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Production of valuable chemicals via multiphase catalytic pyrolysis of hazardous waste expanded polystyrene using low cost $CaCO_3$ solid base catalyst

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In the present research work, multiphase catalytic pyrolysis (in-situ catalytic cracking) of waste expanded polystyrene (WEPS) has been carried out using calcium carbonate ($CaCO_3$) as a solid base catalyst. The multiphase catalytic pyrolysis of WEPS has been conducted at different temperatures ranging from 400°C to 700°C at a heating rate of 15 °C/min and feed to catalyst ratio of 20:1. The thermal pyrolysis of WEPS has produced a maximum liquid yield of 94.37 wt.% at a reaction temperature of 650°C and heating rate of 15 °C/min. Whereas, the maximum liquid yield of 85.99 wt.% is obtained at a reaction temperature of 550°C and heating rate of 15 °C/min for the multiphase catalytic pyrolysis. The GC-FID analysis confirm that the thermal pyrolysis oil is mainly composed of benzene (0.62 wt.%), toluene (10.21 wt.%), ethylbenzene (0.55 wt.%) and styrene (84.74 wt.%). Whereas, the pyrolysis oil obtained from multiphase catalytic pyrolysis using $CaCO_3$ catalyst contains very high styrene content of 93.24 wt.% along with a very low amount of fuel range hydrocarbons benzene (0.25 wt.%), toluene (2.09 wt.%) and ethyl benzene (0.52 wt.%). Thus, the present study clearly indicates that the basic catalyst $CaCO_3$ shows the high selectivity towards the styrene monomer.

Keywords: Catalyst; $CaCO_3$; Multiphase; Pyrolysis; Styrene; WEPS

Introduction

Globalization and modernization have increased the massive production of plastics as they have versatile properties such as low cost, lighter in weight, corrosion resistance[1], strength, flexibility, durability, lightweight, mouldability, electrical and chemical insulation[2]. Recently, consumption of expanded polystyrene (EPS) is increasing rapidly because of its excellent properties such as sound insulation, thermal insulation, hygiene[3], economical, environmentally sustainable, high strength to weight ratio, and moisture resistance[4]. However, waste expanded polystyrene (WEPS) is responsible for many environmental issues especially land and water pollution because of its non-biodegradable nature[5]. EPS is a more common litter in marine and freshwater environments worldwide[6]. The burning of WEPS leads to the penetration of chemicals into the environment, and the release of toxic gases such as COx, NOx, SOx into the environment[7]. Thus, the management of WEPS via suitable waste management technique is necessary. The available options for plastic waste management are recycling and landfilling. As per the ASTM standard recycling is classified into four categories i.e., primary, secondary, tertiary and quaternary (incineration)[8]. Among all these plastic waste management processes, most of the researchers adopt the pyrolysis process because it is more flexible than other recycling methods. In general, the pyrolysis process converts waste plastic into three valuable products viz., pyrolysis oil, pyrolysis gas and solid residue[9]. Furthermore, the process can be easily optimized to maximize the production of any of these constituents by altering the process parameters such as residence time, process temperature, heating rate etc[10]. Pyrolysis is defined as the method where, waste plastic is thermally and chemically destructed in the absence of oxygen, resulting in value-added products[11]. The pyrolysis oil produced from the pyrolysis of waste plastic can be used in multiple applications such as boilers, furnaces, diesel engines and turbines. The pyrolysis gas also has a substantial calorific value that can be used to compensate the overall energy demand of the pyrolysis process plant[9]. The solid residue can be used as the adsorbent or can be used as a fuel[12]. However, catalytic pyrolysis has become more popular as compared to thermal pyrolysis because of

its various advantages such as lower the reaction temperature by reducing the activation energy of the reaction, improve the selectivity towards the target products, and increase the yield of lighter hydrocarbons[13].

It is already reported in the open literature that the thermal pyrolysis of polystyrene (PS) mainly produced styrene monomer. Whereas, solid acid catalysts are more selective towards benzene, toluene and ethylbenzene as compared to styrene monomer. However, solid base catalysts are more selective toward styrene monomer[14]. Zhang *et al.* (1995) investigated the pyrolysis of polystyrene using various basic catalysts such as MgO, CaO, BaO, K_2O, and acidic catalysts such as SiO_2/Al_2O_3, HZSM-5 at a pyrolysis temperature of 623 K. They reported that the solid base catalysts show very high selectivity towards the styrene monomer as compared to the thermal or acid-catalyzed degradation[15]. Achilias *et al.* (2007) examined the catalytic pyrolysis of polystyrene using base (BaO) and acid catalyst (FCC) in a fixed bed reactor. The pyrolysis oil obtained from base catalyst BaO contained a very high percentage of styrene monomer (69.6 wt.%) even higher than the thermal pyrolysis (63.9 wt.%). Whereas, pyrolysis oil produced from acid catalyst FCC contained only 45.1 wt.% of styrene monomer[16]. Ukei *et al.* (2000) also reported that the solid bases were more effective catalysts than solid acids for the degradation of PS into styrene monomer. This was attributed to differences in the degradation mechanisms of PS over solid acids and bases[17]. Inayat *et al.* (2021) conducted the catalytic pyrolysis of polystyrene in batch and semi-batch using magnesium oxide (MgO) as a catalyst. It was found that more than 80 wt.% of styrene yield was recovered at a reaction temperature of 500°C from batch and semi-batch reactor arrangements both[18]. Hussain *et al.* (2020) studied the catalytic pyrolysis of polystyrene using Portland cement as a solid base catalyst. They also reported a higher styrene yield (63.17 %) in pyrolysis oil using Portland cement as a catalyst as compared to thermal pyrolysis (42.14 %)[19].

In this context, the most abundant naturally occurring mineral in the earth's crust calcium carbonate ($CaCO_3$) was selected as a catalyst for the multiphase catalytic pyrolysis of WEPS to enhance the styrene content in the pyrolysis oil as the styrene monomer used for the production of various polymers and copolymers, including polystyrene, styrene-acrylonitrile, acrylonitrile butadiene styrene, and styrene butadiene rubber[20]. The annual production of styrene monomer is over 30 million tonnes per year and a steady increase is expected in the following years, mainly in the part of the world knowing a rapid development[21]. In this research work, the reactor arrangement used for the multiphase catalytic pyrolysis of WEPS offers enough contact between the vapour of hydrocarbon molecules and catalyst particles. Moreover, no additional heating arrangement is required for the vapour phase catalytic reaction makes the process economical. Additionally, the reactor design/arrangement is very compact facilitating easy handling and less maintenance.

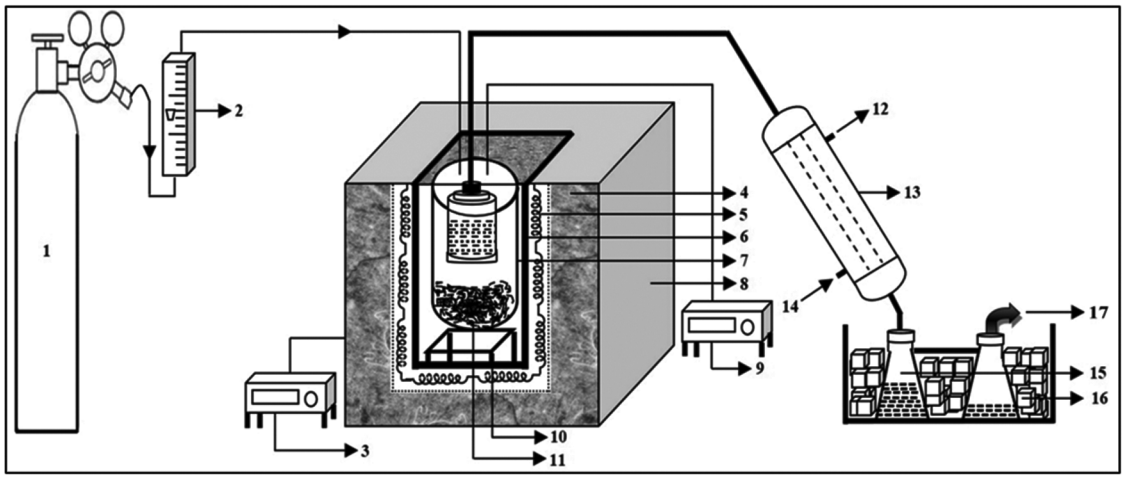
Experimental Section

Raw materials

The WEPS in the form of large sheets of thermocol: $\{C_6H_5\text{-}CH{=}CH_2\}_n$) was collected from the dumping zone of IIT (BHU), Varanasi, India. The collected large sheets of thermocol sheets were manually cut into small pieces of the average size of 80 mm × 80 mm. Then, small pieces of thermocol were placed inside the oven at a temperature of 85°C for 60 min resulting in brittle pieces of the average size of 40 mm × 40 mm. The calcium carbonate ($CaCO_3$) was purchased from the local market of Varanasi, India. The lumps of calcium carbonate were ground into fine powder. Thereafter, the prepared fine powder was screened through the sieve of mess size 63 μm.

Experimental method

The schematic of the experimental setup is shown in Fig. 1. The main pyrolysis unit mainly consists of two reactors i.e., a large primary reactor and a small secondary reactor which, placed inside the primary reactor and connected at the neck using threaded connecter. The detailed design of primary and secondary reactor has already been published elsewhere[22]. The raw material thermocol/WEPS of 50 g was always used for thermal and catalytic pyrolysis both. The raw material was heated by an electrical furnace at a selected temperature and heating rate. The electrical furnace was attached to the proportional integral derivative (PID) controller to maintain the required temperature and heating rate. The achieved target temperature was maintained for 30 min for each experiment. One additional thermocouple was used to measure the temperature of the reactor during the



(1) Nitrogen cylinder	(7) Reactor	(12) Water outlet
(2) Rotameter	(8) Furnace	(13) Condenser
(3) PID Controller for furnace	(9) Thermocouple for measuring the inside	(14) Water inlet
(4) Insulation	temperature of Reactor	(15) Collecting vessels for the collection of pyrolysis oil
(5) Heating coils	(10) Stand for reactor	(16) Ice in the ice bath
(6) Refractory brick wall	(11) Feed material	(17) Gas outlet

Fig. 1 — Scematic of experimental set-up for pyrolysis of WEPS

pyrolysis reaction. The feed material WEPS was kept inside the primary reactor for thermal pyrolysis. Whereas, for multiphase catalytic pyrolysis, feed material with the required amount of catalyst was placed inside the primary reactor and the same amount of catalyst was placed in the secondary reactor in the form of four-layer catalytic bed made by glass wool. In a multiphase reactor arrangement, hydrocarbon vapours come out from the bottom of the primary reactor after liquid phase catalytic pyrolysis of WEPS and then escape through the secondary reactor consisting of a multilayer catalytic bed. The secondary reactor increases the interaction between the catalyst particles and hydrocarbon vapours[22].

The inert atmosphere was maintained inside the pyrolysis reactor by flowing the nitrogen gas at a flow rate of 200 mL/min throughout the pyrolysis process. The leak-proof condition was maintained using a gasket at the periphery of the primary reactor. Thermal and multiphase catalytic pyrolysis of WEPS was carried out at different temperatures ranging from 400°C to 700°C at a heating rate of 15 °C/min using feed to catalyst ratio of 20:1. The non-condensable gases (NCG) and condensable gases (CG) were passed through the copper tube condenser. The tap water was continuously flown through the outer tube of the condenser for the condensation of condensable vapours.

The outlet of the condenser was connected with the two conical flasks for the collection of pyrolysis oil which, was kept in the ice bath and connected in series. The residue was collected from the bottom of the reactor after the completion of the pyrolysis reaction. The pyrolysis gas was collected in a gas holder at the extreme end of an ice bath. The liquid, solid and gaseous yields were calculated from the following equations:

$$\text{Liquid yield (wt.\%)} = \frac{\text{weight of liquid}}{\text{weight of total feed}} \times 100 \quad \text{... (1)}$$

$$\text{Solid yield (wt.\%)} = \frac{\text{weight of solid}}{\text{weight of total feed}} \times 100 \quad \text{... (2)}$$

$$\text{Gas yield (wt.\%)} = \frac{\text{weight of gas}}{\text{weight of total feed}} \times 100 \quad \text{... (3)}$$

Where, weight of gas = [weight of total feed – (weight of liquid + weight of solid)][23]

Analysis of WPS and Pyrolysis Oil

The proximate analysis of WEPS was examined as per ASTM standard IS 1350-1959 guidelines. Thermogravimetric analysis was carried out using thermo gravimetry analyser (Shimadzu TGA-50), North America in the temperature range of 25°C to 800°C at a heating rate of 15 °C/min under nitrogen environment. The gas chromatography was used to conduct the compositional analysis of pyrolysis oil using gas chromatograph (NUCON 5765), Centurion Scientific, India, in flame ionisation detector (FID) mode equipped with SE – 30 and 10% chromosorb W

packed stainless-steel column. The nitrogen gas was used as a carrier with the flow rate of 40 mL/min while compositional analysis of pyrolysis oil. The bomb calorimeter (IP 12/63T) was used to record the higher heating value (HHV) of pyrolysis oil. The carbon residue of thermal and multiphase catalytic pyrolysis oil was measured using Rams bottom carbon residue apparatus (IP 14/65). The flash and fire point of pyrolysis oil were obtained using Cleveland open cup apparatus as per the ASTM D 92 standard.

Results and Discussion

Proximate analysis of WEPS/thermocol

The proximate analysis is defined as the standard technique to measure the moisture content, volatile matter, fixed carbon and ash content. Table 1 shows the proximate analysis of WEPS. It should be noted from Table 1 that the feed material WEPS contains very high volatile matter of 99.8 wt.% which confirms the higher conversion of WEPS into condensable and non-condensable gases[24]. The fixed carbon and ash content were found to be 0.18 wt.% and 0.02 wt.%, respectively. The proximate analysis also confirms the absence of moisture which reduces the possibility of moisture contamination in pyrolysis products.

Thermogravimetric Analysis of WEPS

The thermogravimetry analysis (TGA) is generally used to investigate the thermal stability and thermal degradation behaviour of various materials and their mixtures. The trend and temperature range of degradation depend on various parameters like material type, heating rate, temperature, etc[25]. Thus, TGA was used to determine the degradation behaviour of WEPS with respect to reaction temperature. Fig. 2 shows the thermogravimetry (TG) and derivative thermogravimetric (DTG) curves of WEPS in the temperature range of 25°C to 800°C under a nitrogen atmosphere. It is seen from Fig. 2 that the WEPS showed a single-stage degradation that began at the temperature of 360°C and 99 wt.% of degradation was completed at a temperature of 600°C (Table 2). It can be noted from Table 2 that 50 wt.% of WEPS was degraded at a temperature of 422°C whereas, 90 wt.% of degradation was take place at a temperature of 440°C. It is seen from DTG curve, the maximum degradation takes place at a temperature of 428°C (Fig. 2).

Table 1 — Proximate analysis of WEPS

Physicochemical property	Amount (wt.%)
Moisture content	0.0
Volatile matter	99.8
Fixed carbon	0.18
Ash content	0.02

Effect of temperature on product yield

The influence of reaction temperature was examined for thermal and multiphase catalytic pyrolysis in the temperature range of 400°C to 700°C at a heating rate of 15 °C/min. The feed to catalyst ratio of 20:1 was used to conduct the multiphase catalytic pyrolysis using $CaCO_3$ catalyst. Fig. 3 shows the effect of temperature on the product yield of thermal and multiphase catalytic pyrolysis of WEPS. It should be noted from the Fig. 3 that liquid yield increases with an increase in a reaction temperature for thermal pyrolysis up to 650°C. Beyond the reaction temperature of 650°C, liquid yield goes down due to the stronger cracking of C-C bonds that takes place at higher temperatures, which gives rise to lighter hydrocarbons with shorter carbon chains[26]. The maximum liquid yield of 94.37 wt.% was obtained from thermal pyrolysis at a reaction temperature of 650°C and a heating rate of 15 °C/min. However, the gaseous yield of 5.55 wt.% was obtained at the same temperature of 650 °C and a heating rate of 15 °C/min for thermal

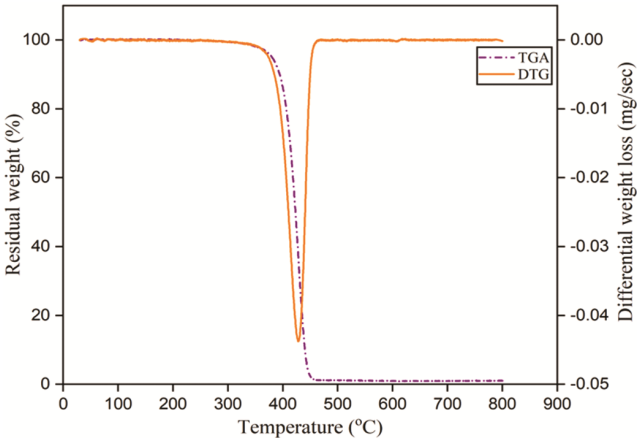


Fig. 2 — TG/DTG curve of WEPS

Table 2 — TG analysis data of waste expanded polystyrene (WEPS)

Weight loss (%)	Temperature (°C)
Initial Decomposition Temperature (IDC)	T_{IDC} =360
10	T_{10} = 394
50	T_{50} = 422
90	T_{90} = 440
99	T_{99} = 600

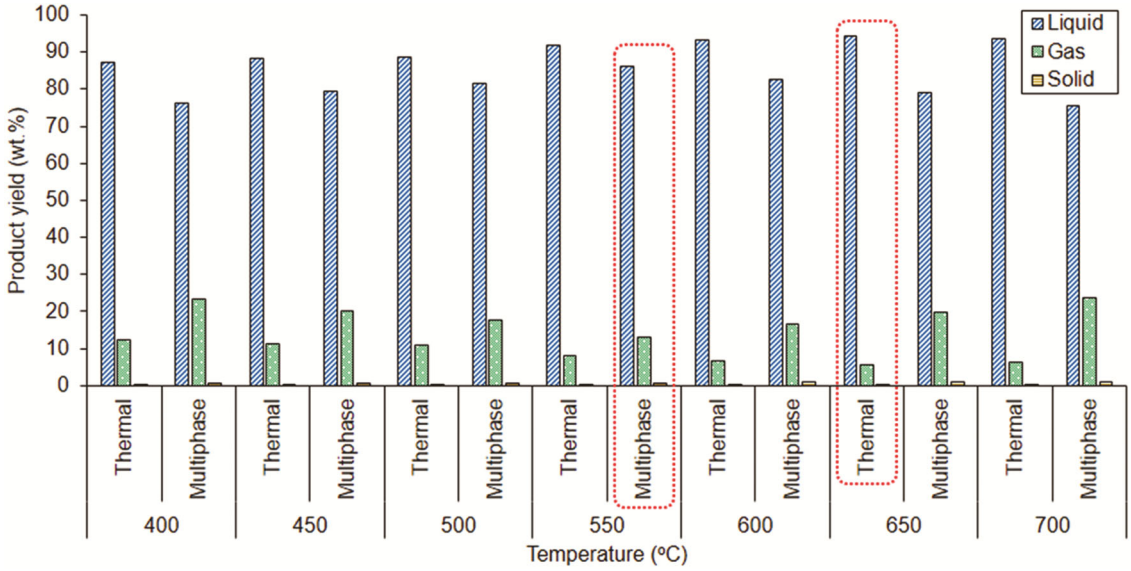


Fig. 3 — Effect of temperature on product yield of thermal and multiphase catalytic pyrolysis process

pyrolysis. A similar trend between liquid yield and temperature was also found for the multiphase catalytic pyrolysis of WEPS using $CaCO_3$ catalyst. The liquid yield increases with an increase in temperature up to 550°C, thereafter the liquid yield get decreased. The maximum liquid yield of 85.99 wt.% was obtained at a reaction temperature of 550°C and a heating rate of 15 °C/min for the multiphase catalytic pyrolysis. The gaseous yield of 13.20 wt.% was obtained for multiphase catalytic pyrolysis. It can be noted from Fig. 3 that the liquid yield was found to be lower for multiphase catalytic pyrolysis as compared to the thermal pyrolysis at each pyrolysis temperature. It is due to the two-stage catalytic cracking i.e., liquid phase catalytic cracking in primary reactor and vapour phase catalytic cracking in secondary reactor which, enhances the gaseous range hydrocarbons.

Analysis of pyrolysis oil

Gas chromatography of pyrolysis oil

The gas chromatography (GC) analysis of pyrolysis oil was conducted to determine the lower aromatic benzene, toluene and ethylbenzene and monomer styrene. The GC-FID analysis gives the percentage peak area of components with respect to their specific retention time. Therefore, the calibration characteristics were plotted for benzene, toluene, ethylbenzene and styrene monomer to convert the % peak area of each component into wt.%. The calibration characteristics for each component were plotted between concentration (wt.%) versus %area already been published elsewhere[22].

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.

Fig. 4 shows the comparison of GC characteristics for thermal and multiphase catalytic pyrolysis oil obtained at optimum temperature i.e., 650°C for thermal pyrolysis and 550°C for multiphase pyrolysis with commercial fuels kerosene and diesel. The peaks for benzene, toluene, ethylbenzene and monomer styrene were found at the retention time of 1.76 min, 3.13 min, 4.94 min and 5.56 min, respectively. It can be noted from Fig. 4 that at higher retention time most of the components of thermal and multiphase catalytic pyrolysis oil were matched with commercial fuels kerosene and diesel.

Table 3 shows the concentration of benzene, toluene, ethylbenzene and styrene monomer for thermal and multiphase catalytic pyrolysis oil. It should be noted from Table 3 that the thermal pyrolysis contains 0.62 wt.% of benzene, 10.21 wt.% of toluene, 0.55 wt.% of ethylbenzene and 84.74 wt.% of styrene monomer. Whereas, a very high styrene content of 93.24 wt.% along with a very low amount of fuel range hydrocarbons benzene (0.25 wt.%), toluene (2.09 wt.%) and ethylbenzene (0.52 wt.%) was found in the multiphase catalytic pyrolysis oil obtained using $CaCO_3$ as a catalyst.

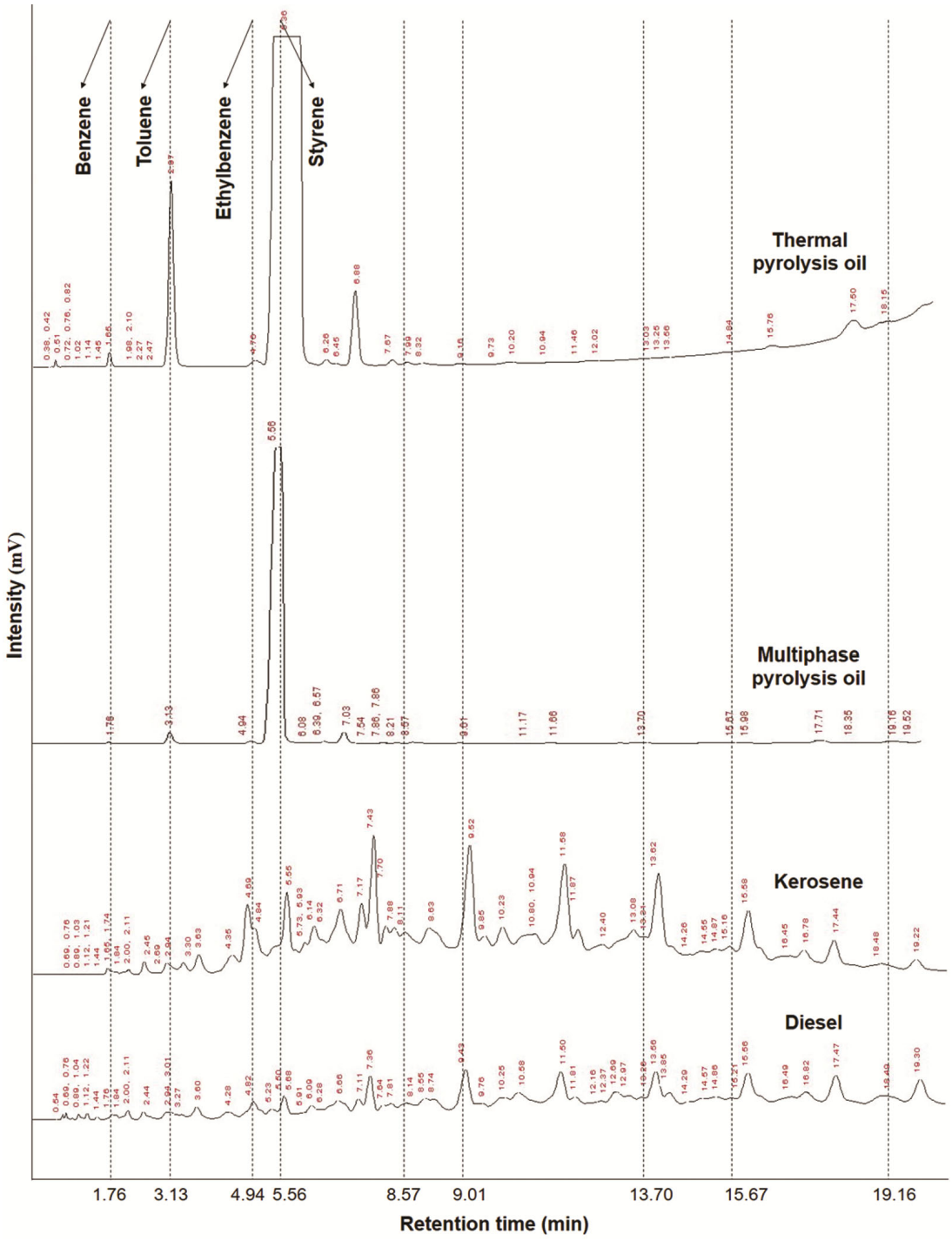


Fig. 4 — GC characteristics of thermal and multiphase catalytic pyrolysis oil and comparison with commercial fuels kerosene and diesel

Table 3 — Product yield and aromatic content of thermal and multiphase catalytic pyrolysis oil obtained at optimum temperature

Pyrolysis Temperature (°C)	Pyrolysis type	Liquid (wt.%)	Gas (wt.%)	Benzene (wt.%)	Toluene (wt.%)	Ethylbenzene (wt.%)	Styrene (wt.%)
650	Thermal	94.37	5.55	0.62	10.21	0.55	84.74
550	Multiphase	85.99	13.20	0.25	2.09	0.52	93.24

It may be due to the higher selectivity of solid base catalyst $CaCO_3$ towards styrene monomer as compared to the thermal pyrolysis. In the present study, the styrene was considered as the desired product and also found in very high quantity (93.24 wt.%) thus, the mechanism for the depolymerization of WEPS into styrene monomer using a basic catalyst is given in Fig. 5(a-b). The degradation of polystyrene using a basic catalyst proceeds through the formation of anions (Fig. 5a)[27]. Zhang *et al.* (1995) reported that the rate of polystyrene depolymerization increases in the presence of base catalysts due to an increase in the rate of initiation when a proton attached to a backbone tertiary carbon is removed by the base catalyst[15].

Facile chain scission may occur when a C-C bond beta to the anionic center is cleaved. The newly formed end-chain anion may then undergo the same type of cleavage, resulting in depolymerization that affords progressively shorter end-chain anions and monomer. However, a depropagating anionic chain may potentially terminate by recovering a proton from the catalyst surface as indicated in Fig. 5b[27].

Physicochemical properties of pyrolysis oil

The physicochemical properties of thermal and multiphase catalytic pyrolysis obtained at optimum temperature with commercial fuels kerosene and diesel are reported in Table 4. The higher heating value (HHV) or gross calorific value (GCV) shows the energy content of fuel[28]. The HHV of thermal pyrolysis oil was found to be low (9816 cal/g) as compared to the multiphase catalytic pyrolysis (11972 cal/g) due to the presence of long-chain

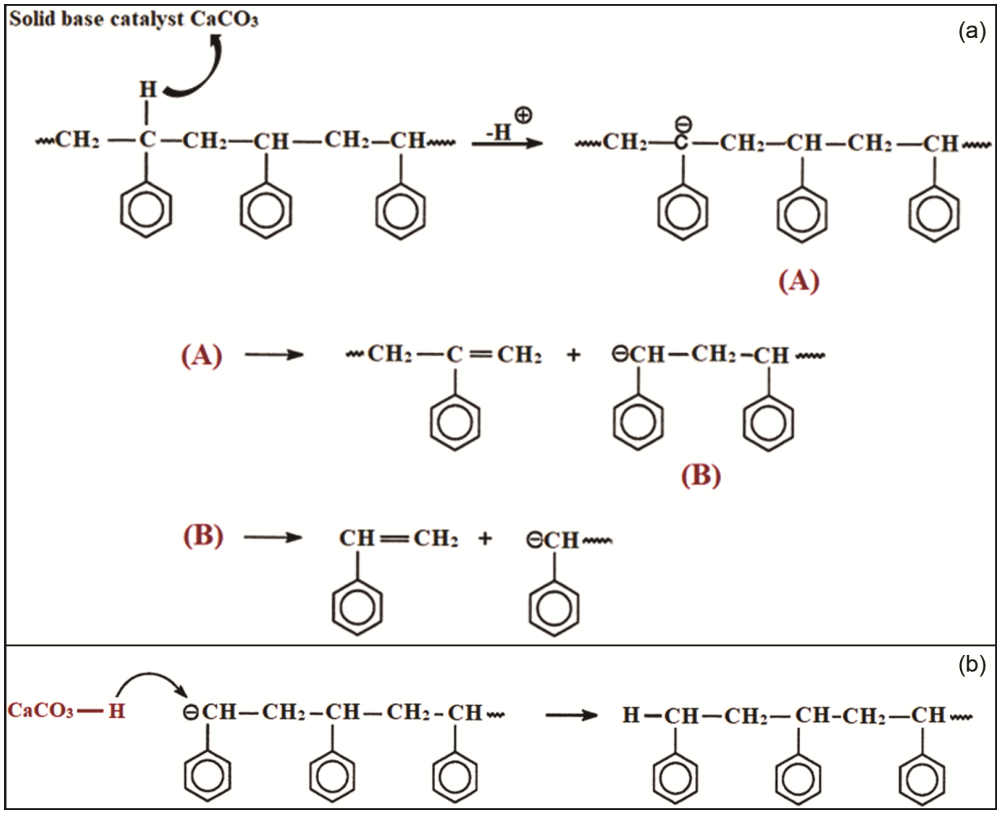


Fig. 5 (a) — Mechanism for depolymerization of WEPS in the presence of base catalyst[27] and (b) termination mechanism for depropagating polystyrene chains due to abstraction of proton from the catalyst[27]

Table 4 — Physicochemical properties of thermal and multiphase catalytic pyrolysis oil obtained at optimum conditions and comparison with standard commercial fuel

Physicochemical Properties	Thermal pyrolysis oil	Multiphase catalytic pyrolysis oil	Kerosene	Diesel
Calorific value (cal/g)	9816	11972	11052	10717
Carbon residue (wt.%)	1	0.68	0.13	1.14
Flash point (°C)	58	46	42	48
Fire point (°C)	62	48	45	50

carbon compounds in thermal pyrolysis oil[29]. The HHV of multiphase catalytic pyrolysis oil (11972 cal/g) was higher than the commercial fuels kerosene (11052 cal/g) and diesel (10717 cal/g)[30] indicating the potential for the use of multiphase catalytic pyrolysis oils as fuel. It may be due to the presence of lighter hydrocarbons because of two-stage catalytic cracking.

The carbon residue is defined as the tendency of the oil to form a carbonaceous solid, when the fuel is combusted in the absence of a large excess of air or when the fuel is subject to evaporation and pyrolysis. The high carbon residue may lead to the coking of fuel injector nozzles in a diesel engine or spray combustion orifice[31]. The carbon residue of multiphase catalytic pyrolysis oil (0.68 wt.%) (Table 4) was lower than the commercial diesel (1.14 wt.%) and higher than the kerosene (0.13 wt.%)[32]. The flash and fire point indicates the maximum temperature at which fuel can be stored and handled without serious fire hazard[33]. The flash point (46°C) and fire point (48°C) of multiphase catalytic pyrolysis oil were lower than the flash (58°C) and fire point (62°C) of thermal pyrolysis (Table 4) oil due to the presence of lower range hydrocarbon molecules in multiphase catalytic pyrolysis oil. The multiphase catalytic pyrolysis oil could be recommended for the cooking stoves, generator sets and diesel engines.

Conclusion

The waste expanded polystyrene (WEPS) converts into useful monomer styrene via multiphase catalytic pyrolysis using basic solid catalyst calcium carbonate ($CaCO_3$). The low-cost calcium carbonate catalyst was found to be effective for the degradation of polystyrene to diesel-grade fuel. The secondary reactor enhances the interaction between hydrocarbon vapours and catalyst particles. The maximum liquid yield of 94.37 wt.% at a reaction temperature of 650°C and 85.99 wt.% at a temperature of 550°C was found for the thermal and multiphase catalytic pyrolysis. The styrene content of 84.74 wt.% was found for thermal pyrolysis. Whereas, styrene content of 93.24 wt.% was recorded for the multiphase catalytic pyrolysis oil. The physicochemical properties of multiphase catalytic pyrolysis oil were found to be better as compared to the thermal pyrolysis oil. Furthermore, the HHV of multiphase catalytic pyrolysis oil was found to be higher than the commercial fuels kerosene and diesel.

References

1 Kumar S, Prakash R, Murugan S & Singh R K, Performance and emission analysis of blends of waste plastic oil obtained by catalytic pyrolysis of waste HDPE with diesel in a CI engine, *Energy Convers Manag*, 74 (2013) 323.

2 Das P & Tiwari P, The effect of slow pyrolysis on the conversion of packaging waste plastics (PE and PP) into fuel, *Waste Manage*, 79 (2018) 615.

3 Dan O & Trofimova L, A study of the properties of forming mixtures containing polystyrene wastes, *J Cast Mater Eng*, 5 (2021) 14.

4 Chen W, Hao H, Hughes D, Shi Y, Cui J & Li Z X, Static and dynamic mechanical properties of expanded polystyrene, *Mater Des*, 69 (2015) 170.

5 Kan A & Demirboga R, A new technique of processing for waste-expanded polystyrene foams as aggregates, *J Mater Process Technol*, 209 (2009) 2994.

6 Song Y K, Hong S H, Eo S, Han G M & Shim W J, Rapid production of micro-and nanoplastics by fragmentation of expanded polystyrene exposed to sunlight, *Environ Sci Technol*, 54 (2020) 11191.

7 Uttaravalli A N, Dinda S & Gidla B R, Scientific and engineering aspects of potential applications of post-consumer (waste) expanded polystyrene: A review, *Process Saf Environ Prot*, 137 (2020) 140.

8 Singh R, Singh N, Fabbrocino F, Fraternali F & Ahuja I P, Waste management by recycling of polymers with reinforcement of metal powder, *Compos B: Eng*, 105 (2016) 23.

9 Sharuddin S D, Abnisa F, Daud W M & Aroua M K, A review on pyrolysis of plastic wastes, *Energy Convers Manag*, 115 (2016) 308.

10 Lam S S, Liew R K, Jusoh A, Chong C T, Ani F N & Chase H A, Progress in waste oil to sustainable energy, with emphasis on pyrolysis techniques, *Renew Sust Energ Rev*, 53 (2016) 741.

11 Tejaswini M S, Pathak P, Ramkrishna S & Ganesh S P, A comprehensive review on integrative approach for sustainable management of plastic waste and its associated externalities, *Sci Total Environ*, 825 (2022) 153973.

12 Martin-Lara M A, Pinar A, Ligero A, Blázquez G & Calero M, Characterization and use of char produced from pyrolysis of post-consumer mixed plastic waste, *J Water*, 13 (2021) 1188.

13 Anene A F, Fredriksen S B, Saetre K A & Tokheim L A, Experimental study of thermal and catalytic pyrolysis of plastic waste components, *Sustainability*, 10 (2018) 3979.

14 Park J J, Park K, Kim J S, Maken S, Song H, Shin H, Park J W & Choi M J, Characterization of styrene recovery from the pyrolysis of waste expandable polystyrene, *Energy Fuels*, 17 (2003) 1576.

15 Zhang Z, Hirose T, Nishio S, Morioka Y, Azuma N, Ueno A, Ohkita H & Okada M, Chemical recycling of waste polystyrene into styrene over solid acids and bases, *Ind Eng Chem Res*, 34 (1995) 4514.

16 Achilias D S, Kanellopoulou I, Megalokonomos P, Antonakou E & Lappas A A, Chemical recycling of polystyrene by pyrolysis: Potential use of the liquid product for the reproduction of polymer, *Macromol Mater Eng*, 292 (2007) 923.

17 Ukei H, Hirose T, Horikawa S, Takai Y, Taka M, Azuma N & Ueno A, Catalytic degradation of polystyrene into styrene and a design of recyclable polystyrene with dispersed catalysts, *Catal Today*, 62 (2000) 67.
18 Inayat A, Klemencova K, Grycova B, Sokolova B & Lestinsky P, Thermo-catalytic pyrolysis of polystyrene in batch and semi-batch reactors: A comparative study, *Waste Manage Res*, 39 (2021) 260.
19 Hussain Z, Imtiaz M, Naz M Y, Khan K M, Abd El-Salam N M & Ibrahim K A, Thermal and clinker-catalyzed pyrolyses of polystyrene waste using the portland cement solid-base catalyst, *Asia-Pac J Chem Eng*, 16 (2021) e2556.
20 Miller R R, Newhook R & Poole A, Styrene production, use, and human exposure, *Crit Rev Toxicol*, 24 (1994) S1.
21 Leite B, da Costa A O & da Costa E F, Multi-objective optimization of adiabatic styrene reactors using generalized differential evolution 3 (GDE3), *Chem Eng Sci*, 265 (2022) 118196.
22 Verma A & Pramanik H, Multiphase pyrolysis of waste expanded polystyrene and in-situ hydrogenation of pyrolysis oil on silica-alumina supported nickel catalyst for the production of fuel range paraffinic and aromatic hydrocarbons, *Indian J Chem Technol*, 30 (2023) 461.
23 Gaurh P & Pramanik H, A novel approach of solid waste management via aromatization using multiphase catalytic pyrolysis of waste polyethylene, *Waste Manage*, 71 (2018) 86.
24 Verma A, Sharma S & Pramanik H, Pyrolysis of waste expanded polystyrene and reduction of styrene via in-situ multiphase pyrolysis of product oil for the production of fuel range hydrocarbons, *Waste Manage*, 120 (2021) 330.
25 Abbas-Abadi M S, Van Geem K M, Fathi M, Bazgir H & Ghadiri M, The pyrolysis of oak with polyethylene, polypropylene and polystyrene using fixed bed and stirred reactors and TGA instrument, *Energy*, 232 (2021) 121085.
26 Lopez A, De M I, Caballero B M, Laresgoiti M F, Adrados A & Aranzabal A, Catalytic pyrolysis of plastic wastes with two different types of catalysts: ZSM-5 zeolite and Red Mud, *Appl Catal B*, 104 (2011) 211.
27 Woo O S, Ayala N & Broadbelt L J, Mechanistic interpretation of base-catalyzed depolymerization of polystyrene, *Catal Today*, 55 (2000) 161.
28 Verma A, Sharma S & Pramanik H, Synthesis and efficient use of low-cost natural red clay catalyst for the production of upgraded fuel oil using pyrolysis of waste expanded polystyrene and in situ vapour phase hydrogenation, *Int J Energy Res*, 46 (2022) 15463.
29 Lam S S, Russell A D, Lee C L & Chase H A, Microwave-heated pyrolysis of waste automotive engine oil: Influence of operation parameters on the yield, composition, and fuel properties of pyrolysis oil, *Fuel*, 92 (2012) 327.
30 Pramanik H & Gaurh P, Production and characterization of pyrolysis oil using waste polyethylene in a semi batch reactor, *Indian J Chem Technol*, 25 (2019) 336.
31 Gupta A D, Gupta A & Varshney L, An assessment of fuel from disposed plastic containers for desel engine, *Int J Bio-resour Stress Manage*, 10 (2019) 166.
32 Ahmad W, Ahmad I, Ishaq M & Ihsan K, Adsorptive desulfurization of kerosene and diesel oil by Zn impregnated montmorollonite clay, *Arab J Chem*, 10 (2017) S3263.
33 Hakeem I G, Aberuagba F & Musa U, Catalytic pyrolysis of waste polypropylene using Ahoko kaolin from Nigeria, *Appl Petrochem Res*, 8 (2018) 203.