
CHAPTER 3

EXPERIMENTAL

This chapter describes the detailed experimental method for waste expanded polystyrene (WEPS) pyrolysis followed by *in-situ* hydrogenation for the production of target products benzene, toluene and ethylbenzene (BTE) using commercial catalysts ZSM-5 ammonium powder and Nickel on silica-alumina and synthesized catalyst natural red clay. The feed preparation, characterization of feed, synthesis of catalyst from natural red clay, characterization of synthesized catalyst using various analytical techniques like scanning electron microscope/energy dispersive X-ray spectroscopy (SEM-EDX), X-ray diffraction (XRD), Brunauer-Emmet-Teller (BET) surface area, Fourier transformed infrared spectroscopy (FTIR) and catalyst regeneration process are also discussed in this chapter. The characterization of pyrolysis oil using various characterization methods such as gas chromatography (GC) coupled with flame ionization detector mode (FID) mode, Fourier transformed infrared spectroscopy (FTIR), gross calorific value (GCV), carbon residue and flash and fire point are discussed at the end of this chapter.

3.1 Materials

The waste sheets of thermocol, which is also known as expanded polystyrene (EPS) or styrofoam, was used as the feedstock in the pyrolysis process. The WEPS/thermocol was collected from the waste yard of Indian Institute of Technology (BHU), Varanasi. This waste EPS/thermocol was mostly packaging materials of equipments and chemicals.

Commercial and laboratory synthesized catalysts both were used to investigate their individual performance for the pyrolysis of WEPS and performance comparison in terms of liquid yield and BTE production.

The commercial catalysts used were ZSM-5 ammonium powder (NH₄-ZSM-5) and Nickel on silica-alumina catalyst. The catalyst ZSM-5 ammonium powder of surface area 400 m²/g with SiO₂ to Al₂O₃ mole ratio of 200-400:1 was procured from Alfa Aesar, USA (Table 3.1).

Table 3.1 Specifications of ZSM-5 ammonium powder catalyst.

Catalyst	Surface area (m ² /g)	SiO ₂ /Al ₂ O ₃
ZSM-5 ammonium powder	400	200-400:1

The Nickel on silica-alumina powder with 66 ± 5 % Ni was also procured from Alfa Aesar, USA. The specification of Nickel on silica-alumina catalyst are mentioned in Table 3.2.

Table 3.2 Specifications of Nickel on silica-alumina catalyst.

Catalyst	Nickel content	Form	Solubility
Nickel on silica-alumina catalyst	66±5%	Powder	Insoluble in water

The other catalyst, was synthesized from natural red clay which was collected from Chandauli district of Uttar Pradesh near Devdari and Rajdari waterfall. The place Devdari and Rajdari waterfall is situated 60 km away from IIT (BHU) campus, Varanasi. The pictorial view of natural red clay is given in Figure 3.1. The natural red clay is rich in mineral matter mainly silica and alumina which plays catalytic role in pyrolysis of WEPS and further hydrogenation process.

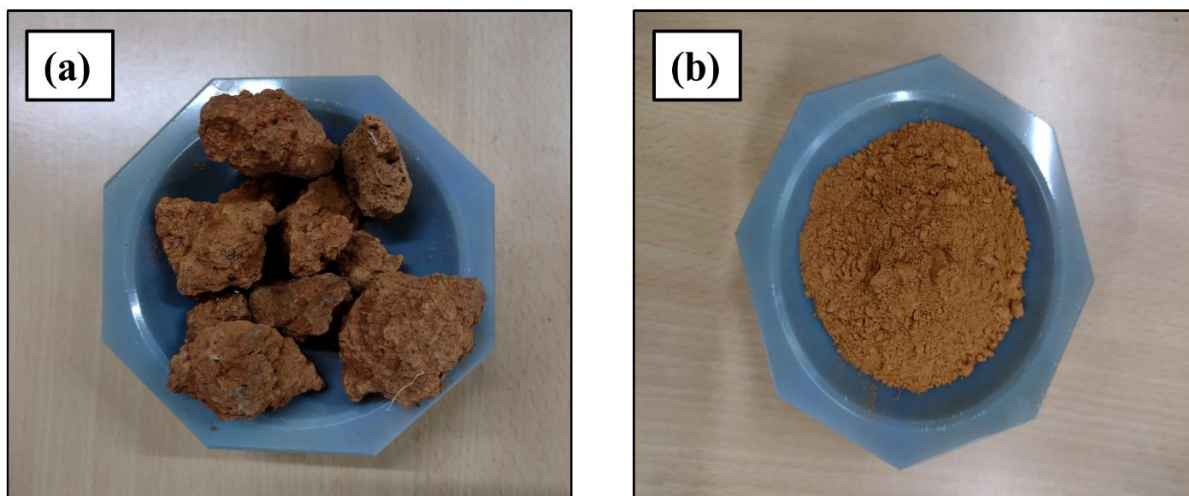


Figure 3.1 Pictorial view of natural red clay (a) lump of red clay (b) grounded natural red clay.

To determine the BTE content in the pyrolysis oil, high purity HPLC grade benzene, toluene and ethylbenzene were procured from Fisher scientific, India, S D fine-chem Limited, India, and Avra synthesis private Limited, India, respectively.

3.2 Experimental setup

Figure 3.2 shows the schematic of the experimental set up used for the pyrolysis of WEPS and *in-situ* hydrogenation of pyrolysis products. Four types of reactor arrangements were used for the pyrolysis of WEPS using thermal and catalytic process which are presented in Figure 3.3 (a-d) systematically. The main reaction unit consists of two parts; one large primary reactor and another small secondary reactor (Figure 3.4 a-b), which was placed inside the primary reactor having attached at the neck of the primary reactor using a threaded connector (Figure 3.3 c-d). Figure 3.4 (a-b) shows the detailed view of secondary reactor with internal arrangements of the four-layer catalyst bed.

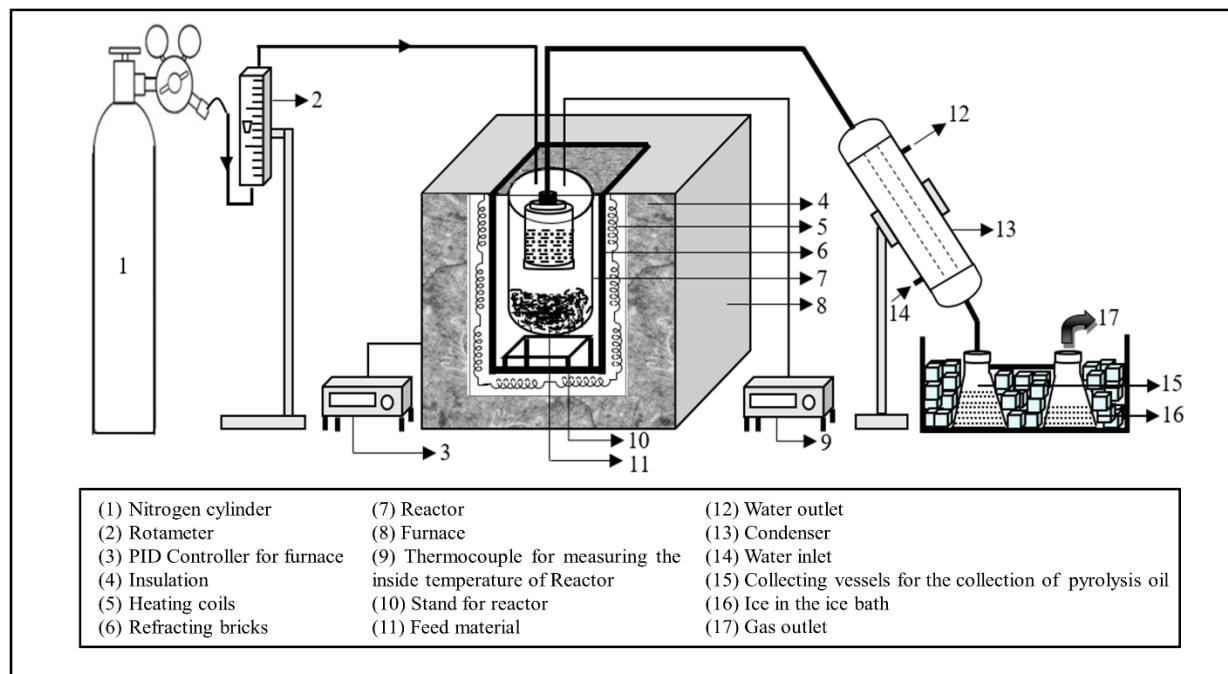


Figure 3.2 Schematic of the experimental setup for the pyrolysis of WEPS.

The pyrolysis of WEPS was started keeping the WEPS always in the primary reactor. The secondary reactor was used for vapour phase catalytic reactions only. It should be noted that the bottom of the secondary reactor consisting of perforated stainless steel bottom plate (Figure 3.4b) for escaping vapour molecules generated in the primary reactor. The height (L) of the primary reactor was 155 mm and the inner diameter (D) was 99.3 mm (Figure 3.3a). The detailed dimension of the secondary small reactor is presented in Figure 3.4b. The thermal pyrolysis was performed in a reactor arrangement which is shown in Figure 3.3a while catalytic pyrolysis was performed in different types of reactor arrangements such as liquid phase/A-type (Figure 3.3b), vapour phase/B-type (Figure 3.3c) and, liquid and vapour phase both (multiphase)/AB-type (Figure 3.3d). The catalyst particles were mixed with feed for liquid phase/A-type reactor arrangement (Figure 3.3b). Whereas, the catalyst was placed in four layers within the secondary reactor using glass wool for B-type/vapour phase reactor

arrangement (Figure 3.3c). In this reactor arrangement (B-type), liquid range hydrocarbon vapour comes out from the bottom of the primary reactor due to thermal pyrolysis of polystyrene and then escapes through the secondary reactor consisting of multilayer catalytic bed (Figure 3.4a).

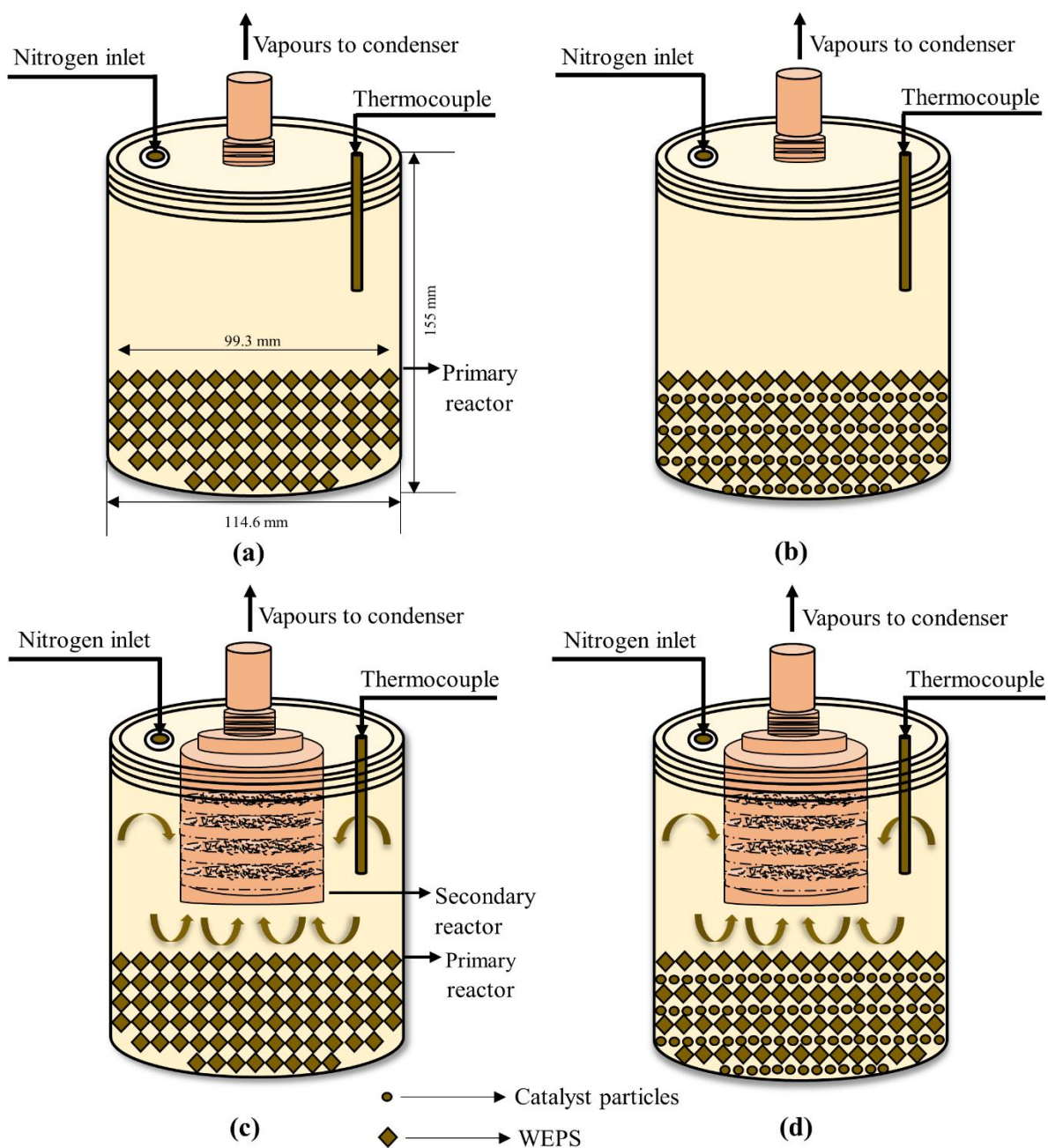


Figure 3.4 Reactor arrangements (a) thermal (b) A-type/liquid phase (c) B-type/vapour phase (d) AB-type/multiphase catalytic pyrolysis.

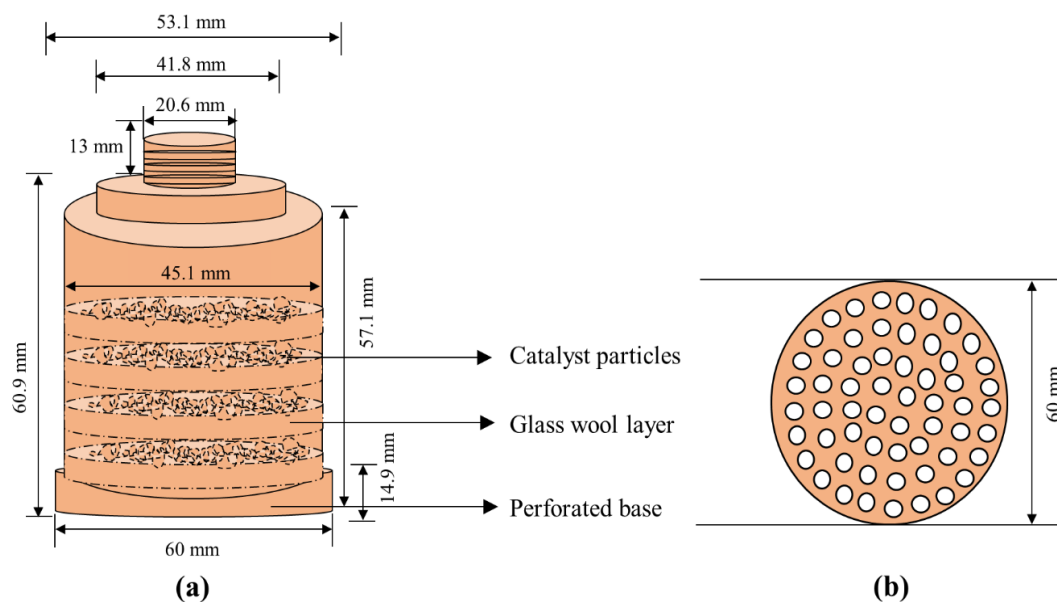


Figure 3.5 Detailed diagram of (a) secondary reactor (b) perforated base of secondary reactor.

Whereas, in multiphase/AB-type arrangement, required amount of catalyst was mixed with feed and fed to the primary reactor and then, same amount of catalyst was distributed in the secondary reactor in the form of four layered catalytic bed as mentioned earlier (Figure 3.3d). Pure nitrogen gas from cylinder was purged in the primary reactor through rotameter. All vapours and gases were generated during the experiment was passed through the copper tube condenser followed by an ice bath containing two conical flasks in series (Figure 3.2). Pyrolysis oil was collected in the conical flasks while gases are collected in a gas holder at the extreme end of the ice bath. The photograph of experimental setup is given the Appendix A-1.

3.3 Method

3.3.1 Feed preparation

The WEPS/thermocool was collected from the waste yard of Indian Institute of Technology (BHU), Varanasi (Figure 3.6a-b). Because of expanded form of polystyrene, volume of WEPS

was very high per unit mass and thus, before using WEPS as feed, EPS required pretreatment for the volume reduction, to accommodate WEPS within the reactor. First of all, the collected large sheets of thermocol were manually cut into small pieces of size 80 mm x 80 mm using a sharp edge knife. Thereafter, the volume of WEPS was reduced by placing the cut pieces of WEPS in an oven at a temperature of 85 °C for 1 hr which resulting in brittle mass of average size 40 mm x 40 mm (Figure 3.6b).

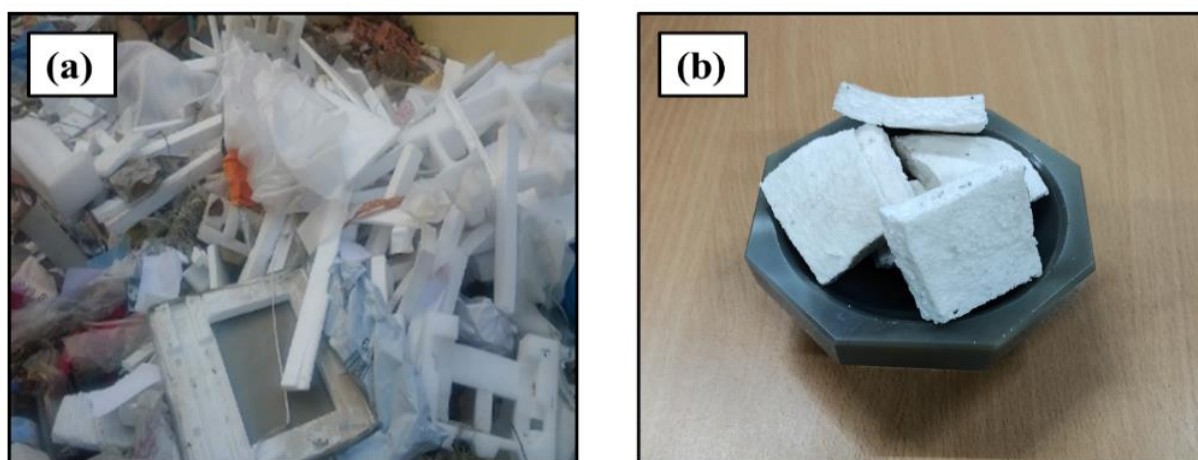


Figure 3.6 Photographic view of (a) collected waste expanded polystyrene, (b) WEPS after processing via heat treatment.

3.3.2 Feed characterization

As it is already discussed in the literature review that the feed characterization is important before using it as a feedstock for the pyrolysis process. In this context, the feed WEPS was characterized by the proximate analysis and thermogravimetric analysis (TGA).

3.3.2.1 Proximate analysis

Proximate analysis of WEPS was done following American society for testing materials (ASTM) test methods (IS 1350-1959) to determine the moisture content, ash content, volatile matter, and fixed carbon.

3.3.2.2 Thermogravimetry analysis (TGA)

Thermogravimetry analysis is a very useful analysis for investigating the behaviour of material and stability with temperature in an inert or in an oxidizing atmosphere. Thus, the thermal behaviour of WEPS was examined using thermo gravimetry analyser (Shimadzu TGA-50), North America, over a temperature range of 25-800 °C at a constant heating rate of 15 °C/min in nitrogen flow of 50 mL/min by taking of 6 mg sample in the platinum pan.

3.3.3 Catalyst syntheiss from natural red clay

The red clay was collected from Chandauli district of Uttar Pradesh near Devdari and Rajdari waterfall, which is 60 km away from IIT (BHU) campus, Varanasi to synthesize the catalyst from natural red clay, The collected natural red clay was washed with tap water followed by distilled water to remove dirt like impurities and then dried in a hot air oven for 24 hours at a temperature of 108 °C to remove any free moisture present in dirt-free red clay. The dried and clean red clay was then screened through a sieve of 63 µm mesh size (ASTM 230) to remove the larger particles. Some part of clean, screened, and fresh red clay was used as a catalyst directly without calcination and designated as RC. The remaining part of red clay was calcined in a muffle furnace at five different calcination temperatures, i.e., 600 °C, 700 °C, 800 °C, and 900 °C for 5 hours in static air and designated as RC-600 (calcined at 600 °C), RC-700 (calcined at 700 °C), RC-800 (calcined at 800 °C) and RC-900 (calcined at 900 °C), respectively. The flow diagram for the synthesis method of catalyst from natural red clay is given in Figure 3.7. The calcination of red clay was done to improve the catalytic properties of the calcined red clay catalysts. The synthesized red clay catalysts were characterized using different characterization techniques SEM-EDX, BET, XRD, and FTIR.

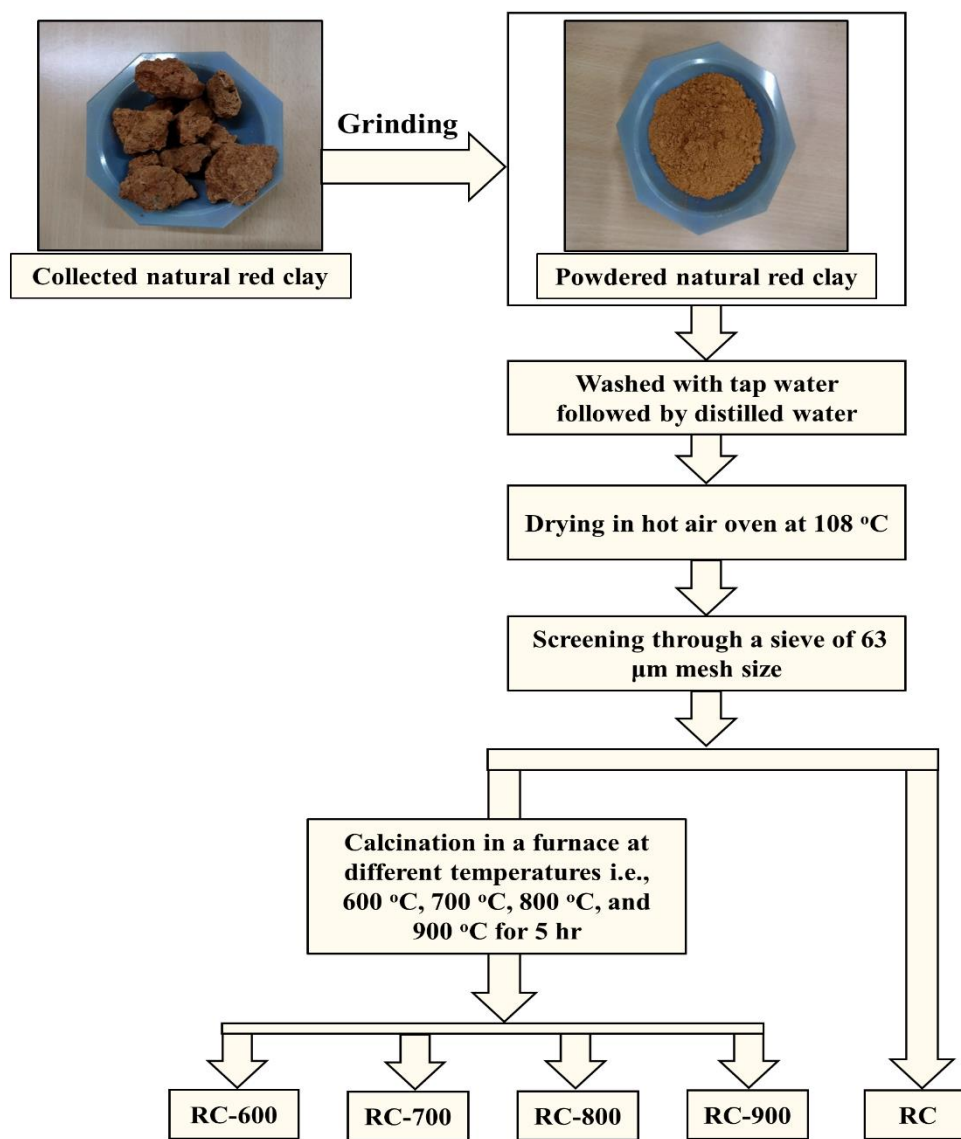


Figure 3.7 Flow diagram for synthesis of catalyst from natural red clay.

3.3.4 Catalyst characterization

The characterization of catalyst is very important for determine its suitability for the specific process. Therefore the characterization of catalyst synthesized from natural red clay was performed using various techniques such as scanning electron microscope-energy dispersive X-ray spectroscopy (SEM-EDX), X-ray diffraction (XRD), Brunauer-Emmet-Teller (BET) surface area, Fourier-transformed infrared spectroscopy (FTIR).

3.3.4.1 Scanning electron microscope-energy dispersive X-ray spectroscopy (SEM-EDX)

The scanning electron micrographs were taken on a high resolution scanning electron microscope (HR-SEM) Nova Nano SEM 450 (FEI Company, USA) equipped with Hikari Pro energy dispersive X-ray detector (EDAX Inc, USA). The powdered samples deposited on a sample holder with an adhesive carbon tape and sputtered with gold.

3.3.4.2 X-ray diffraction (XRD)

The high resolution XRD pattern of all the synthesized red clay catalysts were recorded using Smart Lab 9 kW Powder type high resolution X-ray diffractometer (Rigaku, Japan) to identify the various minerals present in the powdered red clay samples. The XRD pattern for all synthesized catalysts were recorded with a scan speed of 5 °C/min and a scan range of 5 ° to 100 °.

3.3.4.3 Brunauer-Emmet-Teller (BET) surface area

BET surface area analysis determine the total surface area of a solid by suspending a powdered sample in an inert gas bath and measuring the adsorption of gas molecules to the surface and its porous structures. The surface area of red clay catalysts were determined using a smart sorb 92/93 surface area analyzer (Smart Instruments Company Pvt. Ltd., India) at liquid nitrogen temperature (-196 °C) using physisorption. Prior to measurement, each sample was degassed at a temperature of 300 °C for 10 hr. The nitrogen adsorption/desorption isotherms were used to determine the specific surface areas using the BET equation.

3.3.4.4 Fourier transformed infra-red spectroscopy (FTIR)

The FTIR spectra of all synthesized red clay catalysts were recorded on Nicolet summit spectrophotometer (Thermo Fisher Scientific, USA) as KBr pallets in the range of wavenumber 4000 cm^{-1} to 400 cm^{-1} . The powdered samples and analytical grade KBr were dried at $100\text{ }^{\circ}\text{C}$ overnight prior to conduct the FTIR analysis. Fourier transformed infrared spectrophotometer was set to a resolution of 4 cm^{-1} prior to analysis.

3.3.5 Pyrolysis process for the production of BTE

The pyrolysis of WEPS followed by *in-situ* hydrogenation was performed in a semi batch reactor as mentioned in the experimental setup section (page no. 48). The WEPS feed material of 50 g was placed in the primary reactor and heated by an electrical furnace at a specified temperature and heating rate. The nitrogen gas was flown into the reactor at a rate of 200 mL/min for maintaining the inert atmosphere inside the reactor and it also helps for sweeping out the products from the reactor. The gasket in between the lid and reactor was used for maintaining the leak proof conditions. The thermal and catalytic pyrolysis was performed at different holding time in the range between 10 min-60 min, and varying heating rates from $5\text{ }^{\circ}\text{C}/\text{min}$ - $25\text{ }^{\circ}\text{C}/\text{min}$. The catalytic pyrolysis was performed at different feed to catalyst ratio of 10:1, 20:1, 30:1 and 40:1. The multiphase catalytic pyrolysis was performed keeping the equal/same amount of catalyst in the secondary reactor as that of liquid phase. The thermal and catalytic pyrolysis were performed in the temperature range of $400\text{ }^{\circ}\text{C}$ to $700\text{ }^{\circ}\text{C}$ with temperature interval of $50\text{ }^{\circ}\text{C}$. The non-condensable and condensable gases were passed through a two stage cooling process. First through a copper tube condenser having inner tube and outer shell side. The tap water was continuously flowing through the shell side of

condenser for the condensation of condensable vapours passing through the inner tube. The outlet of the condenser was connected with the two conical flasks which were joined in series and kept in the ice bath in the second stage cooling for the collection of pyrolysis oil. The solid residue collected from the bottom of the reactor after the completion of the pyrolysis reaction. The non-condensable vapours was collected as gas using a gas holder at the extreme end of an ice bath. The liquid, solid and gaseous yield were calculated from the following equations:

$$\text{Liquid yield} = \frac{\text{weight of pyrolysis oil}}{\text{weight of total feed}} \times 100 \quad (3.1)$$

$$\text{Solid yield} = \frac{\text{weight of residue}}{\text{weight of total feed}} \times 100 \quad (3.2)$$

$$\text{Gaseous yield} = \frac{\text{weight of gas}}{\text{weight of total feed}} \times 100 \quad (3.3)$$

Where, weight of gas = [weight of total feed - (weight of pyrolysis oil+weight of solid residue)]

3.3.6 Catalyst regeneration

The catalyst regeneration process consists of two steps; step one (i) combustion process to remove the deposited coke from the pores of catalyst and step two (ii) calcination process to enhance the surface properties. The spent/used catalyst was placed in the crucible without lid and heated at a temperature of 550 °C for ½ hr in a muffle furnace in the combustion process. Thereafter, resulted combusted catalyst was place inside the crucible with lid and heated at the same temperature of 550 °C in a muffle furnace for 5 hr for the calcination.

3.4 Pyrolysis oil analysis

3.4.1 Gas chromatography (GC) analysis

The compositional analysis of pyrolysis oil was obtained by the gas chromatograph, (NUCON 5765), Centurion Scientific, India, in flame ionisation detector (FID) mode with SE-30 10% chromosorb W packed stainless-steel column (2m×2mm). Nitrogen gas was used as a carrier with the flow rate of 40 mL/min. The oven temperature was programmed in the range between 70 °C to 230 °C at 7 °C/min with initial and final hold up time of 10 min. Injector and detector temperatures were 220 °C and 230 °C, respectively. Only 1µL of pyrolysis oil was used for the GC-FID analysis.

3.4.1.1 Estimation of BTE and styrene in pyrolysis oil

The qualitative evaluation of the obtained pyrolysis oil at is very much essential in terms of BTE and styrene content. Thus, the calibration characteristics were plotted to measure the extent of enhancement in yield of benzene, toluene, and ethylbenzene (BTE) and reduction in styrene.

High purity HPLC grade benzene, toluene, ethylbenzene and styrene of different ratios were mixed and each mixture was subjected to GC analysis to get the % peak area of each component for their known weight percent. Finally, the calibration characteristic for each component was plotted i.e., concentration (wt.%) vs peak area (%) as shown in Figure 3.8.

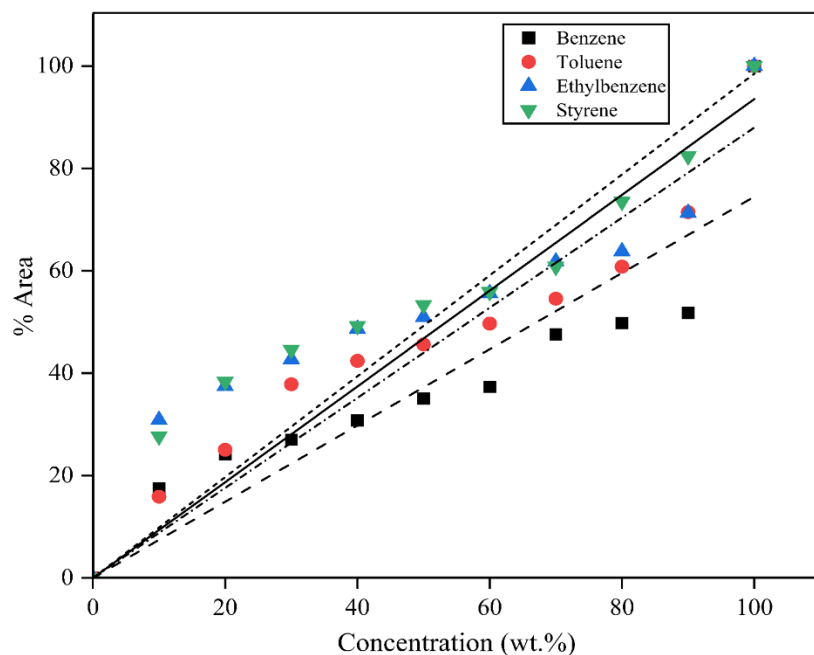


Figure 3.8 Calibration characteristics for benzene, toluene and ethylbenzene (BTE).

3.4.2 FTIR of pyrolysis oil

The functional groups present in the pyrolysis oils were studied by Fourier transformed infrared spectrophotometer thermo-scientific Nicolet iS5 model in the attenuated total reflection (ATR) mode. The FTIR was set to a resolution of 4 cm^{-1} in the range of $500 - 4000\text{ cm}^{-1}$.

3.4.3 Physicochemical properties

3.4.3.1 Gross calorific value (GCV)

The calorific value is the most important property of fuel, which shows the energy content of it. The bomb calorimeter (IP 12/63T) was used to determine the gross calorific value (GCV) of pyrolysis oil. To determine the GCV, 1 g of pyrolysis oil was kept inside the crucible and placed inside the bomb. Thereafter, the bomb was charged with the supply of oxygen up to a

pressure of 25 atm. The pyrolysis oil was ignited and then change in temperature was recorded until it becomes constant. Finally the GCV was calculated using standard formula as mentioned in IP 12/63T method (Verma et al., 2021).

3.4.3.2 Carbon residue

The carbon residue is defined as the amount of carbon remains after combustion. Fuel with higher carbon residue is responsible for the high carbon deposition on engine parts, resulting in overheating and engine knocking (Verma et al., 2022). The carbon residue of pyrolysis oil was obtained using Rams bottom carbon residue apparatus as per IP 14/65 standard (Verma et al., 2021). To determine the carbon residue, 1 g of pyrolysis oil was fed into borosilicate cooking bulb through its capillary. The cooking bulb was placed inside the lead bath and heated at a temperature of 550 °C for 30 min. Thereafter, the cooking bulb was allowed to cool at room temperature and weighted to find out the carbon residue in weight percentage.

3.4.3.3 Flash and fire point

The flash point is also a most important property for fuel. The lower the flash point of a fuel is, the easier the ignition of that fuel. However, fuels with lower flash point required more attention during storage and handling. The flash and fire point of pyrolysis oil were determined using Cleveland open cup apparatus as per the standard of ASTM D 92 (Verma et al., 2021). To determine the flash and fire point, the pyrolysis oil was filled in open cup up to mark and then the temperature of oil was increased slowly. The test flame was ignited and spring handle was rotated over the surface of pyrolysis oil. When the pyrolysis oil was flash momentarily,

this temperature was recorded as the flash point and the fire point is recorded when the pyrolysis oil vapour and air mixture continuously burn at least for 5 seconds.