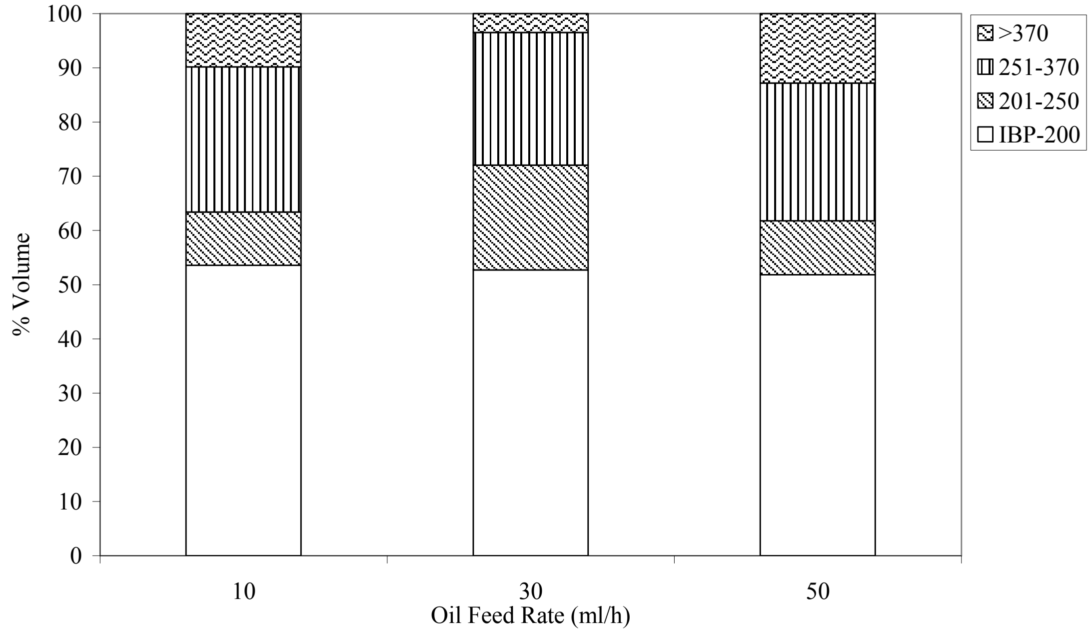


Figure 51 The distillation yields of oil products from upgrading of oil at various oil feed rates using silica alumina-ZnO composite catalyst at the ratio of 1:1.

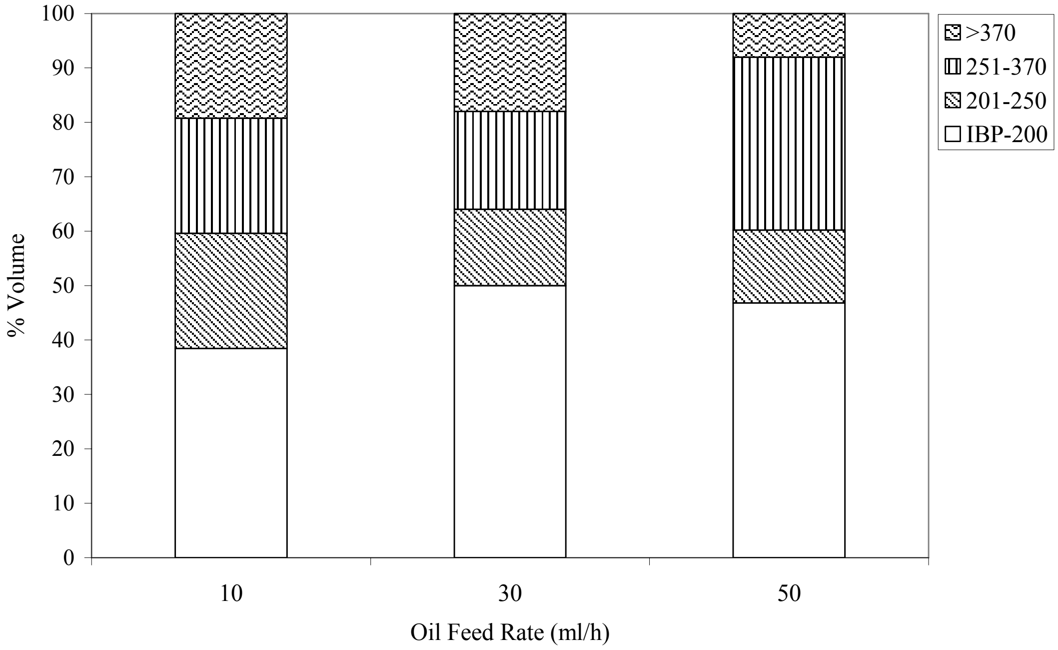


Figure 52 The distillation yields of oil products from upgrading of oil at various oil feed rates using silica alumina-ZnO composite catalyst at the ratio of 1:2.

The feed rate had an effect on product yield and its quality. ZnO composite catalyst showed an increase in cracking activity provided more intermediates (carbonium ions). Therefore, feed rate was used to control the recombination of the intermediates (Aguado *et al.*, 2002).

The fractions of chlorinated hydrocarbon at different feed rates are shown in Figure 53. The feed rate of 30 ml/h of the silica alumina:ZnO (1:1) catalyst provided the lowest fraction of chlorinated hydrocarbon by reducing about 50% from the feed oil.

The fractions of chlorinated hydrocarbon in the upgraded oil from each feed rate were analyzed. Feed rate of 30 ml/h showed a difference in chlorinated hydrocarbon in the upgraded oil using different catalysts at the 90% level of significance, and ranked in order: silica alumina:ZnO (1:2) > silica alumina > silica alumina:ZnO (1:1). Feed rates of 10 and 50 ml/h showed no difference in the chlorinated hydrocarbon in the upgraded oil when using different catalysts.

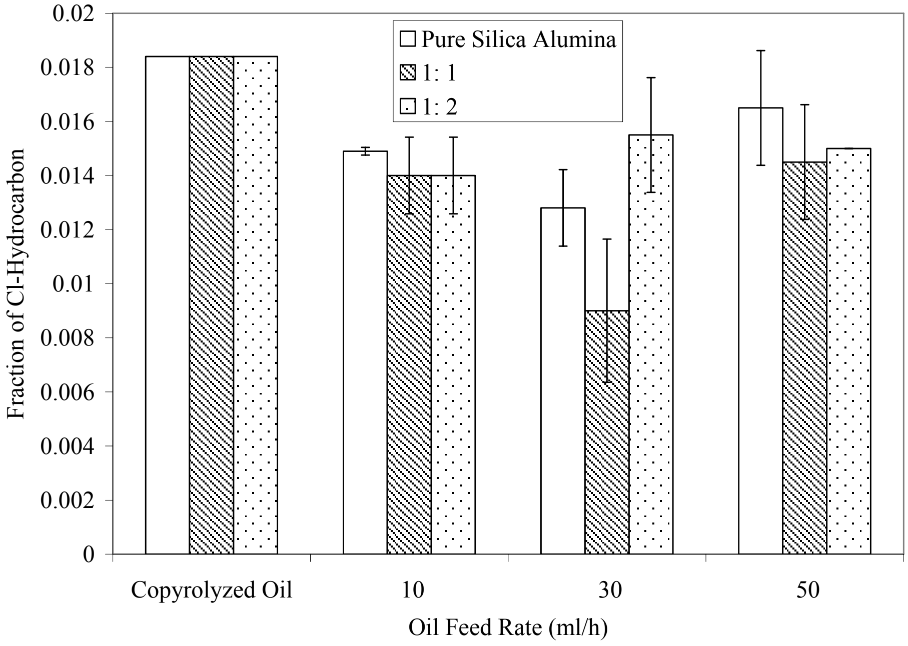


Figure 53 Fractions of chlorinated carbon in oil from upgrading at various feed rates using silica alumina:ZnO ratio of 1:0, 1:1 and 1:2 catalysts.

Figure 54 shows the percent of aromatic, paraffin, and olefin in gasoline fraction. Silica alumina catalyst showed a decrease in paraffin from 52% to 42% and 40% but olefin and aromatic increased slightly about 5% when the feed rate was increased from 10ml/h to 30ml/h and 50ml/h, respectively. On the other hand, silica alumina-ZnO composite catalysts provided an increase in paraffin (10-15%) and decreases in aromatic (20%) and olefin (6.9%) when the feed rate was increased from 10ml/h to 50ml/h.

Oil feed rate had an effect on type of hydrocarbon in gasoline. However, different catalysts fit different feed rates. For some catalysts, high feed rate provided high paraffin because catalyst cracked unsaturated hydrocarbon to paraffin, and short retention time prevented them to reform back to olefin and aromatic compounds. Low feed rate generated reforming of intermediates to olefin and aromatic due to longer reaction time. In the case of silica alumina catalyst, it had low activity of structure rearrangement, therefore, this catalyst needed longer reaction time to produce more paraffin.

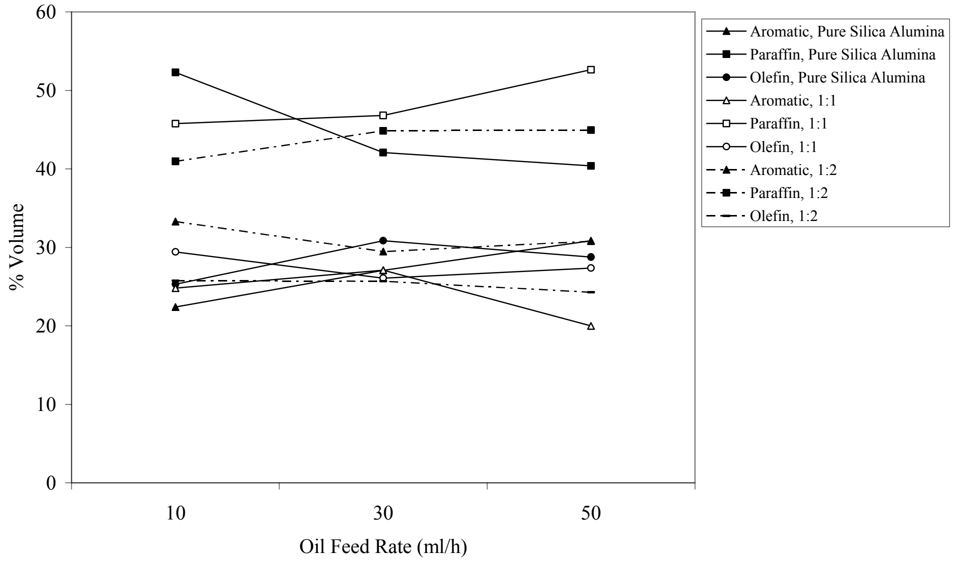


Figure 54 The percents of composition of each hydrocarbon group in gasoline product from reactions at various feed rates using silica alumina:ZnO ratio of 1:0, 1:1 and 1:2 catalysts.

Data of isoparaffin index of gasoline was presented in Table 25. The oil feed rate affected isoparaffin index and also octane number. Silica alumina catalyst showed a decrease in paraffin at higher feed rate in Figure 54 and it also reduced isoparaffin index from 1.44 to 1.04. The composite catalysts showed an increase in isoparaffin index from 1.33 to 3.39 in silica alumina: ZnO ratio of 1:1 and 1.28 to 2.10 in the ratio of 1:2 when the feed rate was increased from 10ml/h to 50ml/h. Octane numbers showed the same tendency with isoparaffin index and were in the range of 94-113.

From this result, silica alumina showed different result from composite catalysts because silica alumina catalyst had slow isomerization so that it needed longer reaction time, but composite catalyst gave both isomerization and dehydrogenation, simultaneously. Isomerization activity needed shorter reaction time, therefore, high feed rate produced high amount of iso-structure.

Table 25 Isoparaffin index and octane number of gasoline products from upgrading of oil at various oil feed rates

Feed rate	Isoparaffin index	RON	MON
1:0 (Pure Silica Alumina), 10ml/h	1.44	95.39	87.44
1:0 (Pure Silica Alumina), 30ml/h	1.28	94.51	86.35
1:0 (Pure Silica Alumina), 50ml/h	1.04	92.77	84.33
1:1, 10ml/h	1.33	94.73	86.65
1:1, 30ml/h	2.38	104.31	97.37
1:1, 50ml/h	3.39	112.50	106.71
1:2, 10ml/h	1.28	95.12	86.92
1:2, 30ml/h	1.71	98.61	90.92
1:2, 50ml/h	2.10	102.19	94.92

Note: RON = Research octane number

MON = Motor octane number

The effect of feed rate on the concentrations of benzene, toluene, and xylene in gasoline products from upgrading of oil by silica alumina is shown in Figure 55. The total amount of benzene, toluene, and xylene increased 26% when the feed rate was increased from 10 ml/h to 50 ml/h. The concentration of xylene increased from 0.36 mol/l to 0.60 mol/l but the concentrations of benzene and toluene were not affected by feed rate. The concentrations of benzene and toluene were 0.46-0.50 mol/l and 0.59-0.65mol/l, respectively.

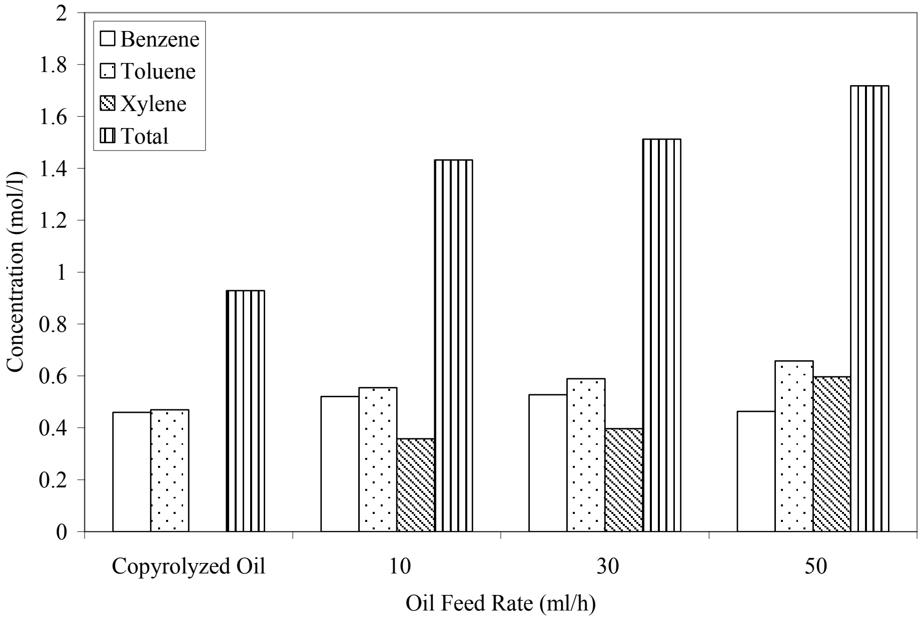


Figure 55 The concentrations of benzene, toluene, and xylene in gasoline products from upgrading of oil at various feed rates using silica alumina catalyst.

Figure 56 shows the effect of feed rate on the concentrations of benzene, toluene, and xylene in gasoline product from upgrading of oil by silica alumina:ZnO (1:1) composite catalyst. Low feed rate of 10 ml/h produced toluene only. Toluene was reduced and benzene was produced when the feed rate was increased to 30 and 50 ml/h. The total concentration of benzene, toluene, and xylene was the highest at the feed rate of 30 ml/h.

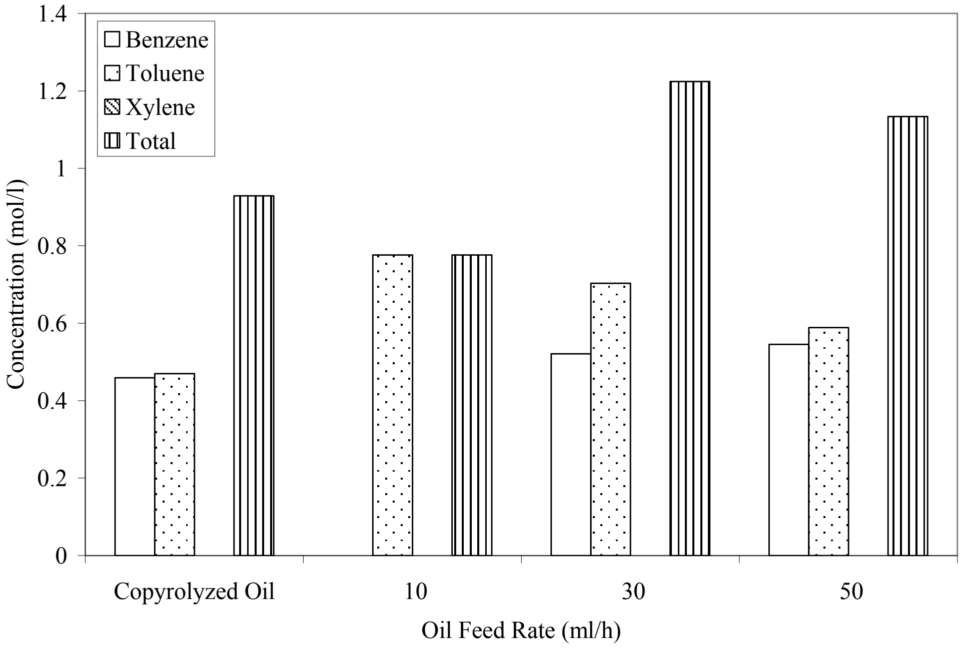


Figure 56 The concentrations of benzene, toluene, and xylene in gasoline from upgrading of oil at various feed rates using silica alumina:ZnO (1:1) composite catalyst.

The concentrations of benzene, toluene, and xylene in gasoline products from upgrading of oil by silica alumina:ZnO (1:2) composite catalyst are shown in Figure 57. The amounts of benzene, toluene, and xylene obtained at the feed rate of 10 ml/h and 30 ml/h were not much different but at high feed rate of 50 ml/h the amount of toluene increased from 0.49 mol/l to 0.93 mol/l. Therefore, total concentration of benzene, toluene, and xylene at high feed rate of 50 ml/h increased 50% from feed rate of 30 ml/h.

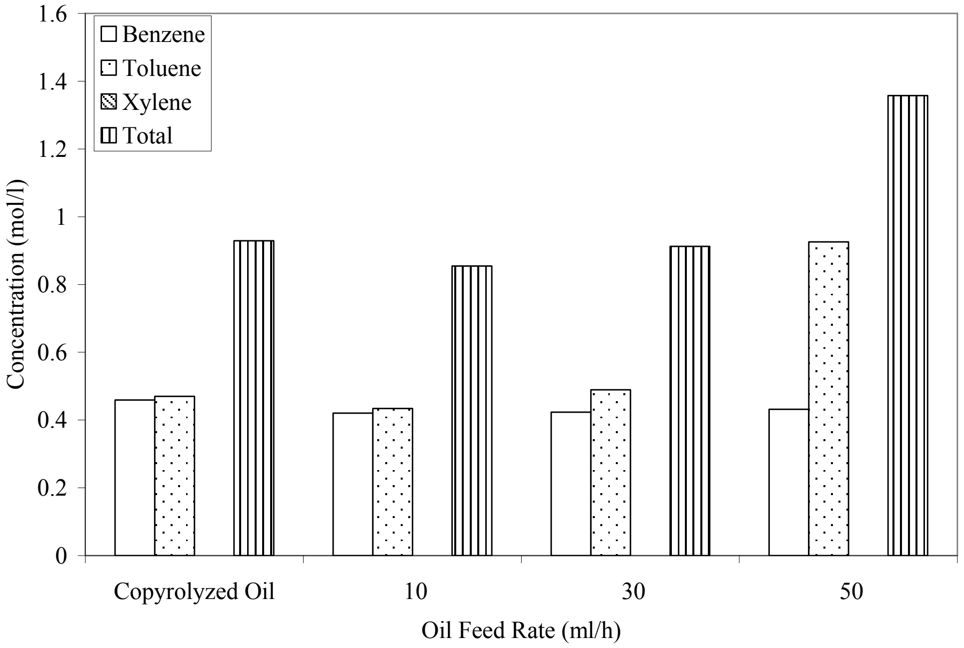


Figure 57 The concentrations of benzene, toluene, and xylene in gasoline from upgrading of oil at various feed rates using silica alumina:ZnO (1:2) composite catalyst.

The feed rate had a significant effect on the concentrations of benzene, toluene, and xylene in the upgraded oil. The high feed rates increased the concentration of benzene, toluene, and xylene because fast reaction promotes rearrangement of structure and prevent recombination to larger molecules.

From the study of upgrading of copyrolyzed oil, silica alumina-ZnO catalyst at the ratio of 1:1 and feed rate of 30ml/h were good conditions which provided high oil yield (60.3%), highest reduction in chlorine in oil (50%) and high octane number (>100).

In the case of investment, the economic analysis is shown in Appendix I. The operating cost of the experiment was calculated and compared with the oil prices in August, 2006. The study showed the oil obtained costs 36.67 baht per month while the operating cost was 1875.25 baht per month the high operating cost was from the use of electric heating reactor. However, the conventional municipal waste treatment uses incineration method which provides available heat energy, therefore, in industrial scale the reactor can use energy from partial combustion of the waste to replace the electricity in order to reduce the operating cost.