METHODOLOGY

The experiment consists of three parts. The first part is the study of the removal of hydrogen chloride gas from copyrolysis of cattle manure and polyvinyl chloride, and to determine the optimum conditions for the best HCl reduction by using statistical method. The second part is to investigate kinetic parameters of copyrolysis reaction of PVC and cattle manure. The last part is to upgrade the pyrolyzed oil by bi-functional catalysts.

1. Copyrolysis of polyvinyl chloride and cattle manure

Polyvinyl chloride and cattle manure mixture at a specified ratio was pyrolyzed in a tubular reactor. The reactor is made of stainless steel 316 tube (ID = 76.2mm.) and placed in an electrical furnace which is controlled by PID controller.

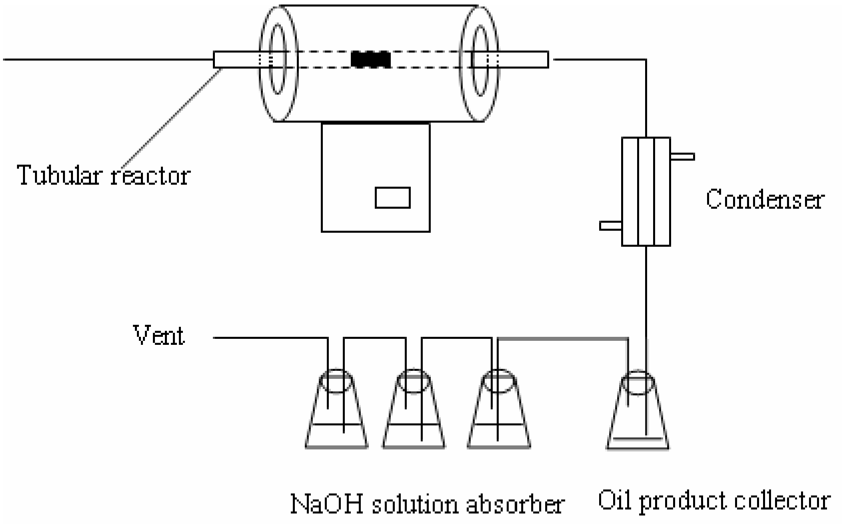

Figure 4 Copyrolysis process diagram

The reaction parameters studied are reaction temperature (250-450°C), holding time (0-60 min), heating rate (1-5°C/min), and the ratio of PVC:cattle manure (1:1, 1:3, and 1:5). The mixture of PVC and cattle manure at a specified ratio was loaded in the reactor. The reactor was heated at a specified heating rate to a specified reaction temperature and held at that temperature for a specified holding time at space time of 1.3 s^{-1}. Each condition was repeated three times. The pyrolysis process diagram is shown in Figure 4. The HCl reduction was determined by titration the remaining sodium hydroxide with hydrochloric acid using phenolphthalein as an indicator.

1.1 Screening factor by 2^k factorial design

Four factors eg., heating rate, reaction temperature, reaction time and PVC:cattle manure ratio, were considered by two level factorial designs. The 16 experimental conditions which followed design matrix in Table 3 are shown in Table 5.

Table 5 Experimental conditions according to factorial design.

Standard order	Run order	PVC: cattle manure	Reaction temperature (°C)	Heating rate (°C/min)	Holding time (min)
8	1	1:5	450	5	0
6	2	1:5	250	5	0
14	3	1:5	250	5	60
3	4	1:1	450	1	0
16	5	1:5	450	5	60
13	6	1:1	250	5	60
4	7	1:5	450	1	0
9	8	1:1	250	1	60
5	9	1:1	250	5	0
1	10	1:1	250	1	0
10	11	1:5	250	1	60
12	12	1:5	450	1	60
15	13	1:1	450	5	60
11	14	1:1	450	1	60
2	15	1:5	250	1	0
7	16	1:1	450	5	0

1.2 Optimize experimental conditions by Box-Behnken method

Box-Behnken statistical design method was used to determine the optimal conditions which provided high efficiency of HCl reduction. It was three-level design for fitting response surfaces. The statistical results were calculated by the Minitab program. Since factorial design showed non-interaction between reaction time and other factors, only three factors were studied: heating rate, reaction temperature and the ratio of PVC: cattle manure. The experimental conditions of Box-Behnken design which followed design matrix in Table 4 is shown in Table 6.

Table 6 Experimental conditions according to Box-Behnken design.

Standard order	Run order	PVC:cattle manure	Heating rate (^{o}C/min)	Reaction temperature (^{o}C)
6	1	1:5	3	250
1	2	1:1	1	350
13	3	1:3	3	350
8	4	1:5	3	450
11	5	1:3	1	450
10	6	1:3	5	250
7	7	1:1	3	450
5	8	1:1	3	250
3	9	1:1	5	350
14	10	1:3	3	350
12	11	1:3	5	450
9	12	1:3	1	250
15	13	1:3	3	350
2	14	1:5	1	350
4	15	1:5	5	350

2. Kinetics study of copyrolysis of PVC with cattle manure

Three ratios of PVC to cattle manure were studied: 1:1, 1:3, and 1:5. The mixture of PVC powder and cattle manure, at a specified ratio, was loaded in a simultaneous DSC-TGA (SDT 2690, TA instrument) which is controlled by Thermal Advantage software. The dynamic degradation and isothermal degradation were studied. The dynamic measurement was carried out at a specified constant heating rate. Four heating rates were chosen: 1, 5, 10, and 20^{o}C/min. The isothermal measurement started at a target temperature with a heating rate of 20^{o}C/min. Three target temperatures: 440, 450, and 460^{o}C, were studied with isothermal degradation. Both isothermal and dynamic measurements were repeated three times.

3. Upgrading of pyrolyzed oil

Oil which was derived from copyrolysis of mixed plastics and cattle manure at the optimum conditions from the first part was upgraded by catalysts to improve the quality of the oil. Metal oxide-acid composite catalyst was of interest to be used in upgrading the oil because metal oxide provided dechlorination activity and acid catalyst gave structure rearrangement to obtain high quality oil (Tang *et al.*, 2003; Zhou *et al.*, 2004). ZnO-silica alumina and Fe_2O_3-silica alumina were used in this study because ZnO and Fe_2O_3 had good dechlorination activities (Tang *et al.*, 2003; Uddin *et al.*,1999) and silica alumina is a conventional acid catalyst used in petroleum refinery. Therefore, the composite of these catalysts was of interest for upgrading the oil. This section can be divided into three parts: catalyst preparation, upgrading reaction, and product analysis.

3.1 Catalyst preparation

The catalysts used are $SiO_2Al_2O_3$, ZnO-$SiO_2Al_2O_3$, and Fe_2O_3-$SiO_2Al_2O_3$. The ZnO-$SiO_2Al_2O_3$ catalyst was prepared at two $SiO_2Al_2O_3$:ZnO molar ratios: 1:1 and 1:2. The composite catalyst was prepared by precipitation method. $Zn(NO_3)_2$ was dissolved in water and precipitated on $SiO_2Al_2O_3$ by adding ammonia solution. The catalyst was dried at a temperature of 150^{o}C and calcined at a temperature of 550^{o}C. Fe_2O_3-$SiO_2Al_2O_3$ composite catalyst was prepared by the same method but using Fe $(NO_3)_3.9H_2O$.

The catalysts were characterized by nitrogen adsorption (Autosorb1), and X-ray diffraction to determine surface area, and crystal structure of catalyst, respectively.

3.2 Upgrading reaction

Upgrading reactor is a vertical fixed bed reactor. The reactor is a stainless steel 316 tube with 0.95 cm diameter and 40 cm long. It is placed in an electrical furnace. Syringe pump was used to feed the pyrolyzed oil to the reactor. The experiment starts with heating the tube reactor, which has a bed of catalyst, to the reaction temperature of 430^{o}C and then the pyrolyzed oil is pumped by a syringe pump to the reactor at a specified feed rate. Three feed rates are studied: 10, 30, and 50 ml/h. The liquid product is condensed in a condenser. The process diagram is shown in Figure 5.

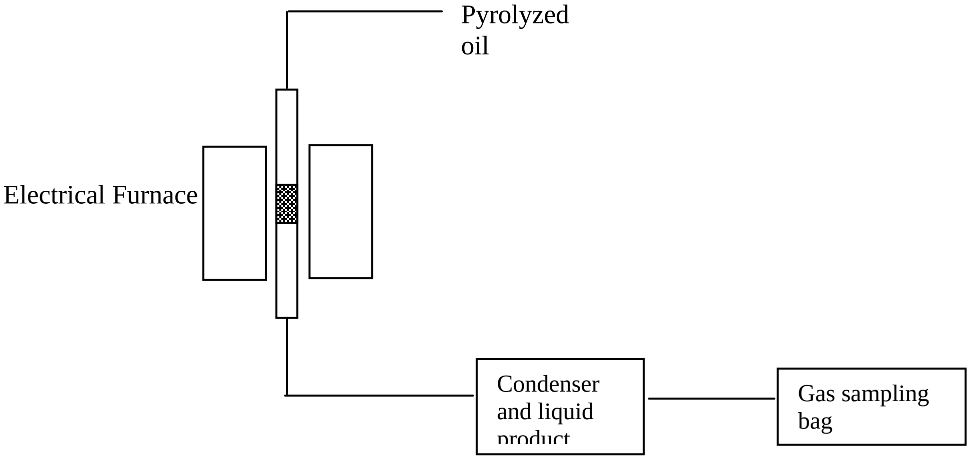

Figure 5 Upgrading process diagram

3.3 Analysis of products

3.3.1 Determination of product composition

The upgraded oil was distilled to four fractions by boiling point: gasoline (initial boiling point (IBP-200^{o}C), kerosene (201^{o}C-250^{o}C), gas oil (251^{o}C-370^{o}C) and residue (>370^{o}C) following ASTM D-86. The gasoline product was analyzed for the composition of benzene, toluene and xylene (BTX) by gas chromatograph (Varian, CP3800) connected with PONA capillary column and FID detector. The injection port temperature was 220^{o}C and the split ratio was 20. The column temperature was started at 50^{o}C and increased at a rate of 3^{o}C/min to 170^{o}C, after that the column was heated to 220^{o}C at a heating rate of 20^{o}C/min. The total time was 42.5 min.

The chlorinated hydrocarbon in oil was determined by nuclear magnetic resonance (Bruker, ADVAVCE DPX300). The amount of chlorinated compounds reduction was found by comparing area of peak at the 2 ppm chemical shift of no manure to that of the presence manure and to that of the upgrading oil.

3.3.2 Determination of octane number by ^{1}H Nuclear Magnetic Resonance Spectrometry

This research determined the octane number of gasoline fraction by Nuclear Magnetic Resonance technique following the work of Myers *et al.* (1975). The spectrum pattern of hydrocarbon compounds in gasoline fraction from NMR is shown in Figure 6.

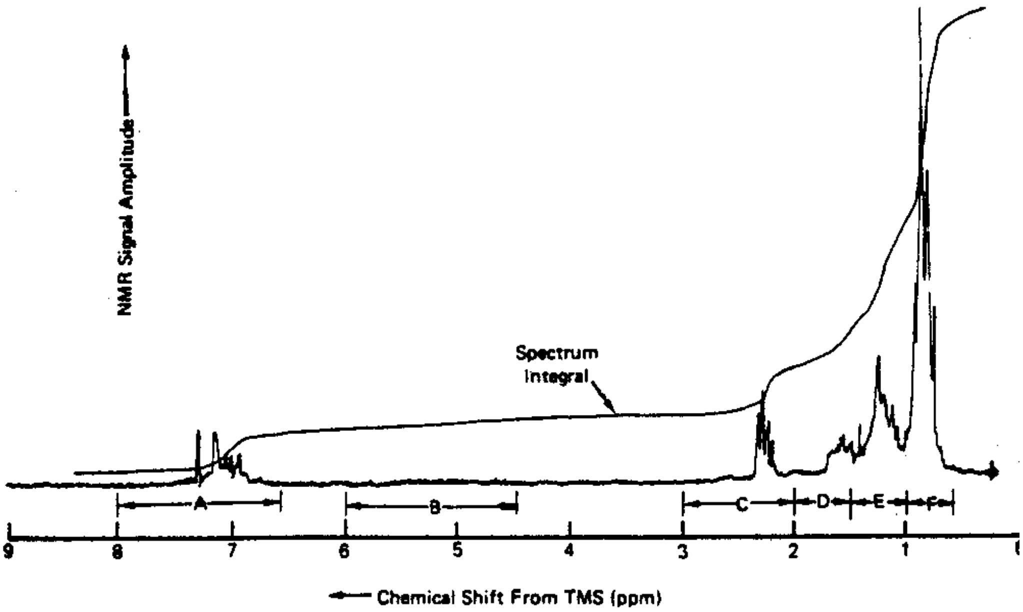

Figure 6 Nuclear Magnetic Resonance graph of gasoline fraction

Sources: Myers *et al.* (1975)

From Figure 6, chemical shift was divided into 6 ranges as shown in Table 7.

Table 7 The chemical shift of proton of each hydrocarbon compound.

Proton type	Chemical shift region
Ring aromatic	6.6 to 8.0 ppm (A)
Olefin	4.5 to 6.0 ppm (B)
α-Methyl	2.0 to 3.0 ppm (C)
Methine (CH, paraffins)	1.5 to 2.0 ppm (D)
Methelene (CH_2, paraffins)	1.0 to 1.5 ppm (E)
Methyl (CH_3, paraffins)	0.6 to 1.0 ppm (F)

The areas of NMR peaks in each range were used to calculate the amounts of aromatic, paraffin, and olefin compounds by equations 19-21.

Aromatics, vol % = $[(A+C/3)\ 0.97\times10^2] / [(A+C/3)0.97+ (D-2B+E/2+F/3)1.02+3.33B]$ (19)

Paraffins, vol% = $[(D-2B+E/2+F/3)1.02\times10^2] / [(A+C/3)0.97+(D-2B+E/2+F/3)1.02 +3.33B]$ (20)

Olefins, vol% = $[3.33B\times10^2] / [(A+C/3)0.97+(D-2B+E/2+F/3)1.02+3.33B]$ (21)

The amounts of paraffin, olefin, and aromatics were used to determine an octane number of gasoline fraction by equations 22-24.

Isoparaffin index (CH_3:CH_2)= 2F:3E (22)

Research octane number (RON) = 80.2 + 8.9 (isoparaffin index) + 0.107 (aromatics (23)

Motor octane number (MON) = 70.8 + 10 (isoparaffin index) + 0.101 (aromatics) (24)