

PREFACE

The aromatization of low valued readily available hydrocarbons in refinery has been of great interest over the past two decades to manufacture highly valued marketable products. In the recent past, the pyrolysis of municipal solid wastes (MSW) has been considered as a potential and innovative alternative for treating MSW, which resulting in different chemicals and fuel range hydrocarbons. The MSW disposal is one of the major problems in most developing countries. In Varanasi city, India about 22 wt.% of municipal wastes consists of waste plastics e.g., low density polyethylene (LDPE), high-density polyethylene (HDPE), polyethylene terephthalate (PET), polypropylene (PP), polystyrene (PS), and poly vinyl chloride (PVC). About 50–70% of the total plastic waste is packaging materials which are derived from polyethylene, polypropylene, polystyrene, and polyvinyl chloride. On an average, polyethylene makes up the greatest fraction of all plastic wastes (39 wt.%), followed by polypropylene (24 wt.%) and polystyrene (7 wt.%). Moreover, waste plastic has become a key component of MSW, as being used in a wide range of products due to its durability, light weight, and low cost. However, waste plastic is a major threat to environment and living being due to its non-degradability and carcinogenic properties of colouring dyes. The methods of waste plastics disposal are landfilling (79 wt. %), incineration (12 wt. %) and recycling (9 wt.%), respectively. These methods require large space and pollutes soil, air and water bodies. The energy contained in plastic waste is lost in these disposal route. Thus, pyrolysis of municipal plastic waste is gaining attention in small cities and town due to its high acceptability in efficiently conversion of plastics waste to valuable energy products without any polluting gas emissions. On the other hand, plastic waste incineration releases nitrogen oxides (NO_x) and sulfur oxides (SO_x), which pollute our environment. As we know, pyrolysis of waste

plastic gives wide range of hydrocarbon molecules and many of them are low valued product. Thus, aromatization of waste plastics mainly polyethylene, polypropylene and polystyrene via pyrolysis could be good option to convert waste plastic to value added products such as benzene, toluene, ethylbenzene and xylene (BTEX). The thermal and catalytic pyrolysis both were carried out for performance comparison in terms of liquid yield and BTEX quality.

The raw material waste plastic polyethylene (PE), polypropylene (PP) and polystyrene (PS) was collected from the municipal dumping zone of Varanasi city, India. The PE waste (carry bag), PP waste (disposable glasses) and PS waste (thermocool boxes) were first subjected to water washing and dried in open sunlight. The average size of the cut plastic pieces used in the experiment was approx. 4 mm X 4 mm. The catalyst used were ZSM-5 ($\text{SiO}_2/\text{Al}_2\text{O}_3 = 30:1$, Alfa Aesar, USA) and the synthesized catalyst derived from waste fly ash (Panki thermal power plant, Kanpur India) for the catalytic pyrolysis of plastic waste. The sieved fly ash (mesh size 230 A.S.T.M-240 B.S.S) was calcined in a muffle furnace at four different temperatures i.e., 600 °C, 700 °C, 800 °C and 900 °C in static air for 5h. The calcined fly ash catalysts were designated as FAN (uncalcined), FA-600 (calcined at 600 °C), FA-700 (calcined at 700 °C), FA-800 (calcined at 800 °C) and FAN-900 (calcined at 900 °C). All the catalysts were characterized using SEM-EDX, FTIR and BET analysis to check the suitability of utilizing it as catalysts for the pyrolysis of waste plastics.

The treated and shredded waste plastic sample of 50 g was fed to the reactor made of mild steel of 123 mm outer diameter, 112 mm inner diameter and 135 mm height. The reactor was then properly sealed with a gasket to prevent the products leakage. The dimension of the reactor was fixed based on standard design criterion of appropriate L/D ratio of 1.2. This improves vapor recirculation inside the reactor and minimizes pressure drop. The

thermal and catalytic pyrolysis were performed at the temperature ranging from 500 °C to 800 °C. A catalyst bed was installed in the vapor phase (A-type), liquid phase (B-type) or both, liquid and vapor phase (C-type)/multiphase to perform pyrolysis batch by batch, respectively. A porous stainless-steel plate was used to support the catalyst. The thermal and catalytic pyrolysis of Plastic waste were performed in nitrogen atmosphere (10 ml/min) varying time upto 30 minutes at different temperatures 500 °C, 600 °C ,700 °C and 800 °C, respectively. The catalytic pyrolysis of waste plastics were performed using commercial ZSM-5 and laboratory synthesized catalyst from waste natural fly ash of thermal power plant. Catalytic pyrolysis was performed at different feed to catalyst ratio using similar operating conditions as that of thermal pyrolysis.

Scanning electron microscopy (SEM), Energy-dispersive X-ray spectroscopy (EDX) and Fourier Transform Infrared spectroscopy (FTIR) was performed to investigate the surface morphology of fly ash derived catalyst. It was found that that most of the particles were spherical in shape with high porosity. The fly ash consists of spherical, vitreous particles of different size. BET analysis shows that surface area and pore volume both increases with the increase in calcination temperature from 600 °C to 800 °C. Whereas, further increase in temperature to 900 °C, surface area gets reduced. The maximum surface area and (Si/Al) ratio of FA-800 catalyst were 310 m²/g and 16.03, respectively.

The compositional analysis of pyrolysis oil was evaluated by gas chromatograph (NUCON 5765) using flame ionization detector (GC-FID). Flash and fire point of pyrolysis oil were obtained using Cleveland open cup apparatus (ASTM D 92). Carbon residue of pyrolysis oil was obtained using Rams bottom Carbon Residue Apparatus (IP 14/65). The density of pyrolysis-oil was measured according to ASTM D 1298 standard method. The bomb calorimeter (IP 12/63 T) was used to determine the gross calorific value (GCV) of pyrolysis oil.

The in-situ pyrolysis and aromatization of plastic waste on synthesized FA catalyst and commercial ZSM-5 catalyst using different types of catalyst arrangements (A-type, B-type and C-type) were studied. The optimum calcination temperature of fly ash for catalyst synthesis was 800 °C, as FA-800 catalyst showed excellent performance for aromatization of pyrolysis product irrespective of reactor arrangements. Thermal and catalytic pyrolysis of plastic wastes (PE, PP and PS) were thoroughly and systematically investigated in nitrogen environment. The experimental results on catalytic pyrolysis of Plastic wastes PE, PP and PS show that the developed process (C-type/multi-phase) could be a very good option for production of mainly aromatics BTEX. The maximum liquid yield and aromatic content (BTEX) at the temperature of 700 °C for thermal pyrolysis of polyethylene 68.02 wt. % and 10.75 wt. %, for polypropylene 86.34 wt.% and 30.9 wt. %, for polystyrene 96 wt.% and 13.57 wt. % were obtained respectively. The maximum BTEX yield for catalytic pyrolysis using C-type/multi-phase reactor arrangement on FA-800 at the same temperature (700 °C) were obtained 22.11 wt.% for PE, 43.43 wt.% for PP, 20.93 wt.% for PS respectively. Whereas, for ZSM-5 catalyst, maximum BTEX yield of 39.47 wt.% for PE, 53.09 wt.% for PP, 26.86 wt.% for PS were obtained respectively. The physicochemical properties of the pyrolysis oil show that it can be used as alternative fuels and as a source of valuable chemicals such as benzene, toluene, ethyl benzene or xylene (BTEX).

The suitability/stability of synthesized catalyst fly ash (FA) derived catalyst was tested and compared the results with commercial ZSM-5 catalyst. The results show that catalyst can be use upto 2nd run without regeneration process. However, regenerated catalyst gives almost same result as of fresh catalyst used. The detail study on the reactor shows that the reactor arrangement C-type/multiphase (vapor and liquid phase) catalytic pyrolysis of waste plastic is a breakthrough process from the technological point of view, as it

produces maximum aromatics/BTEX in comparison to any other process. Nevertheless, the same reactor arrangement (C-type/multiphase) can be operated without catalyst i.e., thermal pyrolysis mode also, giving valuable products thus, protecting environment and saving energy.

The results obtained are discussed and presented in this thesis. The thesis comprises of five subsequent chapters, as described below in brief. In the general introduction about the present scenario of MSW and plastic consumption, plastic waste, pyrolysis process and pyrolysis catalysts are discussed in Chapter 1. Chapter 2 presents the literature review and specific objectives of the thesis. Chapter 3 describes the experimental details related to the plastic waste pyrolysis and aromatization e.g., raw material, experimental setup fabrication, catalyst synthesis and characterization, pyrolysis product characterization, studies on pyrolysis and catalyst regeneration. Chapter 4 presents result and discussion based on the characterization of catalyst, product yield, product oil characterization and catalyst regeneration. Finally, chapter 5 summarizes the essential and conclusion of the thesis and some useful recommendation for future work in the area of waste plastic pyrolysis for BTEX production. The appendixes and the references are provided at the end of the thesis.