OPTIMIZATION OF ACID ACTIVATION CONDITIONS FOR MABISIAN CLAY AND ITS APPLICATION IN PYROLYSIS OF MIXED PLASTIC WASTE

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Abstract- In this study, acid modification of Myanmar Natural clay was optimized and conducted the catalytic pyrolysis of mixed plastic wastes in the fixed bed reactor. Mabisian clay was activated using sulphuric acid at various acid concentrations (2-10M), reaction temperature (60-100ºC) and contact times (1-3 hr). In this process, response surface methodology (RSM) based on Box-Behnken experimental design was applied. RSM results showed close agreement between experimental and predicted value. The physicochemical properties of modified samples were characterized by X-ray fluorescence spectroscopy (XRF), X-ray diffraction (XRD), Fourier transformed infrared spectroscopy (FTIR) andscanning electron microscope (SEM). The chemical treatment increased the Si/Al ratio from 1.405 to 3.102 and decreased the size of clay structure. Product fuel was analyzed by using Gas Chromatography and Mass Spectrometer (GC/MS) and GC/MS result showed product fuel consist of gasoline 58.51%, naphtha (74.9%), kerosene (25.8%), diesel oil (25.8%), grease (5.28%), fuel oil (1.97%) and greases and wax (0.28%).

Keywords- Acid activation, Sulphuric acid, Myanmar Natural Clay, Pyrolysis, Response surface methodology

I. INTRODUCTION

The disposing of plastic waste has been accepted as a world -wide environmental problem. Liquefaction of waste plastics has been interesting as an important technology to solve environmental protection problems. The problem of plastics wastes cannot be solved by land filling and incineration, because suitable and safe depots are expensive. Incineration increases the growing emission of harmful, greenhouse gases, e.g. NO_x, SO_x, CO_x, etc. The two important categories of recycling are mechanical recycling and chemical recycling. Chemical recycling is virtually a thermal method. In chemical recycling method, the long alkyl chains of polymers are broken into a mixture of lighter hydrocarbons. This is one of the prospective ways to utilize waste polymers [11]-[16].

Acid activation has been widely studied as chemical treatment methods for improving the surface and catalytic properties of fibrous clays and has been noted to induce changes in crystal structure of aluminosilicate minerals due to the dissolution of structural ions and/or rearrangement of the structure [2]. The method involves leaching of the clays with inorganic acids, causing disaggregation of clay particles, removal of mineral impurities, and dissolution of the external layers, thus changing the chemical composition and the structure of the clays. The solubility of the clay minerals in acid is of fundamental importance because it reveals certain attributes of the clay minerals [18]. From a practical standpoint, solubility characteristics are important in determining the utility of various clays as sources of aluminum and for the production of porous materials.

Natural untreated clays can be modified by organic and inorganic acid in order to improve the surface, catalytic properties of fibrous clays and to induce changes in crystal structure [1], [3]. Acid-modified clays is interested not only because of their low cost but also because the structure and dimension of their pores appear more suitable, compared to zeolites, for the cracking of larger molecules [2].

Acid modification of Mabisian Clay was investigated and optimized by applying response surface methodology (RSM) based on Box-Behnken design. Response surface methodology (RSM) is a useful statistical technique which has been applied in research into complex variation process. The multiple regression and correlation analyses are used as tools to assess the effects of two or more independent factors on the dependent variable. Its main advantage is the reduced number of experimental runs required to generate sufficient information for a statistically acceptable results. RSM has been successfully applied for optimization of acid activation in clay.

The purpose of this study was to investigate optimum conditions for acid activation for Mabisan clay and apply in pyrolysis of mixed plastic waste.

II. MATERIALS AND METHOD

A. Material

Mabisan clay was collected from Department of Research and Innovation (MSTRD). Raw materials used for this study are mixed plastic wastes (High density polyethylene, Low density polyethylene, Polypropylene and Polystyrene), natural catalysts and starch powder All chemicals used were analytical reagent grade, obtained from Able Chemical, Mandalay. Distilled water was utilized in all experiments.

B. Modification of Myanmar Natural Clay

The experiments were conducted using the following parameter: acid concentration (2-10 M), reaction temperature (60-100 ºC) and reaction time (1-3 hr). In the acid modification process, around 30 g of clay put in the two- neck flask bottom flask. Afterwards, the various concentration of sulphuric acid solution was poured in the reaction flask equipped with reflux condenser in order to avoid the evaporation during the experiment. The resulting suspension was heated under stirring condition and the measurement of the time was started. After acid modification, the slurry was filtered and the precipitate was washed thoroughly with distilled water till the filtrate was free from sulphate ions. The acid–activated samples were dried in an oven. The dried clays were calcined at 500ºC for 2 hr. The acid activated clay is designated as MM-1 to MM-15. The raw clay is designated as MM-0.

C. Pyrolysis of Mixed Plastic Waste

The experiment was carried out by loading 200 g of mixed plastic waste into the fixed bed reactor and 20 g of catalyst into the catalyst bed. Nitrogen was passed through before starting experiment to remove oxygen from the reaction medium. The reactor was heated with an electric furnace at a rate of 5ºC min^{-1} to reach the desired temperature. The reactor temperature was controlled and monitored by a set of temperature controller and thermocouple. The effluent gases were cooled in a condenser unit to separate condensable gases from the non-condensable gases. The condensable gases were collected in liquid form and then characterized.

D. Characterization techniques

The raw and acid treated Mabisian clay materials were characterized by X-ray fluorescence spectroscopy (XRF), X-ray diffraction (XRD), Fourier transformed infrared spectroscopy (FTIR) and scanning electron microscope (SEM). The pyrolytic oil was analyzed by gas chromatography coupled with mass spectrometry detector (GC-MS).

RESULT AND DISCUSSION

E. Optimization of Acid Modification

Box -Behnken response surface design which involves three factors and requires three levels were used to identify which factors of the acid modification process had significant effects on the response, Si/Al ratio of the catalyst. A correction was established with p-value for both responses at the 95 % confidence level. Three factors, namely: acid concentration, reaction temperature, reaction time were selected for the experiment. These factors were examined at three different levels as shown in Table I and Table II show the independent variables and Box-Behnken design matrix for modification of Myanmar Natural clay.

A full quadratic model was used for statistical analysis in order to correlate the Si/Al with the operating variables. The form of the full quadratic model for the first step is as shown in Equation:

$$Si/Al = 7.316 + 0.05313\ X1 - 1.6288\ X2 - 0.12444\ X3 - 0.012275\ X12 + 0.16533\ X22 + 0.000679\ X3 + 0.00348\ X1*X2 + 0.001295\ X1*X3 + 0.013677\ X2*X3$$

Table I

INDEPENDENT VARIABLE FOR BOX-BEHNKEN DESIGN

Variable	Symbols	Level		
		(-1)	0	(+1)
Acid Concentration [M]	X_1	2	6	10
Time [hr]	X_2	1	2	3
Temperature [ºC]	X_3	60	80	100

The analysis of variance (ANOVA) for the experimental results of the Box–Behnken Design is also shown in Table III. The value of P-value for the model is less than 0.05 which indicated that it is a significant and desire model. The value of lack of fit "p value" (more than 0.05) is not significant. It was showed that the quadratic model was valid for the present study. For the model fitted, the coefficient of determination (R^2) was 99.88 %, which indicated that the model adequately represented the real relationship between the parameters chosen and 99.88 % of the variations could be explained by the fitted model.

Table II

BOX-BEHNKEN DESIGN FOR ACID MODIFICATION

Run	X_1	X_2	X_3	Si/Al	Predicted Value
1	6	1	100	2.23641	2.24039
2	2	1	80	1.60913	1.60828
3	6	2	80	1.84172	1.83833
4	2	3	80	1.86679	1.87553
5	6	2	80	1.82360	1.83833
6	6	3	100	3.08813	3.08251
7	10	1	80	1.71993	1.71118
8	6	1	60	2.00942	2.01504
9	10	2	60	1.48597	1.48909
10	6	2	80	1.84967	1.83833
11	6	3	60	1.76700	1.76303
12	10	2	100	2.46386	2.46862
13	2	2	100	2.13391	2.13079
14	2	2	60	1.57027	1.56550
15	10	3	80	2.03318	2.03404

Figure 1-3 showed the three dimensional response surface plots to study the interactions among the various selected factors and to determine their optimum values. The plots were generated by plotting the response using the z-axis against two independent variables while keeping the other two independent variables at their zero level.

Figure 1 showed the effects of acid concentration and reaction temperature at constant reaction time of 2hr. The decrease Si/Al ratio was observed at the acid concentration of 2M and 10M. The lower reaction

time gave the negative influence on Si/Al ratio. The optimum conditions were acid concentration of 6M and reaction temperature of 100ºC.

The effect of reaction time and temperature at constant acid concentration of 6M was showed in Figure 2. According to this Figure, the highest reaction time and reaction temperature give the highest Si/Al ratio. Maximum Si/Al ratio was found at reaction time of 3hr and reaction temperature of 100ºC.

Figure 3 describes the effect of acid concentration and reaction time at constant reaction temperature of 80ºC. Figure showed the acid concentration of 2M and 10M decreased Si/Al ratio while the acid concentration 6M increased the Si/Al ratio. Therefore, using higher concentration of acid gave the excessive leaching of Al^{3+} ion. However, the reaction time induced the positive effective of Si/Al ratio. The optimum conditions were acid concentration of 6M and reaction time of 3hr.

Table III
ANALYSIS OF VARIANCE FOR ACID MODIFICATION

Source	DF	Adj SS	Adj MS	F-Value	P-Value
Model	9	2.28772	0.25419	1893.55	0.000
Square	3	0.54323	0.18108	1348.90	0.000
Error	5	0.00067	0.00013		
Lack-of-Fit	3	0.00031	0.00010	0.59	0.680
Pure Error	2	0.00036	0.00018		
Total	14	2.28839			

F. XRF characterization

The XRF characterization was performed to know the chemical compositions of the minerals present in the clay and the subsequent chemical changes that occurred due to acid treatment. The results of chemical analysis of the parent and acid treated clay as shown in Table IV. The parent clay contains the alumina and silica in major quantities while other minerals such as magnesium, calcium, potassium, zinc and titanium are present in trace amounts. The Al, Mg, Ca and Fe contents in the acid treated material decrease progressively whereas the Na and K content slightly increase after the acid treatment. Silica content increased due to the acid treatment, therefore, the Si/Al ratio increased. The decrease in the alumina content in the acid treated sample can be assigned to the leaching of Al^{3+} ions form.

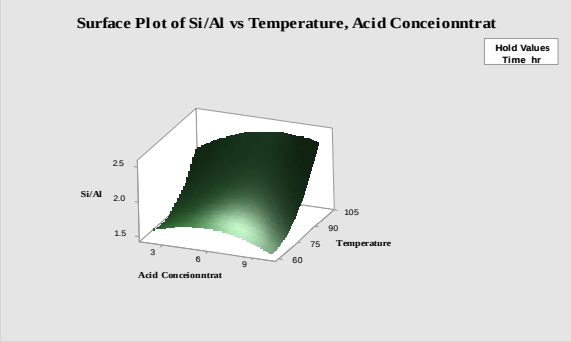


Fig. 1 Response surface of Si/Al ratio Vs Acid Concentration and Temperature

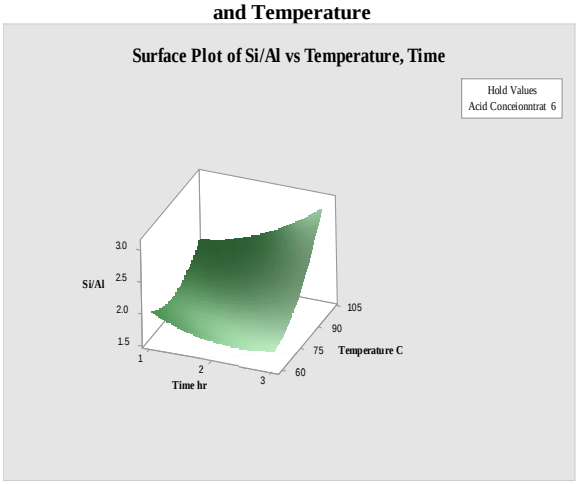


Fig. 2 Response surface of Si/Al ratio Vs Temperature and Time

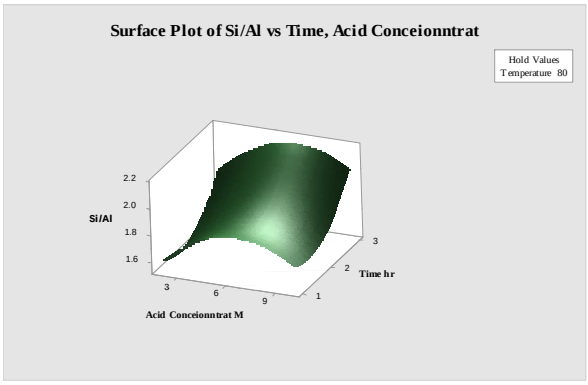


Fig. 3. Response surface of Si/Al ratio Vs Acid Concentration and Time

Table IV
CHEMICAL COMPOSITION OF UNTREATED AND ACID TREATED CLAY

Composition	Untreated Clay	Acid treated Clay
O	38.5	35.7
Na	0.095	0.12
Mg	0.182	0.135
Al	19.73	9.315
Si	27.73	29.83
Cl	-	0.05129
P	0.01	0.00484
S	0.014	0.01761
K	0.842	0.88
Ca	0.022	0.00799
Ti	0.312	0.3556
Cr	0.012	0.0102
Fe	1.453	0.8376
Ni	0.004	0.003
Zn	0.002	0.00144
Ga	0.003	0.00185
Rb	0.0046	0.00543
Sr	0.002	0.00189
Zr	0.0112	0.01438

G.Fourier Transform Infrared (FT–IR) Analysis

The FT–IR spectra of the raw and acid activated samples in the wave number range of 4000–500 cm^{-1}

to study the effect of acid-leaching on the clay mineral. The FTIR spectra of parent and acid treated clay as shown in Figure 4. It is clear that there were some structural modifications on the clay sample as a result of acid activation. The untreated sample show absorption band 547.8, 695.36, 796.63, 911.4, 1002.05, 1051.24, 1114.89, 3457.52, 3620.51, 3696.7 cm^{-1}. In the O-H stretching region, the parent and acid treated clay shows two prominent bands at 3620.51, 3693.7 cm^{-1} corresponds to Al-OH stretching [4],[8]. Leaching causes the intensity of absorption band at 3620 cm-1 to decrease after acid activation. It is due to the removal of octahedral cations, causing the loss of water. In the hydroxyl groups, lying between the tetrahedral and octahedral sheets give the absorption at 3696 and 3620 cm^{-1}. Again, well resolved strong bands in the 908 -916 cm^{-1} and 795-800 cm^{-1} region are due to Al-Al-OH stretching and Al-Mg-OH stretching in untreated and treated clay which changed in shape and position due to structural changes in the tetrahedral cations [5]. The intensities of O-H and Al-OH stretching bands observed at 911 and 916 cm-1 decreased after acid-activation. This cause the partial depletion of Al, Mg and Fe from the clay structure according to the changes in chemical composition In the1000-1002 cm^{-1} region, main functional groups were Si-O and Al-OH [6]-[7].

H.XRD analysis

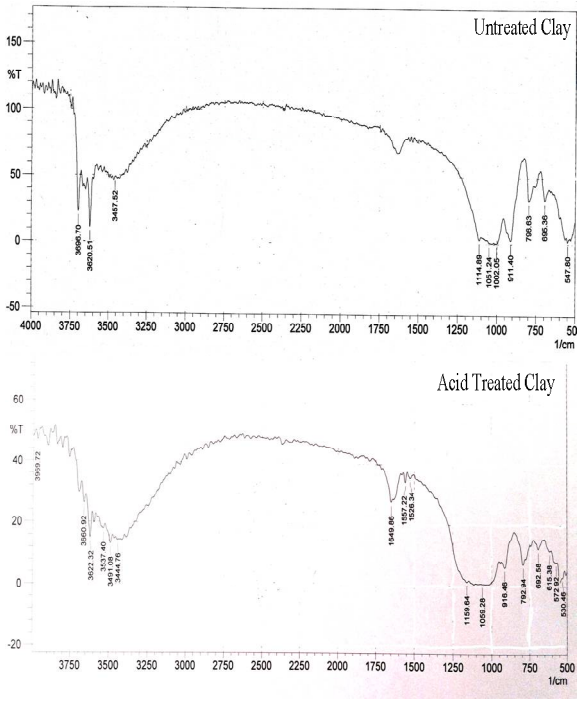
The structural changes of the clay material due to acid treatment were studied using X-ray diffraction technique. The XRD patterns of natural and acid treated clay based on the optimization of the acid treated process were given in Figure 5. Leaching of the clay with sulphuric acid produces important mineralogical changes as can be seen from XRD patterns. The major peaks of the clay are 20.583, 20.734, and 26.538, at 2ɵ respectively. After the acid treatment, the intensity of the clay moderately increases. This indicates that the crystallinity of the clay is considerably affected by acid activation. Therefore, the increase in intensity and narrowing of the peak may be related to the increase of crystallite size and decrease of the mean lattic strain [10] - [11].

E. SEM analysis

The scanning electron micrographs of the untreated and acid treated clay samples are presented in Figure 6 which shows the morphological features. The SEM image untreated clay reveals the presence of large particles that appeared to have been formed by several flaky particles stacked together in form of agglomerates. The SEM images of acid treated clay show different particles morphology. The micrographs of acid treated clay indicated the disaggregation and decrease the size of clay structure on acid treatment.

F. Pyrolysis of Mixed Plastics

Pyrolysis reactions were carried out at the temperature range 200- 450ºC by using plastic to catalyst ratio 10:1. The yield of pyrolytic product was calculated based on the feed of the mixed plastic waste. The yields of liquid fuel were 75.8% and gases was17.124%. In addition, product fuel was analyzed by using Gas Chromatography and Mass Spectrometer (GC/MS) and GC/MS result showed product fuel has gasoline 58.51%, naphtha (74.9%), kerosene (25.8%), diesel oil (25.8%), lubricating oil (5.28%), fuel oil (1.97%) and greases and wax (0.28%). Fuel is ignited and fuel can be used internal combustion engines.



Wave number

Fig. 4 FTIR result of untreated and acid treated clay

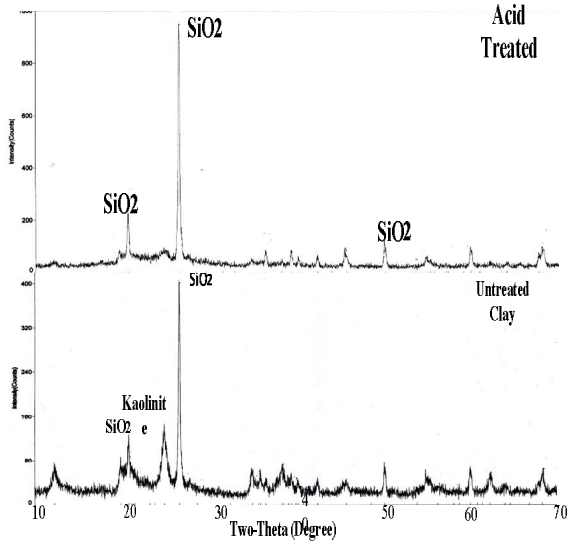


Fig. 5 XRD results of untreated and acid treated clay

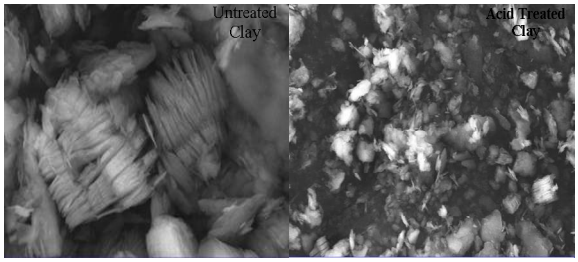


Fig. 6 SEM images for natural and acid treated clay

CONCLUSION

The optimum condition for acid activation of clay was determined with the aid of the Box-Behnken design. The pyrolysis of mixed plastics waste was conducted by using the acid treated clay based on the optimum condition. The optimum conditions of acid treated clay were found that acid concentration 6M, reaction time 3hr, reaction temperature 100ºC within the selected range. Acid activation at optimized conditions was found to significantly alter the clay structure and consequently improve the pyrolysis of mixed plastic wastes. The activated clay was found to increase Si/Al ratio from 1.405 to 3.102 and decrease the size of clay structure on acid treatment. Furthermore, the increase in intensity may be related to the increase of crystallite size and decrease of the mean lattic strain according to the XRD result. The yields of liquid fuel were 75.8% and gases was17.124%. In addition, product fuel has gasoline 58.51%, naphtha (74.9%), kerosene (25.8%), diesel oil (25.8%), grease (5.28%), fuel oil (1.97%) and greases and wax (0.28%). Fuel is ignited and fuel can use internal combustion engines. Therefore, the acid activated clay can be applied for the pyrolysis of mixed plastic waste as catalyst supports.

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