

Mixed Plastic Wastes Pyrolysis in a Fluidized Bed Reactor for Potential Diesel Production

Aida Isma M. I., Salmiaton A., and Nur Dinie K. B.

Abstract—Disposing of waste to landfill has becoming undesirable to the legislation pressures, rising costs and the poor biodegradable quality of polymer used. Feasible study on converting mixed plastic wastes by applying catalytic pyrolysis into valuable products had been carried out. Thermogravimetric analysis under various heating rates and particle sizes were determined. A 15 g/h of fluidized bed lab scale of fast pyrolysis unit was used. The pyrolysis processes were carried out at temperature of 400 °C for 2 hours in non-catalytic and catalytic conditions with ratio catalyst to mixed plastic waste of 10:90. The properties of liquid products were analysed and compared using Fourier Transform Infrared Spectroscopy (FTIR) and High-Pressure Liquid Chromatography (HPLC). Under the experimental conditions, the maximum liquid yields with and without catalyst were 20 and 35 ml, respectively. FTIR results revealed that those functional groups detected are similar with commercial diesel together with HPLC results indicating diesel concentration.

Index Terms—Mixed plastic wastes, pyrolysis, catalytic, diesel.

I. INTRODUCTION

The problem of solid waste disposal is growing throughout the world, as a result of industrialization and population growth. The huge population increase couple with the improved living conditions of people lead to a dramatically increase of the consumption of plastics worldwide. The major usages of plastic are packaging, households and domestic products, electrical and electronic goods as well as building, construction and automotive industries. It was estimated that 170 million tons of plastics were produced worldwide during the year 2003 [1]. Based on statistics for the Western Europe, the annual 2003 total consumption of plastic products was estimated at 48.8 million tons corresponding to 98 kg/capita [2]. In the United States, the total amount of plastic in municipal solid waste (MSW) was approximately 30 million tons, which was represented as 11.7% of total MSW in 2006 [3]. Recycling plastic wastes by chemical reactions such as pyrolysis has made it possible to recover enormous energy recovery [4].

Pyrolysis could be an alternative to landfill or incineration for these rejected streams. In the pyrolysis process (heating in

an oxygen free atmosphere), the organic components of the materials are decomposed generating liquid and gaseous products, which can be useful as fuels and/or feedstock of chemicals for other chemical processing [5]. The yield and the composition of the products influence by a range of pyrolysis process parameters, including the type of waste, reactor system, gas residence time, contact time, heating rate, temperature, pressure ranges, presence of catalyst and presence of hydrogen gas or hydrogen donor compound [6]-[9].

Temperature has been the most influenced factor and has been one of the common studied operating parameter affecting the process of thermal cracking of the plastics, and as a consequence has a strong effect on the pyrolysis products and on the secondary reactions [10]-[12]. Several authors have studied the influence of operating parameters [13]-[18] and type of equipment [19]-[24] on pyrolysis of one or a selected amount of components of the MSW. The influence of catalyst on the yield and composition of products has been extensively investigated [25]. Many of the research have been carried out on a single plastic or in simple plastic mixtures, whilst there are few data on plastics collected from real municipal plastic wastes.

The dominant components of waste plastics such as polypropylene (PP), polystyrene (PS) and polyethylene (PE) are rich in carbon and hydrogen, which are the building blocks of petroleum. Therefore, the possibility of converting mixed plastic waste into liquid fuels is a productive alternative for plastic recycling. The aim of this work was to investigate the thermal degradation of plastic waste in a fluidized bed with and without catalyst for potential diesel production. The effects of heating rate and the particle size were also evaluated.

II. EXPERIMENT

A. Raw Material

The plastic mixture used in this study was a simulated fraction of that found in MSW of Kuala Lumpur, Malaysia. Mixed plastic wastes that consist of PE, PP and PS with ratio of 5:3:1 were cut into smaller sizes (5mm × 5mm) and mixed. The proximate value was characterized using Thermogravimetric Analyzer (Mettler Toledo, TGA/SDTA 851, USA). Experiment was repeated by adding a fluidized catalytic cracking (FCC) catalyst for process enhancement and product selectivity. The ratio of catalyst to mixed plastics was 10:90.

B. Solvents and Others

Locally available 99.9% pure N₂ gas and HPLC grade hexane, toluene and dichloromethane (DCM) solvents from

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Fisher Scientific were used in the reactions.

C. Proximate Analysis

Ten milligrams of the sample at particle size of 1, 2, 2.5 and 4 mm were heated from room temperature to 600°C with different heating rate of 5, 10, 20 and 30°C/min under nitrogen (N_2) with a constant flow rate of 20 mL min⁻¹. Fig. 2(a) and 2(b) shows the thermogravimetric (TG) and derivative thermogravimetric (DTG) curves of mixed plastic wastes.

D. FTIR Analysis

The FTIR spectra were recorded by applying an attenuated total reflectance (ATR) crystal. The instrument used was a spectrophotometer of Perkin Elmer, Spectrum One. The resolution of the equipment was 4 cm⁻¹. The FTIR spectrum in the significant ranges of 4000 to 650 cm⁻¹ was measured and recorded. A commercial software spectrum v.5.0.1 (Perkin - Elmer LLC 1500F2429) was used to process and calculate all data from the spectra. The elemental compositions value of bio-oil was determined.

E. HPLC Analysis

HPLC analyses were carried out using *n*-hexane as the solvent. The column used was the amino propyl silica-dual column (25 cm × 4.6 mm). The instrument used was the Waters 515 with UV and RI detectors. The 16 priority polyaromatic hydrocarbons (PAHs) in the pyrolysis products and in a commercial diesel were analyzed with High Performance Liquid Chromatography (HPLC) equipped with wavelength scanning ultraviolet (UV) detector.

F. Pyrolysis

All experiments took place in the Combustion Laboratory of Chemical and Environmental Engineering Department, Universiti Putra Malaysia, Serdang, Selangor DarulEhsan, Malaysia. The pyrolysis experiments were performed using an unstirred fluidized-bed bench scale reactor made of stainless steel with a diameter of 52 mm and a height of 36.5 cm. A schematic diagram of the reactor is shown in Fig. 1. Two different pyrolysis experiments were performed: (1) Non-catalytic plastic pyrolysis, and (2) Catalytic plastic pyrolysis.

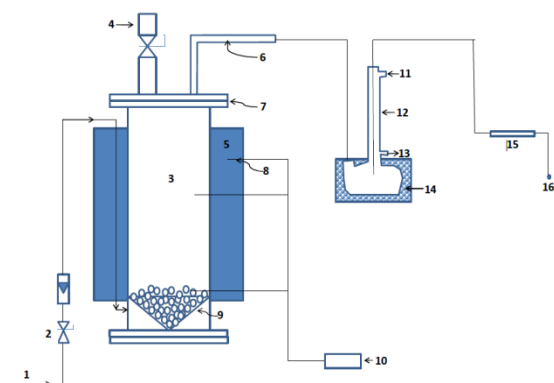


Fig. 1. Schematic diagram of experimental setup. (1) N_2 gas inlet, (2) flow meter, (3) lab scale reactor, (4) feeder, (5) electric furnace, (6) gas discharge, (7) flange, (8) thermocouple, (9) distributor, (10) temperature control panel, (11) cooling water supply, (12) condenser, (13) cooling water outlet, (14) ice bath, (15) silica gel, (16) flue gas outlet.

Approximately 30 ± 5 g of dried plastic samples were pre-blended together with 100 g of inert sand and was placed

in the reactor and after all the connections were made, sweeping gas flow rate of 9L/min was adjusted and measured by a flow meter. The heating rate of 10°C min⁻¹ was kept constant in all experiments. The sample was pyrolysed to the final pyrolysis temperature of 400°C for 2 hours. The pyrolysis experiment was repeated using FCC catalyst. The pyrolysis was performed to determine the influence of temperature and time on the yield of pyrolysis products.

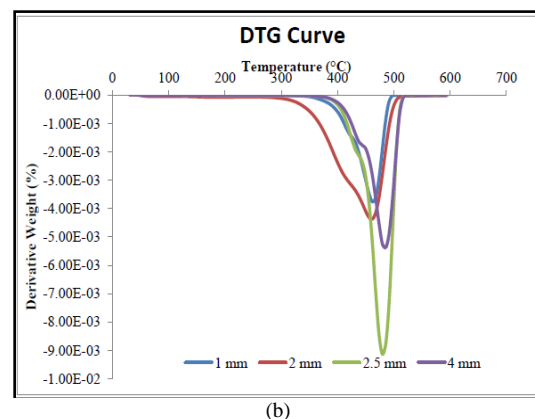
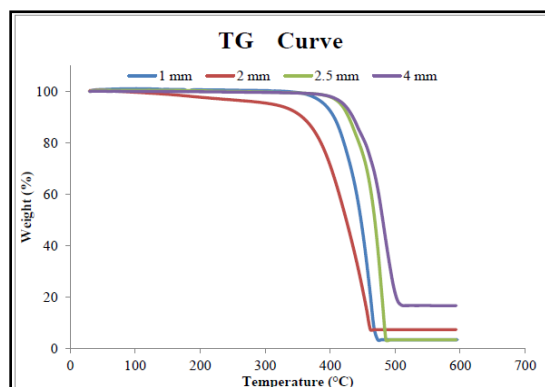
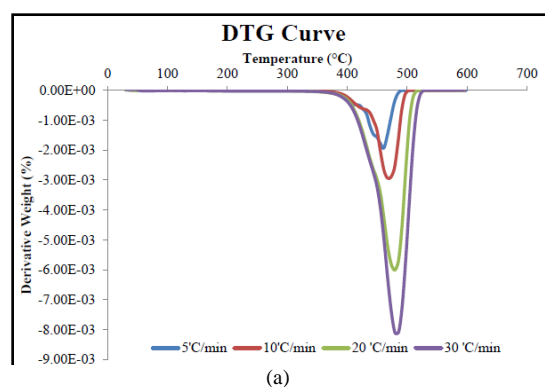
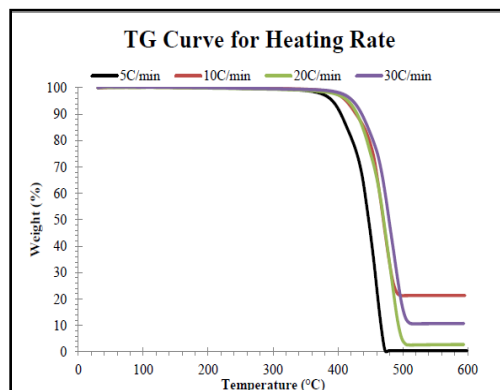


Fig. 2. TG and DTG plots of mixed plastics waste: (a) at different heating time, (b) at different particle size.

The pyrolysis liquid products were collected by condensing in condenser and cold traps maintained at about 0°C to 5°C and were washed by DCM. The liquid obtained from the maximum pyrolysis yield were characterized using FTIR and HPLC.

III. RESULTS

A. Pyrolysis Yields

Chemical properties and distribution of separated hydrocarbon compounds were strongly dependent on the reaction conditions and material fed into the reactor [26], [27]. The liquid yields obtained with the two mentioned pyrolysis method, are presented in Table I. It can be stated that the catalyst plays an important role in pyrolysis product distribution, producing more liquids.

TABLE I: PRODUCT YIELDS FROM THE PYROLYSIS OF MIXED PLASTIC WASTES

Methods	Liquid (DCM + diesel)mL
Non-catalytic condition	20
Catalytic condition	35

B. Heating Rate and Particle Size Effects

For a better understanding of the thermal behavior of the samples, the TGA plots are presented as shown in Fig. 2. Fig. 2a shows the weight loss of samples as a function of heating rate of 5, 10, 20 and 30°C/min and Fig. 2(b) shows the degradation at different particle sizes of 1, 2, 2.5 and 4 mm. As portrayed in the figures, all plastics loss its weight at temperature of approximately 400°C. As the heating rates increase, the peaks are shifted towards the high range of temperature. The analysis of differential thermo-gravimetric (DTG) curves also shows that best particle size of 2.5 mm decomposed at 400°C.

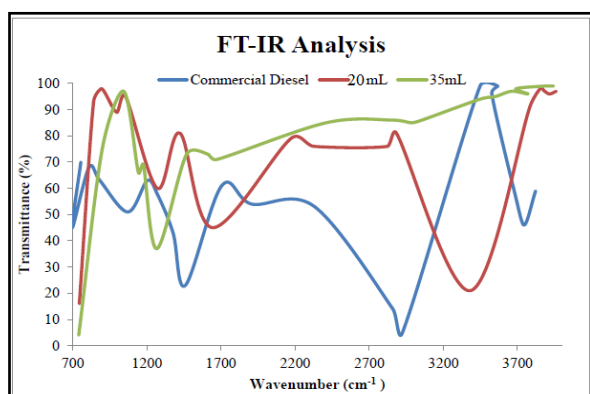


Fig. 3. FTIR results for commercial diesel, liquid containing dichloromethane (DCM) and diesel.

C. FTIR Analysis

The contents of C and H are important indicators for the quality of the liquid products. The chemical structure of the pyrolysis yields and the commercial diesel was confirmed by recording their IR spectra. Fig. 3 shows the FTIR spectra of the commercial diesel, the experimental yields at 20 and 35mL, respectively. As observed, liquid containing DCM and diesel at 20 and 35 ml show almost the same curves as the commercial diesel. The spectra shows that various functional groups occurring in abundance and represented by broad

absorption bands in a regions of hydroxyl groups (3570-3200 cm^{-1}), methylene stretch (2865-2845 cm^{-1}) and aromatic C-H in plane bend (1225 – 920 cm^{-1}).

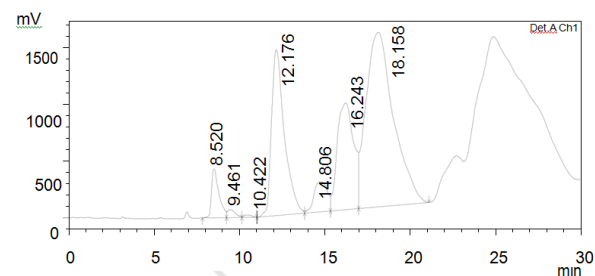
D. HPLC Analysis

The concentration of diesel increased sharply with presence of FCC catalyst temperature of 400 °C. This is because catalyzed reactions have lower activation energy resulting a higher reaction rate at the same temperature as shown in Table II.

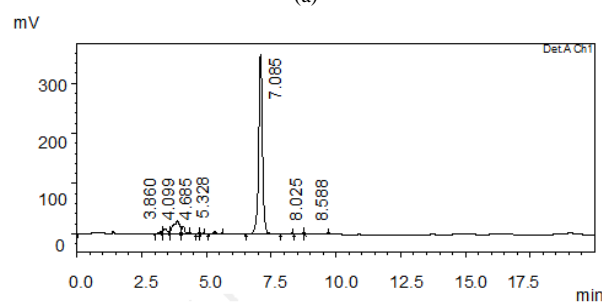
TABLE II: DIESEL YIELD (CONCENTRATIONS) FOR ALL CONDITIONS AND METHOD

Conditions / Method at temp. 400 °C	Area at the retention time	Diesel yield (mg/L)	Liquid (DCM + Diesel), mL
Normal condenser:			
Non-catalytic	9,732	1,734.62	20
Catalytic	58,113	10,358.00	15
Improved condenser:			
Catalytic	151,379	26,981.64	35

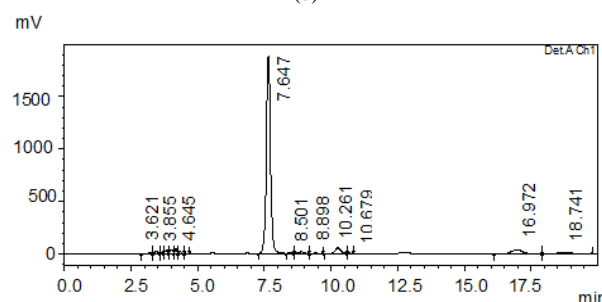
The determination of aliphatics (mainly saturates) and aromatic groups (mono, di and poly-aromatics) in the liquid products obtained from the pyrolysis of mixed plastic wastes are of great importance for their utilization. Fig.4(a) shows the HPLC results of a commercial diesel from Malaysia, Fig. 4(b) HPLC results of non catalyst at 20 mL, Fig. 4(c) HPLC results of catalyst at 15 mL and Fig. 4(d) HPLC results with the presence of catalyst at 35 mL. It should be noted that the compound found in the experimental yield support the presence of the potential diesel production.



(a)



(b)



(c)

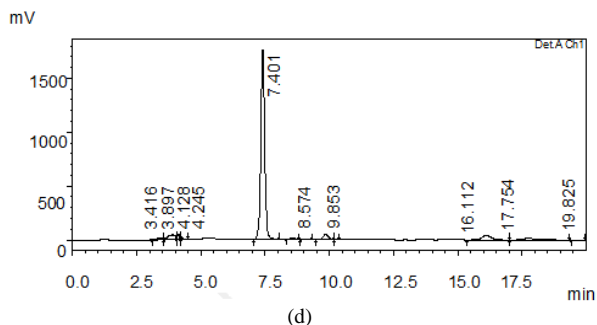


Fig. 4. HPLC spectra of diesel concentration: (a) commercial diesel, (b) non catalyst 20ml, (c) with catalyst (15ml), (d) with catalyst (35ml).

IV. CONCLUSION

Pyrolysis is an attractive alternative for recycling mixed plastic wastes and the use of catalyst can significantly enhance the process. It can be concluded that FCC catalyst is an effective catalyst which enhances the production of aromatic liquid products. Pyrolysis products may be used as an alternative fuels or as a source of valuable chemicals.

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