CHAPTER 2

LITERATURE REVIEW AND OBJECTIVES

In this chapter, literature review and all aspects on production of BTEX from waste polyethylene (PE), polypropylene (PP) and polystyrene (PS) as raw material have been discussed systematically. This chapter-2 is divided into several parts which covers raw materials mainly pyrolysis feedstock, catalyst material, catalyst characterization, pyrolysis product characterization, pyrolysis reactor type/ design, pyrolysis process, aromatization and effect of different process parameters on product yield benzene, toluene, ethylbenzene, xylene (BTEX). Based on detailed literature review, the objectives of the thesis are finalized.

2.1 Literature review

2.1.1 Raw materials

Raw materials are classified into two major classes (i) Pyrolysis feedstock and (ii) catalyst materials which are discussed in this section below.

2.1.1.1 Feedstock waste plastics

Feedstock selection is very crucial step for BTEX production using pyrolysis followed by aromatization. The global report on municipal solid waste (MSW) reveals that the polyethylene (PE) contributes highest amount of 39 wt. % followed by polypropylene (27 wt. %), polyvinyl chloride (17 wt. %), polyethylene terephthalate (8 wt. %) and polystyrene (4 wt. %) (PlasticsEurope, 2017). Apart from the world report on MSW and its composition, the similar published report of Varanasi city, India was thoroughly studied (Srivastava et al., 2014). The detailed study shows that the MSW of Varanasi city is a good source of waste plastic which could be converted to valuable chemicals via thermochemical

process/pyrolysis. There are certain criterion which must be followed for the feedstock selection for pyrolysis and aromatization like availability, suitability to decompose or breakdown to smaller molecules and should be non-hazardous. The availability of such feedstock could be found in municipal solid waste as discussed in Introduction (page no.2).

Table 2.1 Types of waste plastics and their suitability for pyrolysis process.

Types of plastic	**Suitability for pyrolysis**	**Remarks**	**References**
Polyethylene (PE)	Very good for pyrolysis	(i) Required temperature is high (T>500 ^{o}C) (ii) In thermal pyrolysis it converts into wax instead of liquid oil.	Lee, (2012), Miskolczi et al., (2009)
Polypropylene (PP)	Very good for pyrolysis	(i) Required temperature is high. (ii) Produces high aromatic compounds in catalytic pyrolysis.	Miskolczi et al., (2009)
Polystyrene (PS)	Very good and gives excellent fuel properties	(i) Low temperature required (ii) Produces less viscous oil as compared to PP and PE	Lee (2009), Siddiqui and Redhwi (2009)
Polyethylene terephthalate (PET)	Not suitable	(i) Produces Benzoic acid	Thorat et al., (2013)
Polyvinyl chloride (PVC)	Not suitable	(i) Produces hazardous chlorine gas	Lopez et al., (2011a), Lopez-Urionabarrenechea et al., (2012)

Table (2.1) shows the different type of waste plastic and their suitability for pyrolysis process. The result in Table (2.1) indicates that the waste plastics viz PE, PP and PS are most likely the best material for the production of pyrolysis oil using pyrolysis process. The polyvinyl chloride (PVC) and polyethylene terephthalate (PET) are discarded here as

pyrolysis of PET produces benzoic acid and PVC produces hazardous chlorine gas thus it is not eco-friendly. From the above discussion, it is clear that the PE, PP and PS could be recommended as a feedstock material for pyrolysis process.

Polyethylene (PE) are of different types, as discussed in the Introduction section (page no. 2). High-density polyethylene (HDPE) is a stiff plastic used for more robust plastic packaging like laundry detergent containers as well as for construction applications or trash bins. HDPE has a long linear polymer chain with low branching and high degree of crystallinity which gives high strength. Due to its high strength, HDPE is broadly used in manufacturing of toys, oil containers, detergent bottles and milk bottles etc. Low-density polyethylene (LDPE) has weaker intermolecular force, low tensile strength and hardness due to more branching than HDPE. Moreover, LDPE has better ductility, less crystalline and easily molding properties than HDPE. It is commonly used in the manufacturing of plastic bags, wrapping foils for packaging, trash bags and many such items. The waste LDPE is second the largest plastic waste in MSW due to its huge consumption in daily life (Michael, 2010). Thus, pyrolysis of the waste LDPE has received more attention by many researchers (Aguado et al., 2007; Bagri, R. and Williams, P.T., 2002; Marcilla et al., 2009; Onwudili et al., 2009; Uddin et al., 1997) than HDPE as it is found in large quantity in MSW as solid non-biodegradable waste, produces better quantity of oil and easy to recover energy.

Polypropylene (PP) is a thermoplastic polymer which is produced via chain-growth polymerization from the monomer propylene. Polypropylene has a good chemical and heat resistance. The melting point of PP is 160 ^{o}C and the density is lower than polyethylene. However, polypropylene has higher hardness and rigidity in comparison to other plastic materials. All these properties make PP preferable in plastic industry. The miscellaneous applications of PP include storage boxes, office folders, disposable glasses, buckets, car

bumpers, carpets, furniture, container etc. There is significant increase in PP waste due to high demand of PP in our daily life and thus, pyrolysis of PP could efficiently be converted to valuable liquid range hydrocarbons consisting of BTEX. Jung et al., (2005) has shown that BTX yield in the oil increases with the increase in reaction temperature. Ma et al., (2015) stated that PP pyrolysis gives higher aromatic yield i.e., toluene, ethyl benzene, styrene and many other compounds in comparison to other plastic waste. Several researchers have investigated different parameters to characterize the liquid oil yield for the PP pyrolysis (Ahmad et al., 2015; Demirbas, 2004; FakhrHoseini and Dastanian, 2013; Sakata et al., 1999).

Polystyrene (PS) is made of styrene monomers obtained from the liquid petrochemical. Polystyrene is a synthetic aromatic hydrocarbon polymer made from the monomer styrene. Polystyrene can be solid or foamed. General-purpose polystyrene is clear, hard, and rather brittle. It is an inexpensive resin per unit weight. The structure consists of a long hydrocarbon chain with phenyl group attached to every other carbon atom. PS has properties such as; heat resilience, durability, strength and lightness. PS is commonly used in disposable glasses and plates, food packaging, electronic items, medical, appliances and toys. As the polystyrene is non-biodegradable and hazardous material thus the suitable way to convert waste PS is pyrolysis process (Demirbas, 2004; Filip et al., 2013; Lee et al., 2002; Liu et al., 2000; Onwudili et al., 2009; Shah and Jan, 2014) which gives valuable hydrocarbon as obtained in the case of polyethylene and polypropylene.

In this context polyethylene, polypropylene and polystyrene are found suitable for pyrolysis process followed by aromatization to obtain valuable product benzene, toluene, ethylbenzene and xylene (BTEX).

2.1.1.2 Catalyst material

The main role of the catalyst in the pyrolysis process is to speed up the chemical reaction, however catalyst itself should remain unchanged towards the end of the process. Catalysts are commonly used for the optimization of product distribution and to increase the product selectivity in a chemical process and product manufacturing. In some product manufacturing such as commercial fuels diesel, kerosene, gasoline and C2–C4 olefins, which have a huge demand in petrochemical industry, catalytic degradation is particularly interesting (Elordi et al., 2009). The rate of reaction increases or speeds up due to decrease in activation energy of the process on using catalyst. Thus, catalyst reduces the optimum temperature required and this is very crucial since the pyrolysis process requires high energy due to high endothermicity that hinders its commercial application. The usage of catalyst may help in saving energy as heat generation is one of the most expensive in industry. Besides that, catalyst has been also tried by many researchers for product upgrading via cracking, aromatization and isomerization to improve the hydrocarbon distribution in order to obtain pyrolysis liquid that had similar properties to the conventional fuel such as gasoline and diesel (Sharuddin et al., 2016). The commonly used catalyst material for pyrolysis, aromatization and isomerization are silica-alumina (SiO_2/Al_2O_3) based ZSM-5. The other catalysts are solid acid catalysts which are used in plastic waste pyrolysis include molecular sieves, such as silica alumina (Karagöz et al., 2003; Kim and Kim, 2004; Luo et al., 2000; Sakata et al., 1999), zeolites (Anders et al., 1990; Corma et al., 1985; Manos et al., 2000; Mordi et al., 1994), and MCM-41 (Aguado, J. et al., 1997; Marcilla et al., 2003; Pierella et al., 2005). Amongst the numerous kinds of zeolites investigated in polyolefin pyrolysis, Beta (Anunziata and Pierella, 1999), USY (Arthur et al., 1999), ZSM-11 (Pierella et al., 2005), REY (Songip et al., 1993, 1994), FCC (Degnan, 2000; Habib Jr et al., 2002; Prasad and Singh, 2011), Mordenite (Mordi et al., 1994; San

You et al., 1999), ZSM 5 (Mastral et al., 2006; Seo et al., 2003) are the most commonly used. Other catalytic materials such as clays (montmorillonite, saponite) (Manos et al., 2001), reforming catalysts, activated carbon, metal oxides, metal complexes of the type $M(AlCl_4)_n$ (M = Li, Na, K, Mg, Ca, Ba; n = 1,2), and alkali metal carbonates or alkaline metal carbonates have also been tested for polymer degradation (Buekens and Huang, 1998). The common features shared by the different zeolite catalysts are proper acid strength, pore size and pore structure. Generally, the level of the catalyst activity in polyolefin pyrolysis increases with increasing number of acid sites (Ohkita et al., 1993). The product distribution of the catalytic degradation of high-density polyethylene on different zeolites yields hydrocarbons from C3 to C15. The structure of the zeolitic framework has shown a significant influence on the product distribution. ZSM-5 showed the highest catalytic activity on cracking of heavy hydrocarbons to small gaseous hydrocarbons and formation of aromatics (Mastral et al., 2006; Seo et al., 2003). Pyrolysis of waste plastics using ZSM-5 yields greater percentage of gaseous products than oil. This extraordinary yield is explained due to a strongly acidic property and a unique larger intra crystalline pore channel structure of ZSM-5 which helps in excellent catalytic efficiency on cracking, isomerization and aromatization. The larger intra crystalline pore channel structure allows more cracking of the heavy petroleum chemicals. In addition, ZSM-5 possesses a smaller pore diameter (5.4–5.6A˚) among zeolites. Since, the initially degraded materials on the external surface of catalyst can be dispersed into the smaller internal cavities of catalyst, the degraded molecules can be further breakdown to the smaller size of gaseous hydrocarbons, leading to the remarkably high gas yield (Mastral et al., 2006). Thus, the commercial ZSM-5 catalyst can be used as a suitable catalyst material for the production of valuable hydrocarbon such as BTEX from waste plastics PE, PP and PS (Gaurh and Pramanik, 2018a).

There is a scope of manufacture catalyst from many natural solid wastes for the catalytic cracking of plastic wastes as only few natural catalysts are used for pyrolysis process such as natural zeolite (NZ) (Miandad et al., 2017; Syamsiro et al., 2014), Red Mud (Lopez et al., 2011a). Activated carbon catalysed plastics cracking yield normal alkanes and the amount of iso-alkanes is very small. When Pt impregnated on activated carbon was tested, the aromatic yield is reported to reach as high as 50 % of the plastic sample and it was suggested that this is due to a good combination of cracking and dehydrocyclization activities of the catalyst (Balakrishnan and Guria, 2007). 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 cracking of waste plastics due to its uncontrolled and excessive use. In this context, hazardous solid waste of thermal power plant i.e., "fly ash" could be used as catalyst material which is rich source of natural silica and alumina those are trapped in the fuel coal from its origin.

Table 2.2 Country wise fly ash production and utilization (Ram and Masto, 2014).

Country	Year	FA generation (million tons)	FA utilization (million tons)	FA utilization (wt. %)
India	2010-11	131.9	73.13	55.79
China	2010	480	321.6	67.0
USA	2011	59.9	22.98	38.36
Australia	2008	14.50	4.584	32.0
Japan	2006	10.96	10.65	97.2
Canada	2007-08	6.087	1.881	31
Israel	2012	1.445	1.359	94.05
Germany	2010	15.26	15.26	100
Turkey	2012	24.0	2.4	10

Fly ash is the main combustion by-product of coal fired power plants and huge amount of fly ash is produced by the almost all developed and developing countries as reported by Earth science reviews (Ram and Masto, 2014) (Table 2.2). Unfortunately, more than half of fly ash is disposed of in land filling because it finds no other suitable and economical application. The huge production of fly ash is extremely worrying because of the unplanned disposal. In India, fly ash (FA) is being generated at the rate of nearly 132 million tonnes per annum (MTPA) from thermal power plants in 2011-12 (Table 2.2).

There are serious environmental health hazards associated with fly ash. In addition, the land requirement envisaged for disposal of fly ash is about 50,000 acre, with an annual expenditure of about Rs. 500 million for transportation. These problems clearly spell out the fact that utilization of fly ash is absolutely essential. As a consequence, several investigations have been carried out in order to exploit this waste material into value added material. Over the last few years, fly ash has been gaining ground in finding solutions to environmental problems using it as an active ingredient in cement manufacturing and brick making, which is not sufficient (Table 2.3) (GOI, 2016).

Table 2.3 Fly ash utilization in India 2015-16.

Mode of fly ash utilization	**Amount (wt. %)**
Cement	41.97
Bricks and Tiles	12.85
Reclamation of low laying area	11.21
Mine filling	10.91
Ash dyke raising	7.67
Others	7.32
Roads and flyovers	4.87
Agriculture	2.15
Concrete	1.00
Hydro power sector	0.04

Due to unique composition of fly ash (Malik et al., 2016) i.e., quartz, mullite, subordinately hematite and magnetite, carbon, and a prevalent phase of amorphous aluminosilicate (Bayat, 1998; Hall and Livingston, 2002; Hower et al., 1996; Koukouzas et al., 2006; Kukier et al., 2003; Mishra et al., 2003; Sokol et al., 2000) makes fly ash an important source material in zeolite synthesis. Thus, fly ash has been chosen for catalyst synthesis for the production of valuable products BTEX via pyrolysis of waste PE, PP and PS.

2.1.2 Catalyst characterization

Detailed studies related to the catalyst shows that catalyst plays vital role in pyrolysis process for the production of BTEX. Therefore, catalyst characterization is also important to know its stability, particle size, morphology, textural properties and acid strength for the process. Many researchers have used different characterization techniques such as X-Ray Diffraction (XRD), Fourier Transformed Infrared Spectroscopy (FTIR), Brunauer-Emmett-Teller (BET) and Scanning Electron Microscope/ energy dispersive X-ray spectroscopy (SEM-EDX) for catalyst characterization. Tamizhdurai et al., 2018 used XRF, XRD, BET, FT-IR, HR-SEM, HR-TEM and NH_3-TPD analyses to evaluate the particle structure, size and acid strength of ZSM-5 catalyst and suggested that ZSM-5 zeolite catalysts have excellent catalyst activity. Nabavi et al., 2019 evaluated the stability of colloidal ZSM-5 catalyst by SEM, XRD, NMR and NH_3-TPD and showed that the framework of crystals synthesized in fluoride media was more stable than the framework of crystals synthesized. Hamidzadeh et al., 2018 proposed a new, simple and cheap procedure to synthesize the ZSM-5 zeolite with high purity and characterized it by XRD, BET, FT-IR, FE-SEM, NH_3-TPD and TG-DTA. Qiao et al., 2019 studied the pore characteristics, crystallinity, morphology and acidity of the ZSM-5 zeolites by XRD, SEM, TEM, N_2-adsorption, Al MAS NMR and NH_3-TPD. The phase analyses of the alumina fly

ash were performed by Wang et al., 2019 using XRD, the microscopic morphologies by SEM and suggested that rate increases on increasing the mole ratio of carbon: alumina. Miandad et al., 2017 used natural and synthetic zeolite catalysts in a small pilot scale reactor for catalytic pyrolysis of four major types of plastic wastes such as PE, PS, PP, and PET and showed that potential of natural and synthetic zeolite catalysts as an alternative promising cheap catalyst in pyrolysis technology by FT-IR, SEM-EDX, BET and TGA analysis. Fekhar et al., 2018 characterized Ni/ZSM-5, Ni/SAPO-11, red mud and $Ca(OH)_2$ containing catalyst and concluded that the aromatic, branched and unsaturated hydrocarbon content increased by the use of catalysts. ZSM-5 based catalysts show high efficiency in aromatization reaction.

It is clear from the above literature review that catalyst characterization in necessary for the determination of its physical and chemical characteristics which are responsible for its performance in the present study of pyrolysis process.

2.1.3 Pyrolysis product characterization

The pyrolysis oil produced by the pyrolysis process of various plastic wastes were characterized by many researchers using different characterization techniques such as, Fourier transform infrared spectroscopy (FT-IR), detailed hydrocarbon analyser (DHA), bomb calorimeter, nuclear magnetic resonance spectroscopy (NMR), gas chromatography coupled with mass spectrophotometry (GC-MS) and other ASTM standard methods. Das (Das and Tiwari, 2018) performed slow pyrolysis of plastic waste and characterized pyrolysis oil using FT-IR, NMR, GC-FID and concluded that pyrolysis oil are lighter with low viscosity, high octane number and having high calorific values, mostly consist of paraffinic and olefinic hydrocarbons having very low pour point and flash point. Gao (Gao and Xu, 2019) performed FT-IR, NMR and TG analysis of pyrolysis oil. The results

indicated that pyrolysis oil had the same structure and thermostability with commercial fuel, which suggested that pyrolysis oil had economic value. Rehan et al., 2017 investigated the pyrolysis oil by GC-MS, bomb calorimeter, dynamic and kinematic viscosities, flash and fire point and density measurements and concluded that the produced liquid oils can be suitable for energy generation and heating purposes after the removal of acid, solid residues and contaminants. The other characterization methods such as API gravity, viscosity, density, ash. Octane number, pour point, flash point, aniline point and diesel index were performed to determine the liquid oil characteristics (Ahmad et al., 2015; Blazso, 2006; Cepeliogullar, Ozge and Putun, Ayse E, 2013; Desai and Galage, 2015; Manickaraja and Tamilkolundu, 2014; Pinto et al., 1999; Sarker et al., 2011). Thus, it is important to evaluate and characterize the pyrolysis oil which might give different compositions depending on feedstock source and the pyrolysis conditions used.

2.1.4 Reactor type/design

The type of reactors has an important impact in the mixing of the feed materials and catalysts, residence time, heat transfer and efficiency of the reaction towards achieving the final desired product. Most of the plastic pyrolysis in the laboratory scale were performed in batch, semi-batch or continuous-flow reactors such as fluidized bed, fixed-bed reactor and conical spouted bed reactor (CSBR) (Abbas-Abadi et al., 2013; Abbas-Abadi et al., 2014; Adnan et al., 2014; Adrados et al., 2012; Aguado, R. et al., 2002; Artetxe et al., 2013; Bagri, R. and Williams, P.T., 2002; Ballice, 2001; Cardona and Corma, 2000; Cepeliogullar, O. and Putun, A. E., 2013; Choi et al., 2010; Elordi et al., 2012; Elordi et al., 2009; Garcia et al., 2005; Jan et al., 2010; Kim and Kim, 2004; Lee et al., 2002; Lee and Shin, 2007; Lee, 2008; Miskolczi, N. et al., 2004; Olazar et al., 2009; Renzini et al.,

2011; Saad et al., 2015; Seo et al., 2003; Shah et al., 2010; Uemura et al., 2001). The advantages and downsides of each reactor are discussed in this section.

The selection of reactor is a key factor which determines mainly the mixing, quality of heat transfer, gas and liquid phase residence times, and the escape of primary products. A wide range of reactors have been used on a lab-scale in plastic pyrolysis. The reactor set-ups investigated so far are categorized as batch reactor, semi-batch reactor, continuous flow reactor, modifications or combinations of either of these. Mostly studied reactor is batch and semi-batch type due to their simplicity, easy to fabricate and handle. A common variable in batch and semi-batch operations is the nitrogen gas use which maintains inert atmosphere within the reactor also helps in removing volatiles from the reactor vessel. The products are then collected by passing the vapors through a condensation system. Due to high temperature operation, the reactors are made out of pyrex or stainless steel. A key disadvantage observed with these reactors is the high reaction time. From an industrial viewpoint, continuous reaction systems are preferred to batch set-ups for operational reasons (Ohkita et al., 1993; Park et al., 1999). Recently many researchers have been reported on semi-batch reactor for the pyrolysis of waste plastics. In fixed bed semi-batch reactor, polymer and catalysts samples are heated separately and reacted by vapor phase contact. Degraded polymer fragments are carried to the catalyst bed/mesh by a carrier gas, in most cases N_2 or due to high vapor pressure of the hydrocarbon products at the bottom of the reactor. It should be noted that the catalysts are generally placed in the vapor phase in a fixed bed semi-batch reactor (In-situ). For simple catalytic batch process, catalyst is thoroughly mixed with the feed material waste plastics and thus, catalyst is only at liquid phase (Gaurh and Pramanik, 2018a; Gaurh and Pramanik, 2018b). Some reactors are also arranged for two stage ex-situ catalytic process. In this arrangement, first reactor breakdowns the plastic material either by thermal or catalytic process followed by the

further catalytic reaction either cracking or aromatization of hydrocarbon molecules in a second reactor (Ex-situ). This type of arrangement also gives wide range of valuable products due to ex-situ selective cracking (Castello et al., 2018; Choi et al., 2017; Duan et al., 2017; Luo and Resende, 2016). Although fluidized bed reactors and continuous flow reactors are in practice, but they have many disadvantages which are broad residence time distribution of solids due to intense mixing, attrition of bed internals and catalyst particles, difficulty in scale-up, defluidization problems, requires large amounts of catalysts, low liquid yields due to 'over cracking' (Aguado, J. et al., 2002; de la Puente et al., 2002; De Lasa, 1992; del Remedio Hernández et al., 2005; Joo and Guin, 1998; Mahgoub and Al-Khattaf, 2005; Mastellone et al., 2002; Mertinkat et al., 1999; Miskolczi, N et al., 2004a; Miskolczi, N et al., 2004b; Murata et al., 2002; Serrano et al., 2003). In this perspectives, semi-batch reactor is selected for the pyrolysis of waste plastics in the present study. The reactor arrangement are discussed in detail in the experimental section (Page no. 39).

2.1.5 Types of chemical process involved

During the thermochemical conversion of plastic materials, various types of reactions might take place within the reactor. Among them cracking/ pyrolysis and aromatization are the key reactions which control the product composition. In the following section, pyrolysis process and aromatization are discussed.

2.1.5.1 Pyrolysis process

Pyrolysis is generally defined as the breaking of molecules and controlled heating of a material in the absence of oxygen. In plastics pyrolysis, the macromolecular structures of polymers are broken down into smaller molecules or oligomers and sometimes monomeric units. Further degradation of these subsequent molecules depends on a number of different

conditions including presence of catalysts, residence time, temperature and other process conditions. The pyrolysis reaction can be carried out with or without the presence of catalyst. Accordingly, the thermochemical reaction will be named as thermal or catalytic pyrolysis. Since majority of plastic used are polyolefins, so extensive research has been done on this polymer which is summarised as below.

2.1.5.1.1 Thermal Pyrolysis

Thermal cracking or pyrolysis, involves the degradation of the polymeric materials by heating in the absence of oxygen. The process is usually conducted at temperatures between 350 °C to 900 °C to obtain solid residues or carbonized char and a volatile fraction that may be separated into condensable hydrocarbon oil consisting of aromatics, olefins, paraffins, naphthenes, isoparaffins and non-condensable hydrocarbons or gas having high calorific value. The amount of each fraction and their specific composition depends primarily on the process conditions used and the nature of the plastic waste. The amount and the nature of these reactions depend both on the reaction temperature and the residence time of the products in the reaction zone, which is primarily affected by the reactor design. When the molten plastic has the low thermal conductivity and high viscosity, the product characteristics of thermal degradation of heavy hydrocarbons are (i) high production of C_1 and C_2 in the gas product, (ii) olefins are less branched, (iii) some diolefins made at high temperature, (iv) gasoline selectivity is poor i.e., oil products are a wide distribution of molecular weight, (v) gas and coke products are high, (vi) reactions are slow compared to catalytic reactions.

Thermal pyrolysis of both fresh and waste plastics as well as other hydro-carbonaceous sources has been studied widely in the past. A good number of these thermal cracking studies are on polyethylene (Dolezal et al., 2001; Murata et al., 2004; Scott et al., 1990),

polypropylene (Audisio et al., 1984; Bockhorn et al., 1999; Chan and Balke, 1997; del Remedio Hernández et al., 2005; Dolezal et al., 2001; Hayashi et al., 1998; Jakab et al., 2000; Kaminsky, 1985; Kaminsky et al., 2004; Kiang et al., 1980; Kim and Kim, 2004; Lattimer, 1993; Marcilla et al., 2001; Onu et al., 1999; Ranzi et al., 1997; Scott et al., 1990; Seth and Sarkar, 2004; Sørum et al., 2001; Tsuchiya and Sumi, 1969) and polystyrene (Cha et al., 2002; Dolezal et al., 2001; Faravelli et al., 2001; Kim and Kim, 2004; Woo et al., 2000; Woo and Broadbelt, 1998). On the other hand, only a few have worked on the thermal decomposition of other common plastics such as polyvinylchloride (Sakata, Y et al., 1996; Scott et al., 1990), polymethyl methacrylate (Kaminsky et al., 2004), polyurethane (McCaffrey et al., 1995) and polyethylene terephthalate (Sakata, Y et al., 1996). Generally, thermal cracking results in liquids with low octane value and higher residue contents at moderate temperatures, thus an inefficient process for producing gasoline range fuels (Kim and Kim, 2004; Seth and Sarkar, 2004). The gaseous products obtained by thermal pyrolysis are not suitable for use as fuel products, requiring further refining to be upgraded to useable fuel products (Joo and Guin, 1998; Songip et al., 1993). A few researchers have sought to improve thermal pyrolysis of waste plastic which either yielded insignificant improvements or added another level of complexity and costs to the system (Serrano et al., 2003; Seth and Sarkar, 2004). The thermal degradation of polymers to low molecular weight materials requires high temperatures and has a major drawback of wide range random product fraction. However, catalytic pyrolysis provides a means to address these problems and thus, catalytic pyrolysis is discussed in the following section.

2.1.5.1.2 Catalytic pyrolysis

In catalytic pyrolysis, a suitable catalyst is used to carry out the cracking reaction. The presence of catalyst lowers the reaction time and temperature. In addition, catalytic

degradation yields a much finer product distribution of carbon atom number with a peak at lighter hydrocarbons and occurs at considerably lower temperatures (Panda et al., 2010). From an economic perspective, the use of catalyst reduces the cost even further will make this process an even more attractive option. This option can be further optimized by reuse or regeneration of catalysts and the use of achieve catalysts in lesser quantities. This method seems to be the most promising to develop as a cost-effective commercial polymer recycling process to solve the acute environmental problem of plastic waste disposal.

It is also observed that the addition of catalyst enhances the conversion and fuel quality. As compared to the purely thermal pyrolysis, the addition of catalyst in plastic pyrolysis. Significantly lowers pyrolysis temperatures and time. A significant reduction in the degradation temperature and reaction time (Ohkita et al., 1993) under catalytic conditions results in an increase in the conversion rates for a wide range of polymers at much lower temperatures than with thermal pyrolysis (Ding et al., 1997; Lee et al., 2001; Park et al., 1999). It also provides better control over the hydrocarbon products distribution in low density polyethylene (LDPE) (Lee et al., 2002; Park et al., 2002), polypropylene (Hwang et al., 1998; Hwang et al., 2002) and polystyrene (Bagri, R. and Williams, P., 2002; Kim et al., 2002) pyrolysis. While thermal pyrolysis, results in a broad range of hydrocarbons ranging from C5 to C28 (McCaffrey et al., 1995). The selectivity of products in the gasoline range (C5–C12) are much more enhanced by the presence of catalysts (Aguado et al., 2000; Audisio et al., 1984; Park et al., 1999). Moreover, oils obtained by catalytic pyrolysis contain less olefins and more branched hydrocarbon and aromatic content (Ohkita et al., 1993; Seo et al., 2003). However, increases the gaseous product yields to some extent. The dramatic effect of catalytic decomposition of polymers has drawn huge attention for the research in the area of catalysis and polymer degradation. Thus, catalytic degradation of

waste plastics was selected for BTEX production and the same was compared with thermal pyrolysis for similar condition.

2.1.5.2 Pyrolysis with aromatization

The product aromatics mainly BTEX from plastic waste depends on the selective aromatization of lower hydrocarbon, which are formed by the pyrolysis process. When PE, PP and PS are used as raw material and subjected to pyrolysis, then thermal and catalytic both the process might produce BTEX. However, the percentage yield of BTEX obtained is more for catalytic pyrolysis. Aromatization is a chemical reaction in which an aromatic system is formed as shown in equation 2.6 (page no. 29). It can also refer to the production of a new aromatic moiety in a molecule which is already aromatic (Lopez et al., 2011a). Theoretically, this can be achieved by dehydrogenation of existing cyclic compounds such as in converting cyclohexane into benzene or by formation of new cyclic system such as in the cyclotrimerization of acetylene to benzene. Aromatization includes the formation of any aromatic hydrocarbons including heterocyclic and is not restricted to benzene and its derivatives.

2.1.6 Reaction mechanism of plastic degradation

Recent progress in converting plastic wastes into petrochemicals by means of pyrolysis in the absence of a catalyst has been reviewed by Kaminsky (Anndrews, 1992; Kaminsky, 1991). Cullis and Hirschler presented a complete treatment of the mechanism of plastics pyrolysis (Cullis and Hirschler, 1981). They proposed four types of mechanisms of plastics pyrolysis (i) End-chain scission or depolymerization. In this, the polymer is broken up from the end groups producing the corresponding monomers. (ii) Random-chain scission, in which the polymer chain is broken up randomly into uneven length fragments. (iii) Chain-

stripping. The elimination of reactive substitutes or side groups on the polymer chain takes place, which leads to the evolution of a cracking product and a charring polymer chain. (iv) Cross-linking. Formation of a chain network, which often occurs for thermosetting polymers when heated. These different mechanisms and product distributions are related to bond dissociation energies, the aromaticity degrees and the chain defects of the polymers (Buekens and Huang, 1998).

Common waste plastics such as PE, PP and PS have already been tested broadly; the catalysts tested are mainly those used in the petrochemical refinery industry. The laboratory experimental set-up in these studies is mostly reactors; it may be useful to distinguish between two modes of catalyst usage: 'liquid phase contact' and 'vapor phase contact' (Sakata, Yusaku et al., 1996). In 'liquid phase contact', the catalyst is contacted with melted plastics and acts mainly on the partially degraded oligomers from the polymer chains; in 'vapor phase contact', the polymer is thermally degraded into hydrocarbon vapors which are then contacted with the catalyst. In the presence of catalysts, catalytic cracking occurs on the surface interface of the melted polymer and solid catalysts. The main steps of reactions are as follows: diffusion on the surface of catalyst, adsorption on the catalyst, chemical reaction, desorption from the catalyst, diffusion to the liquid phase. The reaction rate of catalytic reactions is always determined by the slowest elementary reaction. The dominant rate controller elementary reactions are the linking of the polymer to the active site of catalyst. But the selectivity of catalysts on raw materials and products might be important. The selectivity is affected by molecular size and shape of raw materials, intermediates and products (Takuma et al., 2000).

2.1.6.1 Reaction mechanism

The cracking of C–C bonds takes place as the result of reactions initiated by thermal or catalytic pyrolysis of waste plastics. It means that thermal and catalytic reactions do not distinct from each other, therefore in discussing thermocatalytic cracking of polymers one has to touch upon both the thermal and catalytic pyrolysis reactions. It is well known, that the thermal cracking of plastics occurs by a radical mechanism, where the initiating radicals are formed by the effect of heat. Catalytic cracking generally proceeds though carbenium ions, which are considered to be produced by the abstraction of hydride ion (Lewis acid) from the polymer or the addition of proton (Bronsted acid) to the polymer ¨ macromolecule in the initial reaction step. Fragments formed in the first cracking reactions cracked further into lower-molecular-weight hydrocarbons on the active sites of the catalyst. Unstable primary fragments are cracked in further decomposition reactions. The following elemental reactions take place both in thermal and catalytic pyrolysis (i) Initiation (ii) formation of secondary radicals, which includes depolymerization, formation of monomers, favourable and unfavourable hydrogen transfer reactions, intermolecular hydrogen transfer (formation of paraffins and dienes), isomerization via vinyl groups and (iii) termination by disproportionation or recombination of radicals (Scheirs and Kaminsky, 2006).

2.1.6.1.1 Initiation

The mechanism of initiation is partly radical in thermocatalytic degradation. The cracking of C–C bonds occurs by homolytic cracking of C–C bonds, at regions with structural faults or distortion of the electron cloud. Catalytic cracking generally proceeds through a carbenium ion, which is considered to occur by the abstraction of hydride ion from polymer or the addition of proton on the polymer macromolecule in the initial step of the reaction (Fig 2.1) as discussed by (Scheirs and Kaminsky, 2006).

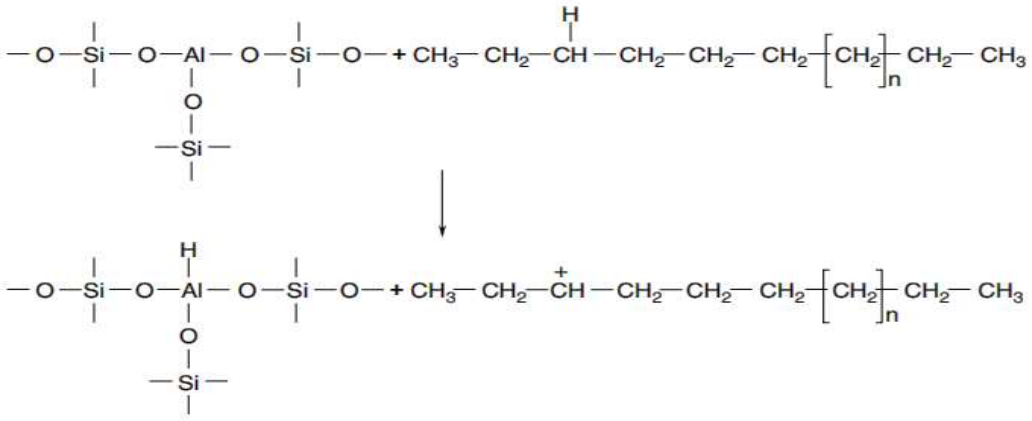
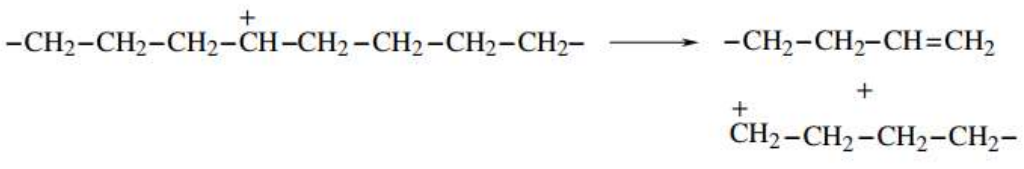


Figure 2.1 Initiation in thermocatalytic cracking

2.1.6.1.2 Formation of secondary unstable compounds

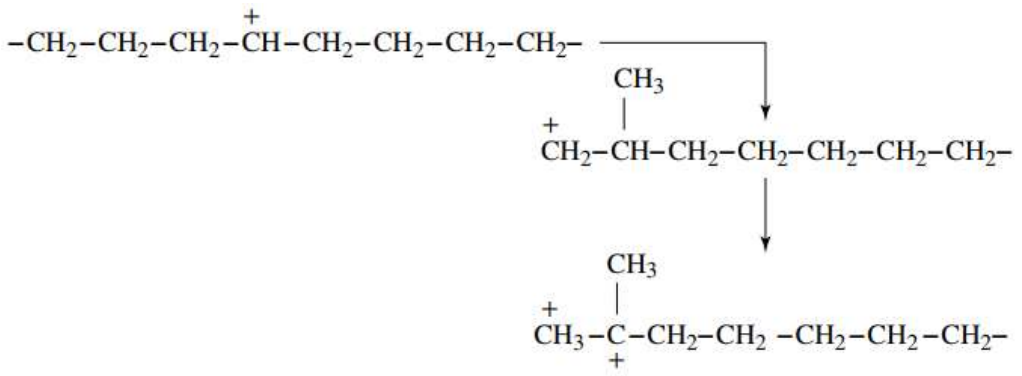
Unstable molecular fragments (radicals and ions) formed in the initiating reaction take part in further decomposition reactions with uncracked macromolecules of polymer or radicals and ions, resulting, among others, in secondary instable compounds of lower molecular weight. Mostly, the β-scission of primary radicals and ions results in monomer. It was found that at lower temperature, intermolecular hydrogen transfer reactions take place followed by β-scission of polymer which leads to stable radicals and ions formation. The polymer chain cracked to a greater degree at higher temperature. Thus, the primary unstable radicals react with alkanes. It is important to note that Diels–Alder reactions causes the formation of aromatics. In these reactions, it is found that the double bond moves toward the end of the framework in the case of nonbranched structures, and that of tertiary carbons in of branched structures. Terminal double bonds turn into internal ones in the case of catalytic cracking, but this is not typical in thermal cracking (Scheirs and Kaminsky, 2006).

1) β-scission



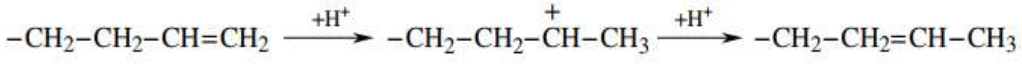
(2.1)

2) Isomerization of carbon framework



(2.2)

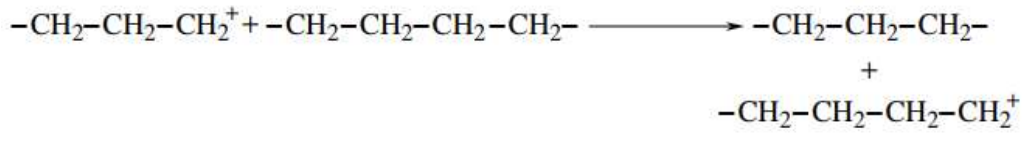
Isomerization of double bond



(2.3)

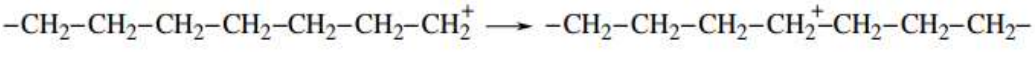
3) Hydrogen transfer reactions

Intermolecular hydrogen transfer reactions



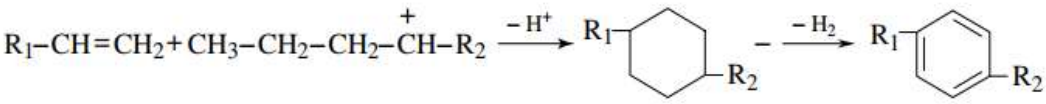
(2.4)

Intramolecular hydrogen transfer reactions



(2.5)

4) Cyclization and aromatization



(2.6)

2.1.6.1.3 Termination with recombination or disproportionation

Primary and secondary unstable molecular fragments formed in the cracking reactions could be stabilized in several ways. Recombination or disproportionation of unstable fragments is one simple way. As a result of recombination, the molecular weight and

branching of products might be significantly increased. It is important to note that both recombination and disproportionation are second-order reactions according to reaction kinetics. Cyclization, aromatization or polycondensation are other ways of termination. Basically, cyclic alkenes, alkenes, mono and polynuclear arenes or coke are formed in these reactions. Termination reactions are principally controlled by the properties of polymers and the temperature.

2.1.7 Pyrolysis for BTEX production

The pyrolysis of waste plastics is affected by a number of process parameters such as temperature (Yoshioka et al., 2004; Ji et al., 2006), retention time (Lopez et al., 2011c; Lee and Shin, 2007), feedstock composition (Troger et al., 2013; Acomb et al., 2015), use of catalyst (Lerici et al., 2015; Miskolczi et al., 2013; Chen et al., 2014), moisture content (Chen et al., 2014), heating rate (Sharma et al., 2014) and particle size (Luo et al., 2010). The important process parameters for product yield e.g., liquid, gas and solid, and BTEX of waste plastic pyrolysis are discussed in the following section.

2.1.7.1 Product yield for thermal pyrolysis

The most important parameters such as reaction temperature, pressure for thermal pyrolysis are presented below.

Table 2.4 shows the literature review on product yield for thermal pyrolysis of waste plastic mainly polyethylene, polypropylene and polystyrene, effectively. Onwudili et al., 2009 performed thermal pyrolysis of waste LDPE in a pressurized batch reactor at 425 ^{o}C to obtain maximum liquid yield of 89.5 wt. %. Lee et al., 2002 used semi-batch reactor for the thermal pyrolysis of PS at 400 ^{o}C. They produced maximum liquid yield of 90 wt. %. Abbas-Abadi et al., 2014 obtained maximum liquid of 92.4 wt. % for PP pyrolysis in semi

batch reactor at 450 °C. It is clear that PE, PP and PS produces maximum amount of liquid yield with minimum amount of gas and solid residue (Table 2.4).

Table 2.4 Product yield of thermal pyrolysis using different types of waste plastics.

Reference	Plastic type	Reactor type	Process parameters	Liquid (wt.%)	Solid (wt.%)	Gas (wt.%)
(Onwudili et al., 2009)	LDPE	Pressurized Batch	Temperature = 425 °C Pressure = 0.8-4.3 Mpa	89.5	0.5	10.0
(Williams et al.,1999)	LDPE	Fluidized Batch	Temperature = 600 °C Pressure = 1 atm	51.0	24.8	24.2
(Abbas-Abadi et al., 2013)	HDPE	Semi batch	Temperature = 450 °C Pressure = 1 atm	91.2	4.7	4.1
(Ahmad et al., 2015)	HDPE	Horizontal steel	Temperature = 350 °C Pressure = 1 atm	80.88	1.88	17.24
(Lee et al., 2002)	PS	Semi batch	Temperature = 400 °C Pressure = 1 atm	90	4	6
(Demirbas, 2004)	PS	Batch	Temperature = 581 °C Pressure = not available	89.5	0.6	9.9
(Abbas-Abadi et al., 2014)	PP	Semi batch	Temperature = 450 °C Pressure = not available	92.4	3.6	4.1
(Ahmad et al., 2015)	PP	Horizontal steel	Temperature = 300 °C Pressure = not available	69.82	1.34	28.84
(Miandad et al., 2017)	Mixed	Batch	Temperature = 600 °C Pressure = not available	49.0	3.9	47.1
(Hopewell et al., 2009)	Mixed	Tubular	Temperature = 800 °C Pressure = 1 atm	73	23.5	3.5
(Miranda et al., 1999)	Mixed	Vacuum batch	Temperature = 400 °C Pressure = 2 kPa	90	5.0	5.0

Apart from liquid yield some efforts have been made to improve the quality of liquid hydrocarbon in terms of BTEX quality. Table (2.5) shows the BTEX yield for the thermal pyrolysis of polyethylene, polypropylene and polystyrene or their mixture studied by the researchers. Cho et al., 2009 used mixed plastic for thermal pyrolysis in a fluidized bed reactor at 660-780 ^{o}C to produce maximum BTEX of 18 wt. %. Ciliz et al., 2004 also used mixed plastic in horizontal quartz reactor at 600 ^{o}C to obtain maximum BTEX of 63 wt. %. Mertinkat et al., 1999 produces 30-40 wt. % BTEX in fluidized bed reactor at 685-738 ^{o}C for thermal pyrolysis of mixed plastic waste.

Table 2.5 The aromatic content (BTEX) in pyrolysis oil obtained by the thermal pyrolysis of waste plastics.

Reference	**Plastic type**	**Reactor type**	**Pyrolysis temperature (^{o}C)**	**BTEX (wt.%)**
(Cho et al., 2009)	Mixed plastic	Fluidized bed	660-780	18
(Mertinkat et al., 1999)	Mixed plastic	Fluidized bed	685-738	30-40
(Li et al., 1999)	Polyethylene	Rotary kiln pyrolyser	850	16.33
(Demirbas, 2004)	Polyethylene	Stainless steel tube	675	5.8
(Kaminsky et al., 2004)	Polyethylene	Fluidized bed	600-800	23.18
(Ciliz et al., 2004)	Mixed plastic	Horizontal quartz reactor	600	63
(Demirbas, 2004)	Polypropylene	Stainless steel tube	875	10.2
(Williams and Slaney, 2007)	Polypropylene	Parr Mini Bench Top	500	10.1
(Scheirs and Kaminsky, 2006)	Polypropylene	Fluidized bed	600-800	25.2
(Demirbas, 2004)	Polystyrene	Stainless steel tube	675	12.1

2.1.7.2 Product yield for catalytic pyrolysis

Table (2.6) summarizes the product yield obtained by the several investigators for the catalytic pyrolysis of waste plastics using various types of catalyst.

Table 2.6 Product yield of catalytic pyrolysis of waste plastics on various catalyst.

Reference	Plastic type	Reactor type	Process parameters	Catalyst	Liquid (wt.%)	Solid (wt.%)	Gas (wt.%)
(Shah and Jan, 2014)	LDPE	Tubular	Temperature = 400 °C Pressure = 1 atm	Al_2O_3	91	0.5	8.5
(Syamsiro et al., 2014)	LDPE	Vacuum Batch	Temperature = 450 °C Pressure = 2 kPa	Silica alumina	93	7	0
(Panda et al., 2010)	LDPE	Rotary drum	Temperature = 500 °C Pressure = 1 atm	β-Zeolite	44	3.4	52.6
(Olazar et al., 2009)	HDPE	Continuous reactor	Temperature = 520 °C Pressure = not available	FCC	58	5.9	36
(Elordi et al., 2009)	HDPE	Conical sprout bed	Temperature = 500 °C Pressure = 1 atm	HZSM-5	64	3	33
(Miandad et al., 2016)	PP	Fixed bed	Temperature = 425 °C Pressure = not available	HZSM-5	68	2.4	29.6
(Lin and Yang, 2007)	PP	Fluidized bed	Temperature = 330-450 °C Pressure = not available	Hybrid FCC	15-87	Not available	Not available
(Adnan et al., 2014)	PS	Batch	Temperature = 400 °C Pressure = not available	Zn catalyst	96.73	3.27	0
(Miandad et al., 2016)	PS	Semi-Batch	Temperature = 500 °C Pressure = 1 atm	FCC	90	6	4

Syamsiro et al., 2014 performed catalytic pyrolysis of waste LDPE using silica alumina catalyst in a vacuum batch reactor at 450 ^{o}C and 2 kPa pressure to obtained maximum liquid yield of 93 wt.%. Miandad et al., 2016 used HZSM-5 as catalyst for the catalytic pyrolysis of PP in a fixed bed reactor at 425 ^{o}C. They produced maximum liquid yield of 68 wt. % and gaseous yield of 29.6 wt. %. Adnan et al., 2014 carried out PS pyrolysis using Zn as catalyst in batch reactor at 400 ^{o}C and obtained 96.73 wt. % liquid yield.

The valuable aromatics (BTEX) have been the key components for many researchers when the catalytic pyrolysis of waste plastic were performed. Lopez et al., 2011 used mixed plastic as feed for the catalytic pyrolysis using ZSM-5 catalyst at 440 ^{o}C in a semi batch reactor to obtain maximum BTEX yield of 78.7 wt. %. Li el at., 2013 used LDPE as feed and ZSM-5 catalyst to produce 28.87 wt. % BTEX in quartz tube at 650 ^{o}C.

Table 2.7 The aromatic content (BTEX) in pyrolysis oil obtained by the catalytic pyrolysis of waste plastics.

Reference	**Plastic type**	**Reactor type**	**Pyrolysis temperature (^{o}C)**	**Catalyst used**	**BTEX (wt.%)**
(Uemichi et al., 1983)	PP	Fixed bed	477	Silica-alumina	10.6
(Li et al., 2013)	LDPE	Quartz tube	650	ZSM-5	28.87
(Pinto et al., 1999)	Mixed	Autoclave	415	NaY powder	30 %
(Achilias et al., 2007)	LDPE	Fixed bed	450	FCC	25.8
(Lopez et al., 2011a)	Mixed	Semi-batch reactor	440	ZSM-5	78.7

It is clear from above literature review that catalyst produces more BTEX content in comparison to thermal pyrolysis of waste plastics due to selective cracking of the

hydrocarbons. Among all the catalyst, ZSM-5 gives better quality of liquid yield in terms of valuable BTEX.

2.2 Objectives

The detailed literature review reveals that waste plastics polyethylene, polypropylene and polystyrene causing environmental degradation and pollution problem and thus, there is a huge scope to convert waste plastics to valuable aromatics benzene, toluene, ethylbenzene and xylene (BTEX). In order to produce valuable BTEX using pyrolysis process, a new innovation in catalyst field is necessary. The development of a stable and active catalyst from natural fly ash could make the pyrolysis process cost effective for the production of BTEX. Using waste plastics as raw materials for the pyrolysis process could reduce the waste and simultaneously produce valuable liquid hydrocarbon BTEX. Thus, a detailed study on the pyrolysis of waste plastics is required to produce BTEX in effective and efficient manner using suitable catalyst and reactor design. Towards the fulfilment of these requirements, the thesis has the following objective:

1. To design and fabricate of the experimental set-up.
2. To synthesize catalyst and its characterization using Fourier-Transformed Infra-Red spectroscopy (FTIR), Scanning Electron Microscope/Energy dispersive X-ray spectroscopy (SEM-EDX), Brunauer-Emmet-Teller (BET) surface area.
3. To study the thermal pyrolysis of waste polyethylene, polypropylene and polystyrene at different temperatures.
4. To study the catalytic pyrolysis in a specially designed reactor to determine optimum conditions of different parameters e.g., feed to catalyst ratio, reaction time, temperature, effect of calcination temperature, catalyst type, different types of reactor arrangements to achieve maximum BTEX yield.

5. To determine the physicochemical properties of pyrolysis oil via GC-FID, FTIR, ASTM distillation, flash and fire point, calorific value, carbon residue.
6. To study the stability of catalyst for pyrolysis process.

The next chapter describes the experimental detail related to the studies on production of BTEX via thermal and catalytic pyrolysis of waste plastic polyethylene, polypropylene and polystyrene, fabrication of experimental setup, preparation of feed material, catalyst synthesis from fly ash, catalyst characterization through Fourier Transformed Infrared Spectroscopy (FTIR), Brunauer-Emmett-Teller (BET) surface area, Scanning Electron Microscope/ energy dispersive X-ray spectroscopy (SEM-EDX), product oil characterization using FTIR, GC analysis, ASTM distillation, flash and fire point, carbon residue and calorific value, catalyst regeneration and its performance study.