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Thermo-catalytic pyrolysis of polystyrene in the presence of zinc bulk catalysts

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ABSTRACT

Zinc bulk catalysts (Zn, ZnO and $ZnCl_2$) were used for the thermo-catalytic pyrolysis of EPSW and were found with high activity and selectivity of products. Thermo-catalytic pyrolysis was carried out using an efficient Pyrex batch reactor. Zn metal catalyst was found as the best catalyst amongst the zinc bulk catalysts for the cost effective pyrolysis of EPSW (expanded polystyrene waste). The yield of liquid products at 450 °C, 120 min heating time and 1:0.2 feed to catalyst ratio was 96.73 ± 0.12 wt.% with 2.47 wt.% toluene, 1.16 wt.% ethylbenzene, 47.96 wt.% styrene monomer and 1.90 wt.% α-methylstyrene. The components of liquid products were separated by fractional distillation and found with further thermal pyrolysis in addition to cyclization and recombination reactions. During the fractional distillation, much product variations were observed. High molecular weight aromatic hydrocarbons decreased with the associated increase of low molecular weight aromatic hydrocarbons, particularly toluene and ethylbenzene.

1. Introduction

Polystyrene (PS) is one of the large consuming plastics and dispensed after use on a large scale in the US and other developing countries. PS is used for households like toys, kitchen utensils, coffee cups, and plates to industrial level, including insulation material, packing material for breakable and food [1,2]. Expanded polystyrene waste (EPSW) is a special goal of concern due its heavy amount refusal by the public and its incredible bulk volume, which causes environmental pollution called "white pollution". EPSW is 10 wt.% of the total plastic wastes, but by volume it could be 40% of the total discarded plastics and occupy more space [2]. EPSW is non-biodegradable, easily spread by wind and it also floats on the surface of water bodies, demolishing the beauty of nature. Throwing to landfill space may cause future construction cracks of roads and buildings [3–7]. To handle polymer wastes, different strategies have been developed, including incineration landfill disposal, mechanical recycling and feed stock recycling. Feedstock recycling *via* thermo-catalytic pyrolysis is the safe alternative to overcome the problem and benefit the important carbon resources into either energy sector or raw chemicals like styrene, toluene and ethylbenzene that are used in the production of new polymers or other substances [8–13].

In pyrolysis processes, the selection of proper reactor and catalyst that affect the pyrolysis temperature and selectivity of products. Various researchers worked on the pyrolysis of PS with the effect of reactor and nature of reactor material, which include various designs of reactors and material such as batch, autoclave (stainless steel reactor), fixed bed, continuous flow and pressure reactors [5,14–17]. Moreover, the addition of numerous types of solvents, different plastic blends, additives, varying conditions and catalysts have been reported to have its impact on the yield of liquid products [18,19].

Huge amount of work is available on the pyrolysis of PS using heterogeneous acidic and basic catalysts with the aim to increase the yield and selectivity of products to a final low cost pyrolysis method [2,20–24]. Among the acidic catalysts, the most commonly used catalysts are zeolites like HZSM5 (acid treated Zeolite Socony Mobil-5), activated charcoal (AC) and silica–alumina (SiO_2/Al_2O_3), fluid catalytic cracking (FCC) catalysts and MCM-41 (mobile composition of matter) [25–29]. Karmore and Madras [26] worked on the thermal pyrolysis of PS by Lewis acid *i.e.* aluminum chloride ($AlCl_3$), ferric chloride ($FeCl_3$), boron triflouride (BF_3) etherate, tin (IV) chloride ($SnCl_4$) in solution and reported that the pyrolysis rate was the highest using $AlCl_3$. Similarly, the heterogeneous basic catalysts have also been reported. They are of good catalytic activity for the pyrolysis of EPSW and enhance the selectivity of component products. The common solid base catalysts are oxides

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of metals [20,30,31]. Ukei et al. [20] studied both heterogeneous acid and base catalysts (metal oxides) for the pyrolysis of PS. It was reported that among the acid and base catalysts, BaO was more effective catalysts for the pyrolysis of PS. Tiwary et al. [32] studied the effect of metal oxides (both alkali and transition metal oxides) at elevated temperature and pressure using solvent.

The race of plastic pyrolysis was also continued using metals as catalyst. Guoxi et al. [33] investigated the pyrolysis of PS using metal powders of Al, Zn, Fe, Ni and Cu, benzene as solvent. It was reported that the order of conversion to styrene monomer was WPS + Al > WPS + Zn > WPS + Fe > WPS + Ni > WPS + Cu > WPS. Hussain et al. [1] studied the pyrolysis of waste PS using Fe mesh by microwave–metal interaction and found 80 wt.% liquid products with rapid pyrolysis rate. It was reported that Fe not only catalyze the reaction, but also work as a synergist. Hussain et al. [34] also reported the co-pyrolysis of PS and Makarwal coal using Cu metal antenna by microwave–metal interaction and obtained significant results. Though a large amount of work is available on the conversion of waste polymers, but most of the studies deal with higher operating and capital cost using expensive solvents and additives. The recent trends of metal investigation, especially of Zn that has been reported to produce higher amounts of styrene monomer after Al metal powder [33] and the high rate of PS conversion using Lewis acid ($AlCl_3$) made our interest to investigate Zn metal, its oxide salt (ZnO) and its Lewis salt ($ZnCl_2$) as catalyst, which have been reported for the pyrolysis of biosludge and kraft lignin [35–37].

The aim of the study was investigating the pyrolysis of EPSW for best catalysts among the zinc bulk catalysts and their comparison with literature reported studies to a final low cost pyrolysis method with the effective catalytic activity and products selectivity. The secondary aim of the work is to separate the pyrolysis products.

2. Experimental

2.1. Materials and methods

EPSW was collected from local market and were used for the pyrolysis experiments. Zn granules (99.9%), ZnO (99.0–100.5%) and $ZnCl_2$ (99%) were purchased from Merck KGaA 64271, Darmstadt, Germany and were used as such for the pyrolysis of EPSW. The pyrolysis experiments were carried out in a Pyrex batch reactor having internal diameter 7 cm and height 22 cm and provided with airtight lid shown in Fig. 1. The reactor was assembled in an external electrical heating furnace coupled with temperature controller, which could operate up to 1000 °C. The reaction temperature was measured by thermocouples that were in direct contact with the reactor and reaction mixture. The pyrolysis process was carried out at ambient conditions. The EPSW samples were pretreated at 150 °C for 20 min to reduce its bulk volume by 20 times and to evolve any gases present. The EPSW samples (5 g each) were pyrolyzed in a mixture with corresponding catalyst (weight to weight percent ratio) without the addition of any additives and solvents. The resultant pyrolysis products were condensed by a water condenser and collected in a cold trap. The pyrolysis products of EPSW were liquids, gases and residue. The process flow of the setup is shown in Fig. 2. The deactivated catalysts left at the bottom of the reactor were recovered by washing several times with *n*-hexane and dried for 1 h at 120 °C followed by heating at 500 °C for 5 h in the same heating assembly [38].

2.2. Fractional distillation

After successful optimization of parameters like pyrolysis temperature, heating time and feed to catalyst ratio, the EPSW samples (100 g) were degraded and bulk liquid products were collected using optimized conditions in the same pyrolysis assembly shown in Fig. 1. The bulk liquid products were then separated using fractional distillation in accordance with PN-81/C-04012 on the basis of boiling point of the products. Fig. 3 demonstrates the distillation setup used in this study. The set-up consists of almost the same assembly that were used in the pyrolysis process with a modified reactor with the same dimensions as mention in Section 2.1 and an additional fractionating column fitted with thermometer. About 200 ml of liquid products was poured in the fractionating reactor with boiling chips to prevent bumping during the process. During the fractional distillation temperature was continuously observed and fractions were collected at various ranges of boiling points. Each fraction was weighed and yield of component products was calculated. The parent liquid products and distillates were also

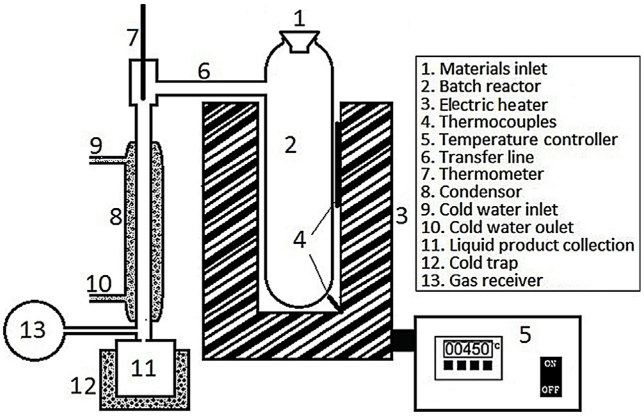

Fig. 1. Schematic diagram of the degradation assembly.

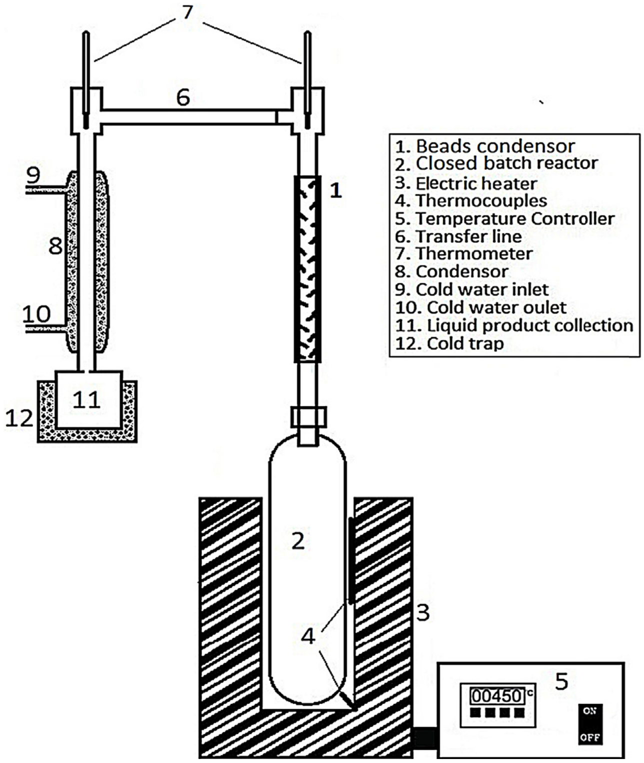

Fig. 2. Schematic diagram of the fractional distillation assembly.