CHAPTER 3
EXPERIMENTAL

This chapter includes the experimental details related to the production of BTEX using commercial and synthesized catalyst from waste plastic polyethylene, polypropylene and polystyrene, preparation of feed material, catalyst synthesis from fly ash, characterization of catalysts through Fourier-Transformed Infra-Red spectroscopy (FTIR), Scanning Electron Microscope/Energy dispersive X-ray spectroscopy (SEM-EDX), Brunauer-Emmet-Teller (BET) surface area, catalyst regeneration process. The product oil was analysed by ASTM distillation, flash & fire point, carbon residue, calorific value, FTIR analysis and gas chromatography with Flame Ionization Detector (GC-FID).

3.1 Material

The statistics of municipal solid waste (MSW), Varanasi city, India shows that major amount of plastic waste consisting of PE, PP, PS, PVC and PET (Table 3.1).

Table 3.1 Plastic waste scenario in Varanasi, India (Srivastava et al., 2014).

Type of plastic waste	Contribution in MSW (wt.%)
Polyethylene (PE)	41
Polypropylene (PP)	24
Polyethylene terephthalate (PET)	13
Poly vinyl chloride (PVC)	3
Polystyrene (PS)	7
Poly lactic acid (PLA)	0.2
Others	11.8

Based on literature survey chapter 2 (Page no. 10), three different types of waste plastics polyethylene (PE), polypropylene (PP) and polystyrene (PS) have been considered for the experimental study in detail via pyrolysis process. All waste polyethylene, polypropylene and polystyrene were collected from the municipal dumping zone of Varanasi city, India.

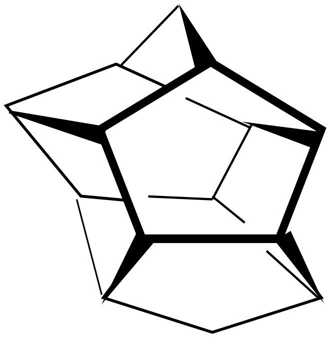


Figure 3.1 Pentasil unit of commercial ZSM-5 catalyst (Cejka and Bekkum, 2005).

In the present study two types of catalysts commercial ZSM-5 catalyst and fly ash synthesized natural catalyst were used. The commercial catalyst ZSM-5 was procured from Alfa Aesar, USA. Zeolite Socony Mobil–5 (ZSM-5) is an aluminosilicate zeolite belonging to the pentasil family of zeolites (Fig 3.1). Its chemical formula is $Na_nAl_nSi_{96-n}O_{192}\cdot16H_2O$ ($0<n<27$) (Cejka and Bekkum, 2005). The mole ratio of SiO_2:Al_2O_3 was taken 30:1 of commercial ZSM-5 catalyst in this study. The surface area of commercial ZSM-5 catalyst was 400 m^2/g.

Table 3.2 Chemical composition of fly ash (Malik et al., 2016).

Components	**Amount (wt. %)**
SiO_2	53.56
Al_2O_3	27.71
Fe_2O_3	5.53
MgO	0.91
CaO	4.50
K_2O	0.94
Na_2O	0.37
Others	6.48
Ignition loss	5.88

The other catalyst used for pyrolysis process in present study was natural catalyst derived from waste fly ash of thermal power plant. The chemical composition of fly ash (FA) is shown in Table (3.2).

To determine BTEX in the liquid yield of waste plastic pyrolysis, analytical grade benzene (Fisher scientific, India), toluene (S D fine-chem ltd., India), ethylbenzene (Avra syn. pvt. ltd., India) and xylene (Avra syn. pvt. ltd., India) were used in GC-FID test.

3.2 Experimental Setup

Fig (3.2) shows the schematic of experimental set up of pyrolysis process consist of a semi batch reactor. The treated and shredded waste plastic polyethylene, polypropylene and polystyrene sample of 50 g was fed to the reactor made of mild steel of 123 mm outer diameter, 112 mm inner diameter and 135 mm height. The reactor was then properly sealed with gasket to prevent the products leakage. The dimension of the reactor was fixed based on standard design criterion of appropriate L/D ratio of 1.21. This improves vapor recirculation inside the reactor and minimizes pressure drop. The thermal pyrolysis was performed in the reactor arrangement as shown in Fig (3.3a**)**. Catalytic pyrolysis was performed in three different phases within the reactor batch by batch systematically keeping the catalyst in A type-vapor phase, B type-liquid phase and C type-vapor and liquid (multiphase), respectively (Fig 3.3b-d). A porous stainless-steel plate was used to support the catalyst in the study as shown in Fig (3.4a-b). A thin layer of ceramic wool was used to make the catalyst bed through which vapors of alkanes and gases could easily diffuse with a better catalyst-vapor interaction. The product vapors were collected via a water condenser followed by two conical flask which was keep in an ice bath. The photograph of experimental setup is shown in the Appendix-A1.

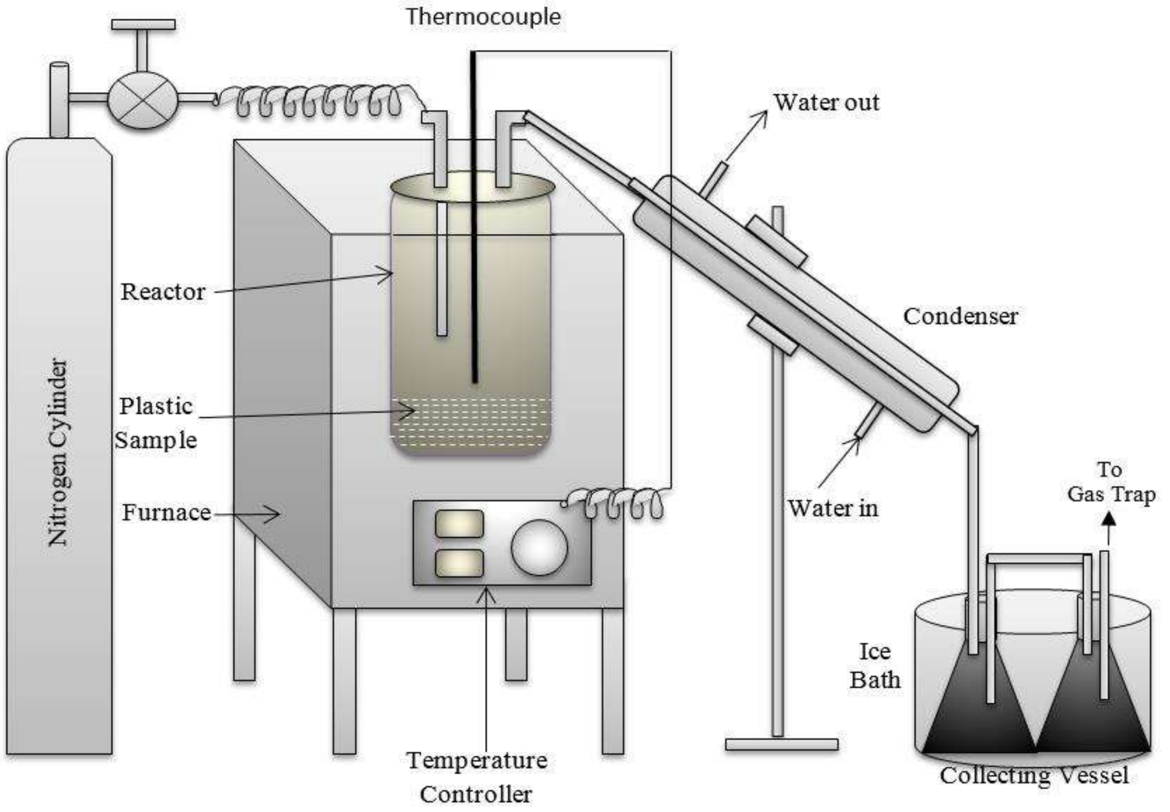


Figure 3.2 Schematic of experimental set-up.

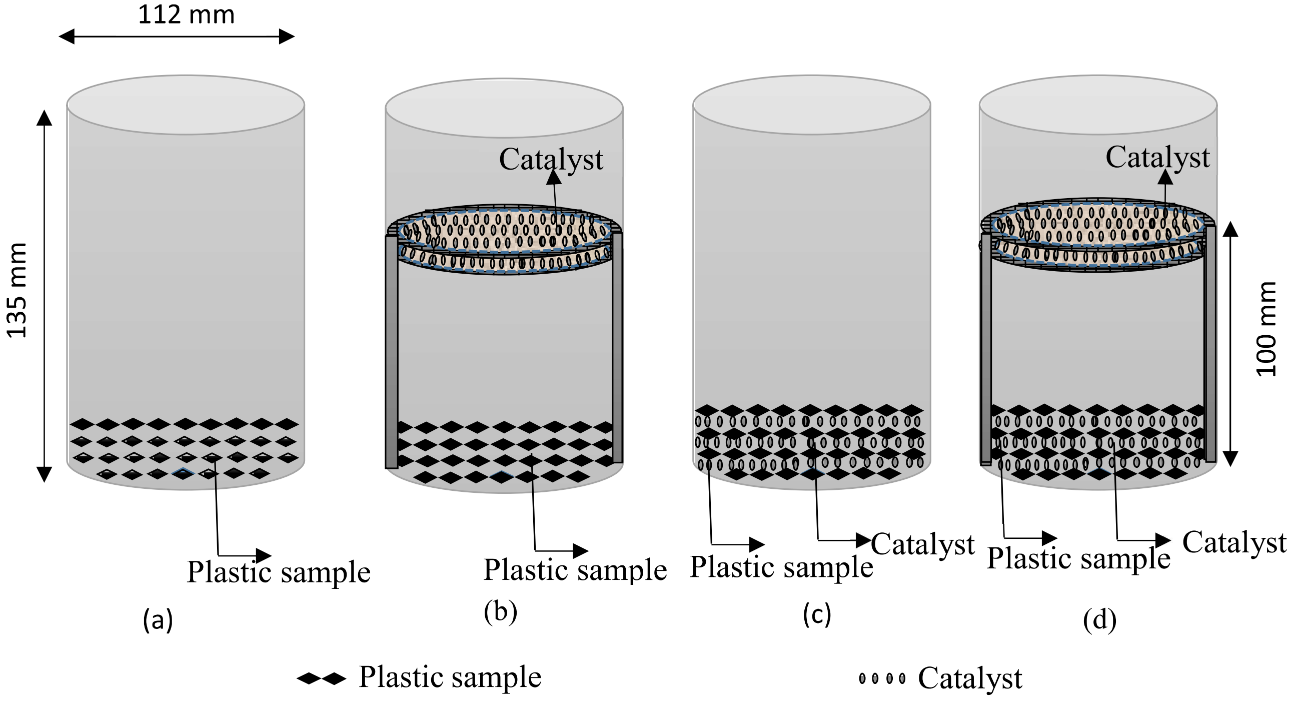
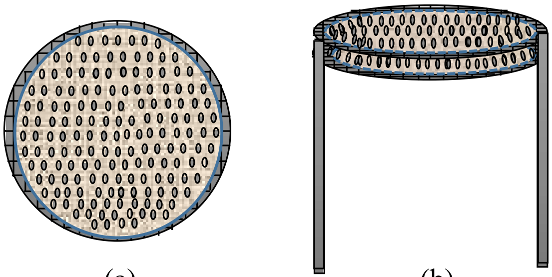


Figure 3.3 Internal detail of reactor set-up (a) Pure thermal pyrolysis (b) A-type (catalyst in vapor phase) (c) B-type (catalyst in liquid phase) and (d) C-type (catalyst in both liquid and vapor phase).



(a) (b)

Figure 3.4 Catalyst bed (a) top view (b) side view

3.3 Method

3.3.1 Feed preparation

The waste polyethylene (PE), polypropylene (PP) and polystyrene (PS) were collected from the municipal dumping zone of Varanasi city, India. The PE waste in the form of carry bag, PP waste in the form of disposable glasses and PS waste in the form of waste boxes used for chemical transport and other accessories were collected. These waste plastics were first cleaned with water to remove other impurities then dried in open sunlight to remove free moisture. The dried PE and PP were shredded into small pieces (4 mm X 4 mm) using scissors manually to accommodate more samples in the reactor and melting faster. The dried PS waste was broken into small pieces and heated at 150 ^{o}C to obtain flakes. The volume of the PS samples was reduced 25 times (final size was 5 mm X 5 mm). The size reduction was done to increase the heat transfer surface area of the material during melting process.

(a) (b) (c)

Figure 3.5 Pictorial view of feed materials (a) polyethylene, (b) polypropylene and (c) polystyrene

3.3.2 Catalyst synthesis from fly ash

The catalyst was synthesized from waste fly ash (FA) which was collected from the Panki thermal power plant in Kanpur, India. The collected fly ash was thoroughly washed with water to remove mud, dirt and any other suspended impurities before the calcination of fly ash. The washed fly ash was then dried in an oven for overnight at a temperature of 108 °C to remove moisture. Dried fly ash was screened through a sieve of mesh size 230 (A.S.T.M.) [240 B.S.S. or 63 μm] to remove the unburnt carbon and larger particles. A fraction of the resulted raw fly ash without calcination was used in the pyrolysis process and designated as "FAN" i.e., untreated fly ash. The remaining of part of the washed and dried fly ash was calcined in order to improve physicochemical properties of synthesized catalysts in terms of BET surface area and Si/Al ratio. The fly ash was calcined in a muffle furnace at four different temperatures i.e., 600 °C, 700 °C, 800 °C and 900 °C in static air for 5 h in which improved surface area of the FA catalyst and surface Si/Al ratio followed by removal of sulfur and other impurities. The calcined fly ash catalyst were designated as FA-600 (calcined at 600 °C), FA-700 (calcined at 700 °C), FA-800 (calcined at 800 °C) and FA-900 (calcined at 900 °C). All the catalysts were characterized using SEM-EDX, FTIR and BET analysis to check the suitability of utilizing it as catalysts for the pyrolysis of waste polyethylene, polypropylene and polystyrene for BTEX production.

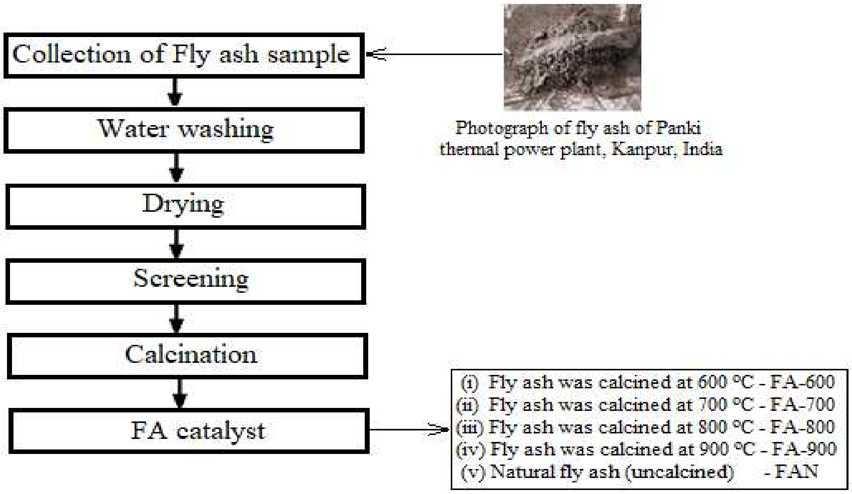


Figure 3.6 Block diagram of synthesis method of catalyst from fly ash

3.3.3 Catalyst characterization

The characterization of catalyst is one of the major aspects of catalyst development. The performance of synthesized catalyst could be predicted by the proper characterization. The structure, composition and chemical properties of catalyst helps for better understanding of the relationship between catalyst properties and catalytic performance. The characterization technique that are applied in the present study are (i) Fourier Transformed Infrared Spectroscopy (FTIR), (ii) Brunauer-Emmett-Teller (BET) surface area and (iii) Scanning Electron Microscope/ energy dispersive X-ray spectroscopy (SEM-EDX). It should be noted that the characterization techniques were applied to fly ash synthesized catalyst only. For some cases ZSM-5 was characterized with reference to BET surface area and FTIR analysis, as ZSM-5 commercial and standard, procured from Alfa aesar, USA.

3.3.3.1 Fourier-transform infrared spectroscopy (FTIR)

The FTIR analysis was carried out with Thermo-Nicolet 5700 model. The Ominc software was used to correct the medium's background material used during analysis. Fourier transformed infrared spectrophotometer was set to a resolution of 4 cm^{-1}, in the range of 500–4000 cm^{-1} using Nujol mull as reference.

3.3.3.2 Brunauer-Emmett-Teller (BET)

The specific surface area and pore volume were analysed using Micromeritics ASAP 2020 analyzer by physical adsorption of N_2 at boiling temperature of liquid nitrogen (−196°C). A known weight of sample was loaded into the chamber and degassed for 8 h with nitrogen purging prior to analysis. A relative pressure range of 7.5 mm Hg to 750 mm Hg was selected for multipoint BET surface area calculation. The pore volume was evaluated at a relative pressure of 0.99 mm Hg. The average pore diameter and pore size distribution were calculated using the Barrett-Joyner-Halenda (BJH) method. This result of BET surface area and pore volume are shown in chapter 4 (page no. 139 for commercial ZSM-5 catalyst and page no. 103 for fly ash derived catalyst).

3.3.3.3 Scanning Electron Microscope/Energy dispersive X-ray spectroscopy (SEM-EDX)

The SEM-EDS were recorded on ZEISS EVO 18 SEM coating of quorum Q150R ES having model number 51-ADD0048. Specific surface area and pore volume of synthesized catalysts were analysed using smart sorb 92/93 surface area analyzer using nitrogen physisorption at liquid nitrogen temperature.

3.3.4 BTEX production using pyrolysis of waste plastics

The target aromatics benzene, toluene, ethylbenzene and xylene (BTEX) were produced via pyrolysis using shredded and treated waste polyethylene, polypropylene and polystyrene in a semi-batch reactor as mentioned in the experimental setup section (Page no. 39). The plastic feed of 50 g was fed to the reactor batch by batch systematically. The nitrogen gas was fed into reactor at the rate of 10 mL/min to ensure there is no oxygen and to maintain inert atmosphere inside the reactor. Adequate precautions were taken to make sure that there is no leakage before we start the experiment. The thermal pyrolysis of waste plastic sample were performed at different temperatures 500 ^{o}C, 600 ^{o}C, 700 ^{o}C and 800 ^{o}C, respectively. The time for each set of experiments were maintained for 35 min. Catalytic pyrolysis was performed at different feed to catalyst ratio of 10:1, 20:1 and 30:1 using similar operating conditions as that of thermal pyrolysis. During the reaction the gas and vapor mixture was allowed to pass through the metal tube which was connected at the top of the reactor. The tube was attached to a copper tube condenser followed by an ice bath to decrease the vapor temperature gradually and reduce the vapor loss at the collecting end. The tube was covered with wet jute to enhance rate of vapor cooling. Two conical flasks in series were kept in the ice bath and pyrolysis oil was collected as condensate. The benzene, toluene, ethylbenzene and xylene (BTEX) were present in the pyrolysis oil. The produced gas was trapped using gas holder at the extreme end of ice bath condenser. The liquid, gas and solid yields were calculated using following Eqs. (3.1 to 3.3):

$$Liquid\ Yield\ = \left(\frac{wt.of\ liquid}{wt.of\ total\ feed}\right) \times 100 \tag{3.1}$$

$$Gas\ Yield\ = \left(\frac{wt.of\ gas}{wt.of\ total\ feed}\right) \times 100 \tag{3.2}$$

$$Solid\ Yield\ = \left(\frac{wt.of\ solid}{wt.of\ total\ feed}\right) \times 100 \tag{3.3}$$

where, wt. of gas = [wt. of total feed - (wt. of liquid + wt. of solid)] (Muhammad et al., 2015). The method of BTEX evaluation in the pyrolysis oil is discussed thoroughly in the section 3.4.3 (page no. 47).

3.3.5 Catalyst regeneration

Regeneration process of used catalyst consists of two steps (i) combustion process and (ii) calcination process. In combustion process, used catalyst was heated in a crucible without lid under oxygen flow at the temperature of 550 °C in a muffle furnace for 30 min to remove coke by combustion process. In calcination process, the combusted sample was kept in a crucible with lid/under nitrogen flow at same temperature for 5 h in a muffle furnace for the calcination process. Fig.3.7 and Fig 3.8 shows the pictorial view of fresh, used and regenerated ZSM-5 and FA-800 catalyst, respectively. The black colour of used catalyst (Fig 3.7b and Fig 3.8b) shows the coke formation on the surface of catalyst.

(a) Fresh (b) Used (c) Regenerated

Figure 3.7 Pictorial view of (a) fresh (b) Used and (c) regenerated ZSM-5 catalyst.

(a) Fresh (b) Used (c) Regenerated

Figure 3.8 Pictorial view of (a) fresh (b) Used and (c) regenerated FA-800 catalyst

3.4 Pyrolysis product analysis

3.4.1 FTIR of the pyrolysis oil

FT-IR analysis was carried out with Thermo-Nicolet 5700 model. The Ominc software was used to correct the medium's background material used during analysis. Fourier transformed infrared spectrophotometer was set to a resolution of 4 cm^{-1}, in the range of 500–4000 cm^{-1} using Nujol mull as reference.

3.4.2 Gas chromatography (GC) analysis

The compositional analysis of pyrolysis oil was evaluated by gas chromatograph (NUCON 5765) using flame ionization detector (FID) with a SE-30 10 % chromosorb W packed stainless steel column (2 m x 2 mm). Nitrogen was used as a carrier gas at the rate of 40 mL min^{-1}. The oven column temperature ranged from 70 °C to 230 °C; programmed at

7 °C min^{-1} with initial and final hold time of 10 min. Injector and detector temperatures were 220 °C and 230 °C, respectively. The injection method was used for analysis of 1μl sample. The percentages of the individual constituents were calculated by electronic integration of the FID peak areas without response factor correction.

3.4.3 BTEX evaluation of the pyrolysis oil

The calibration characteristics were developed for the evaluation of BTEX in the pyrolysis oil obtained by the thermal and catalytic pyrolysis of PE, PP and PS. HPLC grade benzene (Fisher scientific, India), toluene (S D fine-chem ltd., India), ethylbenzene (Avra syn. pvt. ltd., India) and xylene (Avra syn. pvt. ltd., India) were procured to get the calibration characteristics. Benzene, toluene, ethylbenzene and xylene were mixed in different ratios to get a mixture of known composition and their GC data (% Area) for the same. GC-FID of these mixtures were performed for the calibration characteristics of benzene, toluene, ethylbenzene and xylene as shown in Fig (3.9).

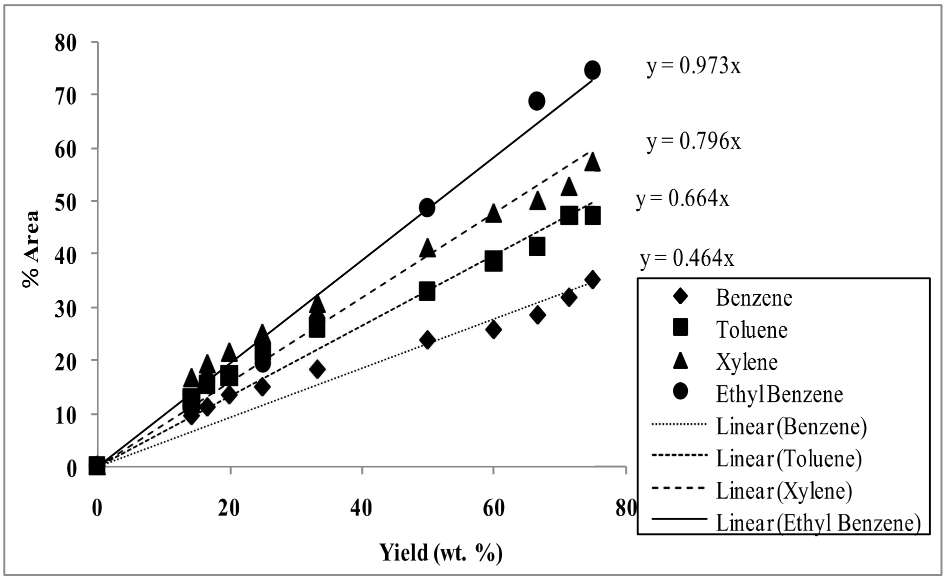


Figure 3.9 Calibration characteristics for benzene, toluene, ethyl benzene and xylene.

3.4.4 ASTM distillation

ASTM distillation of pyrolysis oil was obtained using ASTM D86 method. In this test 100 ml of sample is distilled in a standard flask. The distillate was condensed in a brass tube condenser, surrounded by crushed ice-water mixture to maintain temperature at 0 °C. First drop from the condenser must be available in 5 to 10 min after heating started, at which the recorded temperature was mentioned as initial boiling point (IBP) of the sample. The vapour temperature was recorded at each successive 5 ml distillate collected in a measuring cylinder. The test continues in the same way till the bottom of the flask shows dryness, the temperature recorded corresponds to final boiling point (FBP). The % distillate collected after condensation of vapour and its corresponding temperature was recorded to get the experimental ASTM distillation characteristics. The experimental characteristics were compared with the standard plot as reported in standard literature (Perry and Green, 2007).

3.4.5 Flash and fire point

Flash and fire point of pyrolysis oil were obtained using Cleveland open cup apparatus (ASTM D 92). Flash point is defined as the minimum temperature at which the vapours from oil sample will give a momentary flash on application of standard flame under specific test conditions. The pyrolysis oil was filled up to the mark and the temperature of the oil was slowly and uniformly raised at a rate of 3 °C per min. Test flame was lighted and spring handle was rotated at every 1 °C raise in thermometer. When oil sample burns momentary or flash occurred, flash point temperature was noted. Fire point temperature was noted when the oil vapours can burn continuously for at least 5 S and it occurs after the flash point, by 3-4 °C.

3.4.6 Carbon residue

Carbon residue of pyrolysis oil was obtained using Ramsbottom Carbon Residue Apparatus (IP 14/65). The sample of 1 g was carefully fed into a glass coking bulb which has a capillary end. The coking bulb was kept in a heating lead bath at a temperature of 550 ºC. The oil sample was allowed to decompose for 20 min. After heating is over, the bulb is cooled and weighted to find the carbon residue formed. This was done to check the propensity of cracking of pyrolysis oil at high temperature.

3.4.7 American Petroleum Institute (API) gravity

The API gravity of pyrolysis oil is calculated using the oil sample specific gravity, which is the ratio of density of oil to that of water $(\frac{15.6\ ℃}{15.6\ ℃})$. The API gravity of the pyrolysis oil sample was calculated by the following equation (3.4):

$$\text{Deg. API} = \left(\frac{141.5}{\rho_{pyrolysis\ oil}}\right) - 131.5 \tag{3.4}$$

Where, $\rho_{\text{pyrolysis oil}}$ = specific gravity of fraction at $(\frac{15.6\ ℃}{15.6\ ℃})$

The API gravity is used to classify oil as light, medium, heavy, or extra heavy. As the “quality” of oil is the largest determinant of its market value, the API gravity is exceptionally important for each fraction of oil sample. The oil quality and types are reported as follows (Tiab and Donaldson, 2004):

Light oil : Deg. API > 31.1

Medium oil : Deg. API between 22.3 and 31.1

Heavy oil : Deg. API < 22.3

Extra Heavy oil : Deg. API < 10.0

3.4.8 Gross calorific value (GCV)

The bomb calorimeter (IP 12/63T) was used to determine the GCV of solid residue (coke) and pyrolysis oil. The GCV test was performed by weighing 1 g of sample. The sample was kept inside the bomb and the bomb was charged with oxygen from a cylinder to a pressure of 25 atm. The sample was ignited and the change in temperature at equal interval of time was recorded until it reaches at steady state. Finally, GCV was calculated using standard calculation method as specified in IP 12/63T.