CHAPTER 2
LITERATURE REVIEW AND OBJECTIVES

2.1 Literature review

In this chapter, literature review and various factors related to the pyrolysis of waste expanded polystyrene (WEPS) followed by *in-situ* hydrogenation for the production of benzene, toluene and ethylbenzene (BTE) are discussed in detail. This chapter-2 includes the selection of feed, feed characterization, catalyst material, characterization of catalyst, pyrolysis process, reactor design, mechanism for BTE production, and various effective pyrolysis parameter for the BTE production. Based on the literature review, research gaps are identified on the pyrolysis of WEPS and then the research objectives of the thesis are finalized, which are and listed at the end of this chapter.

2.1.1 Raw materials

The raw materials are divided in to two broad categories (i) feedstock and (ii) catalysts used for the pyrolysis process.

2.1.1.1 Feedstock for the pyrolysis process

The selection of feed stock is very crucial for the BTE production from waste plastics via pyrolysis followed by hydrogenation. As per reported literature, most of the studies have been published on the pyrolysis of waste plastics like high density polyethylene (HDPE), low density polyethylene (LDPE), polypropylene (PP) for the production of aromatic hydrocarbons mainly benzene, toluene, and ethylbenzene (BTE). Only few studies have been focused on the production of BTE from waste expanded polystyrene (WEPS) pyrolysis. The thermal pyrolysis

of WEPS primarily produces styrene monomer (Park et al., 2003), which is not a fuel component and very toxic. Even catalytic pyrolysis of WEPS produces pyrolysis oil rich in styrene monomer. This is the major drawback of polystyrene pyrolysis. It is already mentioned in the chapter 1: Introduction (page no. 4) that the polystyrene is the third largest waste plastic found in municipal plastic waste (MPW). As per the society of the plastic industry (SPI), EPS is a Type 6 plastic (Jasso et al., 2019). The expanded polystyrene (EPS) is a versatile thermoplastic polymer that has been adopted in different applications such as for making trays, plates, bowls, boxes, insulation, and packing materials (Uttaravalli et al., 2021). Although, EPS has many preferred properties, it suffers from poor biodegradability and pollute the environment in various ways such as land pollution, water pollution and air pollution. The worldwide production of EPS is around 15 million metric tons (MMT) per annum and most of which ends up in a landfill. As a result of its widespread use and poor rate of recycling, EPS is viewed as one of the major postconsumer waste products (Uttaravalli et al., 2021). The contribution of WEPS in municipal plastic waste (MPW) is around 10 % by weight in India. However, by the volume it could be 40 % which is highest among all other types of plastic waste because of its low density (Adnan et al., 2014). The EPS is a common marine litter (Song et al., 2020) consumed by marine animals, leading to choking or intestinal obstruction (Ramanan et al., 2018). The incineration of WEPS releases harmful poly-aromatic hydrocarbons, can cause serious health issues after prolonged exposure (Chauhan et al., 2008). However, EPS has a high calorific content estimated to be 47 MJ/kg (Listiani et al., 2015) therefore, the energy and chemical recovery are reasonable approaches to convert WEPS into high valuable aromatics benzene, toluene and ethylbenzene (BTE). In view of this, in the

present study waste expanded polystyrene (WEPS) was selected as raw materials or feed stock for the production of valuable fuel oil rich in BTE.

2.1.1.1.1 Feed characterization

The characterization of feed for the pyrolysis process is very essential to know the composition of feed like C, H, N, S, O and impurities. There are various characterization techniques such as thermogravimetric analysis (TGA), ultimate analysis and proximate analysis to characterize the feed for the pyrolysis process. The TGA of polystyrene (PS) is performed to know its thermal stability and decomposition behaviour at various temperatures.

The proximate analysis determines the volatile matter, fixed carbon, moisture and ash content. The decomposition temperature of waste polystyrene helps in deciding the pyrolysis temperature. Whereas, ultimate analysis of PS is conducted to determine the elemental composition such as carbon, hydrogen, nitrogen, sulphur and oxygen. Ahmad et al., 2020 used thermogravimetric analysis to know the thermal stability of PS. They reported that the decomposition of PS started at about 360 $^\circ$C and decomposition ended at about 460 $^\circ$C. Miandad et al., 2019 also used TGA of waste PS to determine the optimum temperature for thermal degradation. They reported that the initial degradation of PS started at 330 $^\circ$C and maximum degradation was achieved at a temperature of 470 $^\circ$C. Suriapparao et al., 2018 determined the volatile matter, fixed carbon and ash content of PS using proximate analysis. Very high volatile matter of 99.5 wt.%, fixed carbon of 0.5 wt.% and 0.0 wt.% of ash content was found in the PS, as reported by Suriapparao et al., 2018. Similarly, Mohapatra et al., 2021 reported the volatile matter of 98.24 wt.%, moisture content of 0.25 wt.%, ash content of 0.99 wt.% and fixed carbon of 0.52 wt.% for PS. Whereas, the volatile matter of 100 wt.% was

reported by Selvaganapathy et al., 2020. Babajo et al., 2021 determined the C H N S and O content for the PS using ultimate analysis. They reported the very high carbon content of 89.10 wt.%, hydrogen of 8.02 wt.%, nitrogen of 0.22 wt.%, sulphur of 0.01 wt.% and oxygen of 2.65 wt.% for feed PS. Parejo et al., 2019 reported the carbon content of 91 wt.%, hydrogen content of 8.8 wt.%, oxygen content of 0.3 wt.%, nitrogen and sulphur content of 0.0 wt.% for the PS. However, the carbon content of 87.53 wt.%, hydrogen content of 8.86 wt.%, oxygen content of 3.29 wt.% and sulphur content of 0.0 wt.% for PS was reported by the Li et al., 2022. Thus, in the present work, the feed waste expended polystyrene (WEPS) was characterized by the important thermogravimetry and proximate analysis.

2.1.1.2 Catalysts for pyrolysis

The catalysts play a key role during the pyrolysis of WEPS and other waste plastics which produce high percentage of target molecules via pyrolysis of WEPS, selective cracking, aromatization and hydrogenation of product hydrocarbon molecules in the selective reaction process. Thus, the use of catalyst in the pyrolysis process is increasing. The catalyst also lowers the reaction temperature, reduce time of reaction. The pyrolysis oil obtained from the catalytic pyrolysis of WEPS is rich in fuel range hydrocarbons and thus, the oil does not need any further treatment for upgradation. Whereas, the pyrolysis process without catalyst or thermal pyrolysis of WEPS/other waste plastics mainly produced low quality pyrolysis oil which cannot be used for any application without upgradation (Salem et al., 2017). The catalyst improve the quality of pyrolysis oil however, it reduces the liquid yield because high surface area of catalyst facilitates the better contact between the reactants and the surface of catalyst which facilitates the formation of gaseous range hydrocarbon molecules via cracking reaction. It is already

reported in the literature, mostly acid catalysts are used for the cracking of polyethylene (PE), polypropylene (PP) and polystyrene (PS). Whereas, various zeolites like protonated Y-zeolite (HY), protonated β-zeolite (Hβ) and protonated zeolite (HZSM-5) (Ma et al., 2017a) catalysts or zeolite based catalyst such as spent FCC catalyst (Lee, 2008; Lee, 2002) are frequently used for the catalytic pyrolysis of PS because of selectivity and abundant Brønsted and Lewis acid sites (Ma et al., 2016). Many researchers Inayat et al., 2022; Jung et al., 2021; Fuentes et al., 2021; Ojha and Vinu, 2015; Williams and Bagri, 2004; Rehan et al., 2017; Xue et al., 2017; Miandad et al., 2017; Hall and Williams, 2008; Williams et al., 1993; and Syamsiro et al., 2014 used zeolite catalyst for the pyrolysis of polystyrene (PS).

The ZSM-5 zeolite is generally used because of its unique crystalline structure that allows more cracking of the high molecular weight hydrocarbons, and a higher ratio of silica to aluminum (Si/Al) also leads to high thermal stability (Seo et al., 2003). Furthermore, ZSM-5 has smaller pore diameter among all other types of zeolites (Seo et al., 2003) and thus, it acts as a molecular sieve. The ZSM-5 belongs to the family of pentasils with pore diameters of about 5.5 Å as shown in Figure 2.1.
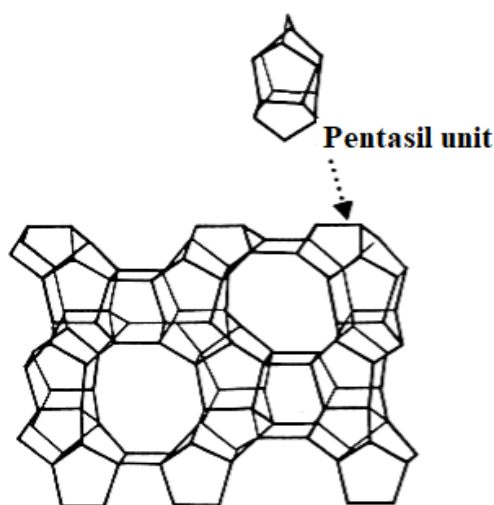
Figure 2.1 Schematic drawing of the structure of ZSM-5 (Kalogeras and Vassilikou-Dova, 1998).

The crystalline frame work of zeolites are mainly consist of $[SiO_4]^{4-}$ and $[AlO_4]^{5-}$ tetrahedral joined by a shared oxygen atom and extended infinitely in a three dimensional network (Elaiopoulos et al., 2010; Mgbemere et al., 2017). The general chemical formula of zeolites based on their crystallographic unit cell is $M_{a/b}[(AlO_2)_a(SiO_2)_y]_cH_2O$.

Where, M is either an alkali metal or an alkaline earth metal cation, b represent the valency earth metal cation, c is the amount of water of crystallization per unit cell of the zeolite while a and y represent the total number of the $[SiO_4]^{4-}$ and $[AlO_4]^{5-}$ tetrahedral in a unit cell of the zeolite. The ratio y/a normally has a value that ranges from 1 to 5, but in the case of a silica based zeolites, the values of y/a can range from 10 to 100 (Mgbemere et al., 2017).

Apart from zeolites, some other transition metal oxide e.g., Nb_2O_5, NiO/Nb_2O_5 (Amjad et al., 2022), NiO/ZrO_2 (Amjad et al., 2021), Zn, ZnO, $ZnCl_2$ (Adnan et al., 2014), CuO (Nisar et al., 2020) have also been used for the catalytic pyrolysis of polystyrene (PS). The transition metals enhance the liquid yield and promote the production of hydrogen (H_2) due to the moderate acid strength and dehydrogenating activity resulted from the metal active phase (Li et al., 2017).

Amjad et al., 2021 used NiO deposited over ZrO_2 carrier as catalyst for the catalytic pyrolysis of PS in a semi batch reactor. The catalysts based on different loading (2 %, 5 %, 10 % and 15 %) of NiO deposited over ZrO_2 carrier were prepared. A comparative analysis, based on styrene monomer formation, pointed out that the 10% NiO/ZrO_2 as the best catalysts for the catalytic pyrolysis process as it reduced the formation of styrene monomer. They also reported that the 10 % NiO catalysts having acidic sites, were more selective towards the formation of aromatics such as toluene and ethylbenzene other than styrene monomer. The NiO/ZrO_2 catalyst also produced diesel range fuel with reduced styrene content. Ma et al., 2017b also used Fe and Ni modified ZSM-5 and MCM-41 catalysts in a two-stage fixed bed reactor to

conduct the catalytic pyrolysis of brominated high impact polystyrene (Br-HIPS). The modified catalysts of Fe/ZSM-5 and Ni/ZSM-5 exhibited prominent cracking performance, resulting in the formation of single ring aromatic yield, including toluene, ethylbenzene, cumene and styrene monomer. However, the formation of styrene monomer while using the Fe/ZSM-5 was more as compared to the Ni/ZSM-5 catalyst. In the view of this, commercial catalysts ZSM-5 ammonium powder and Nickel on silica-alumina were used for the catalytic pyrolysis of WEPS for the production of valuable aromatics benzene, toluene and ethylbenzene (BTE).

Generally zeolites are synthesized using sodium ion to neutralize the framework. The commercial catalyst ammonium ZSM-5 ($SiO_2:Al_2O_3$ =200-400:1) powder was used in the present study due to its excellent catalytic activity towards the formation of better liquid yield containing aromatics hydrocarbons as reported in the published literature (Lopez et al., 2011b; Santos et al., 2018). Very high silica content in ammonium ZSM-5 provides the higher Bronsted acid sites for the production of target products BTE. The ammonium type ZSM-5 provides additional Bronsted acid sites NH_4^+ which helps in selective cracking (Perra et al., 2014; Lanzafame et al., 2017).

However, this sodium ion can easily replace by other ions such as magnesium, potassium and ammonium. The ammonium zeolite is generally prepared by the reaction of sodium zeolite with ammonium nitrate (NH_4NO_3) and the corresponding chemical reaction is given below:

$$NaZ_{(s)} + NH^+_{4(aq)} \Leftrightarrow NH_4Z_{(s)} + Na^+$$
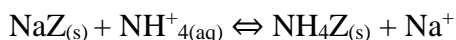
Another commercial catalyst Nickel on silica-alumina was also used because nickel improve the hydrogen production (Wang and Wang, 2011) during the pyrolysis of PS, which helps in

the formation of ethylbenzene via hydrogenation reaction. The presence of nickel on silica-alumina support also increased the gasoline fraction in the pyrolysis oil (Syamsiro et al., 2014). Recently, clay based catalyst has become very popular to reduce the process cost and also allows green chemistry of production. The clay minerals such as kaolinite, illite, vermiculite, and montmorillonite are composed of silica tetrahedral sheets combined with alumina octahedral sheets and further classified into 1:1 and 2:1 layered clay minerals (Figure 2.2). Clay minerals with a 1:1 layer structure are composed of one tetrahedral sheet and one octahedral sheet. Whereas, in the 2:1 layer structure one octahedral sheet is sandwiched between two tetrahedral sheets as mentioned in Figure 2.2 (Gardolinski, 2005).
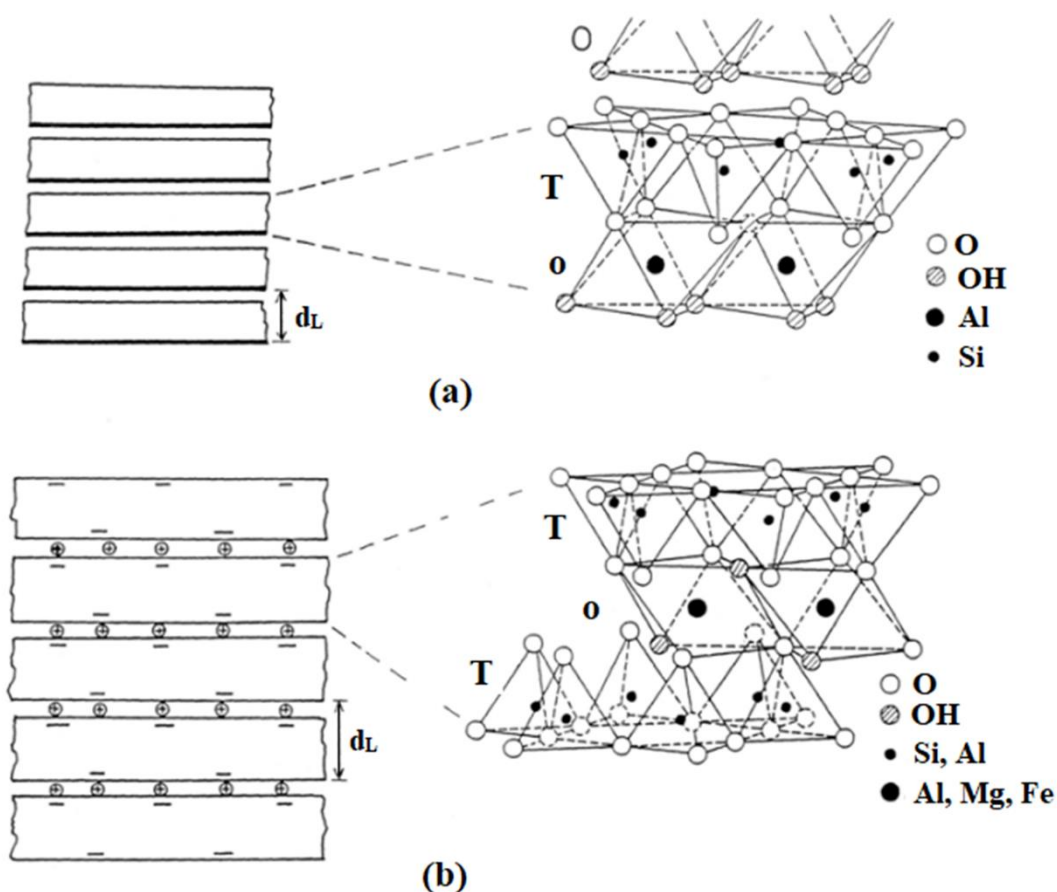
Figure 2.2 Structure of a 1:1 clay mineral layer (a) and of a 2:1 clay mineral layer (b) (the interlayer cations are depicted on the schematic drawing of the layered structure on the left) T = tetrahedral sheet, O = octahedral sheet, d_L = basal spacing of the crystal (Gardolinski, 2005).

Although, clays are less active than zeolites below 600 K, their performance becomes superior to zeolite with increasing temperature (Peng et al., 2022). Clays are widespread, easily available and low-cost chemical substances. Both in their native state and in numerous modified forms, clays are versatile materials that catalyze a variety of chemical reactions such as hydrogenation, cyclization, alkylation, isomerization, and several more (Nagendrappa, 2010). The mild acidity of clay based catalyst does not support the over cracking. It has been confirmed by the detailed characterization of pyrolysis oil obtained by pyrolysis of polystyrene (PS) over clays are mostly in the gasoline range for PS pyrolysis and diesel range for other plastics (Peng et al., 2022). The layer structure of clays makes it possible to tailor a porous network by intercalating sheets with so-called pillars, thus creating a two-dimensional network of interconnected micropores with dimensions larger than those of the zeolites (Peng et al., 2022). The Brønsted acid sites are present in the clay lattice hydroxyls and Lewis sites in the pillars of the materials, respectively (Peng et al., 2022). As per reported literature, clay-based catalysts are good candidates as low-cost catalysts for plastic waste pyrolysis (Fadillah et al., 2021).

Various natural clays such as bentonite (Dewangga et al., 2019), halloysite, pyrophyllite and montmorillonite (Cho et al., 2006) have been used for the catalytic pyrolysis of polystyrene (PS) because of their acidic nature. The use of natural catalyst in place of commercial one would undoubtedly reduce the cost of waste EPS pyrolysis. Therefore, apart from these two commercial catalysts, one natural catalyst synthesized from red clay was also used in this study for the production of aromatic hydrocarbons BTE. The high silica content of red clay provides higher Bronsted acid sites which, makes it suitable as a catalyst for the pyrolysis of waste expanded polystyrene (WEPS). Thus, there is a high possibility of using red clay synthesized

catalysts for pyrolysis of waste plastics to reduce the cost of the pyrolysis process. The red clay mainly contains silica oxide and alumina oxide as the main component. The detailed composition of red clay is given in Table 2.1 (Uddin, 2017).

Table 2.1 Composition of natural red clay.

Various components	wt.%
SiO_2	41.10
Fe_2O_3	6.05
Al_2O_3	31.48
TiO_2	1.49
CaO	0.28
NaO	0.62
K_2O	1.77
MgO	0.35

In this perspective, the catalyst synthesized from natural red clay was also used as a catalyst for the catalytic pyrolysis of WEPS in the present study.

2.1.1.2.1 Catalyst characterization

It is already reported in the literature, the catalyst plays a key role in the pyrolysis process for the production of target products. Thus, the characterization of catalyst is one of the predominant aspects of catalyst development. The proper characterization of catalyst is very important aspect to determine the overall performance of the catalyst. Thus, the characterization of catalyst by means of morphology, surface area, and acidic sites using various analytical techniques are very important to know its suitability for the pyrolysis process. Most of the researchers have used various characterization techniques such as scanning electron microscopy/energy dispersive X-ray (SEM-EDX) (Khalil et al., 2020; Ahmad et al., 2013; Zhang et al., 2019; Sun et al., 2018; Nisar et al., 2019), X-ray diffraction

(XRD) (Yao et al., 2021; Jing et al., 2021; Li et al., 2016; Benedetti et al., 2017), X-ray photoelectron spectroscopy (XPS) (Sun et al., 2018; Wang et al., 2021; Socci et al., 2019; Chen et al., 2020), Brunauer-Emmett-Teller (BET) (Li et al., 2016; Miskolczi et al., 2019; Su et al., 2019; Panda, 2018), Fourier transform spectroscopy (FTIR) (Gaurh and Pramanik, 2018b; Munir and Usman, 2018; Aboul-Enein et al., 2019; Xie et al., 2008), pyridine Fourier transform infrared spectroscopy (py-FTIR) (Amjad et al., 2021; Amjad et al., 2022; Munir and Usman, 2018; Renzini et al., 2009; Panda et al., 2020) to characterize the catalyst for the pyrolysis process.

Amjad et al., 2022 used various analytical techniques such as BET surface area, XRD, XPS, and py-FTIR to characterize the Nb_2O_5, and NiO/Nb_2O_5 catalyst for the pyrolysis of polystyrene (PS) in a semi batch reactor. The Nb_2O_5 catalyst showed a BET surface area of 4.612 m^2/g whereas, NiO/Nb_2O_5 catalyst showed slightly less BET surface area of 4.52 m^2/g. However, the nitrogen adsorption-desorption isotherm obtained using BET surface area analysis confirmed the Nb_2O_5 and NiO/Nb_2O_5 showed a similar type IV isotherm according to the International Union of Pure and Applied Chemistry (IUPAC) nomenclature with a H3 hysteresis loop. The type IV isotherm with H3 hysteresis represents a plate like structure with slit shaped pores and the capillary condensation. The addition of NiO to Nb_2O_5 resulted in an increase in the adsorbed quantity ensured the higher mesoporous volume in the NiO/Nb_2O_5 catalyst. An adsorption isotherm provides information about the maximum amount of adsorbate that can be absorbed by the adsorbent at a particular pressure. In the 1985 IUPAC recommendations physisorption isotherms were grouped into six types (Thommes et al., 2015) as it is seen in Figure 2.3 (Rahman et al., 2019). Type-I(a) isotherm is found for narrow microporous adsorbent having a pore size < ~1 nm. The Type-I(b) isotherm is mainly

characterized by monolayer adsorption. The uptake continuously increases with pressure and reaches a plateau at saturation pressure. Type-II isotherm is characterized by multilayer adsorption and nearly analogous to the Type-I(b) shape; the only difference between the two is the absence of the plateau in Type-II. The uptake continuously increases even when the pressure ratio is close to unity (Rahman et al., 2019).
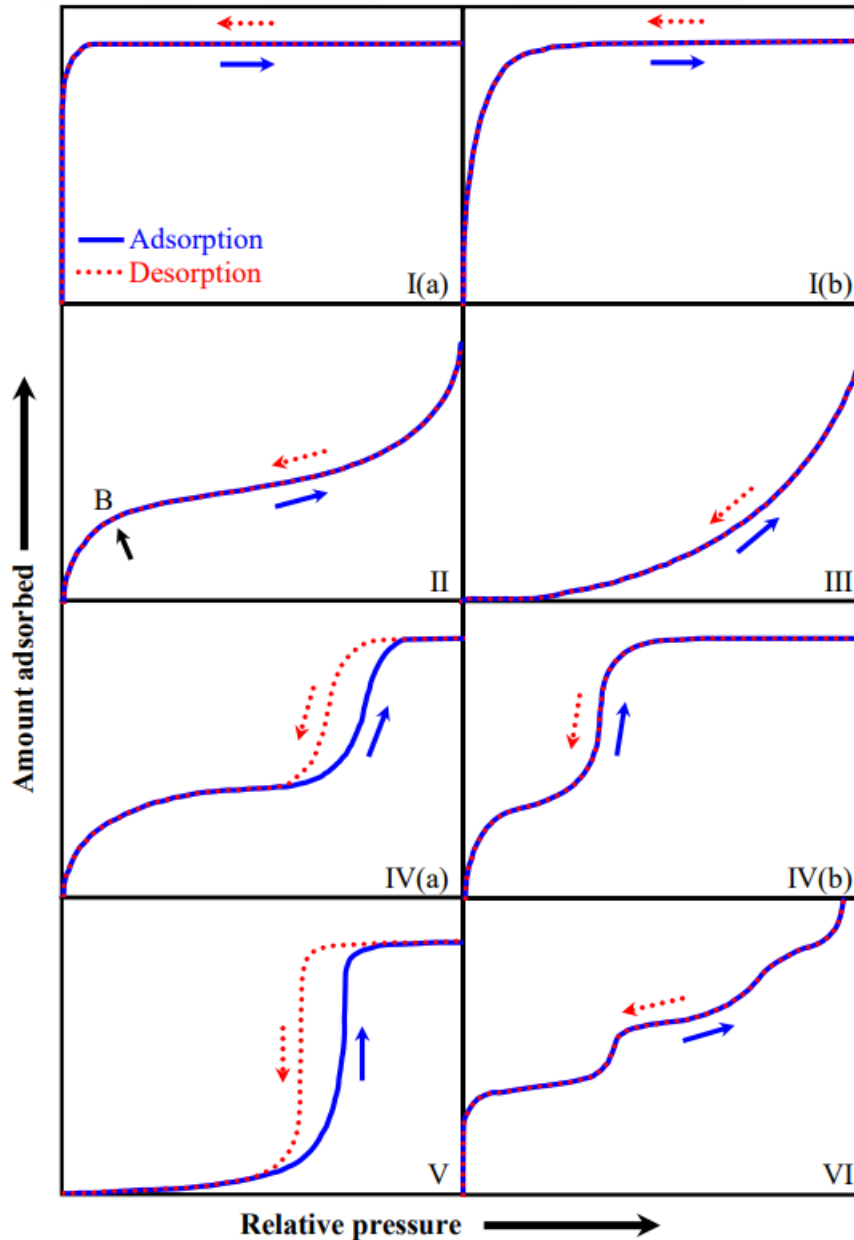
Figure 2.3 Physisorption isotherm classification (© 2015 IUPAC) (Rahman et al., 2019).

The shape of the Type-III adsorption isotherm is convex. At low pressures, the uptake is low, but it increases sharply at high pressures. Depending on the pore width, Type-IV isotherm is divided into two types, one with hysteresis and another without hysteresis, i.e., Type-IV(a) (pore width greater than 4 nm) and Type-IV(b) (pore width smaller than 4 nm), respectively. The type-IV(b) is observed for the adsorbent having cylindrical and conical mesoporous with a smaller width, which is entirely reversible closed at the tapered end (Rahman et al., 2019). Whereas, Type-V is distinguished by its characteristic S-shaped isotherm, and it also demonstrates a hysteresis loop. Finally, in Type-VI, the adsorption occurs in steps (Rahman et al., 2019).

Amjad et al., 2022 carried out the XRD analysis of Ni/Nb_2O_5 to ensure the dispersion of Ni on Nb_2O_5. The XRD analysis revealed well defined peaks indexed to the Nb_2O_5 catalyst (Figure 2.4).
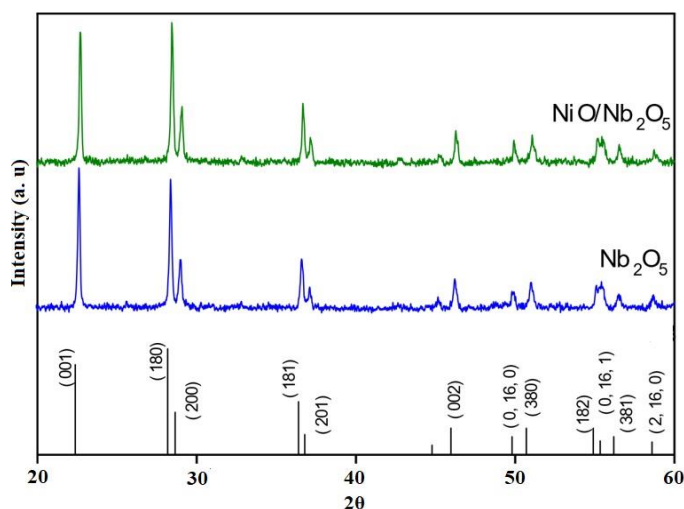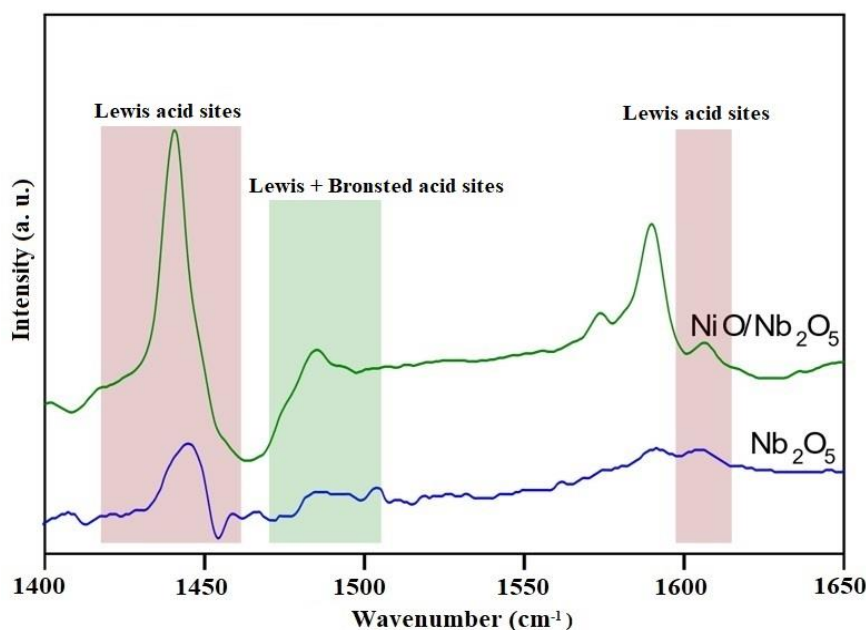

Figure 2.4 XRD pattern of Nb_2O_5 and NiO/Nb_2O_5 catalyst (Amjad et al., 2022).

The reflections of Nb_2O_5 ($2\theta = 22.8$ º, 28.7 º, 29.2 º, 32.7 º, 36.9 º, 46.5 º, 50.1 º, 51.3 º, 55.3 º, and 56.7 º) were indexed to the planes according to the JCPDS card 00-030-0873. The

Ni/Nb$_2$O$_5$ catalyst resulted in peaks at 2θ = 22.7 °, 28.4 °, 29.0 °, 36.6 °, 46.2 °, 49.9 °, 51.0 °, 55.1 °, 56.5 °, and 58.7 ° showing a slight shift towards lower angle (Figure 2.4). This slight shift to lower angles is a sign that NiO is incorporated in Nb$_2$O$_5$ lattice.

The Brosnsted and Lewis acid sites of Nb$_2$O$_5$ and Ni/Nb$_2$O$_5$ catalysts were determined by the py-FTIR spectroscopy (Amjad et al., 2022). The Nb$_2$O$_5$ catalyst showed only a small peak at approximately 1446 cm^{-1}. On the other hand, NiO/Nb$_2$O$_5$ showed a peak at approximately 1446 cm^{-1} and 1591 cm^{-1}. The peak at 1446 cm^{-1} was indicated the Lewis acid sites, and this peak was present in both Nb$_2$O$_5$ (weak intensity) and NiO/Nb$_2$O$_5$ catalysts (high intensity). The peak at approximately 1483 cm^{-1} usually indicated both Bronsted and Lewis sites and was only present with weak intensity in the NiO/Nb$_2$O$_5$ catalyst (Figure 2.5).

Figure 2.5 py-FTIR of Nb$_2$O$_5$ and NiO/Nb$_2$O$_5$ catalyst (Amjad et al., 2022).

The SEM-EDX gives the surface concentration of various elements present in the catalyst along with the surface morphology of the catalyst. Ahmad et al., 2017 used SEM-EDX analysis

to determine the surface morphology and surface elemental composition of the waste brick kiln dust (WBKD) and Zinc oxide impregnated waste brick kiln dust (ZnO/WBKD). The EDX analysis indicated that Si_2O_3, Al_2O_3 and Fe_2O_3 are the major constituents of the waste brick kiln powder. Furthermore, the various inorganic elements i.e., Na, Mg, K, Ca, and Zn were also present in different concentrations ranging from 0.7 wt.% to 5.03 wt.%. It is reported by Ahmad et al., 2017 that the SEM analysis of WBKD indicated the layered morphology with prominent tunnels and large caves (Figure 2.6a). The SEM image of the ZnO/WBKD shows that the surface of catalyst turned into more porous as compared to WBKD (Figure 2.6b).

(a)   (b)
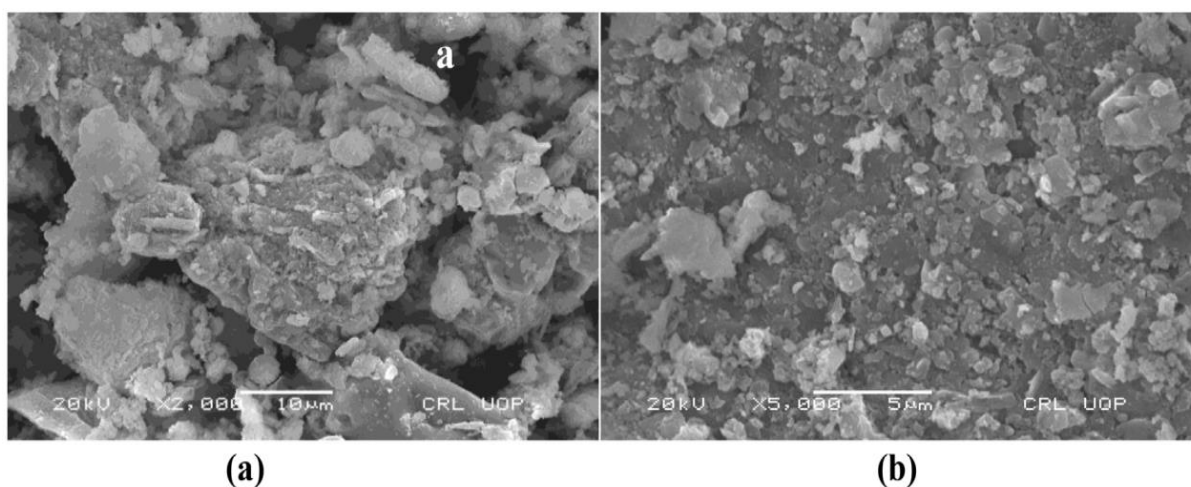
Figure 2.6 SEM images of plain and metal oxide impregnated catalyst (a) WBKD and (b) ZnO/WBKD (Ahmad et al., 2017).

Luo et al., 2020 carried out the pyrolysis of polypropylene (PP) using HCl modified kaoline clay as catalyst. The HCl modified kaoline clay was characterized by the XRD and FTIR analysis before using it as a catalyst. The FTIR analysis of HCl modified kaoline clay reported by Luo et al., 2020 is shown in Figure 2.7. According to Figure 2.7, the FIIR analysis results show that kaolin at 3440 cm^{-1} and 1640 cm^{-1} was the H-O stretching vibration. The characteristic absorption peak neared 1100 cm^{-1} was the stretching vibration of Si-O bond, and

the stretching vibration of Al-OH neared 914 cm $^{-1}$. The characteristic absorption peak in the range of 800 cm^{-1} to 400 cm^{-1} was the flexural vibration of Si-O-Al and Si-O-Si bonds. The active site of the kaolin catalyst is mainly the acid sites formed from tetrahedral aluminum (Al sites and Al species sites). After HCl modification, the Si-O, Al-OH, Si-O-Al and Si-O-Si bond absorption peaks of kaolin were significantly enhanced, which indicated that the catalyst activity was enhanced.
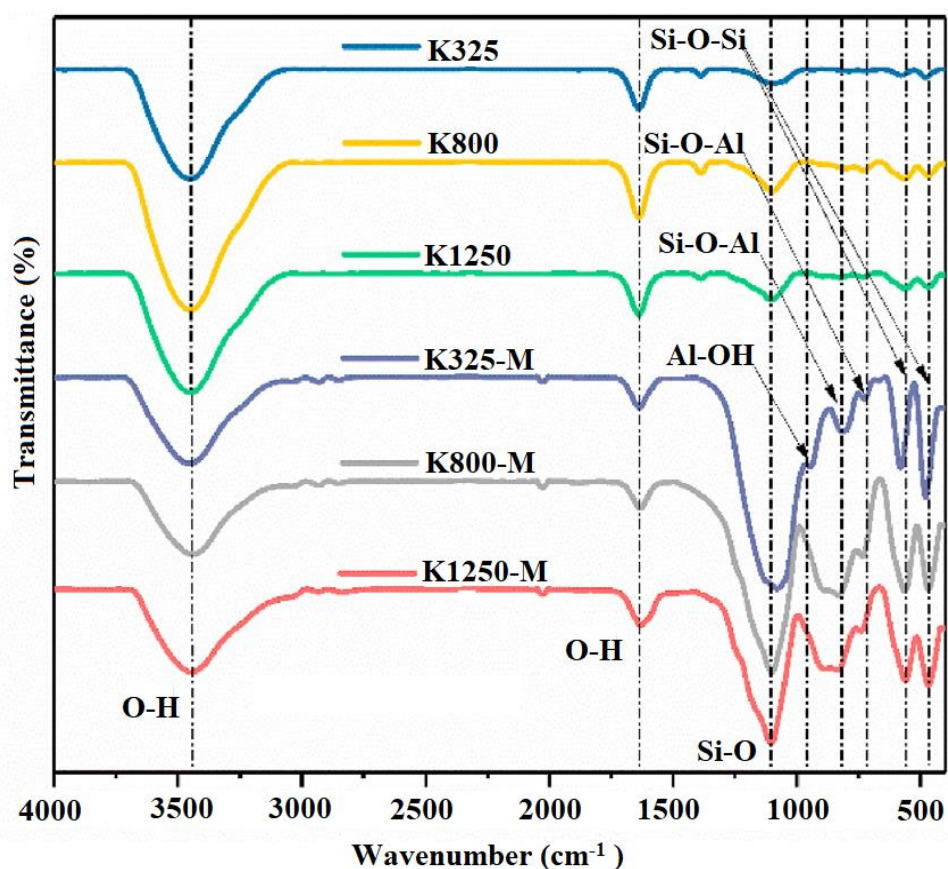
Figure 2.7 FTIR of different kaoline clay K325 (325 mesh of kaolin), K800 (800 mesh of kaolin), K1250 (1250 mesh of kaolin), K325-M (325 mesh of modified kaolin), K800-M (800 mesh of modified kaolin), K1250-M (1250 mesh of modified kaolin) (Luo et al., 2020).

The increase of related functional groups on surface indicated an increase of acid sites, which can promote the decomposition of PP through β-scission reaction and carbonium ion

mechanisms. The XRD analysis of catalyst provides the peaks of various elements present in the catalyst at their respective plane. The different planes obtained from XRD analysis are compared with the standard JCPDS file to identify the elements with their different phases. The XRD analysis of kaoline clay reported by Luo et al., 2020 is mention in Figure 2.8. The crystalline form of kaolin mainly contained $Al_2(Al_{2.8}Si_{1.2})O_{9.6}$, Al_2O_3, SiO_2 and MoO_2. After HCl modification, the crystal shape of kaolin was changed to $Al_2(Al_{2.8}Si_{1.2})O_{9.6}$, Al_2O_3 and SiO_2, while the MoO_2 crystals disappeared.
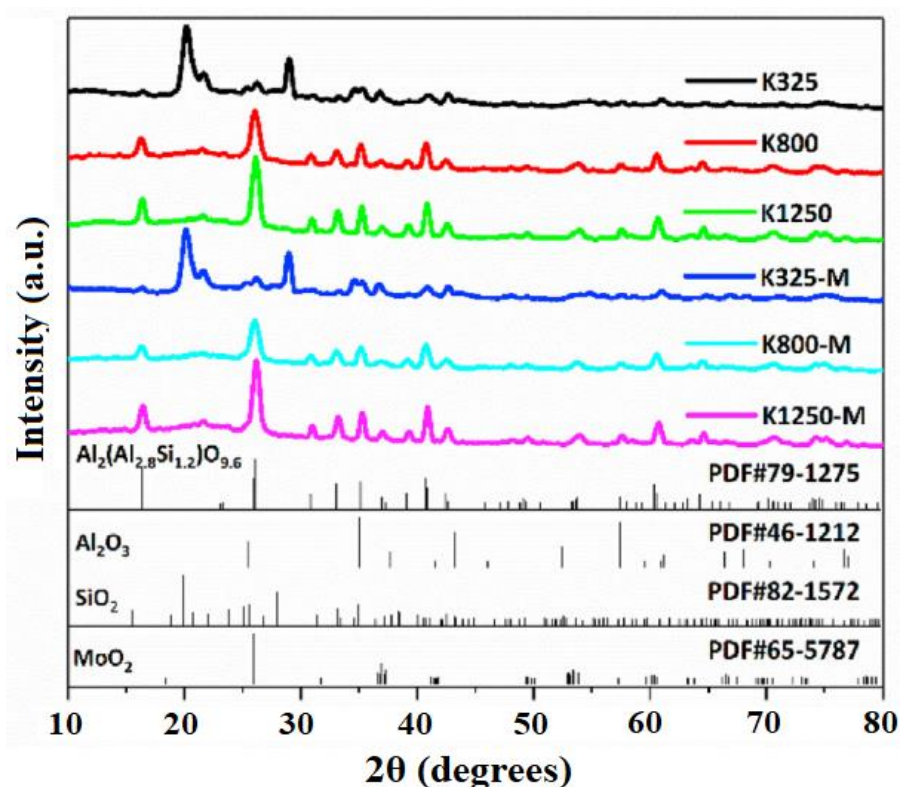

Figure 2.8 XRD of different kaoline clay K325 (325 mesh of kaolin), K800 (800 mesh of kaolin), K1250 (1250 mesh of kaolin), K325-M (325 mesh of modified kaolin), K800-M (800 mesh of modified kaolin), K1250-M (1250 mesh of modified kaolin) (Luo et al., 2020).

It is clear from the above literature review that the catalyst characterization is very important for the determination of its physical and chemical characteristics which are responsible for its

performance to produce target aromatic hydrocarbons benzene, toluene and ethylbenzene (BTE).

2.1.2 Types of reactor/design

The type of reactor/design has major influence on the interaction and degradation behaviour of the feedstock, residence time, heat and mass transfer, efficiency of the process and reaction and cost effectiveness of the pyrolysis process. There are various types of reactors reported in open scientific literature, including batch and semi-batch reactors, fixed and fluidized bed reactors, conical spouted bed reactors (CSBR) and microwave assisted reactors.

The batch reactor is basically a closed system with no inflow and out flow of reactant or products during the pyrolysis process. High conversion in batch reactor can be achieved by leaving the reactant in the reactor for an extended time which is one of its advantages. However, the disadvantages of batch reactor are the variability of product from batch to batch, high labor costs per batch and the difficulty of large scale production. However, semi-batch reactor allows reactant addition or product removal during the reaction. The flexibility of adding reactants over time is an added advantage of the semi-batch reactor in terms of reaction selectivity. Whereas, the disadvantages are same as of batch reactor.

Some researchers used batch (Inayat et al., 2020; Jan et al., 2010; Miskolczi et al., 2004; Adnan et al., 2014; Garcia et al., 2005; Kim and Kim, 2004; Cardona and Corma, 2000; Shah et al., 2010) and semi-batch reactor (Amjad et al., 2022; Amjad et al., 2021; Adrados et al., 2012; Lee and Shin, 2007; Abadi et al., 2014; Rezvanipour et al., 2014; Gaurh and Pramanik, 2018a; Gaurh and Pramanik, 2018b) for the pyrolysis of waste plastics. Some of the batch and semi-

batch reactors were also equipped with stirrer that running at different speed (Sharuddin et al., 2016).

Aljabri et al., 2017 investigated thermal degradation of polystyrene at 250 ^{o}C in a batch reactor and the effect of reaction time and temperature was investigated. The authors found reaction time of 90 min as the optimum time for conversion of waste polystyrene. The liquid fraction collected consisted of styrene, α-methylstyrene, ethylbenzene, 1,2-diphenly propane, 1,3-diphenly butane. Adnan et al., 2014 used batch reactor for the catalytic pyrolysis of polystyrene using zinc bulk catalyst (Zn, ZnO, $ZnCl_2$) in a Pyrex batch reactor. The Zn metal catalyst was found as the best catalyst amongst the zinc bulk catalysts for the pyrolysis of EPSW (expanded polystyrene waste).

Rezvanipour et al., 2014 conducted the pyrolysis of general purpose polystyrene (GPPS) using red mud as a catalyst in a semi-batch reactor. Inayat et al., 2020 used batch as well as semi-batch reactor for the pyrolysis of polystyrene. It was demonstrated that the semi-batch reactor outperformed the batch reactor in terms of liquid yield in both thermal (non-catalytic) and catalytic tests performed at a pyrolysis temperature of 400 °C.

Onu et al., 1999 and Aminu et al., 2020 used two stage process for the pyrolysis of waste plastic. Although, two stage pyrolysis process is not a cost effective because additional heating arrangement is needed to heat the secondary reactor. Moreover, the maintenance and handling is quite tough because of two separate units. Recently, semi batch reactor using various types of reactor arrangements were examined by Gaurh and Pramanik, 2018a for the multiphase catalytic pyrolysis of waste plastic. The developed process enhanced the target aromatic molecules with fuel range hydrocarbons due to *in-situ* aromatization. The process is economical and consumes less energy in comparison to the ex-situ two stage process

(Sharuddin et al., 2016). However, the reamed *in-situ* multiphase pyrolysis of plastic has some limitations like vapour molecules may escape from the reactor without interaction with catalyst present in the vapour phase due to poor design. Only thin layer of catalyst bed was placed at the vapour pahse and thus possibilities of interaction of hydrocarbon molecules with catalyst less in the vapour phase and thereby upgradation of product oil gets hindered. Thus, semi batch reactor with specially designed catalyst bed for *in-situ* vapour phase reactions was selected in the present study for enhancement of the quality of the product oil in terms of BTE and lighter fuel range hydrocarbon molecules.

2.1.3 Types of pyrolysis process

The pyrolysis process involves the chemical transformation (decomposition) of large polymeric molecules in to smaller molecules in an inert atmosphere at high temperature (T) > 300 ºC). The pyrolysis process can be further classified into two broad categories (i) thermal pyrolysis (ii) catalytic pyrolysis as mentioned below.

2.1.3.1 Thermal pyrolysis

Thermal pyrolysis involves the decomposition of polymeric materials by means of thermal energy/heat in an inert atmospheric conditions. Thermal pyrolysis takes place without catalyst therefore, the required temperature for the degradation is high. Thermal pyrolysis process is usually conducted at temperatures in the range between 350 °C to 900 °C. As a result of pyrolysis, three different products i.e., non-condensable gas fraction, liquid fraction (condensable gases) and solid waste are obtained (Almeida and Marques, 2016). The reaction

takes place in a recognized thermal pyrolysis process of waste expanded polystyrene (WEPS) $[(C_8H_8)_n]$ can be expressed as following equation (2.1):

$$[(C_8H_8)_n] + Q \longrightarrow \text{Liquid hydrocarbons} + \text{Gaseous hydrocarbons} + \text{Solid residue} \qquad (2.1)$$
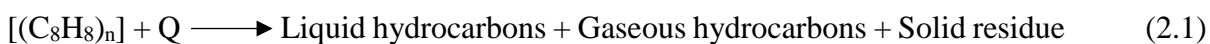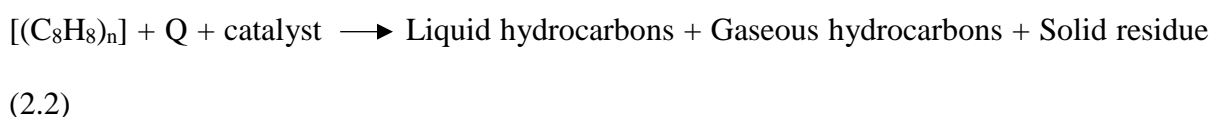
Where, Q is the heat input to conduct the pyrolysis process inside the reactor.

However, liquid fraction obtained from the thermal pyrolysis mainly contains a mixture of higher boiling point-range hydrocarbons (Miandad et al., 2016). The pyrolysis oil obtained from purely thermal pyrolysis having low chemical and fuel value. Thus, further processing is required to enhance the fuel and chemical value of pyrolysis oil. Moreover, thermal pyrolysis is restricted in existing refineries because of non-selective product formation with low octane value (Salem et al., 2017). The product distribution of thermal pyrolysis for a specific reactor design is mainly depends on the temperature and time of reaction. Many researchers Westhuizen et al., 2022; Zayoud et al., 2022; Park et al., 2020; Artetxe et al., 2015; Onwudili et al., 2009; Chauhan et al., 2008; Achilias et al., 2007; Liu et al., 2000; Kim et al., 1999 have been conducted on the thermal pyrolysis of polystyrene (PS). However, the thermal pyrolysis of PS is mainly produces the styrene monomer (Achilias et al., 2007) due to its low activation energy (Park et al., 2003) as compared to other aromatic hydrocarbons like benzene, toluene and ethylbenzene (BTE). It is also reported by Nisar et al., 2019 pyrolysis of PS without catalyst at >500 ^{o}C results in the production of styrene and styrene like compounds. Particularly, for this study, the styrene was considered as the undesired product because it is toxic in nature and a non-fuel type component. In the view of this perspective, the thermal pyrolysis of WEPS was conducted to compare with the liquid yield obtained by catalytic pyrolysis and to determine the enhancement in BTE and reduction in styrene content.

2.1.3.2 Catalytic pyrolysis

The catalytic pyrolysis is more popular as compared to the thermal pyrolysis because it is faster and requires lower temperatures which significantly reduces the energy demand. Moreover, the catalytic pyrolysis produces good quality products due to high selectivity and reduces the need of further upgradation for liquid and gaseous products (Salem et al., 2017). Based on the catalyst phase, pyrolysis process can be further divided into two classes (i) homogenous catalysis cracking and (ii) heterogeneous catalysis cracking. The homogeneous catalytic cracking involve only one phase, in which the feed material i.e., waste plastic and the catalyst are brought in contact in the same phase, ensuring high catalytic activity together with selectivity; and (ii) heterogeneous catalysis cracking, involving more than one phase, the feed and the catalyst reside in different phases (Dwivedi et al., 2019). Aluminium chloride ($AlCl_3$) catalyst is the most commonly used homogeneous catalyst in waste plastic pyrolysis. However, mostly heterogeneous catalysts are widely used for the catalytic pyrolysis due to the fact that the solid catalyst remains with solid residue which can be easily regenerated and reused (Salem et al., 2017). It is already reported in open literature, that the catalytic pyrolysis of PS in the presence of acid catalyst produces more benzene, toluene, and ethylbenzene rather than styrene monomer as compared to the thermal pyrolysis. Interestingly, the catalytic pyrolysis of PS in the presence of base catalyst produces mainly styrene monomer (Park et al., 2003). Many researchers Amjad et al., 2022; Miandad et al., 2017; Adanan et al., 2014; Rezvanipour, et al., 2014; Xie et al., 2008; Moqadam et al., 2015; Dewanga et al., 2019; Lee et al., 2008; Abadi et al., 2018; Gaurh and pramanik, 2020; Shah et al., 2014; Ukei et al., 2000; Cho et al., 2006; Achilias et al., 2007; Ojha and Vinu, 2015 had performed the catalytic pyrolysis of PS using various heterogeneous catalyst for the production of their selected desired products. Moreover,

many researchers (Achilias et al., 2007; Ukei et al., 2000) conducted the catalytic pyrolysis of PS using various basic and acid catalyst to compare the product yield and distribution obtained from basic and acid catalysts. Achilias et al., 2007 conducted the catalytic pyrolysis of PS using basic catalyst i.e., BaO and acid catalyst i.e., FCC catalyst at a temperature of 510 ^{o}C. It was concluded that the, styrene was found to be the main component obtained from the both type of catalyst. However, catalytic pyrolysis over FCC catalyst exhibited low selectivity towards the styrene monomer as compared to the BaO catalyst. Furthermore, the FCC catalyst shows higher selectivity towards the benzene, toluene and ethylbenzene because of the cracking and hydrogenation ability of the acid catalyst FCC. Ukei et al., 2000 also used various basic catalysts i.e., MgO, CaO, BaO, K_2O, and acid catalyst such as SiO_2/Al_2O_3, HZSM-5 to conduct the pyrolysis of PS. It is also suggested by the Ukei et al., 2000 that the, acid catalysts are more prone for the formation of aromatics other than styrene such as benzene, toluene and ethylbenzene. Thus, in the present study, the catalytic pyrolysis of WEPS was conducted in the presence of solid acid catalysts for the production of target molecules BTE. The catalytic pyrolysis of waste expanded polystyrene (WEPS) can be expressed as equation (2.2):

$[(C_8H_8)_n]$ + Q + catalyst $\longrightarrow$ Liquid hydrocarbons + Gaseous hydrocarbons + Solid residue (2.2)

Where, Q is the heat input to conduct the pyrolysis process inside the reactor.

2.1.4 Mechanism for the formation of BTE via thermal and catalytic pyrolysis

In general, cracking and hydrogenation are responsible for producing BTE in the thermal decomposition of polystyrene. Wang et al., 2019 reported the mechanism for the formation of BTE via thermal pyrolysis of WEPS as shown in Figure 2.9.
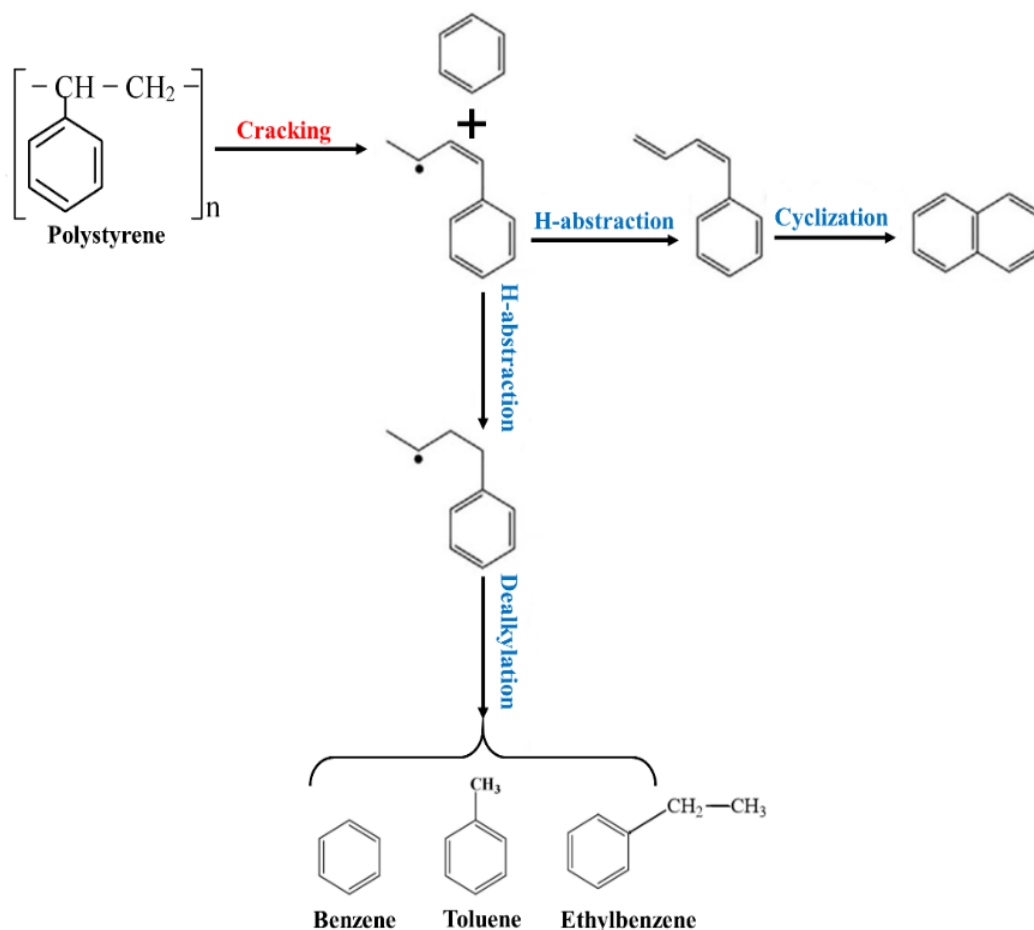
Figure 2.9 Proposed reaction pathway for thermal cracking of polystyrene to form BTE (Wang et al., 2019).

However, the percentage of benzene, toluene and ethylbenzene in the liquid yield is less due to non-selective nature of the reaction process (Gaurh and Pramanik, 2018a). On the other side, the catalytic cracking of polystyrene starts from either the aromatic ring or the aliphatic chain, and protonated styrene dimers are formed because the aliphatic chain is more easily attacked by protons from Brønsted acid sites, which further undergoes cyclization and cracking to generate benzene (Wang et al., 2019).

In catalytic process, ethylbenzene and toluene are formed via hydrogenation reaction (Onwudili et al., 2009). Figure 2.10 shows the reaction pathways for the production of benzene,

toluene, ethylbenzene and styrene during catalytic pyrolysis of WEPS. The degradation of WEPS starts from proton of Bronsted acid sites of catalyst.
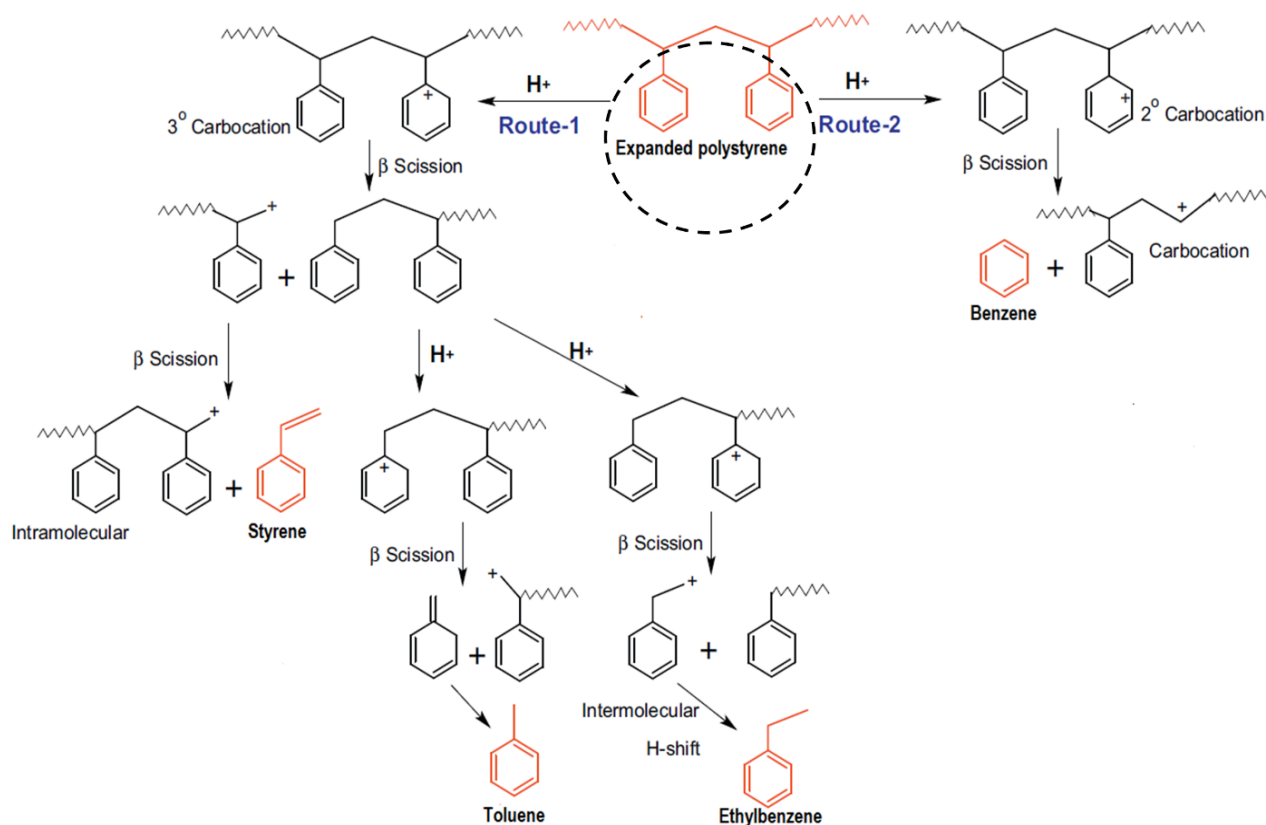
Figure 2.10 Mechanism of formation of major product during catalytic pyrolysis of EPS (Verma et al., 2021).

As mentioned in the Figure 2.10, proton can attack a mid-chain phenyl group either at position 1 or 2 as per path 2 or 1, respectively. Protonation at the position-1 results in the formation of secondary carbocation. However, protonation at position 2 leads to the formation of a more stable tertiary carbocation. The tertiary carbocation produced by route 1 undergoes β-scission to form end chain primary carbocation and a stable polymer chain with benzyl end group. The end chain carbocation can further undergo β-scission to form styrene. The formation pathways of toluene and ethylbenzene involve protonation of the ultimate or penultimate phenyl group in position 1 of the PS chain, respectively. Toluene is formed via β-scission, while

ethylbenzene is formed via β-scission followed by intermolecular proton shift with another polymer or oligomer chain.

2.1.5 Factors affecting the BTE production from PS

The pyrolysis oil, pyrolysis gas and solid residue are obtained after the pyrolysis process as a final product. The composition as well as distribution of these pyrolysis products can be easily altered by changing various pyrolysis process parameters such as feed stock composition (Adnan et al., 2015), feedstock size (Selvaganapathy et al., 2020), reaction temperature (Adnan et al., 2015), reaction time (Adnan et al., 2015), system pressure (Onwudili et al., 2009), heating rate (Singh and Ruj, 2019), type of reactor, reactor design (Zhou et al., 2021), atmosphere of pyrolysis (Xue et al., 2017), flow rate of carrier gas (Pan et al., 2022), catalyst type (Ukei et al., 2000), catalyst amount (Gaurh and Pramanik, 2020) and contact mode of catalyst (Xue et al., 2017). The product composition and distribution obtained from thermal and catalytic pyrolysis at various parameters are discussed below for the selection of effective process parameters in the present study.

2.1.5.1 Production of BTE via thermal pyrolysis of PS

It is already mentioned that the thermal pyrolysis takes place without catalyst. Therefore, the major influencing parameters for thermal pyrolysis are reaction temperature, reaction time, heating rate and reactor design/type. Table 2.2 shows the product distribution and composition based on the thermal pyrolysis of PS. It is seen from the published literature that the thermal pyrolysis of PS mainly produced styrene monomer and BTE very low amount. However, product composition can be altered by controlling the various parameters as mentioned earlier.

Westhuizen et al., 2022 conducted the thermal pyrolysis of PS at a temperature of 550 ºC in a semi-continuous pilot scale reactor to achieve a maximum liquid yield of 82.5 wt.%.

Table 2.2 Liquid yield, BTE and styrene content obtained from the thermal pyrolysis of PS.

References	Reactor type	Important process parameters	Liquid yield (wt.%)	Aromatic content (wt.%)
Westhuizen et al., 2022	Semi-continuous pilot scale reactor	Temperature: 550 ºC	82.5	Benzene: not available Toluene: 4.0 ± 0.3 Ethylbenzene: 4.9 ± 0.8 Styrene: 39.4 ± 3.5
Zayoud et al., 2022	Continuous pyrolysis pilot-scale reactor	Temperature: 550 ºC Pressure: 0.02 bar	94.5	Benzene: not available Toluene: 3.2 Ethylbenzene: 2.1 Styrene: 55.9
Artetxe et al., 2015	Conical spouted bed reactor	Temperature: 500 ºC	Not available	Benzene: 0.44 Toluene: 3.54 Ethylbenzene: 1.28 Styrene: 70.57
Ojha and Vinu, 2015	single shot micropyrolyzer	Temperature: 400 ºC	Not available	Benzene: 0.0 Toluene: 0.0 Ethylbenzene-0.0 Styrene- 81.54
Achilias et al., 2007	Bench scale fixed bed reactor	Temperature: 510 ºC	91.8	Benzene: not available Toluene: 2.0 Ethylbenzene: 0.5 Styrene: 63.9
Ukei et al., 2000	Stainless steel reactor	Temperature: 623 K Reaction time: 3h	80.1	Benzene: not available Toluene: 5.1 Ethylbenzene: 2.4 Styrene: 70.0
Lee et al., 2001	Semi-batch reactor	Temperature: 400 ºC Reaction time: 2h	81.7	Benzene: 0.06 Toluene: 7.73 Ethylbenzene: 8.79 Styrene: 70.08
Kim et al., 1999	Stirred tank batch reactor	Temperature: 400 ºC	94.80	Benzene: not available Toluene: 1.41 Ethylbenzene: 0.09 Styrene: 71.56

The pyrolysis oil mainly composed of toluene (4.0 ± 0.3 wt.%), ethylbenzene (4.9 ± 0.8 wt.%) and styrene (39.4 ± 3.5wt.%). The reported styrene content is very high in comparison to toluene and ethylbenzene. Zayod et al., 2022 performed the thermal pyrolysis in a continuous mode pilot scale reactor under very low pressure of 0.02 bar. Very high styrene yield of 55.9 wt.% was reported. Artexe et al., 2015 used conical spouted bed reactor for the thermal pyrolysis of PS at a reaction temperature of 500 °C. They also reported very high styrene content of 70.57 wt.% with low BTE content. Achilias et al., 2007 reported maximum liquid yield of 91.8 wt.% for the pyrolysis temperature of 510 °C. Total toluene and ethylbenzene of 2.8 wt.% and styrene of 63.9 wt.% were obtained.

Ukei et al., 2000 performed the thermal pyrolysis of PS at a reaction temperature of 623 K for the reaction time of 3h. They reported very high styrene content of 70.0 wt.% in the pyrolysis oil. Lee et al., 2001 and Kim et al., 1999 also reported very high styrene content of 70.08 wt.% and 71.56 wt.% with liquid yield of 81.7 wt.% and 94.80 wt.%, respectively. They reported very low BTE content in comparison to styrene in the pyrolysis oil obtained from WEPS. It is reported in open literature, that the high temperature and retention time, favours the formation of BTE with a decrease in styrene content (Artetxe et al., 2015). Onwudili et al., 2009 reported that the toluene and ethylbenzene formed via further degradation of styrene. Ukei et al., 2000 also reported that high temperature might lead to hydrogenation of styrene due to the secondary reactions that may decrease styrene and increase its derivate compounds. Moreover, it is reported by Shah and Jan, 2014 that the increase in reactor pressure also decreases the production of styrene with the increase in toluene and ethylbenzene. It is seen from the above literature review that the styrene content in the pyrolysis oil by thermal process is very high in comparison to BTE content even at very high temperature.

2.1.5.2 Production of BTE via catalytic pyrolysis of PS

The product yield and product distribution obtained from the catalytic pyrolysis of PS using various acid and basic catalyst is given in Table 2.3. It is clear from the literature review, the catalyst catalytic pyrolysis of PS using acid catalyst are very popular for the production of aromatic hydrocarbons other than styrene. The use of solid acid catalyst decreases the styrene production and increase the production of benzene, toluene, and ethylbenzene (Ukei et al., 2000). Adnan et al., 2014 performed the catalytic pyrolysis of PS using Zn, ZnO, and $ZnCl_2$ catalyst. They reported that the Zn metal catalyst was found as the best catalyst amongst the zinc bulk catalysts for the pyrolysis of PS. The liquid yield of 96.73 wt.% obtained at a temperature of 450 ^{o}C with the feed to catalyst ratio of 1:0.02. The very high styrene content of 47.96 wt.% was found in the pyrolysis oil with very low toluene and ethylbenzene content of 2.47 wt.% and 1.16 wt.%, respectively.

Rezvanipour et al., 2014 conducted the catalytic pyrolysis of PS using red mud catalyst at a reaction temperature of 350 ^{o}C. They reported very high styrene content of 60.32 wt.% in the pyrolysis oil. Moqadam et al., 2015 investigated the catalytic pyrolysis of PS in a semi batch reactor at a pyrolysis temperature of 410 ^{o}C using silica-alumina catalyst. They also reported very high styrene content of 80.98 wt.% in the pyrolysis oil. Lee et al., 2008 and Abadi et al., 2018 were also reported the very high styrene content of 58.99 wt.% and 61.2 wt.% in the catalytic pyrolysis oil, respectively.

Gaurh and Pamanik, 2020 investigated the catalytic pyrolysis of PS using ZSM-5 catalyst at a temperature of 700 ^{o}C in a semi batch reactor. The toluene of 16.57 wt,.% and ethylbenzene of 3.57 wt.% were found in the pyrolysis oil. Although, they did not reported the styrene content of pyrolysis oil.

Table 2.3 Liquid yield, BTE and styrene content obtained from the catalytic pyrolysis of PS.

References	Reactor type	Catalyst used	Important process parameters	Liquid yield (wt.%)	Aromatic content (wt.%)
Adnan et al., 2014	Batch reactor	Zn, ZnO, ZnCl$_2$	Catalyst: Zn Temperature: 450 ºC Feed/Catalyst: 1:0.2 Reaction time: 120 min	96.73	Benzene: not available Toluene: 2.47 Ethylbenzene: 1.16 Styrene: 47.96
			Catalyst: ZnO Temperature: 450 ºC Feed/Catalyst: 1:0.2 Reaction time: 60 min	84.73	Benzene: not available Toluene: 1.80 Ethylbenzene: 0.60 Styrene: 41.45
			Catalyst: ZnCl$_2$ Temperature: 500 ºC Feed/Catalyst: 1:0.1 Reaction time: 60 min	79.60	Benzene: not available Toluene: 2.11 Ethylbenzene: 1.93 Styrene: 40.88
Rezvanipour et al., 2014	Semi-batch reactor	Red mud	Temperature: 350 ºC Feed/Catalyst: 100:15	93	Toluene: 1.67 Benzene and its derivatives: 33.63 Styrene: 60.32
Moqadam et al., 2015	Semi-batch reactor	Silica-alumina	Temperature: 410 ºC Catalyst/feed: 1:20	97.3	Benzene: not available Toluene: not available Ethylbenzene: 0.2 Styrene: 80.98
Lee et al., 2008	Stirred semi-batch reactor	Spent FCC	Temperature: 400 ºC Feed/catalyst: 10:1 Reaction time: 34-42 min	-	Benzene: 2.03 Toluene: 8.95 Ethylbenzene: 16.14 Styrene: 58.99
Abadi et al., 2018	Semi-batch stirred reactor	Used FCC	Temperature: 450 ºC Catalyst/feed: 5(w/w%) Agitatorspeed-50 RPM	93.7	Benzene: not available Toluene: not available Ethylbenzene: not available Styrene: 61.2
Gaurh and Pramanik, 2020	Semi-batch reactor	ZSM-5	Temperature: 700 ºC Feed/catalyst: 20:1	86.2	Benzene: 0.80 Toluene: 16.57 Ethylbenzene: 3.57 Styrene: not available

The detailed literature review on the catalytic pyrolysis of WEPS shows the low styrene content in the liquid yield with higher amount of BTE content in comparison to the thermal pyrolysis. It is expected that the proposed catalytic pyrolysis of WEPS using commercial red clay synthesized catalyst would give better quality of liquid yield with higher BTE content and lower styrene content.

2.1.6 Pyrolysis product characterization

The pyrolysis oil obtained from the pyrolysis process are characterized by the different characterization techniques such as gas chromatography with mass spectroscopy (GC-MS), nuclear magnetic resonance (NMR), Fourier transform spectroscopy (FTIR) and some important physicochemical properties such as gross calorific value (GCV), carbon residue, kinematic viscosity, API gravity, ASTM distillation, flash and fire point.

Nisar et al., 2019 characterized the pyrolysis oil obtained from thermal pyrolysis of polystyrene using GC-MS to determine the various components present in the pyrolysis oil. The pyrolysis oil was also characterized by important physicochemical properties such as density, specific gravity, API gravity, refractive index, viscosity, kinematic viscosity and acid value and compared with the standard fuels such as diesel, gasoline and kerosene. It was clear from the GC-MS analysis the major components of pyrolysis oil were 2-propanone, toluene, 1-hydroxy-2-propanone, styrene and α-methyl styrene. The acid value of polystyrene waste oil was higher than the gasoline and diesel oil but lower than the kerosene oil. Whereas, the specific gravity of pyrolysis oil was higher than the gasoline oil and lies within the range of diesel oil. API gravity of waste oil was lower than the kerosene and gasoline oil while close to the API gravity of diesel fuel. Refractive index of polystyrene oil was 1.471, which was very close to the

refractive index of diesel oil. The viscosity of the polystyrene oil was found out to be 1.132 centipoise at 30 °C, which falls within the viscosity range of kerosene oil (1.2-1.8 centipoise) as reported by Nisar et al., 2019.

Rezvanipour et al., 2014 characterized the pyrolysis oil using GC-MS and various physicochemical properties such as density, specific gravity, API gravity, viscosity, kinematic viscosity, flash point and freezing point obtained from catalytic pyrolysis of polystyrene using red mud as catalyst. The physicochemical properties of pyrolysis oil was also compared with the gasoline, diesel and kerosene. As reported by Rezvanipour et al., 2014, the catalytic pyrolysis oil was mainly composed of styrene, benzene and its derivatives, toluene and ethylbenzene. The density of pyrolysis oil was about 0.82 g/cm^3 close to the kerosene and diesel. The specific gravity value of the pyrolysis oil was about 0.83 close to the commercial fuel diesel. The API gravity value was found to be 39.81 for catalytic pyrolysis oil. The API gravity of pyrolysis oil was found in the range of API gravity of kerosene. The viscosity and kinematic viscosity values of obtained pyrolysis oil were 1.267 centipoises and 1.536 mm^2/s respectively. The viscosity and kinematic viscosity of pyrolysis oil were close to the standard fuel kerosene. However, the flash point of catalytic pyrolysis oil was corresponds to the flash point of gasoline. Whereas, the freezing point value was in close agreement with kerosene freezing point.

Similarly, Sanchez et al., 2022 characterized the thermal pyrolysis of a real mixture of plastic wastes collected from municipal solid waste using specific gravity, refractive index, elemental analysis, GC-MS (gas chromatography-mass spectroscopy), ASTM D86 distillation. Wathakit et al., 2021 used GC-MS, ASTM distillation, kinematic viscosity, surface tension, flash point to characterize the pyrolysis oil obtained from the pyrolysis of mixed waste plastic. Gaurh and

Pramanik, 2018a characterized the pyrolysis oil obtained from waste polyethylene using gas chromatography in flame ionization detector mode (GC-FID), ASTM distillation, FTIR analysis, carbon residue, API gravity, GCV, flash and fire point.

In view of the above mentioned literature review, it is clear that the, characterization of pyrolysis oil using various characterization techniques and physicochemical properties is very important to determine its end use.

2.2 Objectives

The detailed literature review confirms that the pyrolysis of waste expanded polystyrene (WEPS) followed by *in-situ* hydrogenation is the suitable way to convert WEPS into valuable hydrocarbons benzene, toluene and ethylbenzene (BTE) and thereby reducing the environmental pollution problem caused by the WEPS. Furthermore, synthesis of catalyst from natural red clay would reduce the cost of entire pyrolysis process for the production of valuable commodity chemicals and hydrocarbons BTE from WEPS pyrolysis. The developed red clay catalyst from natural red clay could be better alternative of commercial catalyst. Thus, a detailed study on the pyrolysis of WEPS is needed for the production of BTE and fuel range hydrocarbons using different types of catalysts and reactor design. Towards, the fulfilment of these requirements, the thesis has the following objectives:

1. To design and fabrication of reactor and experimental set up for the multiphase catalytic pyrolysis of waste expanded polystyrene (WEPS).

2. To synthesis catalyst from red clay and its characterization using scanning electron microscope/energy dispersive X-ray spectroscopy (SEM-EDX), X-ray diffraction (XRD),

Brunauer-Emmet-Teller (BET) surface area, Fourier transformed infra-red spectroscopy (FTIR).

3. To optimize the different effective process parameters of catalytic pyrolysis such as feed to catalyst ratio, temperature, heating rate, reaction time and reactor arrangements for enhancing the liquid yield, target aromatic hydrocarbons benzene, toluene and ethylbenzene (BTE) and reduction of styrene monomer in the pyrolysis oil.

4. To determine the physicochemical properties of pyrolysis oil obtained from thermal and catalytic pyrolysis using GC-FID, FTIR, flash and fire point, calorific value, carbon residue.

5. To optimize the effective process parameters using RSM-BBD to achieve highest liquid yield for the best reactor arrangement multiphase/AB-type and validated with experimental data.

6. To study the reusability of catalyst for pyrolysis process.

The next chapter 3 describes detailed experimental method and reactor arrangements to conduct the thermal and catalytic pyrolysis of WEPS, feed preparation, characterization of feed, synthesis of catalyst using natural red clay, characterization of synthesized catalyst using various analytical techniques, and characterization of pyrolysis oil using various characterization methods.