CHAPTER 1
INTRODUCTION

The plastics are widely used material in the world due to their malleable properties which helps to mold into varieties of solid objects. These plastics are generally synthetic organic polymers of high molecular mass which are synthesized from petrochemicals by polymerization (Beyene, 2014; Gao, 2010; Stahel, 2016). Polymers are natural or synthetic molecules that are composed of a large number of smaller moieties and monomers which are reacted to form a long chain molecule.

One of the greatest innovations of the millennium is plastic which have certainly occupied a huge market share for their numerous applications. The major reasons for such popularity of plastics are lightweight, does not rust or rot, low cost, reusable and conserves natural resources. The plastics contain mainly carbon and hydrogen, same as hydrocarbon fuels such as diesel and petrol (Forum, 2016; Gao, 2010; Stahel, 2016). They also contain compounds such as chlorine and nitrogen (Kyaw and Hmwe, 2015). About 90 % of plastic is produced from fossil fuel i.e., hydrocarbons which costs about 6 % of the world's global oil consumption (Forum, 2016).

Polymeric materials can be classified broadly into two groups like natural and synthetic, based on their origin. However, classification based on important physical properties like elastic modulus and the degree of elongation are more useful. As per this criterion, polymers can be classified into elastomers or rubber, plastics and fibers. The elastomers or rubbers are characterized by a long-range extensibility that is almost reversible at room temperature. Plastics have only partially reversible deformability, while fibres have very high tensile strength but low extensibility. As discussed earlier, plastics are majorly used polymeric material, which is about 93 %. Whereas, consumption of rubber and synthetic fibres are only 4 % and 3 %, respectively. There are six groups of plastics (i) polyethylene, which are mainly low-density polyethylene (LDPE), linear low-density polyethylene (LLDPE) and high-density polyethylene (HDPE) (ii) polypropylene (PP) (iii) polyvinyl chloride (PVC) (iv) polystyrene which may be solid polystyrene (PS) and expandable polystyrene (EPS) (v) polyethylene terephthalate (PET) and (vi) polyutherane (PUR) (Buekens and Yang, 2014; North and Halden, 2013). The plastics have a wide variety of combinations of properties. Some are very rigid and brittle, while others are flexible, exhibiting both elastic and plastic deformations when stressed and sometimes experiencing considerable deformation before fracture. The literature survey shows that the biggest market shares belong to polyethylene among all the plastics and it is about 39 wt. %. Whereas, polypropylene, polyvinyl chloride, polyethylene terephthalate and polystyrene demands are only 27 wt. %, 17 wt. %, 8 wt. % and 4 wt. %, respectively (PlasticsEurope, 2017). Table (1.1) shows worlds plastic demand divided by different types of plastics in 2016.

Table 1.1 World plastic demand by different types of polymers in 2016 (PlasticsEurope, 2017).

Type of plastic	**Demand (wt. %)**
Polyethylene (PE)	39
Polypropylene (PP)	27
Polyvinyl chloride (PVC)	17
Polyethylene terephthalate (PET)	8
Polystyrene (PS)	4
Others	5

After consumption, most of the waste plastics are collected as municipal solid waste (MSW). Due to the huge consumptions of plastic material, a large portion of municipal solid waste (MSW) contain plastic waste and thus, disposal of MSW is one of the major problems in most developing countries. In general, about 10.67 % of municipal waste consist of waste plastics e.g., low-density polyethylene (LDPE), high-density polyethylene (HDPE), polypropylene (PP), polyvinyl chloride (PVC), polystyrene (PS) and polyethylene terephthalate (PET) (Panda et al., 2010; Pinto et al., 1999). About 50–70% of the total plastic waste is packaging materials which are derived from polyethylene, polypropylene, polystyrene, and polyvinyl chloride (Aguado et al., 2008; Passamonti and Sedran, 2012). The plastic waste has become a key component of MSW, as the plastics are durable, light weight and low-cost.

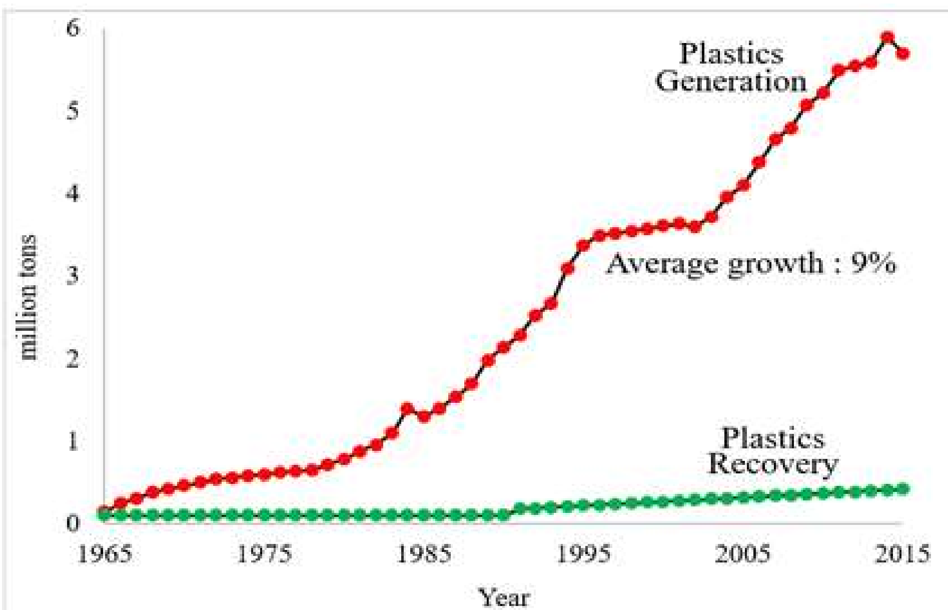

Figure 1.1 Plastics generation and recovery (Weebly, 2018).

The usage of plastics as a packaging material are mainly to keep food fresh longer duration and reduce food waste, due to their barrier properties. This has increased the global volume of plastic for packaging from 17 % to 25 % resulting from a good plastic packaging market (Forum, 2016). In India more than 7.1 Million tons per annum plastic waste is generated as per Central Pollution Control Board report in the year 2018 (C.P.C.B., 2018). Only 9-10 wt. % is recycled and remaining used for land filing. Incineration of waste plastics is not a practical and healthy solution as it emits nitrogen oxides (NOx) and sulphur oxides (SOx), which pollutes our environment. Due to improper waste plastic management, there is a huge gap between plastic generation and recovery. It is seen in the Fig (1.1) that the average growth of plastic generation is about 9 wt.%, whereas rate of plastic recovery per year is very low. World's oldest living holy city Varanasi, India is severely affected by the waste plastics. The MSW of holy city Varanasi, India contain maximum food waste of 32 wt.% followed by plastic waste of 22 wt.%, textile of 10 wt.%, paper of 9 wt.%, glass of 7 wt.% and others about 20 wt.%. Per capita MSW waste generation rate is 800 MT per day, 0.217 kg/person/day in Varanasi city (Srivastava et al., 2014). The published literature shows that plastic waste of Varanasi, India consists of highest amount of polyethylene of 41 wt.%, polypropylene of 24 wt.%, polyethylene terephthalate of 13 wt.%, polystyrene of 7 wt.%), polyvinyl chloride of 3 wt.% and others about 12 wt.% (Georgia, 2013). Thus, plastic waste is a major threat to environment and living being due to its non-biodegradability and carcinogenic properties of coloring dyes (Harding et al., 2007).

From literature survey it is clear that the four major plastic waste are PE (41 wt.%), PP (24 wt.%), PET (13 wt.%) and PS (7 wt.%), which creates huge environmental problems and ecological imbalance in Varanasi, India. As for example the waste polyethylene results in (i) water logging due to blockage in city drainage system (ii) animals mainly cow in many occasions dies as they eat PE when it thrown with food stuffs and (iii) contaminate soil and water body as PE is non-biodegradable. Polypropylene, polyethylene terephthalate and polystyrene waste in the form of plastic glasses, bottles and plates contribute to blockage of drains and gutters, are a threat to aquatic life when they find their way to water bodies, and can cause livestock deaths when the livestock consume them. Furthermore, when filled with rainwater, plastic glasses and plates becomes breeding grounds for mosquitoes, which cause malaria.

In view of this, in the thesis three types of plastic waste PE, PP and PS were considered for the study as a potential raw material to effectively and efficiently convert into value added products via pyrolysis followed by aromatization. PET and PVC were discarded as the pyrolysis of PET produces benzoic acid, which clog the condenser and vapor lines and thus, it is highly dangerous to handling such unstable system (Thorat et al., 2013). Whereas, the pyrolysis of PVC produces hazardous chlorine gas (Lopez-Urionabarrenechea et al., 2012; Lopez et al., 2011a). Pyrolysis process is preferred in small cities and town over processes like incineration due to its high acceptability and efficiently conversion of plastic waste to valuable energy products like benzene, toluene, ethylbenzene and xylene (BTEX) without any gas emissions.

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 (Smiešková et al., 2004). Thus, BTEX were chosen as a target or ideal product of the pyrolysis irrespective of types of plastic used as raw material. Since BTEX have numerous applications, like benzene is primarily used as raw material for ethyl benzene to styrene and cumene to phenol production. The third largest use of benzene is in the production of cyclohexane, a nylon precursor. Toluene, the second largest aromatic in BTEX/Hydrotreated Pygas, is used in refinery streams such as gasoline blending for improvement of octane value. Ethyl benzene is widely used in industrial processes for the manufacture of styrene, which is then used for polystyrene manufacture. Ethyl benzene is also present as a solvent in inks, dyes and in petrol. Xylene is widely used in the production of plastic bottles and polyester clothing and as a solvent with a range of applications from circuit board cleaning to thinning paints and varnishes. Xylene may either be used in refinery streams for gasoline blending or further separated by isomers for chemical applications (Gaurh and Pramanik, 2018a; Gaurh and Pramanik, 2018b; Thongplang, 2016).

Pyrolysis may be purely thermal or catalytic process. In thermal pyrolysis of plastic, no catalyst is used with the feed. Only at high temperature in absence of oxygen plastics/polymers are decomposed to get random product molecules. The catalytic pyrolysis of plastic is a chemical conversion technique that involves breakdown/decomposition of polymers to recover useful products via appropriate route (Malkow, 2004; Shent et al., 1999).

Almost all the reported research work on plastic waste pyrolysis are either thermal or catalytic. No research work on pyrolysis of waste plastic and in-situ multiphase aromatization of lighter hydrocarbon have been reported till date. Thus, in this thesis, multiphase catalytic pyrolysis of selected raw material i.e., waste plastic PE, PP and PS were considered to get better aromatization in both liquid and vapor phase, which could give highest aromatic yield BTEX. The multiphase pyrolysis and multiphase aromatization need two types of reactor arrangement. In the first type, the catalyst could be placed in liquid phase and vapor phase both using a specially design reactors. This has been reported as multiphase catalytic pyrolysis (Gaurh and Pramanik, 2018a). Multiphase catalytic pyrolysis enhances the product quality with the increase in product yield of BTEX due to selective cracking and better aromatization in both liquid and vapor phase. The second type of arrangement may be the combination of thermal and catalytic pyrolysis to improve the product yield and quality as that of multiphase catalytic pyrolysis as mentioned above. In this arrangement liquid phase involves purely thermal pyrolysis followed by catalytic pyrolysis in vapor phase.

The catalyst is one of the most active compounds in the catalytic pyrolysis. Generally, silica-alumina (Si/Al) based ZSM-5 is widely used catalyst in cracking, isomerization and aromatization of large hydrocarbon molecules due to their excellent catalytic properties, thermal stability and acidity (Gaurh and Pramanik, 2018a; Lopez et al., 2011a**)**. The widely used and recommended commercial catalyst is ZSM-5 for the selective catalytic cracking of high molecular petroleum products and different types of plastics/polymers e.g., polyethylene (PE), polypropylene (PP) and polystyrene (PS). However, commercial ZSM-5 is costly which will add cost to the entire process of manufacturing valuable hydrocarbon products like BTEX.

Apart from ZSM-5, so far many articles have been published on catalytic conversion of different types of plastics and polymer to have different types of products mainly valuable chemicals and fuel range hydrocarbon using different types of catalyst. The catalysts tested are red mud (Lopez et al., 2011a), FCC (Lee, 2009), ZSM-5 (Gaurh and Pramanik, 2018a; Lopez et al., 2011a), HZSM-5 (Hernandez et al., 2007; Marcilla et al., 2006; Mordi et al., 1992), $Ca(OH)_2$ (Sarker and Zaidi, 2011), H-mordenite (Mordi et al., 1992), Y-zeolite (Lee, 2012) , Fe_2O_3 (Sarker and Rashid, 2013), Al_2O_3 (Sarker and Zaidi, 2011), natural zeolite (Miandad et al., 2017; Syamsiro et al., 2014), H-theta-1 (Mordi et al., 1992), MCM-41 (Aguado, J et al., 1997; Marcilla et al., 2006; Obalı et al., 2012b), Zeolite beta (Aguado et al., 2000), SAPO-34 (Park et al., 2010), Fe/HZSM-5 (Alyani et al., 2011) and SBA-15 (Obalı et al., 2012a).

It is clear from the above literature survey that there is a still scope of manufacture catalyst from many natural solid wastes for the catalytic pyrolysis of plastic wastes mainly PE, PP and PS as they are extensively used in today's daily life. The pyrolysis of waste plastics in a multiphase reactor is still in the developing stage. Almost no studies on such reactor using waste plastics PE, PP and PS are found in the open literature. Although quite possible that the development work on the pyrolysis of waste plastics using different types of reactor is being carried out, but their detailed studies on various operating parameters are not reported in the present literature to protect/intellectual property right. Thus, considerable research work is still required regarding reactor design, catalyst developments and performance of the process. In this context, this thesis work focuses on the utilization of waste materials fly ash as catalyst for the production of BTEX using multiphase catalytic pyrolysis of plastic wastes polyethylene or polypropylene or polystyrene in a specially designed reactor.

The thesis chapters are 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.