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Performance and reusability assessment of ZSM-5 for the production of lighter aromatics via pyrolysis of waste polystyrene

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The plastic waste poly styrene (PS) has been selected for the conversion to value added useful products using pyrolysis. The thermal and catalytic pyrolysis of polystyrene (PS) are investigated at reaction temperature ranging from 500°C to 800°C for 30 min, as an effective way to recycle polystyrene and produce valuable aromatic hydrocarbons benzene, toluene, ethyl benzene and xylene (BTEX). The catalytic pyrolysis is performed using commercial catalyst ZSM-5 which is reused repeatedly twice and further regenerated to evaluate the stability of ZSM-5 for PS pyrolysis with reference to BTEX formation. The maximum liquid yield of 96 wt. % and 86.2 wt. % are obtained at a temperature of 700°C for thermal pyrolysis and catalytic pyrolysis (fresh catalyst/1st run), respectively. The product analyses show that liquid yield contains substantial amount of BTEX with the increase in temperature for fresh ZSM-5. The BTEX yield is significantly increased for catalytic pyrolysis (fresh catalyst/1st run) i.e., about 75 wt. % for fresh ZSM-5 in comparison to thermal pyrolysis at a temperature of 700°C. There is very minute change in BTEX yield for the 2nd and 3rd run of catalytic pyrolysis using spent catalyst ZSM-5. The maximum aromatic (BTEX) of 23.71 wt. % for fresh ZSM-5 is obtained at the temperature of 700°C. However, spent ZSM-5(3rd run) produced 20.45 wt. % BTEX at the same temperature. The regenerated ZSM-5 produced only 2 wt. % less BTEX yield in comparison to fresh ZSM-5 at the optimum temperature of 700°C. The gas chromatography and other fuel test have been performed for liquid yield characterisation. The characteristics of product prove that the liquid hydrocarbon has potential to use it as fuel.

Keywords: Waste polystyrene, ZSM-5, regeneration, FTIR, GC-FID, BTEX.

The plastic waste recycling has received a great attention due to its huge consumption and unplanned disposal. Our daily life is more or less dependent on the use of plastic in the form of household packaging materials, carry bag, food stuff packaging and many other such plastic items. All these domestic plastic wastes along with organic mass of biodegradable nature are dumped in the municipality dumping ground in unscientific way. Due to non-biodegradable nature of the plastic waste, it contributes more problems to municipal waste management which have generated substantial environmental complications. As the rate of consumption of plastic materials in the world is greatly expanded, more waste plastics are generated. The disposal of waste plastic is mostly achieved by conventional ways such as landfill or incineration. However, these methods have a problem on human health and living being due to the air pollution, water pollution and soil contamination. The economical resistance caused by an increase space use and a disposal cost. Thus, the recycling of plastic wastes has become a predominant subject all over world. The development of technologies acceptable from the environmental friendly and economical is one of the most important key factors. Generally, the recycling methods are classified as (i) material recycling to manufacture plastic products and (ii) chemical recycling to convert some other valuable chemicals. The former is one of the most conventional methods but is limited by difficulties in maintaining the high quality and adequate price of final products, in particular, for the mixture of plastic waste. Thus, application of other procedures such as chemical recycling and energy recovery is required Fig. 1. Moreover, in the developing countries landfill is the main disposal method for waste plastic materials which can lead to ground water contamination. While incineration process generates large amount of toxic gases[1-6]. Recently, pyrolysis as a new method for waste plastic disposal has attracted great attentions[7]. Pyrolysis not only provides an environmentally friendly solution to dispose waste plastic materials,

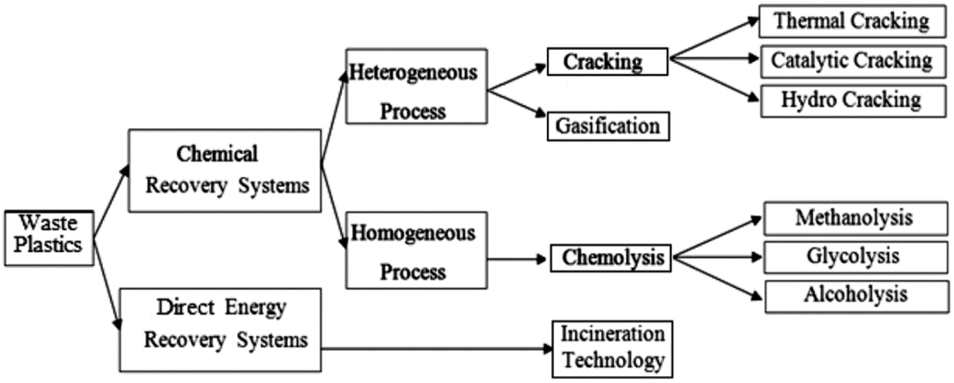

Fig. 1 — Recycle routes of waste plastics.

but also converts those materials into transportable fuels or valuable chemicals[2]. Polystyrene is one of the most important plastics in China with an annual production of 4.7 million tons in 2013[8]. It has been widely used for various applications such as injection mouldings, electrical applications, packaging materials, and consumer goods etc.[9]

The pyrolysis or cracking of plastic waste involves the degradation of the polymeric materials by heating in the absence of oxygen. The pyrolysis may be of three different types, like thermal cracking, catalytic cracking and hydro cracking Fig. 1. The recycling of waste plastics by thermal and catalytic degradation processes can be an important source producing alternative fuel oil from the view point of an economical aspect and contributing to the environmental protection from the view point of an environmental aspect[10]. The process pyrolysis has certain advantage over the incineration and landfill methods, like (i) without segregation and treatment all thermoplastic mixtures can be converted to valuable oils and (ii) lower the pollutant emission and soil contamination. In the pyrolysis, thermal degradation is a simple method for upgrading plastic waste into liquid product at medium temperature (400-600°C) in the absence of oxygen. However, this process requires relatively high energy consumption, due to a low thermal conductivity of waste plastic and to an endothermic reaction by degradation of waste plastic. Moreover, the oil obtained by pyrolysis of plastic wastes has hydrocarbon with wide molecular weight distribution and poor economic value, which does not have a sufficient quality to use as alternative fuel oils[11]. The pyrolysis of polystyrene with high proportion in mixed plastic produces much more unstable heavy compounds with high viscosity as low-grade product[12-13]. The characteristics of these products depend on the nature of plastic waste and process conditions.

Thermal degradation of polystyrene and high-impact polystyrene involving brominated flame retardants or their combinations with antimony oxide have also been the subject of several studies[14]. Oligomeric brominated flame retardants were preferred because of decreased toxicity, and improved mechanical properties, melt flow characteristics and thermal stability among the conventional non-oligomeric types. The use of Sb_2O_3 in combination with halogenated flame retardants was found to increase the release rates of halogens by the generation of antimony halides and oxyhalides during degradation[15]. Isitman and coworkers investigated flammability of polystyrene nanocomposites containing brominated epoxy and/or antimony oxide using limiting oxygen index, LOI and vertical burning ratings (UL-94)[16]. The enhancement in the fire-retardant effectiveness was associated not only with the gas-phase hot radical entrapment by halogenated flame-retardant system coupled but also with the condensed-phase physical action of nanodispersed organo-clay.

Onwudili *et al.*[17] have examined PS pyrolysis in a batch pressurized autoclave reactor for one hour duration at 300-500°C. The heating rate was 10°C/min and pressure 0.31 MPa up to 1.6 MPa. From the experiment, they found that the PS pyrolysis produced a very high liquid oil yield around 97.0 wt. % at a temperature of 425°C. The maximum amount of gas formed was only 2.5 wt. %. The high yield of liquid oil product was also supported by Liu *et al.*[18]. The pyrolysis of PS was piloted using fluidized bed reactor at temperature of 450-700°C. The highest liquid oil obtained was 98.7 wt. % at 600°C. Nevertheless, the amount of liquid oil produced was also considered high at lower temperature of 450°C which was around 97.6 wt. % and it differed by only 1.1 wt. %. In the case when energy saving was the priority, lower temperature was preferable as it could reduce the energy cost incurred. Demirbas[19] performed the PS pyrolysis at 581 °C in a batch reactor. The liquid oil of 89.5 wt. %, gas yield of 9.9 wt. % was obtained. He performed same experiment at 740 °C and the liquid oil of 48.8 wt. %, gas yield of 49.6 wt. % was obtained. Kyong *et al.*[20] have investigated the pyrolysis of PS in a semi-batch reactor at 400 °C at 1 atm. The heating rate used was 7 °C/min. From the experiment, they found that the PS pyrolysis produced a very high liquid oil yield around 90.0 wt.%. Shah *et al.*[21] investigated PS pyrolysis in batch reactor at 500 °C for 150 min. They obtained high amount of liquid yield 96.73 wt. %.

Filip *et at.*[22] performed thermal and catalytic pyrolysis of PS waste over two different samples of natural zeolitic volcanic tuff catalysts comparative with Florisil catalyst and obtained maximum liquid yield of 83.45 wt. % and 90.11 wt. % at 460°C degradation temperature respectively. Wu *et al.*[23] compared the effect of NZ, Fe-NZ, YZ and Fe-NZ catalysts on the product yield, the gas and oil product composition in the two-stage combined pyrolysis and catalytic reforming reactor at both pyrolysis and reforming temperatures of 500°C and found that Fe-NZ catalyst gives excellent performance. Shah *et al.*[24] investigated the catalytic activity and physical characteristics of Cu impregnated catalysts over Al_2O_3, Mmn and AC for the degradation of PS waste and fount that for the selectivity of toluene and ethylbenzene, 15% Cu-Mmn and 20% Cu-AC were good selective catalysts.

PS was less cracked to the gaseous product since PS contained benzene ring that created more stable structure[25]. The calorific value of PS was commonly lower than the polyolefin plastic due to the existence of the aromatic ring in the chemical structure which had lesser combustion energy than the aliphatic hydrocarbon[17]. For PS pyrolysis oil, Onwudili *et al.*[17] reported that the benzene, toluene and ethyl benzene were three main components in the PS oil product that increased with the temperature. On the other hand, styrene monomer kept decreasing with the temperature and this suggest that the styrene radical formed during the degradation process of PS was very reactive. Liu *et al.*[18] also reported the same observation. The styrene and monoaromatics were among the major components in the liquid oil product that they covered around 80 wt.% in the liquid fraction. These components were categorized in the low boiling point fraction of less or equal to 200°C. In most plastics, the usage of catalyst in the process might improve the liquid oil yield, but PS was exceptional. This is because PS degraded very easily without the needs of any catalysts to speed up the reaction and yet 96 wt. % of oil was produced[17]. Thus, PS was the best plastic for pyrolysis since it produced the highest amount of liquid oil production among all the plastics.

It is clear from the thorough literature review that the stability study of the catalyst used in waste plastics pyrolysis has never been perform which is one of the important aspects of commercialization of process technology and products as well. Thus, in this research a special emphasis was given to evaluate and compare the performances of commercial catalyst ZSM-5 in reference to BTEX production from waste polystyrene. Moreover, till date no detailed study on the pyrolysis of polystyrene and thorough characterization of its product has been reported in the open literature. In this work, our main purpose is to investigate the thermal and catalytic degradation behaviour of polystyrene plastic waste. All the experiments were performed at different temperatures in a mild steel semi batch reactor. Products were characterised using different characterisation techniques such as GC-FID, FTIR, ASTM Distillation and Flash and fire point.

Experimental Section

Materials and methods

Waste polystyrene (PS) samples (waste boxes used for chemical transport and other accessories) were collected from the municipal dumping zone of Varanasi city, India. PS samples were cleaned by water washing to remove dirt. They were broken into small pieces and heated at 150°C to reduce the volume of the PS sample i.e., about 25% of its original volume. Compact reduced PS samples were transformed to flakes of 5 mm X 5 mm size. This was done to increase the heat transfer surface area of the material during melting process. The catalyst used was commercial ZSM-5 ($SiO_2/Al_2O_3 = 30:1$). The ZSM-5 was procured from Alfa Aesar, USA.

Experimental set up and method

Figure 2 shows the schematic of experimental set up of pyrolysis process consist of a semi batch reactor. The polystyrene sample of 50 g was filled in

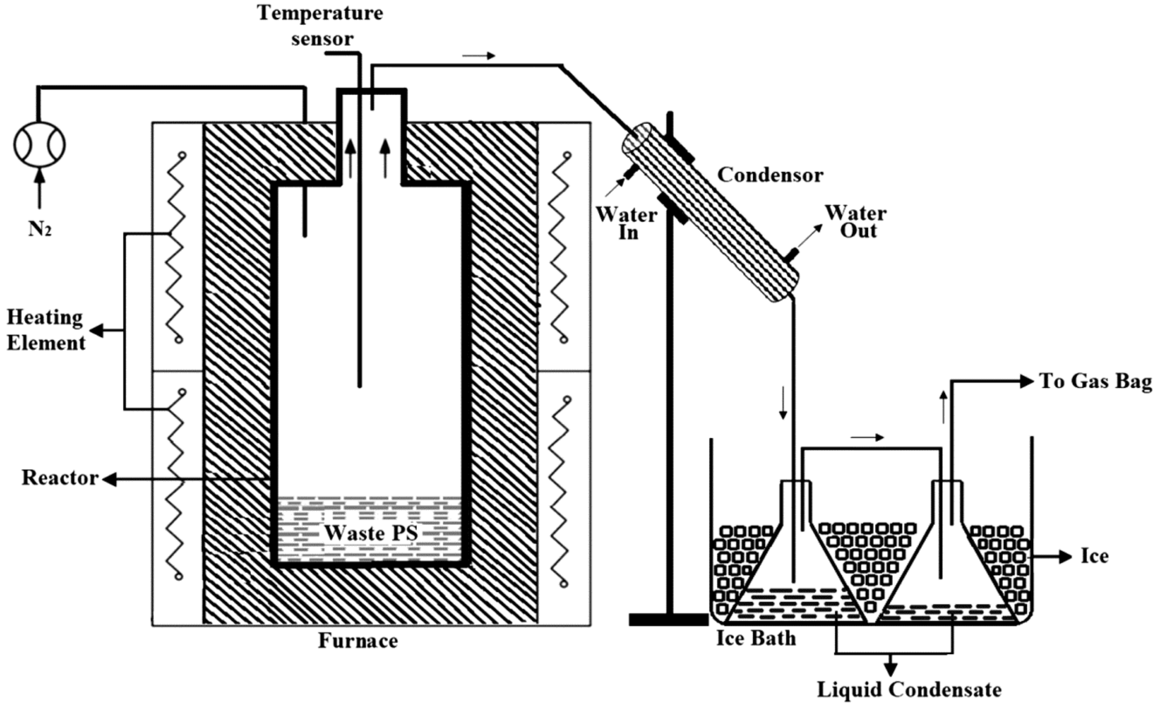

Fig. 2 — Schematic of experimental set up.

reactor made of mild steel with 123 mm outer diameter, 112 mm inner diameter and 135 mm height. The nitrogen gas was introduced into reactor at the rate of 10 mL/min to ensure there is no oxygen in reactor. The pyrolysis experiments of PE were performed at different temperatures of 500°C, 600°C, 700°C and 800°C. The time for each set of experiments were maintained for 30 min. The vapour produces inside the reactor was collected using a pipeline which was connected at the top of the reactor. The pipeline was attached to a copper tube condenser followed by an ice bath to decrease the vapour temperature gradually and reduce the vapour loss at the collecting end. The pipeline was covered with wet jute to enhance rate of vapour cooling. Two conical flasks in series were kept in the ice bath and pyrolysis oil was collected as condensate. The produced gas was trapped using gas holder.

Analysis of liquid hydrocarbon

Flash point is defined as the minimum temperature at which the vapours from oil sample will give a momentary flash on application of standard flame under specific test conditions. Fire point temperature was noted when the oil vapours can burn continuously for at least 5 seconds and it occurs after the flash point, by 3-4 ^{o}C. The flash and fire point were conducted using Cleveland open cup method (ASTM D 92).

Carbon residue of pyrolysis oil was obtained using Ramsbottom Carbon Residue Apparatus (IP 14/65). Proximate analysis of solid residue (coke) was done following ASTM test methods (IS 1350-1959). This is an assay of the moisture, volatile matter, ash content and fixed carbon of a solid residue.

The bomb calorimeter (IP 12/63T) was used to determine the calorific value/ higher heating value (HHV) of solid residue or coke and pyrolysis oil.

The compositional analysis of pyrolysis oil was evaluated by gas chromatograph (NUCON 5765) using flame ionization detector (FID) with a SE-30 10 % chromosorb W packed stainless-steel column (2 m x 2 mm). Nitrogen was used as a carrier gas at the rate of 40 mL min^{-1}. The oven column temperature ranged from 70 to 230°C; programmed at 7°C min^{-1} with initial and final hold time of 10 min. Injector and detector temperatures were 220°C and 230°C, respectively. The injection method was used for analysis of 1 µL sample. The percentages of the individual constituents were calculated by electronic integration of the FID peak areas without response factor correction[15]. The FTIR spectra of liquid fuel obtained in pyrolysis were carried out with Thermo-Nicolet 5700 model. The ominc software is used to correct the medium’s background material used during analysis. Fourier transformed infrared spectrophotometer with a resolution of 4 cm^{-1}, in the range of 500–4000 cm^{-1} using Nujol mull as reference.

ASTM distillation of pyrolysis oil was carried out using ASTM D86 method to get the % distillate vs boiling point range for pyrolysis oil obtained at various temperatures from PS pyrolysis.

Regeneration of catalyst

Regeneration of used catalyst consists of two steps (i) combustion and (ii) calcination. In combustion process, used catalyst was heated in a crucible without lid under oxygen flow at the temperature of 550°C in a muffle furnace for 30 min to remove coke by combustion process. In calcination process, the combusted catalyst sample was kept in a crucible with lid under nitrogen flow at the same temperature for 5 h in a muffle furnace. Figure 3 shows the photographic view of fresh, used and regenerated ZSM-5 catalyst, respectively. The black colour of used catalyst (fig. 3b) shows the coke formation on the surface of catalyst.

Catalyst characterisation

The surface areas and pore volumes of the fresh, used and regenerated samples were measured by Scanning Electron Microscopy (SEM) and Brunauer-Emmett-Teller (BET) analysis. The SEM-EDS were recorded on ZEISS EVO 18 SEM coating of quorum Q150R ES having model number 51-ADD0048. Specific surface area and pore volume of the catalysts were analyzed using smart sorb 92/93 surface area analyzer using nitrogen physisorption at liquid nitrogen temperature.

Results and Discussion

Catalyst characterization

SEM analysis

Figure 4a to Fig. 4c show the surface morphology of fresh, used and regenerated ZSM-5 catalyst. It is seen in the Fig. 4a that most of the particles were spherical in shape with high porosity. The SEM image of Fig. 4b shows that the particles of used ZSM-5 catalyst are covered with pyrolysis residue/coke which is formed during the pyrolysis and aromatization within the reactor. Fig. 4c shows the SEM image of regenerated ZSM-5 which is similar to fresh ZSM-5 (Fig. 4a).

BET surface area analysis

Table 1 shows the surface area and pore volume of fresh, used and regenerated ZSM-5 catalyst. It is seen in the Fig. 4a that the used ZSM-5 catalyst lost a significant portion of its surface area and pore volume as compared to the fresh catalyst. When the spent catalyst was regenerated, the total BET surface area increases and achieved surface properties similar to fresh catalyst. The surface area of fresh ZSM-5 (400 m^2/g) and regenerated ZSM-5 (390 m^2/g) are almost same. The pore volume for fresh and regenerated catalyst is also same. This result indicates

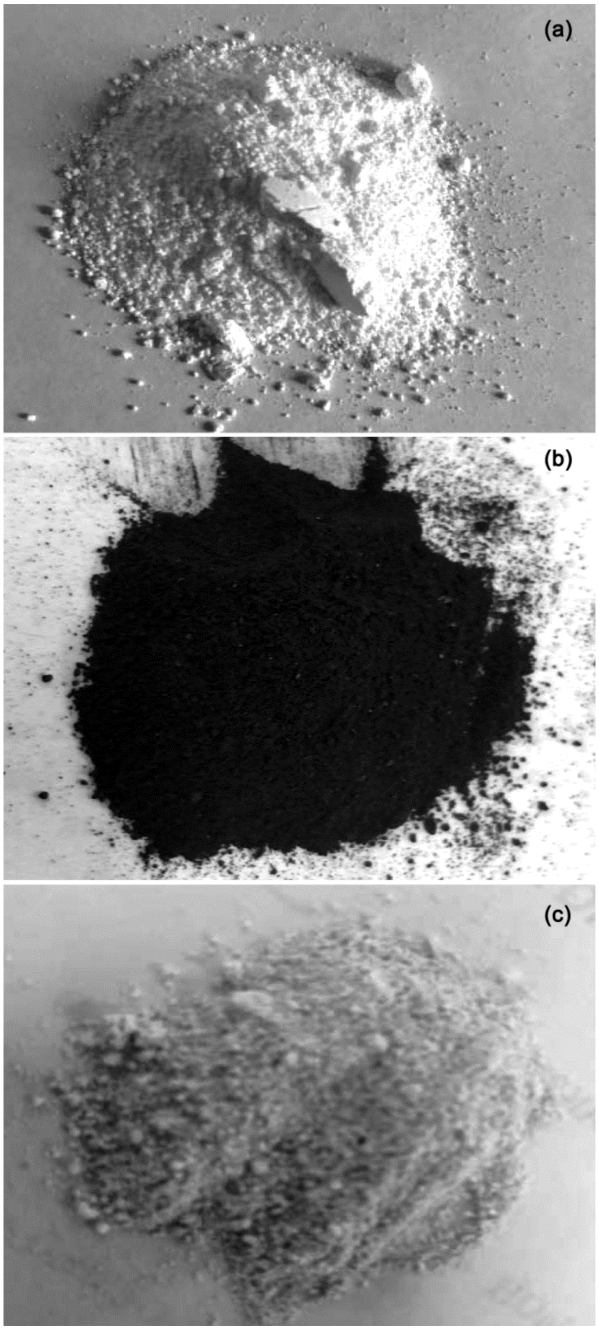

Fig. 3 — Photographic view of (a) Fresh; (b) Used and (c); Regenerated ZSM-5 catalyst.

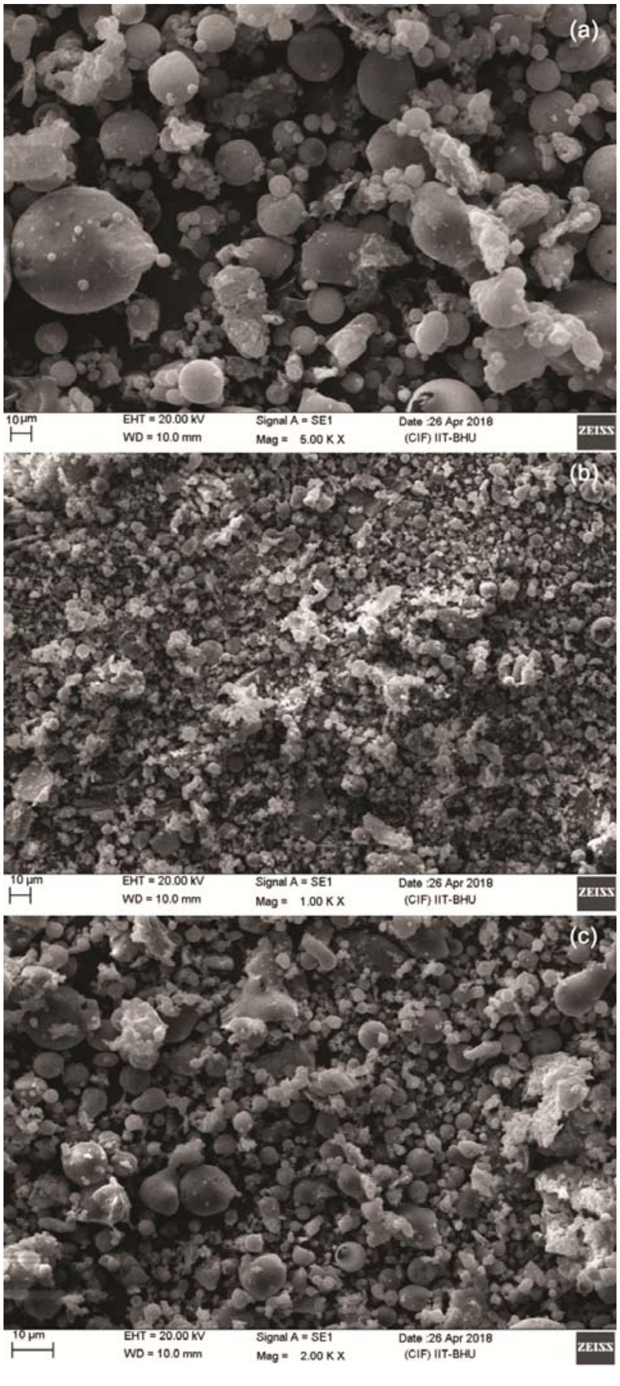

Fig. 4 — SEM images of (a) Fresh ZSM-5; (b) Used ZSM-5 (c) Regenerated ZSM-5 catalyst.

Table 1 — Surface area and pore volume of fresh, used and regenerated catalyst ZSM-5.

Name of catalysts		Surface area (m^2/g)	Pore volume (ml/g)
ZSM-5	Fresh	400	51.56
	Used	312	47.26
	Regenerated	390	50.26

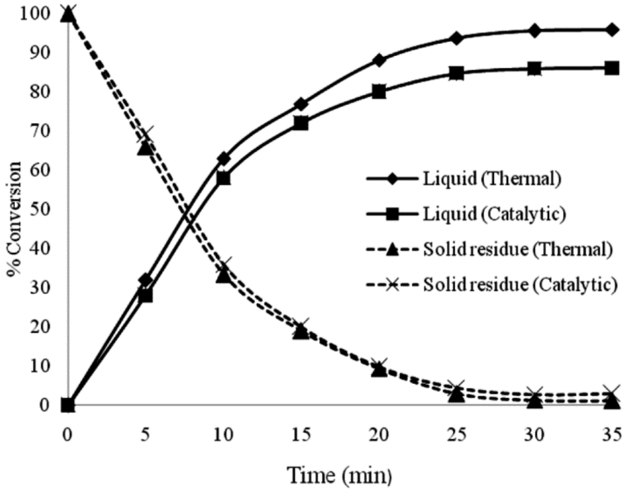

Fig. 5 — Time vs. percentage conversion of liquid and solid yield for thermal and catalytic pyrolysis of polystyrene at the temperature of 700 °C.

that ZSM-5 catalyst can be reused after regeneration process, which is economical.

Effect of reaction time on conversion rate

Figure 5 shows the effect of reaction time on the liquid and solid conversion for thermal and catalytic pyrolysis of polystyrene (PS) at the temperature of 700°C. It is clearly seen in the Fig. 5 that the conversion rate decreases with the increase in reaction time for both thermal and catalytic pyrolysis of polystyrene. This indicates that the reaction time plays vital role for the conversion of waste plastics and achieving maximum product yield.

The conversion rate becomes constant after 25 min for PS. Figure 5 shows that there is no conversion after 25 min of reaction time. Thus, to ensure complete conversion and achieve maximum product yield, the thermal and catalytic pyrolysis of polystyrene was performed for 30 min.

Effect of feed to catalyst ratio

The catalytic pyrolysis of waste polystyrene was performed at different feed to catalyst ratio of 10:1, 20:1 and 30:1. Figure 6 shows the comparison of liquid yield, gas yield and solid residue of catalytic pyrolysis of waste PS at a temperature of 700°C. It is seen form Fig. 6 that the feed to catalyst ratio of 20:1 (PS to ZSM-5) gives maximum liquid yield of 86.2 wt. % because of the large number of active catalytic sites that are responsible for enhancing the liquid yield. On the other hand, feed to catalyst ratio of 30:1 gives lowest liquid yield of 85.58 wt. % with

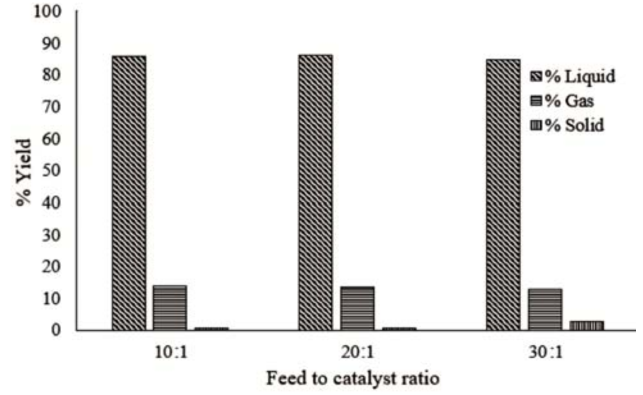

Fig. 6 — Comparison of liquid yield, gaseous yield and solid residue for different feed to catalyst ratio.

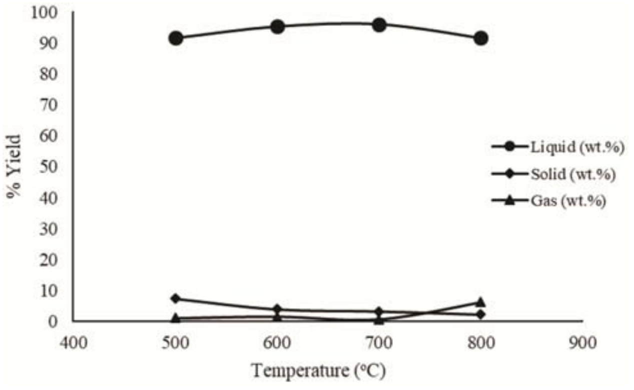

Fig. 7 — Comparison of liquid, gas and solid residue by thermal pyrolysis of PS at different temperatures.

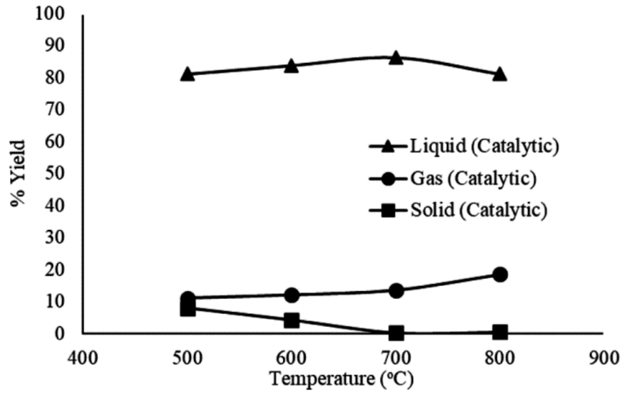

Fig. 8 — Comparison of liquid, gas and solid residue by catalytic pyrolysis of PS at different temperatures.

maximum solid residue of 2.6 wt.%. It may be due to less number of available active sites of catalyst, which is not sufficient to crack polystyrene into more liquid yield. However, 10:1 feed to catalyst ratio gives almost same yield of liquid, gaseous and solid residue as that of 20:1 feed to catalyst ratio. Due to more amount of catalyst active sites in 10:1 feed to catalyst ratio, the process would be less feasible as compared to 20:1 feed to catalyst ratio. Hence, all the catalytic pyrolysis of polystyrene were carried out using 20:1 feed to catalyst ratio.

Product yield of thermal pyrolysis

Figure 7 shows the effect of temperature on liquid, gaseous and solid residue yield for thermal pyrolysis of polystyrene. It is seen in Fig. 7 that the maximum liquid yield of 96 wt.% was obtained for the thermal pyrolysis of polystyrene at the temperature of 700°C. There was about 5.5 wt.% increase in the pyrolysis oil when temperature was increased from 500 to 700°C. Beyond the temperature 700°C, the liquid yield decreased to 91.5 wt.% and gets solidify at the temperature of 800°C. The solid residue coke keeps on decreasing from 7.32 to 2.27 wt.% up to the pyrolysis temperature 800°C for polystyrene. As temperature increases the gaseous product increases and solid char decreases. At high temperature the lower molecular weight hydrocarbon (mainly liquid range) converts into gaseous range hydrocarbons.

Product yield of catalytic pyrolysis

Figure 8 shows the effect of temperature on liquid, gaseous and solid residue yield for catalytic pyrolysis of polystyrene. The pyrolysis oil yield of 81, 83.7, 86.2 and 81 wt.% were obtained for catalytic pyrolysis at the temperature of 500, 600, 700°C and 800°C, respectively. As temperature increases the gaseous product increases and solid char decreases. The optimum condition for the pyrolysis temperature is 700°C, at which maximum liquid yield was obtained. Gaurh *et al.* 2018 a,b[26,27] stated that the use of catalyst resulting in slightly low quantity of liquid yield but improved the quality of liquid oil in terms of aromatics BTEX. At the temperature of 700^{o}C the maximum quantitative wise liquid yield was obtained in thermal pyrolysis and qualitative wise it was obtained in catalytic pyrolysis. At the temperature of 800°C the liquid yield gets solidifies or waxy in nature at room temperature. It may be due to high temperature does not allow high molecular weight hydrocarbons to take further participation in cracking process and it directly goes to condensate.

FTIR spectroscopy of pyrolysis oil

The Fourier transform infrared spectroscopy (FTIR) is an important analysis technique which detects various characteristic functional groups present in the pyrolysis oil. On interaction of an infrared light with oil, chemical bond will stretch, contract, and absorb infrared radiation in a specific wave length range regardless the structure of the rest of the molecules.

Fig. 9 shows the FTIR spectra of liquid fuel obtained at optimized condition by thermal and catalytic pyrolysis of waste PS. The presence of alkanes is detected at 3024 cm^{-1} with C–H stretching vibrations. C=C stretching vibrations at 1680-1600 cm^{-1} indicates the presence of alkenes/fingerprint region. The presence of alkanes is detected by C–H scissoring and bending vibrations at 1461 cm^{-1}. C–H bending vibrations at 966 cm^{-1} indicate the presence of alkenes and the C–H bending vibrations at frequency 722 cm^{-1} indicates the presence of phenyl ring substitution bands.

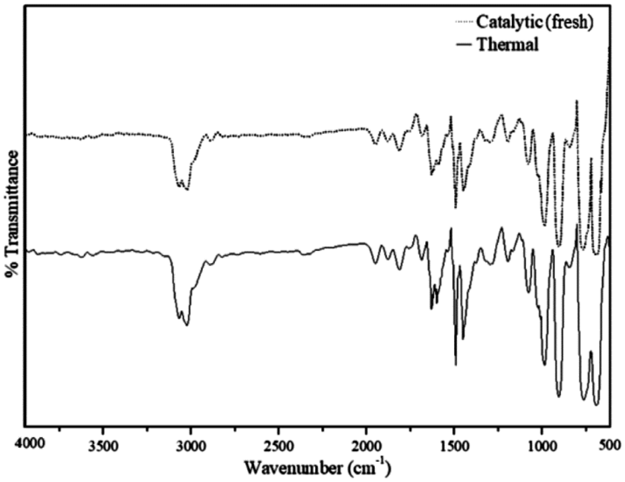

Fig. 9 — FTIR spectra of liquid oil obtained using thermal and catalytic pyrolysis at 700 °C.

ASTM Distillation of pyrolysis oil

The distillation or volatility characteristics of hydrocarbons have an important effect on their safety and performance, mainly in the case of fuels and solvents. The boiling point range gives information on the composition, properties, and behaviour of the fuel. Volatility is the major determinant of the tendency of a hydrocarbon mixture to produce potentially explosive vapors. The distillation characteristics are critically important for both automotive and aviation gasolines, affecting starting, warm-up, and tendency to vapor lock at high operating temperature or at high altitude, or both[28,29].

Figure 10 shows comparison between standard fuel and pyrolysis oil (Thermal and Catalytic pyrolysis) obtained at the temperatures of 700°C of polystyrene. The boiling point range of pyrolysis oil obtained at temperature of 700°C for thermal and catalytic pyrolysis lies in between heavy naphtha and paint

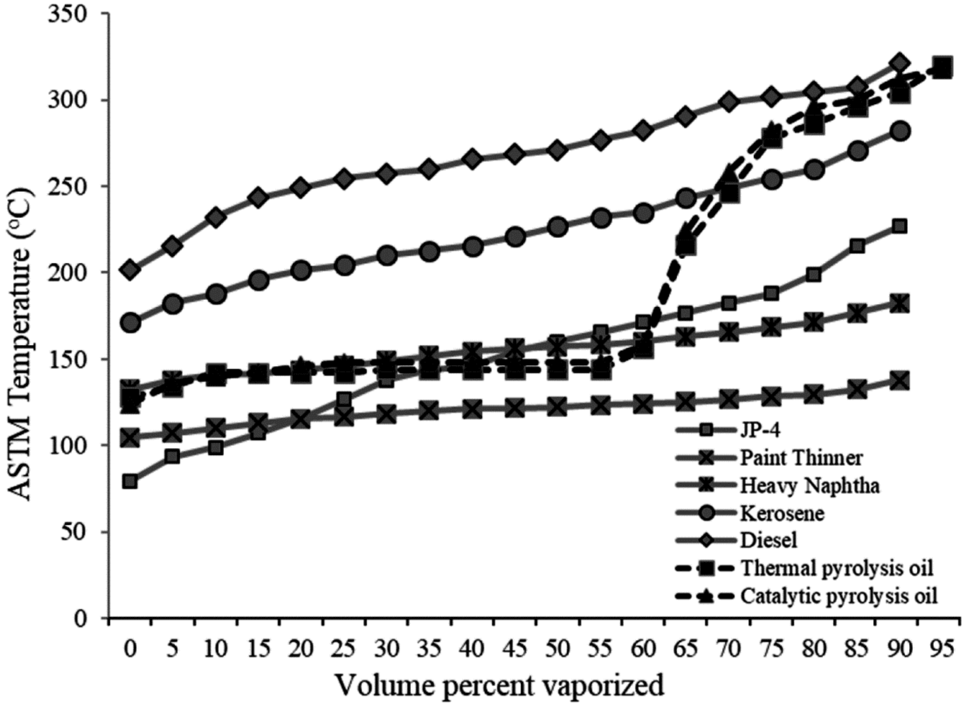

Fig. 10 — Volume percent vaporized vs. Distillation temperature characteristics of pyrolysis oil (Thermal and Catalytic pyrolysis) and standard fuel.

thinner for the recovery of distillate 0-60%. In addition, all the pyrolysis oil obtained lies between JP-4 and kerosene for 60-70% recovery. Whereas, interestingly pyrolysis oil tends to behaves as diesel oil (Fig. 10) above 70% of distillate recovery for thermal and catalytic pyrolysis.

GC-FID analysis of pyrolysis oil

Figure 11 shows the GC-FID of the pyrolysis oil derived by the pyrolysis of the polystyrene at 700^{o}C. It was compared with standard BTEX (benzene, toluene, ethylbenzene and xylene) peaks and retention time as major component in pyrolysis oil obtained from Pyrolysis of polystyrene which are aromatic compounds.

To measure mainly benzene, toluene, ethyl benzene and xylene (BTEX) a calibration curve was used. High purity HPLC grade benzene, toluene, ethyl benzene and xylene were procured from Fisher Scientific, India to get the calibration characteristics. Benzene, toluene, ethyl benzene and xylene (BTEX) were mixed in different ratios to get a mixture of known composition and their GC data (% area) for the same. GC-FID of these mixtures were performed for the calibration characteristics of benzene, toluene, ethyl benzene and xylene as discussed elsewhere [26, 27]. GC-FID of standard/pure benzene, toluene, ethylbenzene and xylene were done to get retention time of individual compounds and the % area of the certain peaks. Retention times of benzene, toluene, ethylbenzene and xylene were found to be at 1.76 min, 3.17 min, 5.18 and 4.97 min, respectively.

The effect of temperature on BTEX yield obtained by the thermal and catalytic pyrolysis of PS are presented in Fig. 12 and its comparison with the commercial fuels are shown in Table 2. From Table 2, it is seen that wt. % of aromatic content in thermal pyrolysis of polystyrene was around 13.58 wt.%. Whereas, it is higher in the case of catalytic pyrolysis (23.71 wt.%). The maximum/highest amount of aromatic content i.e., BTEX was found for the catalyst ZSM-5. The BTEX yield was significantly increased for catalytic pyrolysis i.e., about 75 wt. % in comparison to thermal pyrolysis. It may be due to the very high surface area, high Si to Al ratio (=30) could provide more acidic sites with higher selectivity which produces maximum amount of more aromatics (BTEX).

It is clear that the optimum temperature is 700°C for the production of BTEX using thermal and catalytic pyrolysis of PS. The toluene wt. % is more in the product oil followed by xylene and ethylbenzene wt. %. Thus, the liquid product mixture could be a good source of lighter aromatics BTEX[27].

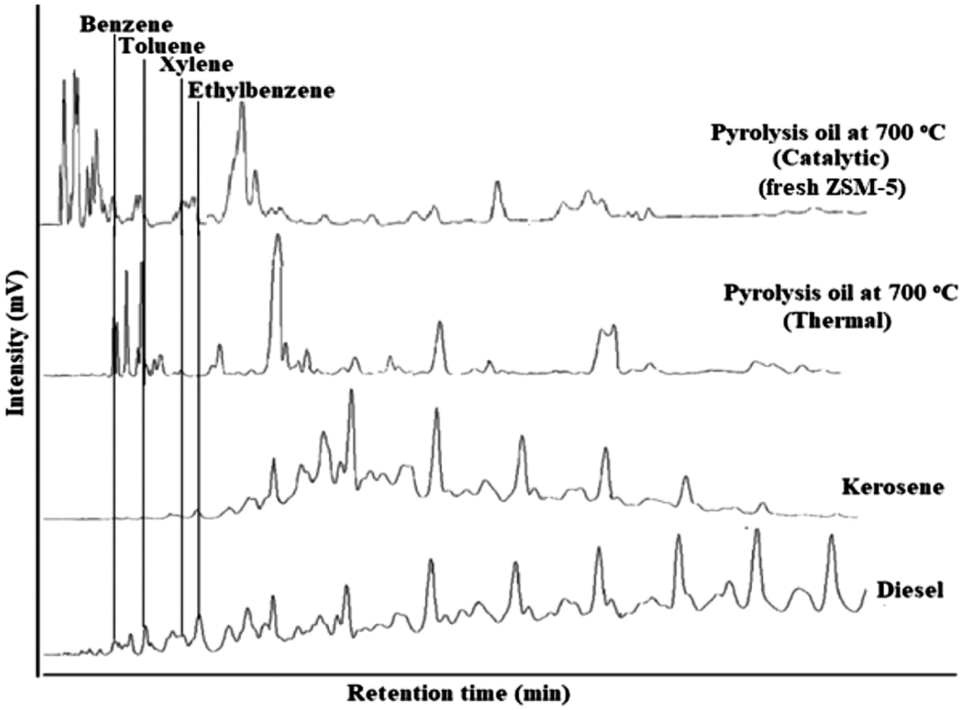

Fig. 11 — Gas chromatography characteristic of kerosene oil (commercial), diesel oil (commercial) and pyrolysis oil obtained from the thermal and catalytic pyrolysis of polystyrene at a temperature of 700 ^{o}C.

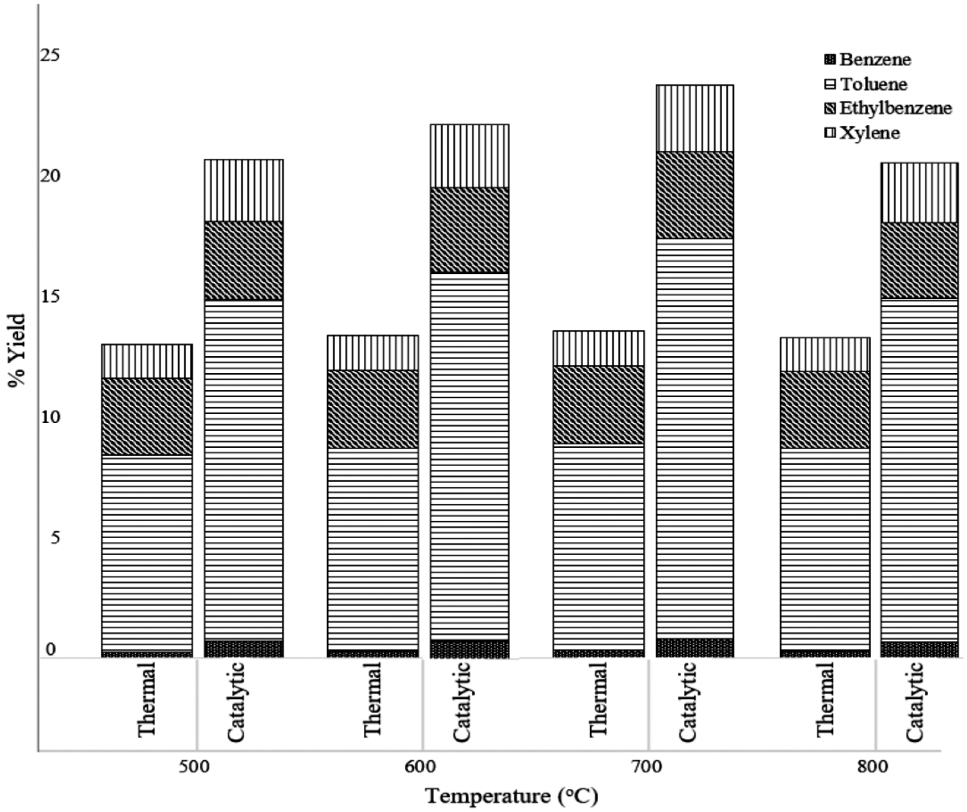

Fig. 12 — BTEX content of pyrolysis oil obtained from thermal and catalytic pyrolysis at different temperatures.

Table 2 — The aromatic content (BTEX) in pyrolysis oil obtained at 700 °C and commercial fuels.

Sources of oil	Benzene (wt. %)	Toluene (wt. %)	Ethyl benzene (wt. %)	Xylene (wt. %)	Total (wt. %)
Thermal pyrolysis	0.31	8.57	3.23	1.47	13.58
Catalytic pyrolysis	0.80	16.57	3.57	2.78	23.72
Commercial diesel	0.15	0.54	4.38	4.26	9.33
Commercial kerosene	0.014	0.0008	2.06	2.00	4.08
Commercial gasoline	0.88	14.88	5.26	15.43	36.45

Performance of regenerated catalyst

The reusability of catalyst for the catalytic pyrolysis of waste polyethylene, polypropylene and polystyrene were checked upto 3rd run. After 3rd run catalyst was regenerated to check its stability and activity. Figure 13 shows the comparison of liquid yield and BTEX for 1st run (fresh catalyst), 2nd run (used catalyst), 3rd run (used catalyst) and 4th run (regenerated catalyst) for catalytic pyrolysis of waste PS at the optimum temperature of 700 °C. It is seen from Fig. 13 that the liquid yield and BTEX decreases to noticeable amount after 2nd run for all the cases. Table 3 shows the comparison of liquid, gaseous, solid residue and BTEX yield for catalytic pyrolysis of PS using ZSM-5 upto 3rd run and regenerated ZSM-5 catalyst. The regenerated catalyst gives comparable yield of liquid, gaseous and solid as that of fresh catalyst. This shows the suitability of ZSM-5 catalyst for pyrolysis process.

Table 3 shows the benzene, toluene, ethylbenzene, xylene and total BTEX of pyrolysis oil obtained at 700°C using fresh ZSM-5 catalyst (1st run), used ZSM-5 catalyst (2nd run), used ZSM-5 catalyst from 2nd run (3rd run) and regenerated ZSM-5 catalyst (4th run).

Physicochemical properties of the pyrolysis oil

The different physical and physic-chemical properties (Table 4) of the pyrolysis oil were measured using standard methods as mentioned in experimental section. Table 4 shows the results of physical property analysis of liquid fuel obtained from thermal and catalytic pyrolysis of waste PS at optimized condition. The appearance of the oil is dark

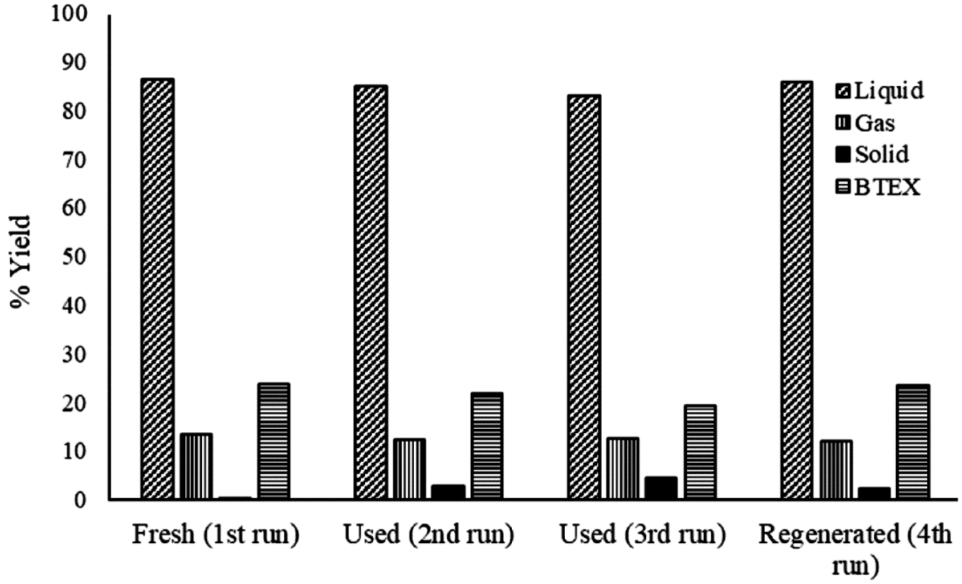

Fig. 13 — Comparison of liquid, gas and solid residue for different number of experiments run at the temperature of 700 ^{o}C.

Table 3 — Benzene, Toluene, Ethylbenzene, Xylene and total BTEX of pyrolysis oil obtained at 700°C.

Number of runs	Benzene (wt.%)	Toluene (wt.%)	Ethylbenzene (wt.%)	Xylene (wt.%)	Total BTEX (wt.%)
1st run (fresh catalyst)	0.79	16.57	3.57	2.78	23.71
2nd run (used catalyst)	0.77	15.15	3.51	2.72	22.15
3rd run (used catalyst)	0.64	14.06	3.32	2.43	20.45
4th run (regenerated catalyst)	0.71	16.45	3.47	2.63	23.26

Table 4 — Physical properties of liquid fuel obtained by thermal and catalytic pyrolysis of waste PS at optimized condition (700°C).

Oil properties	Test method	Result obtained	
		Thermal pyrolysis	Catalytic pyrolysis
Flash point (°C)	ASTM D 92	35	26
Fire point (°C)	ASTM D 92	39	30
Carbon residue (wt.%)	IP 14/65	0.29	0.25
Specific gravity	ASTM D 1298	0.8472	0.8567
API gravity (^{o})	API correlation	35.52	33.67
Calorific value (Cal/g)	IP 12/63 T	7073.37	9726.1

yellowish free from visible sediments. From comparison with other commercial fuels, the density of liquid product can be modified by blending it with commercial fuels. The flash point of the liquid product is in a comparable range which will not cause any trouble in most of the engines. Liquid fuel obtained by catalytic pyrolysis of waste PS has GCV of 9726.1 Cal/g, therefore this liquid product would perform relatively well in engines, which infers the presence of mixture of different oil components such as gasoline, kerosene and diesel in the oil. From this result, it is observed these could be possible feedstock for further upgrading or use of lighter compounds as kerosene.

Conclusions

The experimental results of polystyrene pyrolysis and analyses of products show that the process could be a very good option for production of valuable liquid hydrocarbon suitable for internal combustion engine. In addition, this method may possibly reduce the plastic waste load to dumping ground. The maximum liquid yield of 95.8 % at a temperature of 600°C was obtained by thermal pyrolysis with minimum amount of coke formation (6 wt. %). The pyrolysis temperature of 600°C and 700°C results in the same amount of liquid yield of nearly 96 % by wt for thermal pyrolysis. The flash point and fire point of pyrolysis oil were found to be in the range of kerosene irrespective of pyrolysis temperature. Lower amount of carbon residue of pyrolysis oil (0.29 wt. %) is indication of low char and lesser amount of higher aromatic content. The maximum calorific value of pyrolysis oil was 9726.1 Cal g^{-1} for pyrolysis oil obtained at a temperature of 700°C. GC-FID test of pyrolysis oil at 700°C, confirm that it can be used as commercial fuel after purification. All these ensure that the pyrolysis oil contains low molecular weight paraffinic hydrocarbons and BTEX may be suitable for the use in gasoline and as domestic fuel.

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