CHAPTER 1
INTRODUCTION

Presently, global warming has become one of the major concerns across the globe as it is a global threat for the survival of living beings. Excessive use of fossil fuels mainly coal, petroleum and natural gas (Mittal and Kumar, 2014) which release the harmful gases e.g., carbon dioxide (CO_2), carbon monoxide (CO), methane (CH_4), nitrogen oxides (NO_x), sulphur oxides (SO_x), and hydrocarbon vapours in the atmosphere. All these pollutants are responsible for many critical dieses of human beings such as CO_2 affects the oxygen movement in blood stream, CO causes headache (Dhall et al., 2021), high concentration of methane causes nausea (Samudro et al., 2022), No_x are responsible for the cardiovascular sickness (Dhall et al., 2021). The prolonged exposure of SO_x affects the heart and lungs (Samudro et al., 2022). Some pollutants like NOx, CO_2 and CH_4 cause global warming and thus, minimizing the emission of such harmful pollutants by reducing consumption of fossil fuels using some alternative fuel could be a good option (Zhao et al., 2022). Apart from pollution problem, its limited reserves and uncertainty in supply are some valid reasons which have motivated world researchers to think on alternative fuels. In India, coal, petroleum and natural gas are primarily used as fossil fuels. Where, coal is mainly used for electricity generation in thermal power plants (Kumar et al., 2019). Majority of petroleum fuel is used for road transportation, rail transportation, shipping, and aviation sector (Ramachandra and Shwetmala, 2009). Whereas, natural gas is consumed in the road transportation and fertilizers sectors, in large amount (Reddy and Venkataraman, 2002).

The globalization has increased the transportation via railways, road, shipping, and airways. Moreover, the economic growth of the particular region is mainly depends on the roads, railways, water and air connectivity. These transportation sectors mainly consume the petroleum products as a fuel, which are the major contributor of green-house gases (GHG) (Ramachandra and Shwetmala, 2009). Only road transportation is responsible for the 80 % emission of GHG (Ramachandra and Shwetmala, 2009). Apart from the transportation sector, the petroleum products or petrochemicals are also used as raw material for other products manufacturing. Approximately 4 % of the world petroleum production is directly converted into different types of plastics such as high density polyethylene (HDPE), low density polyethylene (LDPE), polypropylene (PP), and polystyrene (PS) (Ziad et al., 2021). All these plastics are the major contributor of waste in municipal solid waste (MSW) because of their non-biodegradable nature (Dwivedi et al., 2019). Thus, the management of waste plastic is very much important by using proper plastic waste management technique.

The commercial production of plastics started around in the year of 1950 and it is increasing year by year. The global annual production of plastic was 330 million tons in 2016 (Lebreton and Andrady, 2019). Whereas, about 359 million tons of plastic was produced in 2018 (Ziad et al. 2021). Figure 1.1 shows the growth in global yearly production of plastic.

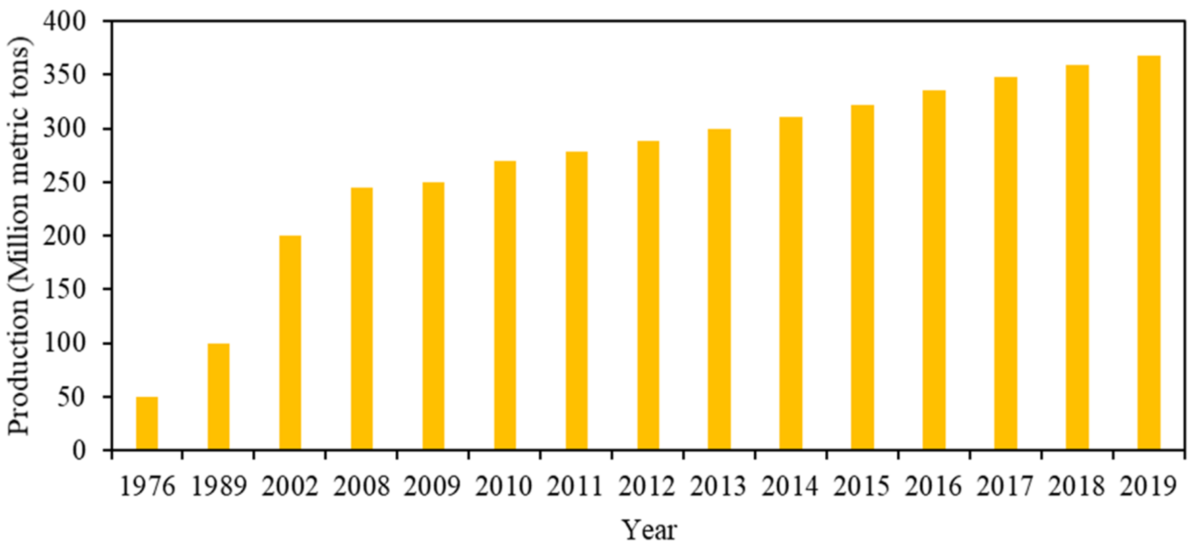

Figure 1.1 Growth in global plastic production (Statista, 2022).

The plastics are used for different types of products manufacturing due to excellent properties such as light weight, durability, low density, corrosion resistance, and high strength (Tulashie et al., 2019; Grigore, 2017). The high production of plastic products leads to accumulation of waste due to its non-biodegradable nature (Dwivedi et al., 2019). It is estimated that there will be 12000 million metric tons of waste plastic on the earth by 2050 if current trend in plastic consumption persists (Chen et al., 2020).

As per ASTM D883 80c standard, plastics are classified in two groups: (a) thermoplastics and (b) thermosets (Alauddin et al., 1995). Thermoplastics are long chain carbon molecules which are independent from each other (Zheng et al., 2005). Thermoplastic can change their state at glass transition temperature (Tg). Thus, thermoplastics can reshaped and recycled via temperature manipulation (Wang et al., 2021) such as polyethylene-terephthalate (PET), low density polyethylene (LDPE), high density polyethylene (HDPE), polyvinyl chloride (PVC), polypropylene (PP), and polystyrene (PS). Whereas, thermoset plastics have three dimensional crossed linked structure such as bakelite and melamine (Zheng et al., 2005) which cannot be recycled to manufacture mouldable new products after first use (Wang et al., 2021).

About 80 % of consumed plastics are thermoplastics, mainly used as packaging material for industrial and domestic goods and 50 % of thermoplastics are in single-use applications. About 20 % to 25 % are used in long-term infrastructures like pipes, cable coatings, and structural materials (Kazemi et al., 2021). Thus, plastic waste consist of different thermoplastic products those are predominantly made from low density polyethylene (LDPE), high density polyethylene (HDPE), polypropylene (PP), polystyrene (PS), polyvinyl chloride (PVC) and polyethylene-terephthalate (PET).

In India, municipal solid waste (MSW) is composed of 51 % biodegradables wastes, 32 % plastic wastes, 7 % paper wastes, and 10 % other wastes such as textile, metal, glass, drain, street sweepings, and silt (Usmani et al., 2020). The composition analysis of MSW shows that the, plastic is the second largest contributor of solid waste which is non-biodegradable. Among all plastic wastes waste expanded polystyrene (WEPS) contributes around 10 wt.% of the total plastic waste. Surprisingly, by volume, it could be 40 % of the total discarded plastics and thus, occupy more space (Adnan et al., 2014). The WEPS is non-biodegradable, highly mobile and escapes from garbage bins and landfills, litters the streets, or ends up polluting water bodies. Tiny expanded polystyrene globules could be orally consumed by animals, leading to choking or intestinal obstruction (Ramanan et al., 2018). The EPS is one of the major post-consumer waste product because of its poor recycling rate (Uttaravalli et al., 2020). Landfilling by WEPS may cause damage to the future construction e.g., cracks to roads and building etc (Verma et al., 2021). Upon incineration of WEPS, it releases harmful polyromantic hydrocarbons (Chaukura et al., 2016). Thus, waste expanded polystyrene waste (WEPS) has caused a major concern due to its heavy amount of disposal by the industries and as domestic waste with large bulk volume, which causes environmental pollution called ‘‘white pollution” (Verma et al., 2021). In this context, proper utilization of WEPS using sustainable and effective waste management technique is the primary need in the present time (Verma et al., 2021).

There are various recycling strategies are used to reduce the WEPS such as primary recycling, secondary recycling, tertiary chemical recycling, and quaternary incineration (Huang et al., 2022). Primary recycling is referred to the recovery of uncontaminated scrap plastic for re-use in similar applications. It is low cost and it has many drawbacks like a limited number of re-use cycles and restriction to industrial materials with minimal contaminations (Lee and Liew, 2021). Secondary recycling is transformation of material by mechanical means. Although, mechanical processing faced significant challenges on the complicated sorting/pretreatment processes (Huang et al., 2022). If the plastic waste is more complex and contaminated then it is more difficult to recycle it mechanically (Salem et al., 2009). Tertiary recycling of waste plastic focuses on the recovery of monomers, fuels and chemicals, resulting in a lower carbon footprint. On the other hand, quaternary recycling/incineration is considered as a linear economy approach where the material is not recycled back to value-added products. Additionally, incineration produces considerable amount of CO_2 emission and other contaminants such as NOx, dioxins and solid particulates. Thus, tertiary recycling is an economically and environmentally feasible way to convert waste plastics into value added products obtained via various thermochemical processes such as pyrolysis, reforming, gasification and chemolysis (Huang et al., 2022). Among these methods, pyrolysis is the best way to manage the plastic waste due to its various advantages over the other thermochemical recycling methods. The pyrolysis is defined as the degradation of organic materials under the effect of heat and in the absence of oxygen (Qureshi et al., 2020). The pyrolysis converts waste plastic into high value added products like pyrolysis oil, pyrolysis gas, and carbonaceous solid residue (Miandad et al., 2019). The liquid oil and gaseous yield are having high calorific value and thus, they are used as fuel (Kasar et al., 2020). The pyrolysis oil obtained from plastic waste has a wide range of applications as a fuel in furnaces, turbines, boilers, and diesel engines without any further treatment (Maffa, 2021). Furthermore, pyrolysis gas can be used for electricity generation in gas turbines or direct firing in boilers without any flue gas treatment (Sharuddin et al., 2016).

The solid residue obtained from plastic waste pyrolysis is very low amount and it may be used as fuel, as an adsorbent and or even as a soil amendment (Lara et al., 2021).

Figure 1.2 shows various applications of pyrolysis products obtained from WEPS pyrolysis i.e., pyrolysis oil, pyrolysis gas and residue. The pyrolysis process can be performed thermally without catalyst or in the presence of catalyst. The non-catalytic or purely thermal pyrolysis does not employ any catalyst and thus, it requires high temperature in comparison to catalytic pyrolysis. Whereas, catalytic pyrolysis is carried out in the presence of catalyst for the production of selective products relatively low temperature than thermal process (Dwivedi et al., 2019). However, in the catalytic pyrolysis, gaseous fraction is enhanced and the liquid oil yield get reduced in comparison to the thermal pyrolysis (Miandad et al., 2016).

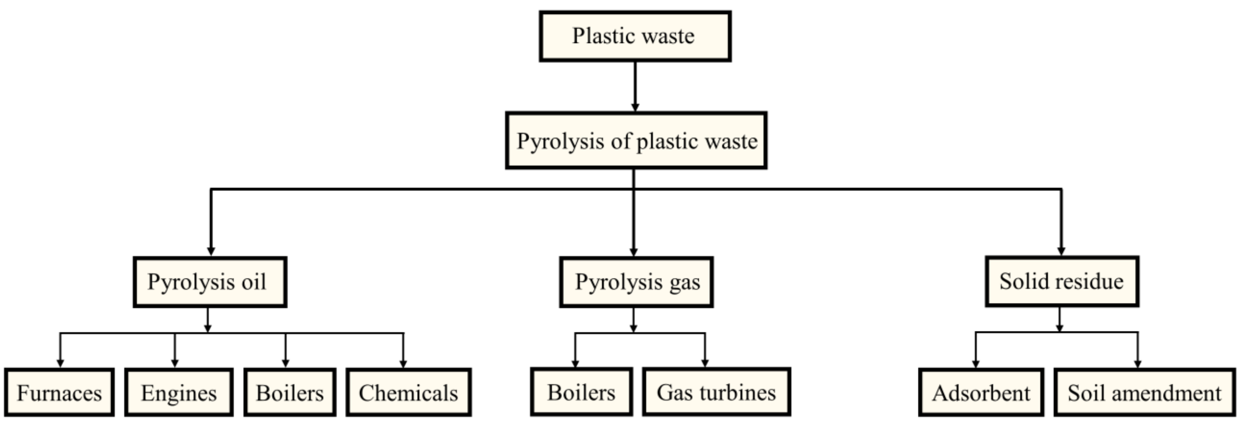

Figure 1.2 Applications of pyrolysis products.

Thus, pyrolysis was selected as an alternative economically viable and non-polluting or less polluting method for the conversion of WEPS into value added products. It is seen from the literature that most of the studies on polyethylene (PE) and polypropylene (PP) pyrolysis are based on the catalytic process as it directly gives fuel range paraffinic and aromatic hydrocarbons in a simple liquid phase reaction using batch or semi-batch type of reactor (Verma et al., 2022).

The major drawback with polystyrene (PS) is that, the thermal pyrolysis of PS mainly produces monomer styrene (84.74 wt.%) (Verma et al., 2021) and derivative of styrene in the pyrolysis oil (Achilias et al., 2007).

The styrene is very toxic in nature and it cannot be used as fuel component because of its auto polymerization tendency (Park et al., 2020). Additionally, the styrene has no major use in other products manufacturing except polystyrene. Thus, reduction of styrene and enhancement in valuable products like benzene, toluene and ethylbenzene (BTE) in the pyrolysis oil is very much essential using a specially designed semi-batch reactor via *in-situ* secondary cracking of product styrene. The benzene, toluene, ethylbenzene (BTE) were considered as major products of the pyrolysis of WEPS because, they have fuel value or can be used as raw material for the production of some other value-added chemicals. The valuable aromatics BTE is used for enhancing the octane rating of gasoline (Verma et al., 2022) and also found in diesel fuel. In addition, benzene has been used widely as a solvent in the manufacture of industrial chemicals, shoe manufacturing, in adhesives, and in the printing industry (Capleton and Levy, 2005). However, it is a minor component of gasoline (Capleton and Levy, 2005). The benzene quantity in gasoline is limited to <1 wt.% to avoid soot formation (Verma et al., 2021). Toluene is an aromatic hydrocarbon is used in the production of various industrial chemicals such as benzene, toluene diisocyanate, phenol, benzyl and benzoyl derivatives, benzoic acid, toluene sulfonates, nitrotoluenes, vinyl toluene, and saccharin and also used as a solvent for paints, lacquers, and adhesives (Donald et al., 1991). Ethylbenzene is primary used for the production of styrene. In addition, it has many minor uses including as a paint solvent, in the semi-conductor industry and as a general solvent. It is also found in paints, lacquers, printing inks, insecticides and solvents (Henderson et al., 2007). Thus, the production of these valuable aromatics BTE from a specially designed reactor would obviously reduce the WEPS disposal effectively. Nevertheless, this developed process would be helpful in saving the fossil fuel to some extent along with the improvement in IC engine performance due to the presence of toluene and ethylbenzene in the product fuel.

The styrene is considered as an undesired aromatic as it is very toxic in nature and not a fuel component. However, significant amount of styrene (47.96 wt.%) was found in pyrolysis oil obtained from WEPS pyrolysis (Adnan et al., 2014). Thus, after separation, it can be mainly used for the production of various resins such as polystyrene, acrylonitrile butadiene styrene (ABS), styrene-butadiene rubber (SBR) etc. Styrene is highly reactive, and it can polymerize rapidly, with the possibility of violent explosions if uncontrolled. Therefore, it is necessary to add polymerization inhibitors for transport and storage of the styrene monomer (Miller et al., 1994).

It is already discussed, that the pyrolysis of polystyrene is very challenging as it produces styrene as a major product when a purely thermal process is performed. In the view of this, selection of catalyst is also very important for the pyrolysis of WEPS to produce target aromatic hydrocarbons BTE. However, many experimental studies suggested that, the pyrolysis of PS in the presence of heterogeneous base catalysts such as BaO (Achilias et al., 2007; Ukei et al., 2000), Mg, MgO, $MgCO_3$ (Shah et al., 2014), CaO, K_2O (Zhibo et al., 1996) are more selective towards the formation of styrene and even higher than the thermal pyrolysis. Whereas, relatively higher yields of benzene, toluene, and ethylbenzene (BTE) are observed in the presence of solid acid catalysts (Soni et al., 2021) such as Nb_2O_5 and NiO/Nb_2O_5 (Amjad et al., 2022), CuO (Nisar et al., 2020), NiO/ZrO_2 (Amjad et al., 2021), silica-alumina (Moqadam et al., 2014), ZSM-5, Y-zeolite (Williamsn and Bagri, 2004), used FCC (Abadi et al., 2014). The acid catalyst reduce the styrene content due to secondary reactions such as hydrogenation and cracking that take place to a greater extent in presence of such catalysts. Due to this reason why styrene yield is usually lower in catalytic pyrolysis oil compared to thermal pyrolysis of polystyrene pyrolysis (Lopez et al., 2011a).

Recently, the focus has shifted to clay catalysts because of their low cost. The low cost catalyst for the pyrolysis process is a key factor for determining the economy of catalytic process because, in a continuously operating plant, it is necessary to have a large amount of catalyst (Maffa, 2021). The clays are mesoporous catalysts used in various organic reactions such as hydrogenation, alkylation, acylation, isomerization, etc (Zhou, 2011). Clays can be used as acidic catalysts in their natural form due to Bronsted and Lewis acidic sites (Nagendrappa, 2002). Structurally, clays are crystalline hydrous alumino-silicates and also contain various other cations (Nagendrappa, 2002). The clay based catalyst can be considered as a green and low-cost catalyst for waste plastics because they are non-toxic and have no disposal problem. As per literature, various commercial grade clays such as sepiolite (Marcilla et al., 2005), kaoline clay (Panda and Singh, 2011), and bentonite (Soliman et al., 2022) were used for the pyrolysis of waste plastics. However, the catalytic degradation of polystyrene using various clays such as natural sepiolite (Jin et al., 2012), bentonite (Parasuram et al., 2013), halloysite clays (Tae et al., 2004), albite and montmorillonite (Cho et al., 2007) have already been examined. It is also reported in the literature, that the clays shows selectivity towards the benzene, toluene and ethylbenzene rather than styrene because of their acidic nature.

Thus, in the present work, catalyst was synthesized from natural red clay as it is rich in silica and alumina like any other natural clay like bentonite (Kyaw and Hmwe, 2015), and kaoline (Gandidi et al., 2018) for the BTE production and styrene reduction via catalytic pyrolysis of WEPS. Two commercial catalysts i.e., ZSM-5 ammonium powder and Nickel on silica-alumina were also used for the catalytic pyrolysis of WEPS and performance comparison with natural red clay synthesized catalyst with commercial catalyst in terms of product yield and BTE content.

Not only the catalyst, the catalyst contact mode also affects the product yield and product composition. In view of this, three different types of catalyst contact modes were considered within the reactor for each type of catalysts viz liquid phase/A-type, vapour phase/B-type and multiphase/AB-type. The details of reactor arrangements for catalytic pyrolysis are discussed in experimental section (page no. 48). Apart from type of catalysts and reactor arrangements, various effective parameters also control the product yield and product composition.

It is seen from the through literature study, although various researches are being carried out on the pyrolysis of polystyrene using various types of commercial and natural catalysts. The detailed information are not being published due to the intellectual property rights. In this perspective, in the present thesis the thorough research work was carried out for the production of valuable aromatics benzene toluene and ethylbenzene (BTE) via multiphase catalytic pyrolysis of waste expanded polystyrene (WEPS).

Various pyrolysis parameters such as temperature, heating rate, and feed-to-catalyst ratio were optimized using ZSM-5 ammonium powder, Nickel on silica alumina, and low-cost red clay catalyst to achieve the highest liquid yield with high BTE content and reduce styrene. Furthermore, the effect of different reactor arrangements that is, liquid phase, vapour phase, and multiphase have been examined to determine the best reactor arrangement for the production of pyrolysis oil, rich in valuable aromatic hydrocarbons benzene, toluene and ethylbenzene (BTE). There is no doubt that such type of detailed investigation on the pyrolysis of WEPS in specially designed laboratory scale semi-batch reactor using above mentioned catalysts is innovative in nature.

The thesis chapters are described below in brief. Chapter 1 describes the general idea about the present scenario of plastic consumption, plastic waste, pyrolysis process, various catalysts used in pyrolysis process. Literature review and research objectives are discussed in Chapter 2. Chapter 3 describes the experimental details related to the pyrolysis process such as raw materials, experimental setup, synthesis and characterization of catalyst, characterization of pyrolysis oil, and studies on catalyst regeneration. Chapter 4 describes the optimization of effective process parameters using RSM-BBD technique for multiphase catalytic pyrolysis. Results and discussion related to the catalyst characterization, product yield, product distribution, process optimization and catalyst regeneration are discussed in the Chapter 5. Chapter 6 summarizes the conclusions and recommendations for the future work for the pyrolysis process of WEPS for BTE production. The references and appendixes are provided at the end of the thesis.