



# Pyrolysis of HDPE into fuel like products: Evaluating catalytic performance of plain and metal oxides impregnated waste brick kiln dust

Imtiaz Ahmad<sup>a,\*</sup>, M. Ismail Khan<sup>a</sup>, Hizbullah Khan<sup>b</sup>, M. Ishaq<sup>a</sup>, Razia Khan<sup>a</sup>, Kashif Gul<sup>a</sup>, Waqas Ahmad<sup>a</sup>

<sup>a</sup> Institute of Chemical Sciences, University of Peshawar, 25120, Peshawar, Khyber Pakhtunkhwa, Pakistan

<sup>b</sup> Department of Environmental Sciences, University of Peshawar, 25120, Peshawar, Khyber Pakhtunkhwa, Pakistan

## ARTICLE INFO

### Article history:

Received 23 December 2016

Received in revised form 25 January 2017

Accepted 1 February 2017

Available online 3 February 2017

### Keywords:

Polyethylene

Pyrolysis

Impregnation

Clays

Metal oxides

Fuels

## ABSTRACT

The work explores the catalytic activities of plain and metal oxides (Fe<sub>2</sub>O<sub>3</sub>, CoO, ZnO, MnO<sub>2</sub> and NiO) impregnated waste brick kiln dust (WBKD) for pyrolysis of high density polyethylene (HDPE) in order to get useful liquid oil that can be used as substitute to petro-fuels. The catalysts prepared in the laboratory were characterized by scanning electron microscopy (SEM), energy dispersive x-rays (EDX) analysis, surface area analysis (SAA) and x-ray diffractometry (XRD). The conversion of HDPE into liquid oil (LO) as a function of concentration of catalysts was studied. Based on the yielding results, ZnO- impregnated WBKD (5%) was found to be highly active. The liquid oils obtained in the thermal and ZnO-impregnated WBKD catalyzed runs were analyzed by using fourier transform infra-red spectroscopy (FTIR) and gas chromatographic-mass spectrometry (GC-MS). While comparing the results with the un-catalyzed thermal run, the ZnO-impregnated WBKD altered the liquid oil composition in terms of carbon range and hydrocarbon group type distributions. The fuel properties of the resultant liquid oils showed fuel values resembling to the generic petro-fuels.

© 2017 Elsevier B.V. All rights reserved.

## 1. Introduction

End of use plastics are disposed off into landfills which remain there for years, create nuisance, and land & water pollution [1–5]. In order to handle disposal issues in an environmentally friendly way, several recycling methods have been proposed in the past [6–8], but none of these proved to be effective in providing an adequate and optimum solution [9,10]. Furthermore, there is much concern with the wastage of plastics as valuable commodity. Being a valuable resource, waste plastics can be chemically recycled not only to get value added fuel like products to meet with the growing demand for alternative energy resources but also to conform to the stringent environmental regulations laid down for safe disposal of such wastes.

A number of recycling processes has been reported in the open literature for resource recovery from waste polyolefins with focus on thermo-catalytic pyrolysis [11,12]. Owing to the fact that the catalysts may alter the product spectrum and reduce the reac-

tion temperature with several other benefits; catalytic pyrolysis is considered to be more practical compared to thermal pyrolysis. A variety of homogeneous catalysts have been tested till date and a number of such catalysts are used to promote a wide range of bond-forming or bond-breaking reactions involving carbon. However, the homogeneous catalysts pose several problems including the difficulty in recovery from the product when become spent/passivated. Heterogeneous catalysts like conventional zeolites [13], mesoporous catalysts [14], nanostructured and hierarchical catalysts were also used in the past with greater success [15]. Among these, the zeolite catalysts were the focus of attention of many researchers in recent years [16–18]. However, most of the catalysts did not prove efficacy in terms of plastic conversion due to fair textural properties, wide range of acidity, high cost, and access of bulky polymer molecules to their active sites [19,20]. These draw backs have necessitated development of novel catalysts with improved activity and selectivity.

Transition metal oxides are enjoying popularity as catalysts in a variety of applications. However, a major problem associated with these catalysts in thermal treatment of hydrocarbons is deactivation by coking [21]. The coke along with several by-products can increase viscosity of reaction mixture and hence reduce heat trans-

\* Corresponding author.

E-mail address: [patwar2001@yahoo.co.in](mailto:patwar2001@yahoo.co.in) (I. Ahmad).

fer coefficient [22]. A number of studies have been reported in the open literature aimed to reduce the build-up of carbon deposition on these catalysts, in order to keep them active throughout the reactions [23,24]. In the present work, we have impregnated transition metal oxides on a waste product (waste brick kiln dust) and evaluated their catalytic performance in comparison with the plain brick kiln dust for pyrolysis of high density polyethylene to get useful liquid oils that could be used as substitute fuel or as feed-stock in chemical industries.

## 2. Experimental section

### 2.1. Materials, and catalysts preparation & characterization

The HDPE pellets were obtained from the local market. The proximate and ultimate analyses are provided in Table 1. The WBKD was collected from a brick kiln, Peshawar, Pakistan and its elemental composition is provided in Table 2. Transition metals salts i.e. FeCl<sub>3</sub> (99%), CoCl<sub>2</sub> (99%), Zn(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O (98%), MnCl<sub>2</sub>·4H<sub>2</sub>O (99%), and Ni(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O (99%) were procured from Merck company and used as metal precursors in impregnation study. The metal salts were impregnated on WBKD by Incipient Wetness method. Before use, the as received WBKD was purified by de-siltation and exhaustive washing with de-ionized water (DI), dried in an oven at 100 °C for 3 h, and sieved using a screen (125 μm).

In a typical procedure, the stoichiometric quantity of each metal salt required for attaining 2 wt% loading on the WBKD was dissolved separately in 100 mL of DI. The solution was transferred to a 400 mL beaker and added 3 g of the WBKD. The resultant slurry was stirred at 70 °C for 5 h using a heating mental cum magnetic stirrer. The impregnated WBKD was recovered by vacuum filtration, and dried in an oven at 90 °C for 24 h, ground and then further calcined at 550 °C for 4 h. All catalysts were prepared in the same fashion, stored in air tight glass vials, and used as such in subsequent pyrolysis experiments.

The surface morphologies of the plain and variously metal-impregnated WBKD were examined by scanning electron microscope (Model JEOL-Jsm-5910; Japan) under high vacuum microprobe. The surface area and pore size analyses were carried out by surface area analyzer (Quantachrome Nova Station A) using nitrogen adsorption-desorption method. The surface area was calculated by the Brunauer-Emmett-Teller (BET) surface area analysis and the pore size & volume were calculated from N<sub>2</sub> sorption-desorption isotherms data using Barrett, Joyner, Halenda (BJH) model. The catalysts were also characterized by using X-ray diffractometer (XRD; model JDX-9C, JOEL, Japan) at room temperature, with CuKα radiation and a nickel filter. The diffraction spectra were obtained using Cu (K-α) radiation having 1.54178 Å wave length.

### 2.2. Pyrolysis experiments

The experimental apparatus consisted of a stainless steel reactor (25.4 cm x 2.1 cm) connected to a 50 mL glass reservoir (pyrex) through a quick fit condenser with water cooling arrangement. The liquid receiving reservoir was connected to an exit through flexible tubing for venting the gas. A high-pressure nitrogen cylinder was used to pressurize/purge the reactor before the start of the pyrolysis to create an oxygen depleted environment. The schematic of the reactor and auxiliary devices is provided in Fig. 1. Samples were pyrolyzed unstirred (quiescent bed) using 2 g of plastic pellets loaded with 0.5–10 wt% catalyst at target temperature (350 °C) and time (30 min). A tube furnace was used to heat the reactor to the desired temperature. The reactor skin temperature was measured by a thermocouple. The vapors leaving the reactor were allowed to flow through a condenser. The condensates were collected in a

reservoir and the uncondensed gases were sent to vent. The yields of the liquid oil were calculated as under:

$$\text{Conversion} = \frac{[(WF) - (WR)]}{WF} \quad (1)$$

$$\text{Liquid yield (wt\%)} = \frac{[(WL)]}{(WF)} \times 100 \quad (2)$$

Weight feed polymer (WF), Weight residual polymer (WR), Weight liquid oil (WL).

### 2.3. Liquid oil analysis

The liquid oils of optimum yields were analyzed by FT-IR and GC-MS. The FT-IR analysis was performed by using Fourier Transform Infrared spectrometer (Model FT-IR Prestige-21, Shimadzu, Japan) in the wave number range of 4000–600 cm<sup>-1</sup> while GC-MS analysis was carried out by using gas chromatograph coupled with MS analyzer (GC-MSQP2010, Shimadzu) under the given experimental conditions:

- I Injector: ADC-201
- II Column: DB-5MS (25 m x 0.25 mm i.d., 0.25 μm)
- III Carrier gas: helium
- IV Flow rate of carrier gas (mL min<sup>-1</sup>): 1.3
- V Split ratio: 50
- VI Injector temperature (°C): 300
- VII Sample injection volume (μL): 1
- VIII Initial oven temperature (°C): 35

The peaks in the chromatograms were identified from the data of mass spectral (MS) library (National Institute of Standards and Technology, NIST MS/MS Database).

The standard fuel oil analyses developed for petroleum based fuels were applied to pyrolysis liquid oils. Density, API gravity, viscosity, carbon residue, ash, flash point, heating value, aniline point, octane number and cetane number were determined and compared with the petroleum-derived products to look for their fuel oil qualities in chemical and thermal applications using standard American Society for Testing and Materials (ASTM)/Institute of Petroleum (IP) designated methods.

## 3. Results and discussion

### 3.1. Characterization of catalysts

The surface area analysis (Table 2) showed that the plain-WBKD has high surface area and small pore dimensions. The BET and BJH surface areas were found to be 74.54 and 300.26 m<sup>2</sup>g<sup>-1</sup> while the pore size and volume were found to be 122.78 Å and 0.92 ccg<sup>-1</sup>, respectively. The results showed that for the catalysts like NiO/WBKD, CoO/WBKD and MnO<sub>2</sub>/WBKD, the BET surface areas determined were decreased to 65, 70 and 62 m<sup>2</sup>g<sup>-1</sup>, respectively whereas the BJH surface area also decreased to 221, 156 and 239 m<sup>2</sup>g<sup>-1</sup>, respectively. A decrease can also be seen in the pore size and volume which may be attributed to the accumulation of metal oxides within the pore mouths upon impregnation/calcination. On contrary, ZnO/WBKD, and Fe<sub>2</sub>O<sub>3</sub>/WBKD, exhibited increased surface areas of 77, and 83 m<sup>2</sup>g<sup>-1</sup>, respectively. Similarly, the pore size and volume also increased which might be resulted by increase in the layers spacing of the WBKD due to pillaring effect exhibited by the metal oxides during impregnation and subsequent calcination. As in the current study, only ZnO/WBKD was found to be the most active catalyst in the cracking of HDPE, therefore, further analyses were performed for this catalyst in comparison with the plain-WBKD.

The mineralogical compositions of the plain and ZnO/WBKD studied by EDX are given in Table 3 while the corresponding sig-

Download English Version:

<https://daneshyari.com/en/article/5134585>

Download Persian Version:

<https://daneshyari.com/article/5134585>

[Daneshyari.com](https://daneshyari.com)