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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

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In this work, thermal and catalytic pyrolysis of waste expanded polystyrene (WEPS) have been investigated in a laboratory designed semi-batch reactor in the temperature range of 400-700℃ and heating rate of 15 ℃/min to produce gasoline range lower paraffins and valuable aromatics i.e., benzene, toluene and ethylbenzene (BTE). Three different type of reactor arrangements i.e., liquid phase/A-type, vapour phase/B-type and multiphase/AB-type have been used to conduct the catalytic pyrolysis of WEPS using nickel on silica-alumina catalyst. The thermal pyrolysis of WEPS produced highest liquid yield of 94.37 wt.% at a temperature of 650℃ and heating rate of 15 ℃/min, whereas, liquid phase/A-type, vapour phase/B-type and multiphase/AB-type catalytic pyrolysis produced highest liquid yield of 88.54 wt.%, 83.21 wt.%, and 81.15 wt.%, respectively, at the same heating rate of 15 ^{o}C/min and at the temperature of 600℃, 550℃, and 550℃, respectively. The pyrolysis oil obtained from thermal pyrolysis mainly contains styrene monomer of 84.74 wt.% and very less BTE content of 11.38 wt.%. Among, the all types of catalytic pyrolysis, AB-type/multiphase pyrolysis produced pyrolysis oil with highest amount of BTE content of 28.56 wt.%. Furthermore, the pyrolysis oil obtained from A-type, B-type and AB-type catalytic pyrolysis contains low styrene content of 69.94 wt.%, 65.67 wt.% and 55.55 wt.%, respectively, as compared to thermal pyrolysis (84.74 wt.%).

Keywords: WEPS, Nickel on silica-alumina, Multiphase, In-situ hydrogenation

The plastic consumption and rate of waste plastic production is at an alarming rate at the present time[1]. Plastics are made from petrochemical hydrocarbons, including some additives such as flame retardants, stabilizers, anti-oxidants, crosslinking agents etc., which makes plastics difficult to be biodegraded[2]. Thus, plastic waste reduction in a sustainable way is a big challenge. Recycling of waste plastic is considered as one of the best solutions for decreasing the waste generated from the used plastic materials. However, plastics have high energy content[3] which promotes the research and development works on thermochemical conversion in the absence of oxygen i.e., pyrolysis of plastic materials into value-added chemicals and fuels[4]. Pyrolysis is an eco-friendly and highly effective method for converting the waste plastic into valuable products as compared to other recycling methods as it can handle the mixed and contaminated plastic waste as a feed[5]. The pyrolysis of plastics has become very popular as it converts plastic waste into energy in the form of pyrolysis oil, pyrolysis gas and solid residue[1]. The pyrolysis oil is widely used as a fuel in boilers, turbines, furnaces, and diesel engines after certain upgradation[6]. The pyrolysis gas can be used for electricity generation in gas turbines without any treatment[7]. Furthermore, the solid residue obtained from pyrolysis process can be used as an adsorbent, as a soil amendment and as a solid fuel[8]. However, the distribution of products in the pyrolysis process depends on the pyrolysis type, reaction conditions, and feedstock[9]. It is seen from the literature that the expanded polystyrene (EPS) is widely used as a construction and packaging material due to several properties such as lightweight, good insulating property for cold insulation, and high impact resistance[10]. The global demand for expanded polystyrene (EPS) is gradually increasing[11]. Due to the large consumption of EPS, it is a common plastic marine debris found in oceans and rivers worldwide[12]. In addition, WEPS contributes 10 wt.% of the total plastic waste, and it could be 40% by volume of the total discarded plastic waste. Thus, presently WEPS requires more concern due to its high disposal by the public and industries[13]. On the other hand, the disposal or burning of WEPS releases harmful chemicals and gases into the environment[14]. In this context, the eco-friendly and versatile method, pyrolysis was adopted for handling the waste generated from the disposal of EPS. The pyrolysis process does not release harmful gasses like incineration[15].

The thermal pyrolysis of polystyrene mainly produces styrene monomer[16-17]. Liu *et al.*[17] investigated the pyrolysis of polystyrene in a fluidized bed reactor in the range of temperature 450°C to 700°C. The highest liquid yield of 98.7 wt.% was obtained at the pyrolysis temperature of 600°C. Very high styrene content of 78.7 wt.% was reported in pyrolysis oil with some mono-aromatics such as benzene, toluene, and ethylbenzene. It was also found that the styrene gets converted into benzene, toluene, and ethylbenzene when pyrolysis temperature is increased beyond 600°C. Aguado *et al.*[18] also suggested the mechanism of polystyrene decomposition at high temperature, resulting in low yield of styrene. Whereas, the catalytic pyrolysis is considered as better process than thermal pyrolysis as it offers advantages such as minimize the reaction temperature, reaction time[19] and enhance the selectivity towards target molecules[20]. A wide range of catalysts such as silica-alumina[21], Y-zeolite[22], β-zeolite[22], HZSM-5[22], MCM-41[23] has been investigated for the catalytic pyrolysis of plastic waste. Lee *et al.*[24] examined the effect of various catalysts such as silica-alumina, HZSM-5, HY, mordenite, natural clinoptilolite zeolite, and synthesized clinoptilolite for the catalytic degradation of polystyrene and suggested that higher acidity of catalyst favoured the production of ethylbenzene by promoting the hydrogenation reaction. Rehan *et al.*[25] also reported the decrease in styrene production and it may be due to high acidity of the catalyst which increases the rate of secondary reactions i.e., further cracking of styrene via hydrogenation or recombination of styrene via H-abstraction followed by cyclization. Park *et al.*[26] also reported that the styrene monomer is easily produced during the pyrolysis of polystyrene due to its low activation energy, whereas, acid catalysts show higher selectivity towards benzene, toluene, and ethylbenzene rather than styrene monomer. On the other hand, basic catalyst shows higher selectivity for styrene. Thus, based on the thorough literature survey, it was found that the acid catalyst promotes the formation of valuable lower aromatic hydrocarbons i.e., benzene, toluene and ethylbenzene (BTE), and thereby reduces the styrene content in the pyrolysis oil. Not only the acid catalyst, reactor arrangement or reactor type also plays a crucial role for the production of target aromatic hydrocarbons such as BTE. Verma *et al.*[27] performed the catalytic pyrolysis of WEPS in three different reactor arrangements i.e., liquid phase, vapour phase, and multiphase. The highest BTE content of 28.12 wt.% was reported for the pyrolysis oil obtained from multiphase reactor arrangement. Whereas, lowest BTE content of 18.98 wt.% was found in pyrolysis oil obtained from the liquid phase reactor arrangement using commercial ZSM-5, ammonium powder as a catalyst. Park *et al.*[28] conducted two-stage pyrolysis of polystyrene that has an auger reactor and a fluidized bed reactor connected in series. It was reported that the reaction temperatures and the type of fluidizing medium effects the product distribution and composition. The maximum yield of 26.3 wt.% was obtained for benzene, toluene, ethylbenzene, and xylenes at a temperature of 780°C in the fluidized bed reactor without use of any catalyst. In addition, styrene yield get decreased as the temperature in the auger reactor increased. It is seen from the thorough literature that, no detailed study on the catalytic pyrolysis of WEPS using nickel on silica-alumina catalyst is reported till date. However, some work on nickel based catalyst for the pyrolysis of municipal plastic waste[29] and high density polyethylene (HDPE)[30] has been performed but not on the pyrolysis of waste expanded polystyrene (WEPS). Furthermore, nickel on silica-alumina catalyst widely used in various hydrocarbon reactions including isomerization, hydrocracking, olefin hydrogenation, etc. The nickel on silica-alumina catalyst exhibits both acidic and hydrogenation activity[31]. It is also suggested by Wang and Wang[29], nickel improves the hydrogen production which may be used in in-situ hydrogenation reaction for the production of ethylbenzene during pyrolysis of polystyrene. Sunarno *et al.*[32] reported the higher selectivity of Ni/silica-alumina catalyst towards the gasoline range hydrocarbon molecules. Due to several benefits of nickel based catalyst, nickel on silica-alumina catalyst was used in the present study for the reduction of styrene content in pyrolysis oil and enhance the valuable lower aromatic hydrocarbons i.e., BTE via in-situ hydrogenation, aromatization, and cyclization. Moreover, appropriate quantity of BTE when blended with gasoline, improves its fuel efficiency and engine performance[33-34].

The BTE also used for numerous industrial and household purposes such as, chemical intermediates, solvents, and cleaners[35]. The principal use of benzene is as a raw material for the synthesis of various compounds such as phenol, cyclohexane, aniline, maleic anhydride, styrene, alkylbenzenes, and chlorobenzenes[36]. Toluene is used as a raw material for variety of applications, including solvents for adhesives, paints and inks[37]. Similarly, ethylbenzene is mainly used as raw material for styrene production[38] and has some applications in the synthesis of other chemicals and as a solvent in inks, rubber adhesives, varnishes, and paints[39]. In the present study, the production of styrene was minimized, as it is not a fuel component because of its high chemical reactivity and rapid polymerization with the possibility of violent explosions [40]. Although, significant amount of styrene was found in the pyrolysis oil, which can be used as raw material for production of polymer and copolymer and a variety of resins[40]. In this study, nickel on silica-alumina catalyst is used for the production of lower range aromatic hydrocarbons BTE. The effect of reactor arrangements, feed to catalyst ratio, heating rate, and temperature were also examined on the product distribution and product composition in order to achieve the optimum conditions for the higher production of lower range parraffins and valuable aromatic hydrocarbons (BTE). In addition, such type of reactor arrangements for catalytic pyrolysis of WEPS using nickel on silica alumina catalyst is not studied till date in open literature. The four-layer fixed catalytic bed used in this study provides easy and enough contact between hydrocarbon vapours and nickel on silica alumina catalyst particles with minimum resistance. Furthermore, the additional heating arrangement is also not required here for the vapour phase catalytic reaction as the secondary reactor is attached inside the primary. On the other side, reactor arrangements are very compact and easy to handle which promotes the application of the reactor for industrial use after scale up.

Materials and Method

Materials

The packing material (thermocol/WEPS) of various laboratory equipments was used as the feed for the pyrolysis process of WEPS. The same procedure of feed material preparation was also adopted here as the previous work published elsewhere[27]. The pictorial view of the collected and treated feed material is shown in Fig. 1a and Fig. 1b, respectively. The nickel on silica-alumina powder with 66 ± 5 % Ni was procured from Alfa Aesar, USA used as the catalyst for the catalytic pyrolysis process.

Experimental method

The WEPS was subjected to the thermal and catalytic pyrolysis in different reactor arrangements as mentioned in Fig. 2(a-d). The detailed schematic of experimental setup is given elsewhere[27]. The main pyrolysis unit mainly consists of two reactors i.e., a large primary reactor (Fig. 2a) and a secondary reactor of relatively smaller diameter and height than those of primary reactor (Fig. 3a-b).

The secondary reactor was placed inside the primary reactor and connected at the ceiling using threaded connecter (Fig. 2c-d). The bottom of secondary reactor is perforated which provides the path to the vapours generated inside the primary reactor (Fig. 3a-b). The raw material thermocol/ WEPS of 50 g was used for each pyrolysis

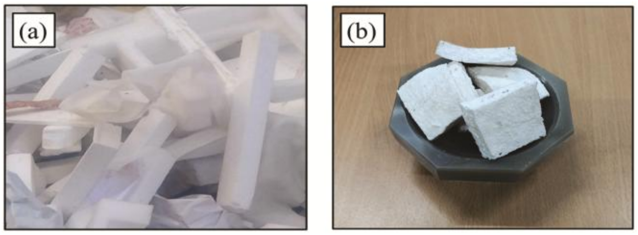

Fig. 1 — Photographic view of (a) collected WEPS, (b) WEPS after processing via heat treatment

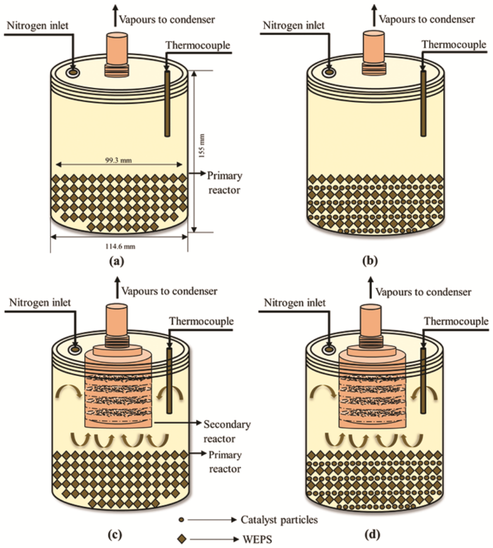

Fig. 2 — Reactor arrangements (a) thermal pyrolysis, (b) liquid phase/A-type, (c) vapour phase/B-type, (d) multiphase/AB-type pyrolysis

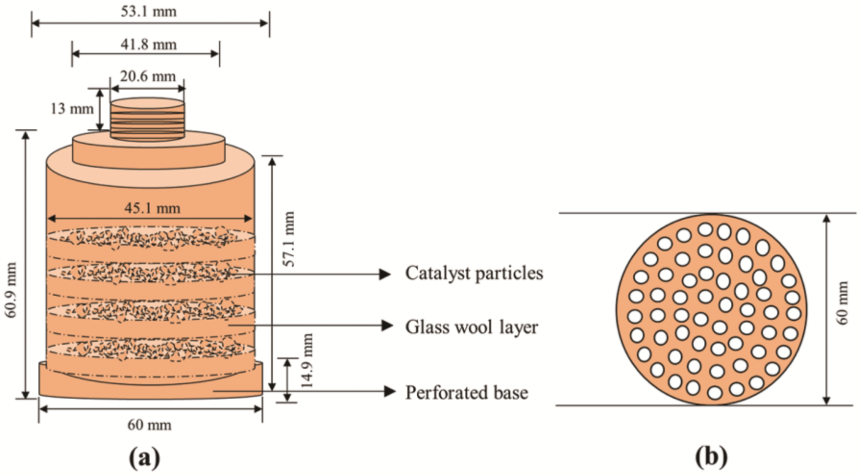

Fig. 3 — Detailed diagram of (a) secondary pyrolysis reactor for the vapour phase reactions, (b) perforated base of secondary reactor

experiment. The raw material WEPS was heated by an electrical furnace at a selected temperature and heating rate. The target temperature of pyrolysis and other secondary reactions was maintained for ½ h for each experiment of pyrolysis. The thermal pyrolysis was conducted in a reactor arrangement as shown in Fig. 2a. Whereas, the catalytic pyrolysis was conducted in three reactor arrangements i.e., liquid phase/A-type (Fig. 2b), vapour phase/B-type (Fig. 2c), and multiphase/AB-type (Fig. 2d). The detailed experimental method is given in our previously published research article[27].

The amount of catalyst was optimized for the A-type catalytic pyrolysis at various feed to catalyst ratio in the range of 10:1-40:1. The effect of heating rate was examined for thermal and catalytic pyrolysis at a varying heating rate in the range of 5 - 25 ^{o}C/min. The effect of temperature was examined in the temperature range of 400^{o}C to 700^{o}C for thermal as well as catalytic pyrolysis.

Analytical methods for characterization of polystyrene and pyrolysis oil

The thermal degradation behaviour of WEPS was investigated thermogravimetrically using TGA instrument (Shimadzu TGA-50, North America) in the temperature range of 25^{o}C to 800^{o}C and at a heating rate of 15 ^{o}C/min in the nitrogen atmosphere by taking 6 mg sample in the platinum pan. The proximate analysis of WEPS was carried out using standard ASTM test methods IS 1350-1959. The gas chromatograph (NUCON 5765, Centurion Scientific, India) was used to conduct the compositional analysis of pyrolysis oil in flame ionisation detector (FID) mode using SE-30 10% chromosorb W packed stainless-steel column. The Fourier transform infrared spectroscopy (FTIR) analysis of pyrolysis oil was performed by Nicolet iS5 spectrophotometer (THERMO Electron Scientific Instruments LLC, USA) to determine the various functional groups present in hydrocarbon molecules. ASTM D86 method was used to obtain the distillation characteristics of pyrolysis oil. The digital bomb calorimeter (RSB-3, Rajdhani Scientific Instruments Co., India, IP 12/63T standard) was used to determine the gross calorific value (GCV) of pyrolysis oil. The flash and fire point of pyrolysis oil were obtained using the Cleveland open cup apparatus as per ASTM D 92 standard. The carbon residue of pyrolysis oil was determined using Ramsbottom carbon residue apparatus as per IP 14/65 standard.

Results and Discussion

Raw material characterization

Thermal and proximate analysis of WEPS

The thermal degradation behaviour of WEPS is very much essential to know for their thermal stability in pyrolysis reactor. The various temperature region of thermal degradation of WEPS was examined using thermogravimetry analyser. The degradation of WEPS starts at a temperature of about 360^{o}C and 99 wt.% degradation occurs at a temperature of 600^{o}C. The detailed discussion on TGA characteristics of WEPS is reported in our previous publication elsewhere[27]. The volatile matter, moisture and ash content of WEPS were determined by the proximate analysis. The high volatile matter of 99.8 wt.%, indicates the higher conversion of WEPS into liquid and gaseous hydrocarbons with low solid residue[41].

The detailed results of proximate analysis of WEPS have been reported in our previous publication[27].

Influence of operating parameters on product yield

Catalyst amount

The effect of catalyst amount on the product yield obtained from A-type catalytic pyrolysis was determined at different feed to catalyst ratio ranging from 10:1 to 40:1, keeping fixed pyrolysis temperature of 600°C, and heating rate of 15 °C/min. The highest liquid yield of 88.54 wt.% was obtained at the feed to catalyst ratio of 20:1. It may be due to the better interaction between active sites of catalyst with reactants. It is clearly seen from the Fig. 4 that the liquid yield of 86.32 wt.%, and 83.65 wt.% were obtained at feed to catalyst ratio of 30:1 and 40:1, respectively.

At high feed to catalyst ratio of 30:1 and 40:1, liquid yield were less as compared to the low feed to catalyst ratio of 20:1 (Table 1). It may be due to the less available active sites of catalyst at high feed to catalyst ratio. Although, active sites are high for the very low feed to catalyst ratio of 10:1, reactant is not sufficient to produce high liquid yield[42].

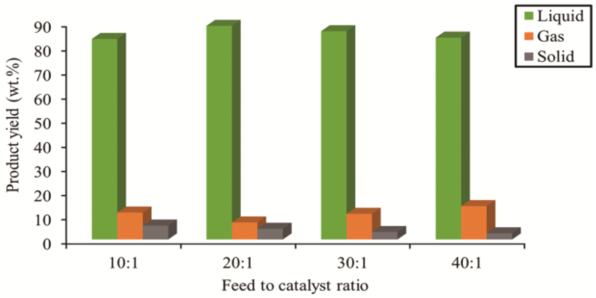

Fig. 4 — Effect of feed to catalyst ratio on product yield of liquid phase/A-type catalytic pyrolysis at 600 °C and heating rate of 15 °C/min

Heating rate

The heating rate is one of the important operating variable affecting the product yield of the WEPS pyrolysis. To determine the effect of heating rate on product yield, the WEPS was subjected to thermal, A-type, B-type, and AB-type pyrolysis at different heating rates ranging from 5 - 25 °C/min, fixed pyrolysis temperature of 550°C, and optimum feed to catalyst ratio of 20:1. The effect of heating rate on product yield can be clearly seen from Fig. 5.

At low heating rates such as 5 °C/min and 10 °C/min, the high gaseous yield was recorded because, under slower heating rates, molecules remained within the reactor for a longer duration as compared to the heating rate of 15 °C/min, which promotes further cracking and production of gaseous range hydrocarbons[43]. However, at very high heating rates such as 20 °C/min and 25 °C/min, a higher gaseous yield was also reported due to the β-scission reaction[27]. The highest liquid yield was obtained at the heating rate of 15 °C/min for thermal as well as catalytic pyrolysis. It may be due to the limited decomposition of relatively higher molecular weight hydrocarbon molecules which, favours the formation of mainly liquid range hydrocarbons. The thermal pyrolysis produced liquid and gaseous yield of 91.69 wt.% and 8.17 wt.%, respectively at the heating rate of 15 °C/min. Whereas, A-type, B-type and AB-type pyrolysis produced liquid yield of 84.17 wt.%,

Table 1 — Effect of feed to catalyst ratio on product yield of liquid phase/A-type catalytic pyrolysis at 600 °C and heating rate of 15 °C/min

Feed to catalyst ratio	Liquid (wt.%)	Gas (wt.%)	Solid (wt.%)
10:1	83.11	11.14	5.75
20:1	88.54	7.04	4.42
30:1	86.32	10.61	3.07
40:1	83.65	13.81	2.54

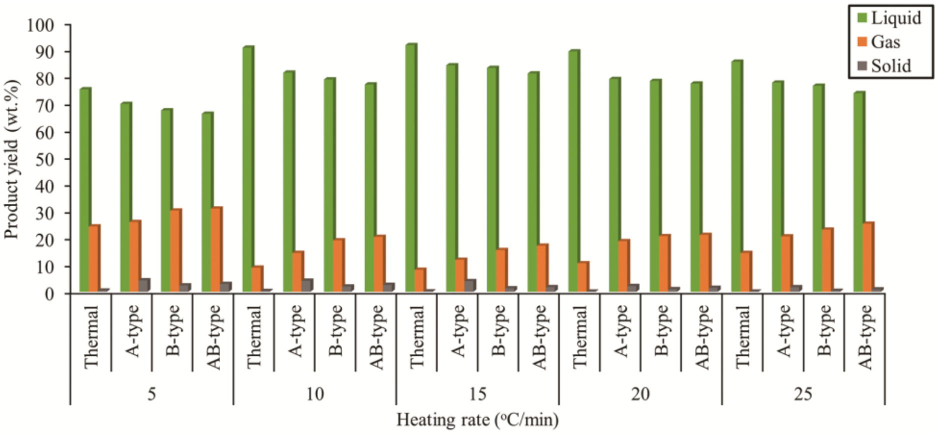

Fig. 5 — Effect of heating rate on product yield of thermal and catalytic pyrolysis of WEPS at pyrolysis temperature of 550 °C

83.21 wt.%, and 81.15 wt.%, respectively, at the same heating rate of 15 ^{o}C/min. The gaseous yield of 11.89 wt.%, 15.50 wt.%, and 17.14 wt.% were obtained from A-type, B-type and AB-type catalytic pyrolysis, respectively, at the heating rate of 15 ^{o}C/min.

Effect of pyrolysis temperature on product yield

The product yield obtained from thermal and catalytic pyrolysis is given in Fig. 6. The effect of temperature on the product yield was determined at different pyrolysis temperature in the range of 400^{o}C to 700^{o}C, at fixed heating rate of 15 ^{o}C/min and feed to catalyst ratio of 20:1. The increase in pyrolysis temperature from 400^{o}C to 650^{o}C caused a significant increase in the liquid yield for thermal pyrolysis. Beyond 650^{o}C, liquid yield get decreased due to the stronger cracking of C-C bond at high pyrolysis temperature, which gives rise to lighter hydrocarbons with shorter carbon chains[19]. The highest liquid yield of 94.37 wt.% was obtained at the pyrolysis temperature of 650^{o}C for thermal pyrolysis. All types of catalytic pyrolysis i.e., A-type, B-type and AB-type pyrolysis produced more gaseous yield as compared to the thermal pyrolysis at each pyrolysis temperature. The catalytic pyrolysis favours the production of lighter hydrocarbons and gases. Furthermore, catalytic pyrolysis improves the selectivity towards the target molecules and reduces the pyrolysis temperature which may lower the energy requirement of the entire process[44]. For A-type catalytic pyrolysis, liquid yield increased with increase in temperature up to 600^{o}C and then decreased. Similarly, for B-type and AB-type catalytic pyrolysis liquid yield increased with increase in temperature up to 550^{o}C and then decreased.

The highest liquid yield of 88.54 wt.%, 83.21 wt.% and 81.15 wt.% were obtained for A-type pyrolysis at a temperature of 600^{o}C, B-type pyrolysis at a temperature of 550^{o}C, and for AB-type catalytic pyrolysis at the temperature of 550^{o}C, respectively. The product yield obtained from thermal and catalytic pyrolysis of all types at their optimum temperature conditions were presented in Table 2. Moreover, among all pyrolysis, the AB-type catalytic pyrolysis produced the highest gaseous yield at each pyrolysis temperature due to the multi-stage catalytic contact of hydrocarbon molecules in liquid phase followed by selective vapour phase catalytic contact within the secondary reactor.

Similarly, B-type catalytic pyrolysis also proceeds through multi-stage cracking i.e., in the first stage molecules crack thermally in liquid phase without catalyst and then cracked hydrocarbon molecules pass through the catalytic bed installed in the secondary reactor. Thus, the B-type catalytic pyrolysis produced little lower gaseous yield as compared to the AB-type catalytic pyrolysis. The AB-type and B-type pyrolysis produced gaseous yield of 17.14 wt.% and 15.50 wt.%, respectively, at the optimum temperature of 550^{o}C. Whereas, A-type catalytic pyrolysis produced gaseous yield of 7.04 wt.% at the optimum temperature of 600^{o}C. The thermal pyrolysis produced lowest gaseous yield of 5.55 wt.% at the optimum temperature of 650^{o}C. It should be noted that, catalysts with higher acidity increase the cracking process that also increased the gas production and thus, liquid yield goes down[25].

Table 2 — Product yield of thermal and catalytic pyrolysis at optimum temperature

Type of pyrolysis	Optimum temperature (^{o}C)	Liquid (wt.%)	Gas (wt.%)	Solid (wt.%)
Thermal	650	94.37	5.55	0.08
Liquid phase/A-type	600	88.54	7.04	4.42
Vapour phase/B-type	550	83.21	15.50	1.29
Multiphase/AB-type	550	81.15	17.14	1.71

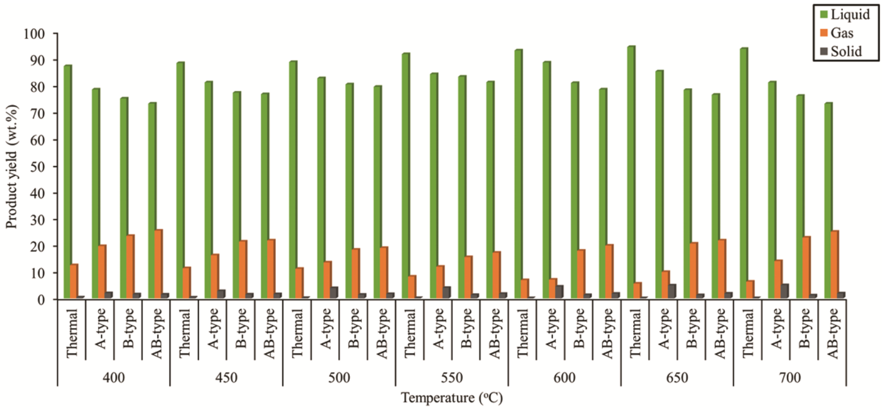

Fig. 6 — Effect of temperature on product yield for thermal and catalytic pyrolysis at a heating rate of 15 ^{o}C/min

Product characterization

GC-FID analysis of pyrolysis oil for determining the BTE content

The qualitative analysis of pyrolysis oil obtained from thermal and catalytic pyrolysis is very much essential to determine its end use. In this context, the calibration characteristics were plotted between concentration (wt.%) vs % area to measure the concentration of benzene, toluene, ethylbenzene (BTE), and styrene. The detailed method for plotting the calibration curve is reported elsewhere[27]. Fig. 7 shows the calibration curve for measuring the BTE and undesired aromatic styrene content present in pyrolysis oil. The styrene is not considered as fuel component. It is very toxic and can polymerize rapidly, which may cause violent explosions[40]. However, styrene is found in large amount in the liquid yield for all types of pyrolysis. Thus, the measurement and separation of styrene from pyrolysis oil is important before its use in IC engines. Similarly, benzene is used as octane booster for the gasoline and amount of benzene in gasoline is limited to less than 1 wt.% because of shoot formation in IC engines.

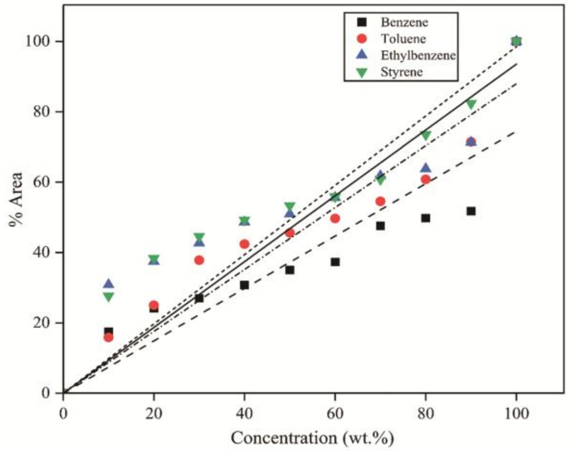

Fig. 7 — Calibration characteristics for benzene, toluene, ethylbenzene and styrene

Thus, the separation of benzene is also essential before the use of pyrolysis oil in IC engines[27]. However, small amount of benzene (< 1 wt.%) in gasoline fuel improves its octane number. The detailed reaction scheme for the formation of target molecules BTE in different reactor arrangements is mentioned in Fig. 8. The reaction scheme-A (Fig. 8)

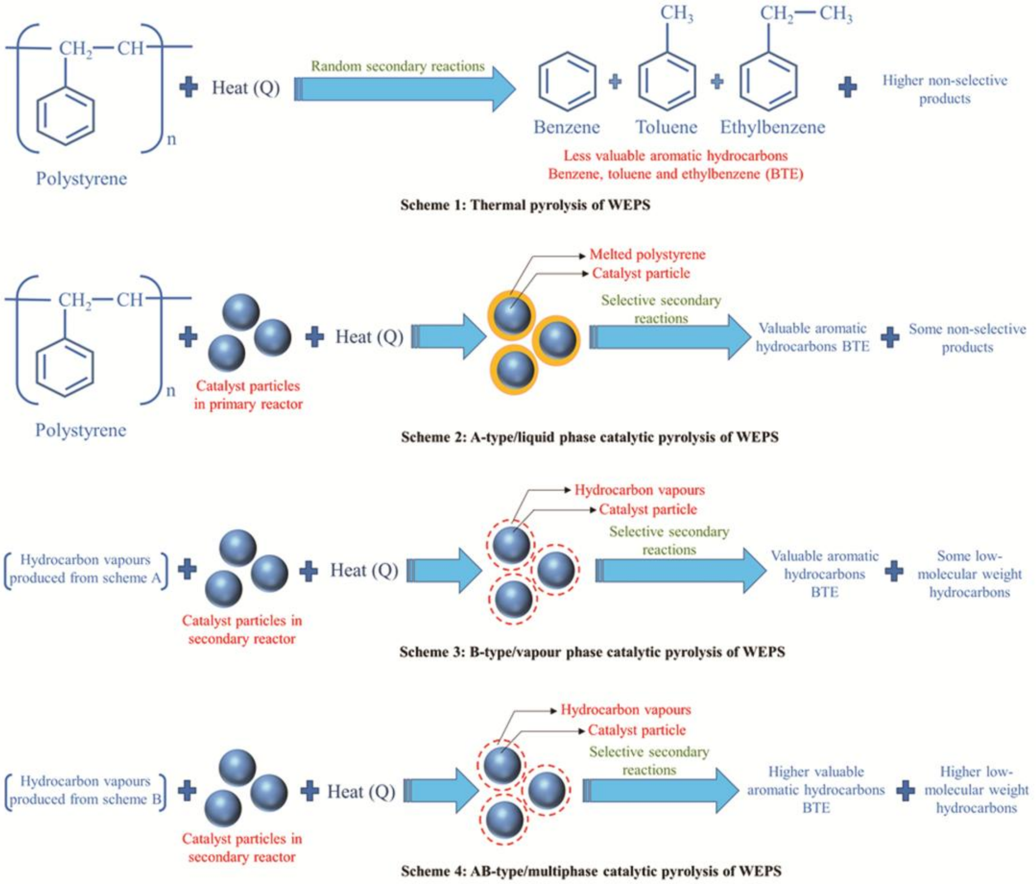

Fig. 8 — Possible reaction scheme for the formation of major product during pyrolysis of WEPS

shows the reaction path way for the thermal pyrolysis of WEPS. Whereas, the reaction scheme-B, scheme-C, and scheme-D (Fig. 8) show the possible reaction path for the A-type, B-type and AB-type catalytic pyrolysis of WEPS using Ni supported on silica-alumina, respectively. For the catalytic pyrolysis, the interactions of liquid polystyrene and product vapours with the catalyst particles are shown in the scheme-B to scheme-D.

Fig. 9 shows the comparison of GC-FID characteristics of pyrolysis oil obtained at optimum heating rate i.e., 15 ^{o}C/min using optimum temperature of 650^{o}C for thermal pyrolysis, 600^{o}C for A-type, and 550^{o}C for B-type, and AB-type pyrolysis, respectively. The peaks of target molecules i.e., gasoline range lower aromatic hydrocarbons i.e., BTE and styrene are highlighted with marker. The concentration of benzene, toluene, ethylbenzene and styrene were calculated from the calibration characteristics (Fig. 7).

The BTE and styrene content of pyrolysis oil obtained from thermal and catalytic pyrolysis i.e., A-type, B-type and AB-type at heating rate of 15 ^{o}C/min and at a temperature ranging from 400 ^{o}C to 700 ^{o}C is given in Table 3.

It is clearly seen from the Table 3 that pyrolysis oil contains maximum BTE content only at optimum temperature i.e., 650^{o}C, 600^{o}C, 550^{o}C and 550^{o}C for thermal, A-type, B-type and AB-type pyrolysis, respectively. It can be seen from the Table 3, thermal pyrolysis produced lowest BTE content of 11.38 wt.% and highest styrene content of 84.74 wt.% at optimum conditions due to the non-selective cracking (Fig. 8, scheme-A). Many authors[16, 45] have also reported that the thermal pyrolysis of polystyrene produced mainly styrene monomer. However, the yield of styrene affected by the temperature of reaction. With the increase in temperature the styrene yield decreases and the production of toluene and ethylbenzene increases due to the further decomposition of styrene at high temperature[46]. Generally, cracking, aromatization, oligomerization, isomerization, and alkylation are responsible for the production of aromatic hydrocarbons in the thermal pyrolysis of

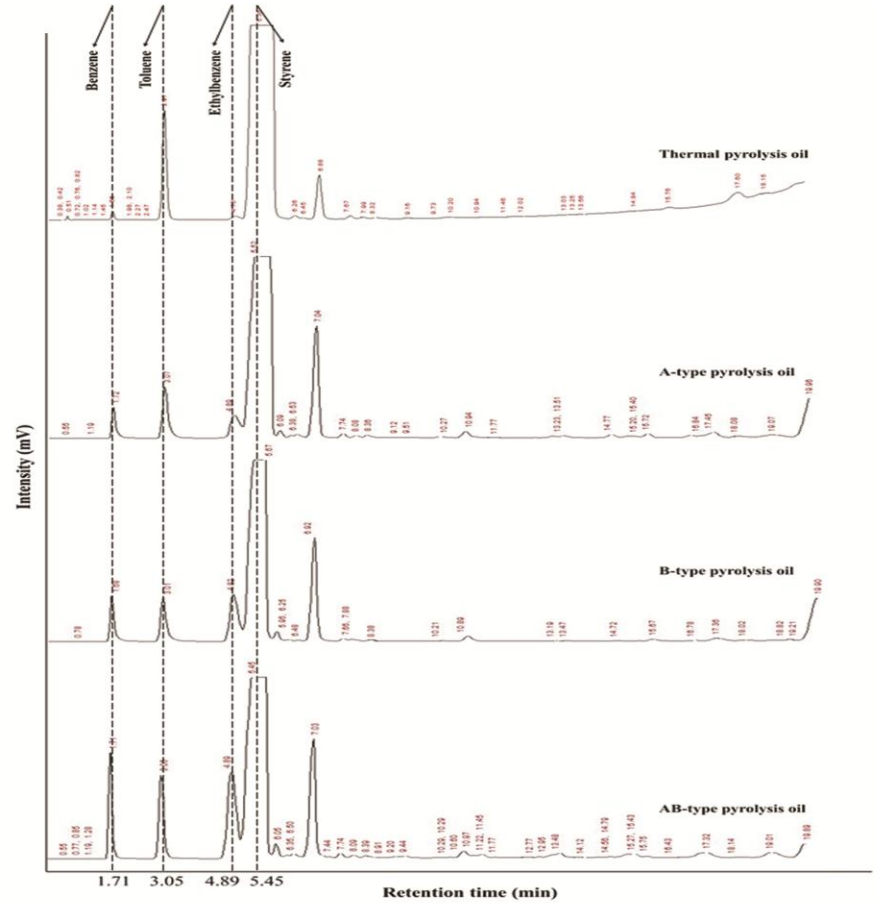

Fig. 9 — Gas chromatographs of thermal and catalytic pyrolysis oil A-type, B-type and AB-type

Table 3 — Aromatics BTE content of thermal and catalytic pyrolysis in the range of temperature 400 °C -700 °C and at the heating rate of 15 °C/min

Temperature (°C)	Reactor arrangement	Liquid (wt.%)	Gas (wt.%)	Benzene (wt.%)	Toluene (wt.%)	Ethylbenzene (wt.%)	Styrene (wt.%)	Total BTE (wt.%)
400	Thermal	87.18	12.45	0.12	3.55	0.29	91.61	3.96
	A-type	78.41	19.63	0.48	2.29	1.34	80.19	4.11
	B-type	75.03	23.45	1.81	3.25	4.48	75.78	9.54
	AB-type	73.12	25.44	2.68	4.27	7.21	69.39	14.17
450	Thermal	88.33	11.33	0.25	4.58	0.32	91.07	5.15
	A-type	81.06	16.19	0.62	3.26	2.13	77.14	6.01
	B-type	77.20	21.33	2.42	3.94	5.68	73.50	12.04
	AB-type	76.65	21.75	3.71	4.75	8.57	64.44	17.02
500	Thermal	88.73	11.1	0.35	6.77	0.34	88.34	7.46
	A-type	82.64	13.5	1.31	4.53	2.97	73.51	8.81
	B-type	80.34	18.28	4.16	5.12	7.40	69.56	16.68
	AB-type	79.42	18.94	5.53	6.16	11.58	59.28	23.27
550	Thermal	91.69	8.17	0.41	6.90	0.36	87.63	7.68
	A-type	84.17	11.89	1.96	5.52	3.62	71.06	11.10
	B-type	83.21	15.5	5.57	6.53	9.28	65.67	21.38
	AB-type	81.15	17.14	8.05	7.55	12.96	55.55	28.56
600	Thermal	93.06	6.85	0.55	8.82	0.49	87.15	9.86
	A-type	88.54	7.04	3.18	6.48	4.33	69.94	13.99
	B-type	80.85	17.9	4.28	5.68	6.59	60.99	16.55
	AB-type	78.43	19.82	6.29	4.75	10.33	52.04	21.37
650	Thermal	94.37	5.55	0.62	10.21	0.55	84.74	11.38
	A-type	85.20	9.93	2.53	5.71	3.45	66.43	11.69
	B-type	78.23	20.57	3.08	4.38	5.70	56.67	13.16
	AB-type	76.44	21.76	4.27	3.58	7.81	48.88	15.66
700	Thermal	93.64	6.27	0.50	7.90	0.56	83.27	8.97
	A-type	81.06	13.99	1.39	5.06	3.06	63.88	9.52
	B-type	76.03	22.84	2.31	3.03	4.48	54.52	9.82
	AB-type	73.11	25.02	3.30	2.19	6.17	45.82	11.66

polystyrene[47]. Furthermore, the catalyst can significantly improve the conversion as well as the selectivity toward the desired products/target molecules[48]. Moreover, in-situ B-type (Fig. 8, scheme-C) and AB-type catalytic pyrolysis arrangements (Fig. 8, scheme-D) improve the diffusion efficiency, which favoured the attack of the aromatic double bond, as the low mass transfer resistance is offered in the vapour phase catalytic reaction in comparison to liquid phase catalytic reaction path of the vapours which produced from the primary reactor. In addition, vapour phase catalytic cracking favoured the secondary reactions within the secondary reactor like hydrogenation, cyclization[49] and aromatization[27] which, are responsible for the formation of gasoline range lower aromatic hydrocarbons mainly benzene, toluene and ethylbenzene. The aromatic ring or the aliphatic chain of polystyrene is more easily attacked by protons from Brønsted acid sites formed protonated styrene dimer, which further undergoes cyclization and cracking to generate benzene. In the presence of acid catalyst, ethylbenzene is formed by the hydrogenation of styrene[49]. Whereas, toluene is produced from ethylbenzene by the cleavage of the -C-C- bond of the ethyl substituent followed by hydrogenation[50]. The AB-type catalytic pyrolysis involves two-stage catalytic cracking i.e., in a liquid phase and the vapour phase both. Thus, AB-type catalytic pyrolysis produced highest BTE content of 28.56 wt.% at a pyrolysis temperature of 550 °C and heating rate of 15 °C/min. The B-type catalytic pyrolysis produced little lower BTE content of 21.38 wt.% at a pyrolysis temperature of 550 °C and same heating rate. However, A-type catalytic pyrolysis yielded lowest BTE content of 13.99 wt.% among all catalytic pyrolysis arrangements because of single stage liquid phase contact between hydrocarbon molecules and catalyst. It is seen from the Fig. 9, AB-type catalytic pyrolysis oil gives the highest peak intensity of ethylbenzene indicating the promotion of

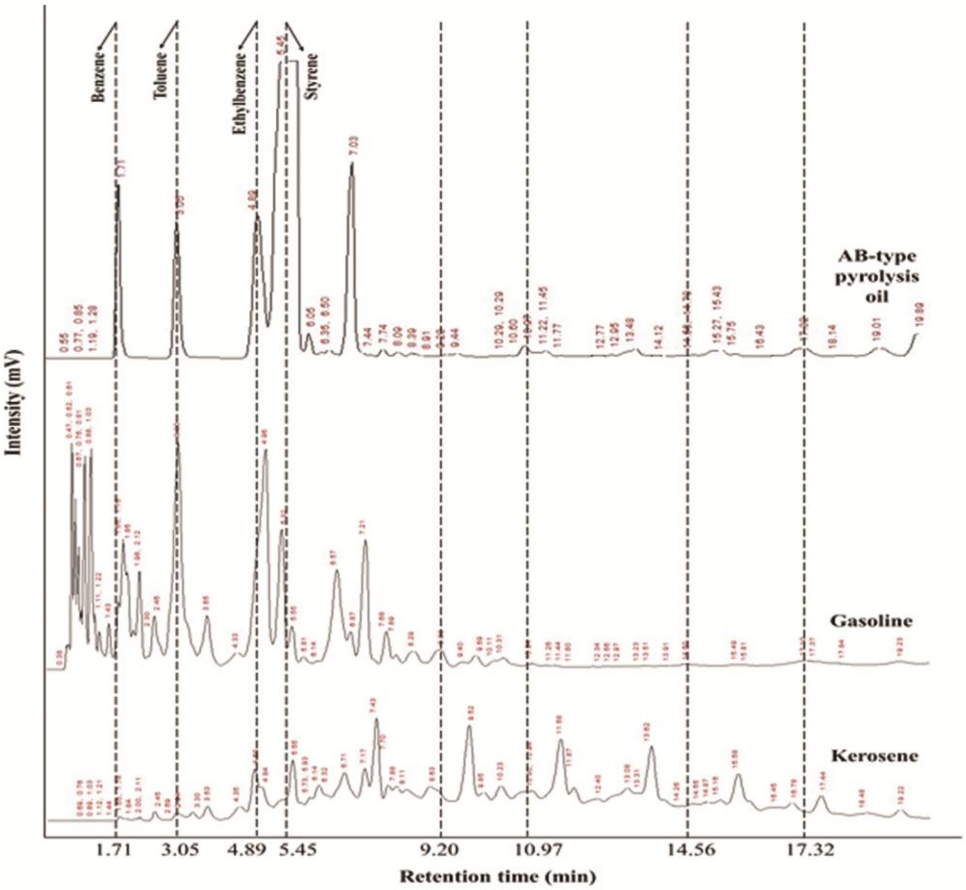

Fig. 10 — Gas chromatographs of AB-type pyrolysis oil, commercial fuel gasoline and kerosene

hydrogen transfer which causes the styrene hydrogenation to ethylbenzene[49]. It is reported by Onwudili *et al.*[50] that there was no direct production of toluene and ethylbenzene. However, these are produced from the reaction of styrene itself. Lopez *et al.*[51] also suggested that styrene decomposes into other aromatic compounds due to the secondary reactions in the presence of acid catalyst. Fig. 10 shows the comparison of liquid yield of AB-type catalytic pyrolysis with standard commercial gasoline and kerosene.

The peaks of benzene, toluene, and ethylbenzene (BTE) appears within the initial zone of residence time of 6 min. The AB-type catalytic pyrolysis oil shows similarities with gasoline. This indicates that the AB-type catalytic pyrolysis oil contains gasoline range lighter hydrocarbons. Thus, quality-wise pyrolysis oil follows an order of multiphase/AB-type > vapour phase/B-type > liquid phase/A-type > thermal pyrolysis oil.

ASTM distillation of pyrolysis oil

The distillation curve is a useful tool for quality assurance of automobile fuel[52]. The ASTM distillation curve is a graphical representation of the boiling temperature of components plotted against the volume fraction distilled[53] which is used to determine the volatility characteristics of liquid fuel[54]. The ASTM distillation curve of pyrolysis oil obtained from the thermal and catalytic pyrolysis at their respective optimum process conditions i.e., heating rate of 15 ^{o}C/min for all types of pyrolysis and temperature of 650^{o}C for thermal pyrolysis, 600^{o}C for A-type/ liquid phase, and 550^{o}C for B-type/vapour phase and AB-type/multiphase along with standard commercial fuels like gasoline and kerosene[55] are presented in Fig. 11.

The distillation curve of catalytic pyrolysis oil i.e., A-type, B-type and AB-type lies between gasoline and kerosene from initial boiling point (IBP) to final boiling point (FBP). However, the distillation curve of

AB-type catalytic pyrolysis oil was close to the commercial fuel gasoline. It means, the AB-type catalytic pyrolysis oil contains gasoline range hydrocarbons which, is also confirmed by GC-FID analysis. The initial and final boiling point of multiphase/AB-type catalytic pyrolysis oil was 48°C and 180°C, respectively. While 50% distilled volume was obtained at 118°C. The initial boiling point of multiphase/AB-type pyrolysis oil was low, revealing that oil contains low molecular weight hydrocarbons. In addition, initial boiling point and low-temperature region of the distillation curve are important while evaluating the ease of engine starting and the potential for vapour lock[56].

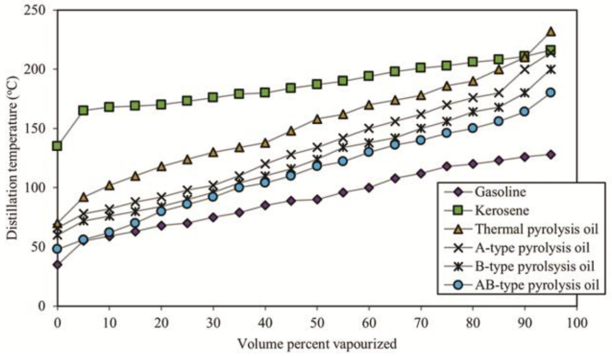

Fig. 11 — ASTM distillation curve of thermal and catalytic pyrolysis oil obtained at optimum conditions with commercial gasoline and kerosene

FTIR spectra of pyrolysis oil

The FTIR spectra of thermal pyrolysis and catalytic pyrolysis oil at their respective optimum process conditions are presented in Fig. 12. The important FTIR peaks with their respective wavenumbers are given in Table 4. The FTIR peaks above 3000 cm^{-1} was related to the aromatic C‒H stretching [57]. The methylene group C-H asymmetric and symmetric stretching vibrations were confirmed by peaks

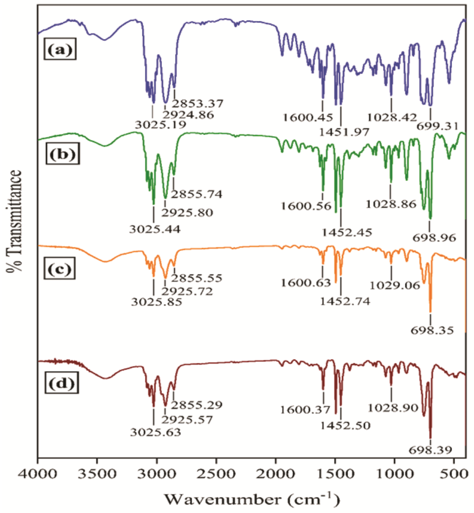

Fig. 12 — FTIR spectrum of thermal and catalytic pyrolysis oil obtained at optimum conditions (a) thermal pyrolysis oil, (b) A-type/liquid phase, (c) B-type/vapour phase, (d) AB-type/multiphase

Table 4 — Functional groups present in the thermal and catalytic pyrolysis oil obtained at optimum conditions

Functional group	Wavenumber (cm^{-1})			
	Thermal pyrolysis	A-type/liquid phase	B-type/vapour phase	AB-type/multiphase
Aromatic C‒H stretching	3081.44	3081.86	3082.35	3081.93
	3058.86	3059.38	3059.95	3059.73
	3025.19	3025.44	3025.85	3025.63
	3000.87			
Methylene C‒H asym stretching	2924.86	2925.80	2925.72	2925.57
Methylene C‒H sym stretching	2853.37	2855.74	2855.55	2855.29
C = C‒C aromatic ring stretching	1600.45	1600.56	1600.63	1600.37
	1582.57	1582.88	1494.62	1494.22
	1493.31	1493.89		
Methyl C‒H asym bend	1451.97	1452.45	1452.74	1452.50
Methyl C‒H sym bend	1367.31	1379.44	1378.19	1377.81
Aromatic C‒H in plane bend	1179.73	1180.33	1155.63	1179.55
	1155.09	1155.46	1074.80	1155.53
	1072.04	1074.46		1073.88
Cyclohexane ring vibrations	1028.42	1028.86	1029.06	1028.90
	965.07	965.20	965.14	965.12
Aromatic C‒H out of plane bend	842.13	842.30	753.06	753.32
	777.54	777.51	698.35	698.39
	752.77	754.22		
	699.31	698.96		

Table 5 — Physicochemical properties of thermal and catalytic pyrolysis oil obtained at optimum conditions

Physicochemical properties	Results obtained					
	Thermal pyrolysis	Catalytic pyrolysis			Commercial fuels	
		A-type	B-type	AB-type	Gasoline	Kerosene
Calorific value (cal/kg)	9816	9985	11240	12750	11315	11052
Carbon residue (wt.%)	1	0.89	0.65	0.45	0.14	0.18
Flash point (°C)	58	48	44	40	22	42
Fire point (°C)	62	54	50	44	25	45

observed between 2935-2915 cm^{-1} and 2865-2845 cm^{-1}, respectively. Similarly, methyl group C-H asymmetric and symmetric bending were confirmed by the FTIR peaks obtained between 1470-1430 cm^{-1} and 1380-1370 cm^{-1}, respectively. The FTIR peaks observed between 1615-1580 cm^{-1} and 1510-1450 cm^{-1} confirmed the C=C-C aromatic ring stretching.

The aromatic C-H in plane bending vibrations were observed in the range of wavelength 1225 cm^{-1} to 950 cm^{-1}. Whereas, aromatic C-H out of plane bending vibrations were observed between wavelength of 900 cm^{-1}-670 cm^{-1}. Furthermore, the FTIR peaks obtained between wavelength of 1055-1000 cm^{-1} and 1005-925 cm^{-1} confirmed the cyclohexane ring vibrations[58].

Physicochemical properties of pyrolysis oil

The important physicochemical properties viz gross calorific value (GCV), flash and fire point, carbon residue of pyrolysis oil obtained from the thermal and catalytic pyrolysis at their respective optimum process conditions is reported in Table 5. The GCV is an important property of fuel which is defined as the energy output due to combustion of a unit mass of fuel in the engine chamber[59-60].

It is seen from the Table 5 that the GCV of oil obtained by catalytic pyrolysis is always higher in comparison to the thermal pyrolysis. Moreover, the GCV of multiphase/AB-type pyrolysis oil is highest i.e., 12750 Cal/g among all pyrolysis oil and even higher than the calorific value of gasoline and kerosene[61]. It is may be due to the high concentration of low molecular weight hydrocarbons in the oil[62]. The GCV of thermal pyrolysis oil was found to be lowest due to the presence of some heavier components in pyrolysis oil. The carbon residue is another property of oil which decides the carbon deposit tendency[63] inside the IC engine due to the cracking of higher molecular weight hydrocarbons. Fuel with high carbon residue > 1 wt.% results in deposition of carbon residue inside engine which causes overheating and knocking[64]. The carbon residue of thermal and catalytic pyrolysis oil with some standard commercial fuels i.e., gasoline and kerosene[65] is also reported in Table 5. The carbon residue of multiphase/AB-type pyrolysis oil is quite low i.e., 0.45 wt.%. Thus, it can be recommended for the IC engines. The flash point is an important parameter for the storage, handling, and transportation of any liquid fuel[66]. Lower flash point leads to the easier ignition of that fuel. However, fire and explosion accidents also have a higher risk of occurrence for the oil having too low flash point[67]. The comparison of flash and fire point of thermal and catalytic pyrolysis oil with standard fuels i.e., gasoline[68] and kerosene[69] is presented in Table 5. It is seen from Table 5 that the multiphase/AB-type catalytic pyrolysis oil has the lowest flash and fire point i.e., 40°C and 44°C, respectively. Thus, it is highly flammable in nature and easily ignites inside the engines. However, it requires more attention during storage, handling and transportation.

Comparison of present work with other studies reported in open literature

The present work is compared with some previous studies based on the pyrolysis of polystyrene. There are various reactors have been used for the pyrolysis of polystyrene. Table 6 shows the comparison of present work with other studies based on polystyrene pyrolysis. Adnan *et al.*[13] used batch reactor for the catalytic pyrolysis of PS using zinc catalyst with feed to catalyst of 1:0.2. The liquid yield of 96.73 wt.% was obtained at a temperature of 450 °C with toluene content of 2.47 wt.%, ethylbenzene of 1.16 wt.%, and styrene content of 47.96 wt.%. However, in the present work the reported toluene (7.55 wt.%) and ethylbenzene (12.96 wt.%) content was significantly high. Rezvanipour *et al.*[70] have studied the catalytic pyrolysis of polystyrene in semi-batch reactor at a temperature of 350°C, and reported the styrene content of 60.32 wt.% which is higher than the present work (55.55 wt.%).

Recently, Zayoud *et al.*[71] used continuous pilot scale reactor for the pyrolysis of polystyrene. However, the reported toluene (3.2 wt.%) and

Table 6 — Comparison of present work with other studies reported in open literature

Reference	Reactor	Catalyst	Parameters	Liquid yield (wt.%)	Aromatic content (wt.%)
Adnan et al., 2014	Batch reactor	Zn	Temperature-450°C Feed/Catalyst-1:0.2 Reaction time- 120 min	96.73±0.12	Benzene-not available Toluene-2.47 Ethylbenzene-1.16 Styrene-47.96
Rezvanipour et al., 2014	Semi-batch reactor	Red mud	Temperature-350°C Feed/Catalyst-100:15	93	Toluene-1.67 Styrene-60.32 Benzene and its derivatives-33.63
Zayoud et al., 2022	Continuous pyrolysis pilot scale reactor	-	Temperature-550°C Pressure-0.02 bar	94.5	Benzene-not available Toluene- 3.2 Ethylbenzene-2.1 Styrene- 55.9
Park et al., 2020	Fluidized bed reactor	-	Temperature-780°C	86.01	Benzene-15.55 Toluene- 9.79 Ethylbenzene and xylene-0.96 Styrene-26.09
Artetxe et al., 2015	Conical spouted bed reactor	-	Temperature-500°C	Not available	Benzene-0.44 Toluene- 3.54 Ethylbenzene-1.28 Styrene-70.57
Present study	Semi-batch multiphase reactor	Nickel on silica-alumina	Temperature-550°C	81.15	Benzene-8.05 Toluene-7.55 Ethylbenzene-12.96 Styrene-55.55

ethylbenzene (2.1 wt.%) contents were found in the pyrolysis oil lower than the present work. Park *et al.*[28] used fluidized bed reactor to reduce the styrene content and valuable aromatics benzene, toluene, and ethylbenzene in the pyrolysis oil obtained from the pyrolysis of PS. They reported the very low ethylbenzene and xylene content (0.96 wt.%) as compared to the present study (12.96 wt.%). However, the styrene content was significantly low (26.09 wt.%), but it required very temperature of 780°C. Artetxe *et al.*[46] conducted the conical spouted bed reactor for the degradation of polystyrene at temperature of 550°C. The obtained pyrolysis oil mainly composed of benzene (0.44 wt.%), toluene (3.54 wt.%), ethylbenzene (1.28 wt.%) and styrene (70.57 wt.%). The benzene, toluene and ethylbenzene content were very less as compared to the present study. Additionally, the styrene content was very high as compared to the present work (55.55 wt.%). In the present study, multiphase reactor arrangement was used to produce the benzene, toluene and ethylbenzene as the major products and to reduce the styrene content. It should be noted that the production of benzene, toluene and ethylbenzene using multiphase reactor arrangement is a cost effective approach because additional heating arrangement is not needed for vapour phase cracking.

Conclusion

The fuel oil of gasoline to the kerosene range was successfully obtained from WEPS via multiphase/AB-type catalytic pyrolysis in a laboratory fabricated innovative reactor which has never been reported by any other scientists in their published articles except in our previous publication as mentioned earlier. In all three catalytic pyrolysis of WEPS i.e., liquid phase/A-type, vapour phase/B-type and multiphase/AB-type, the catalyst used was nickel on silica-alumina. The vapour phase secondary reactions such as in-situ hydrogenation, aromatization, and cyclization reduced the styrene content and enhanced lower hydrocarbons and valuable lower aromatics i.e., benzene, toluene, and ethylbenzene. The thermal pyrolysis produced very high styrene monomer of 84.74 wt.% and low BTE content of 11.38 wt.% at the optimum temperature of 650 °C and heating rate of 15 °C/min. Whereas, AB-type/multiphase catalytic pyrolysis of WEPS produced the highest amount of target molecules BTE of 28.56 wt.% and the lowest amount of styrene content of 55.55 wt.% at the optimum temperature of 550°C, heating rate of 15 °C/min and feed to catalyst ratio of 20:1. Thus, the multiphase pyrolysis oil can be used as rich source of benzene, toluene and ethylbenzene. However, pyrolysis oil obtained from the A-type/liquid phase pyrolysis contains low BTE content of 13.99 wt.%

among all catalytic pyrolysis oil because of single stage catalytic cracking. In addition, the calorific value of pyrolysis oil obtained from multiphase/AB-type was found to be highest among all types of pyrolysis oil even higher than the gasoline because of high content of lower molecular weight hydrocarbons. On the other hand, low flash point (40^{o}C) of multiphase pyrolysis oil indicates the easy ignition in IC engines. Similarly, less carbon residue of 0.45 wt.% indicates the less formation of carbon deposit inside the engine surface. Thus, the AB-type pyrolysis oil could be recommended as an alternative of commercial fuels like gasoline and kerosene. It should be noted that benzene and styrene should be separated from the product oil to have the desired specification of fuel as per the need of IC engines. The management of WEPS could be done efficiently via in-situ hydrogenation aromatization, and cyclization using nickel on silica-alumina catalyst in a laboratory fabricated reactor, which could be scaled up for the commercial production of fuel oil from WEPS and thus, protecting environment.

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