Indian Journal of Chemical Technology
Vol. 27, March 2020, pp. 144-152

In-situ production of valuable aromatics via pyrolysis of waste polypropylene using commercial catalyst ZSM-5

Pramendra Gaurh & Hiralal Pramanik*
Department of Chemical Engineering and Technology,
Indian Institute of Technology (Banaras Hindu University), Varanasi 221 005, India.
E-mail: hpramanik.che@itbhu.ac.in

Received 12 November 2018; accepted 13 November 2019

Waste polypropylene has been subjected to pyrolysis followed by in-situ aromatization in a specially designed semi batch reactor at the temperature ranging from 500 - 800°C. The molecules of interest are valuable aromatics benzene, toluene, ethyl benzene and xylene (BTEX) which appeared highest amount in the liquid mixture. The catalyst used is commercial ZSM-5 (30:1). The catalytic pyrolysis of PP is studied in a semi batch reactor in two different phases, keeping the catalyst in the liquid phase (L-type) and liquid and vapor phase/multiphase (M-type), respectively. The BTEX yield is enhanced significantly using multiphase catalytic pyrolysis of polypropylene. The catalytic performance of ZSM-5 catalyst for PP pyrolysis is evaluated with respect to target aromatics BTEX. The thermal pyrolysis of PP produced maximum liquid yield of 80.56 wt. % at a temperature of 700°C. The commercial catalysts ZSM-5 produced highest liquid yield of 86.3 wt. % for liquid phase (L-type) pyrolysis. The BTEX yield is significantly increased from 30.9 wt.% for thermal pyrolysis to 53.09 wt. % for catalytic multiphase/M-type pyrolysis. Almost 72 % increase in BTEX yield is recorded for catalytic multiphase/M-type pyrolysis in comparison to thermal process. The pyrolysis oil is analyzed using GC-FID, carbon residue test and other fuel testing methods to examine the suitability of its end use and aromatic content.

Keywords: GC-FID, BTEX, Polypropylene, Multiphase pyrolysis, Commercial ZSM-5.

The production of valuable aromatics benzene, toluene, ethyl benzene and xylene (BTEX) from naphtha has increased tremendously due to their high demand in the manufacturing of synthetic fibres, resins, synthetic rubber, explosives, pesticides, detergent and intermediates etc.[1]. The feed stock naphtha comes from the fractionation of crude petroleum which has some limitations, e.g. limited reserves, uncertainty in supply and price hike of crude oil. All these problems have given momentum to think on alternative sources of BTEX production. There is a recent development that BTEX can be produced from waste plastic polyethylene (PE) via multiphase catalytic pyrolysis using commercial ZSM-5 and fly ash synthesized catalyst[2]. The plastic waste is available and abundant in municipal solid waste (MSW) which consist of high percentage of plastic wastes, primarily high density polyethylene (HDPE), low density polyethylene (LDPE), polypropylene (PP), polyethyleneterephthalate (PET),polystyrene (PS) and polyvinyl chloride (PVC)[3].The packaging materials derived from PE, PP, PS and PVCcontributes 50-70 % of the total waste plastic and the percentage share of PP in the total municipal plastic waste is nearly 24.3 wt. %[4]. Thus, the primary aim of the present study is pyrolysis of waste polypropylene using catalytic pyrolysis and in-situ aromatization to produce valuable aromatics BTEX.

Polypropylene (PP) is a hydrocarbon polymer derived from petrochemicals and most commonly used synthetic polymers. Polypropylene is a saturated polymer with linear hydrocarbon chain that has a good heat and chemical resistance. The melting point of PP is160°C and the density is lower than polyethylene. However, polypropylene has higher hardness and rigidity in comparison to other plastic materials. All these properties make PP preferable in plastic industry. The miscellaneous applications of PP include storage boxes, office folders, disposable glasses, buckets, car bumpers, carpets, furniture, container etc. There is significant increase in PP waste due to high demand of PP in our daily life and thus, pyrolysis of PP could efficiently be converted to valuable hydrocarbons BTEX. Jung *et al.*[5] has shown that BTX yield in the oil increases with the increase in reaction temperature. Ma *et al.*[6] stated that PP pyrolysis gives higher aromatic yield i.e., toluene, ethyl benzene, styrene and many other compounds in comparison to other plastic waste. Several researchers have investigated different parameters to characterize the liquid oil yield for the PP pyrolysis. Ahmad *et al.*[7] carried out thermal pyrolysis of polypropylene in a micro steel reactor at the temperature ranging from 250 to 400°C and reported that the maximum liquid yield obtained was about 69.8 wt.% with overall conversion of 98.6 wt. % at the temperature of 300°C. They also stated that on increasing temperature upto 400°C the total liquid yield was reduced to 94.3 wt.% and there is increase in solid residue from 1.3 wt. % to 5.7 wt. %. This indicates that coke formation tendency of the process at higher temperature. However, Sakata *et al.*[8] obtained higher liquid yield of 80.1 wt.%, gaseous yield of 6.6 wt.% and solid residue of 13.3 wt.%, respectively for the thermal pyrolysis of PP at the temperature of 380°C. Fakhrhoseini and Dastanian[9] performed thermal pyrolysis of PP and obtained maximum liquid yield of about 82.12 wt.% at a temperature of 500°C. However, beyond 500°C on increasing temperature, the liquid yield decreases. Demirbas[10] performed thermal pyrolysis of PP in a batch reactor at high temperature of 740°C and obtained 48.8 wt. % liquid yield, 49.6 wt.% gaseous and 1.6 wt.% char. The thorough literature survey on thermal pyrolysis shows that with the increase in temperature liquid yield decreases and coke formation predominates. Moreover, thermal pyrolysis of PP never gives good quality product in terms of composition as the process is non selective. In view of that, considerable efforts have been made to study the catalytic pyrolysis of polypropylene to achieve quality product[11-15]. So far, different types of catalysts have been studied by researchers for the pyrolysis of PP such as H-ZSM-5[11,14], H-mordenite[11], H-theta-1[11], MCM-4[12,14,15], Zeolite beta[13], SAPO-34[16], Fe/HZSM-5[17] and SBA-15[15]. The catalytic pyrolysis always gives selective target molecules relatively at low temperature in comparison to the thermal pyrolysis.

Similar to other polymer studies, many authors have proposed that backbiting reactions are more important and diverse, that occurs during the pyrolysis of polypropylene in comparison to pyrolysis of polystyrene. It may be due to the small methyl substituent groups present in polypropylene, that makes PP more flexible[18]. Along with pyrolysis, product analyses is also a very important part to understand the quality of product formation in terms of composition. To obtain a complete understanding of PP pyrolysis process, various types of analytical techniques have been used. Gas chromatography (GC) is themost common liquid oil characterization method for the product distribution over various catalysts, due to its good performance in separation and high sensitivity[19-24]. It is also widely used to identify the products of decomposition for its short response time[25-27]. To study the degradation behaviors of PP for different catalysts Thermo gravimetry analysis (TGA) is used[28-30] that is also useful for establishing kinetic models.

Onu *et al.*[19] studied the catalytic pyrolysis of PP using two different types of HZSM-5 zeolite and reported that the acidity and steric effect of the catalyst plays vital role in the production of liquid and gaseous yield. Lin *et al.*[21] carried out catalytic pyrolysis of PP in a fluidized-bed reactor at the temperature range of 290°C to 430°C using acidic zeolite catalysts (HZSM-5, HMOR, and HUSY) and non-zeolite catalysts (MCM-41 and SAHA). They obtained maximum amounts of volatile hydrocarbons in the case of acidic zeolite catalyst. Hayashi et al.[31] performed oxidative pyrolysis in a fixed bed reactor at 250°C and found that 90 % of PP was converted into volatiles which mainly consisted of CS_2-soluble oils having a number-average chain length of 10. Saha *et al.*[30] used nano crystalline HZSM-5 as catalyst to perform the catalytic pyrolysis of PP in a TGA apparatus and studied the behavior of TG curves which showed the reaction mechanism in the process. For the detailed information on vapors produced by the decomposition process of the PP, fourier transform infrared spectroscopy (FTIR) was used parallelly with TGA[14]. The open literature on catalytic pyrolysis shows that HZSM-5, HUSY, Hb and HMOR are widely used catalysts for the plastic pyrolysis. Besides, the non-zeolites catalysts such as silica–alumina, MCM-41 and silicalite have also been used in current researches[32]. Thus, zeolites, FCC and silica–alumina are most commonly used catalysts for the plastic pyrolysis.

It is clear from the thorough literature search that till date, no such studies have been carried out on catalytic pyrolysis of plastic wastes polypropylene using innovative reactor design on ZSM-5 catalyst. Thus, the main objectives of this study were to produce useful light aromatic hydrocarbons BTEX by thermal and catalytic pyrolysis of PP and comparison of the BTEX yield for the commercial ZSM-5 catalyst. In this paper, solid residue and gaseous yield are not given emphasis in the discussion, as the primary and main product is liquid yield containing lighter aromatics BTEX. In a nutshell, this paper explores the scope of waste polypropylene management using ZSM-5 catalyst resulting in valuable BTEX.

Experimental Section

Raw materials

Raw material polypropylene was collected from the municipal solid waste dumping ground of Varanasi city, India. The raw material/polypropylene was in the form of disposable glasses. Huge population of Varanasi generates 800 MT per day of MSW and per capita consumption of MSW is about 0.217 kg/person/day[33]. The published report shows that the percentage share of plastic waste polypropylene is about 24 wt. % of municipal plastic waste (22 wt.%). The collected PP waste was first cleaned with water to remove other impurities then dried in open sunlight to remove free moisture. The dried polypropylene was shredded into small pieces (5 mm × 5 mm) using scissors manually to accommodate more PP in the reactor and melting faster. The commercial ZSM-5 (Alfa Aesar, USA) of SiO_2/Al_2O_3 ratio 30:1 was chosen for the catalytic pyrolysis of polypropylene.

Experimental set up and method

The pyrolysis and *in-situ* aromatization of waste polypropylene was carried out in a semi batch reactor made of mild steel of 112 mm inner diameter and 135 mm height (Fig. 1). Poly propylene sample of 50 g was fed into the reactor and sealed properly using gasket to prevent the products leakage. The thermal pyrolysis was performed in the reactor arrangement as shown in Fig. 2a. A catalyst bed (Fig. 2c) of commercial catalyst ZSM-5 was used in the liquid and vapor phase (M-type)/ multiphase to perform pyrolysis of PP batch by batch, respectively. A porous stainless-steel plate was used to support the catalyst. A thin layer of ceramic wool was used to make the catalyst bed through which vapour of hydrocarbons and gases could easily diffuse with a better catalyst-vapor interaction[2,4]. The mass ratio of catalysts distribution in liquid to vapour phase was 1:1 for M-type reactor arrangement. The nitrogen gas was circulated into reactor to remove oxygen and create anaerobic condition inside the reactor. The thermal pyrolysis of PP was performed at different temperatures 500, 600, 700 and 800°C, respectively. The time for each set of experiments were maintained for 35 min. ZSM-5 (Si/Al=30:1) was used for catalytic pyrolysis. Feed to catalyst ratio of 20:1 was maintained for catalytic pyrolysis keeping other operating conditions similar to the thermal pyrolysis.

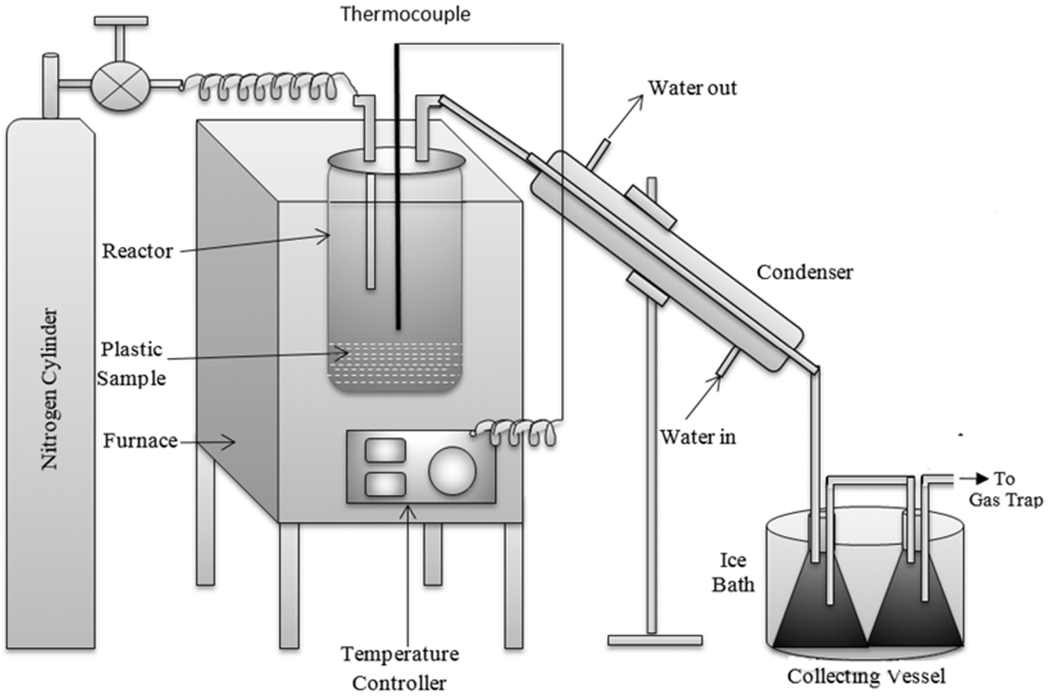


Fig. 1 — Schematic view of experimental set-up.

The product gas and vapour mixture were directed through a condenser of copper made. The copper condenser was attached to an ice-bath to get all condensable vapors as liquid yield in two conical flasks except the non-condensable gases which was collected by a gas trap.

The liquid, gas and solid yields were calculated using following Eqs. (1–3):

$$Liquid\ Yield = \frac{wt.of\ liquid}{wt.of\ total\ feed} \times 100 \qquad \ldots (1)$$

$$Gas\ Yield = \frac{wt.of\ gas}{wt.of\ total\ feed} \times 100 \qquad \ldots (2)$$

$$Solid\ Yield = \frac{wt.of\ solid}{wt.of\ total\ feed} \times 100 \qquad \ldots (3)$$

where, wt. of gas = [wt. of total feed - (wt. of liquid + wt. of solid)][2,4].

Analysis of the reaction products

FTIR analysis was carried out with Thermo-Nicolet 5700 model in the range of 500–4000 cm^{-1} with a resolution of 4 cm^{-1} using Nujol mull as reference. The Ominc software was used to correct the medium's background material used during analysis[2]. The gas chromatograph (NUCON 5765) was used to determine the composition of pyrolysis oil using flame ionization detector (FID) with a SE-30 10 % chromosorb W packed stainless-steel column (2 m × 2 mm)[34]. The Cleveland open cup apparatus (ASTM D 92) gives the flash and fire point of pyrolysis oil. Carbon residue of pyrolysis oil was obtained using Rams bottom Carbon Residue Apparatus (IP 14/65). The density of pyrolysis-oil was measured according to ASTM D 1298 standard method. The API gravity of pyrolysis oil is calculated using the oil sample specific gravity, which is the ratio of density of oil to that of water ($\frac{15.6\ ℃}{15.6\ ℃}$). The API gravity of the pyrolysis oil sample was calculated by the following equation (4):

$$\text{Deg.API} = \left(\frac{141.5}{\rho_{pryolysis\,oil}}\right) - 131.5 \qquad \ldots(4)$$

where, $\rho_{pryolysis\,oil}$ = specific gravity of fraction at $\left(\frac{15.6°C}{15.6°C}\right)$.35,36

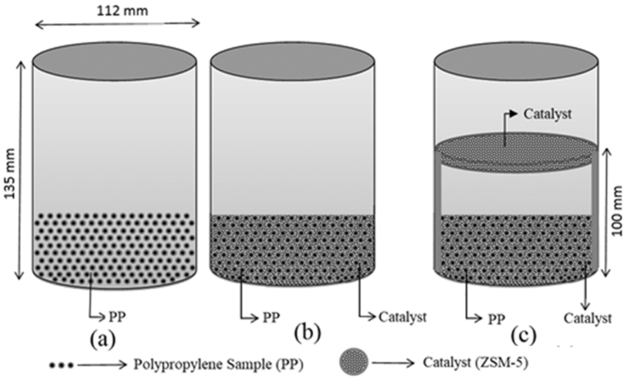


Fig. 2 — Reactor set-up of (a) thermal pyrolysis, (b) L-type (catalyst in liquid phase) and (c) M-type (catalyst in both liquid and vapor phase).

The bomb calorimeter (IP 12/63T) was used to determine the gross calorific value (GCV) of pyrolysis oil.

Results and Discussion

Product yield of pyrolysis process

Effect of reaction time on conversion rate

The effect of reaction time on the conversion rate for thermal and catalytic pyrolysis of polypropylene at a temperature of 700°C is shown in Fig. 3. The % conversion of polypropylene increases with the increase in reaction time and becomes constant after 25 min for both thermal and catalytic pyrolysis. This indicates that the reaction time plays vital role for the conversion of PP and achieving product yield. The Fig. 3 shows that there is no further conversion after 25 min of reaction time. Thus, to ensure complete conversion and achieve maximum product yield, both thermal and catalytic pyrolysis were performed for 30 min[2,4].

Effect of temperature

Figure 4a-d show the comparative study of liquid, gas and solid yields for thermal and catalytic

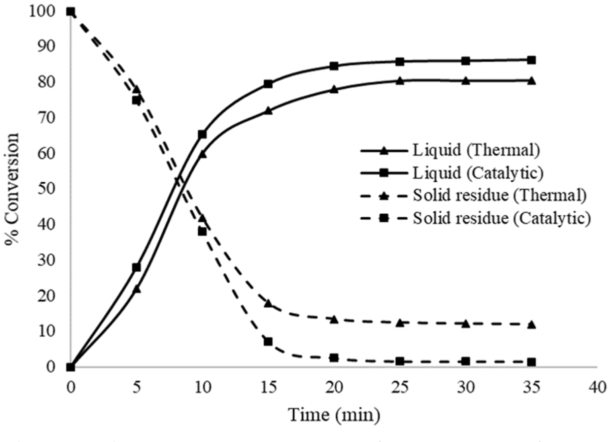


Fig. 3 — Time vs.% conversion rate of polypropylene for thermal and catalytic pyrolysis at 700°C.

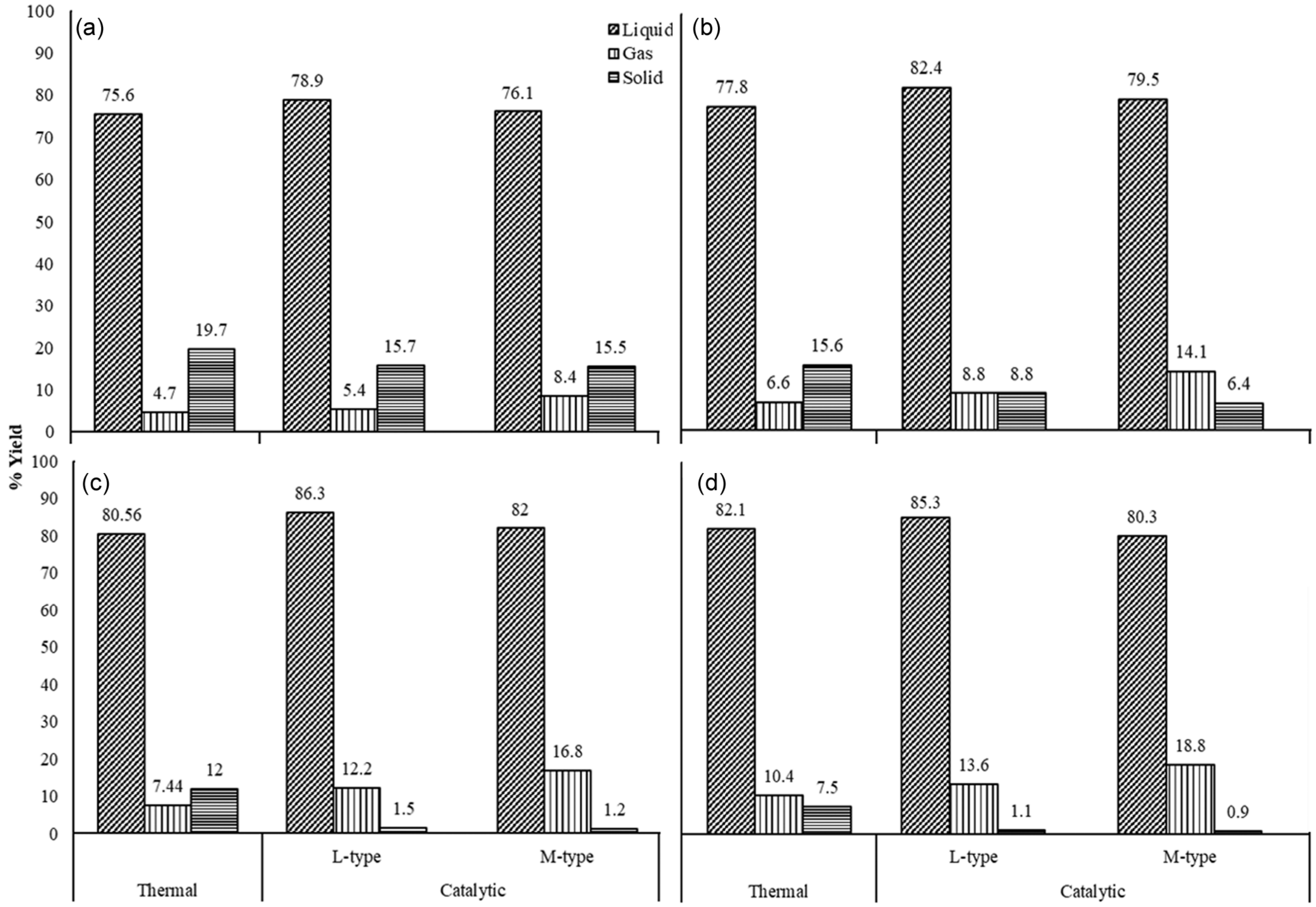


Fig. 4 — Comparison between liquid, gaseous and solid residue obtained by the thermal and catalytic pyrolysis of PP at (a) 500°C, (b) 600°C, (c) 700°C and (d) 800°C.

pyrolysis of polypropylene (PP) at the temperature range from 500°C to 800°C. All the pyrolysis experiments (L-type and M-type) were performed in a same semi batch reactor. The catalytic pyrolysis was performed using commercial catalyst ZSM-5 (Si/Al=30:1). When catalyst is mixed only with feed i.e., L-type/liquid phase reactor arrangement, melted liquid PP interacts with catalyst particles, resulting in liquid range hydrocarbon. Whereas, M-type/multiphase reactor arrangement helps in interaction between active catalyst sites and PP in the bottom of the reactor (liquid phase) followed by interaction of liquid range smaller hydrocarbon molecules with ZSM-5 catalyst in vapor phase giving more aromatics in comparison to thermal pyrolysis and L-type/liquid phase reactor arrangement.

It is seen in the Fig. 4a-d that liquid and gaseous yield increases and solid residue decreases with the increase in temperature for the thermal pyrolysis. The maximum liquid yield of 80.56 wt. % was obtained at a temperature of 700°C for the thermal pyrolysis. However, at a temperature of 800°C, the obtained liquid yield was waxy at room temperature. The solid residue decreases from 19.7 wt. % to 7.5 wt. %, when temperature is increased from 500°C to 800°C. It implies that more decomposition of solid residue takes place at high temperature resulting in more liquid yield and non-condensable gases. Similarly, catalytic pyrolysis at a maximum temperature of 800°C produced waxy liquid yield with respect to all of reactor arrangements (L-type and M-type/multiphase).

Figure 4c shows the product yield obtained from thermal and catalytic pyrolysis using commercial ZSM-5 catalyst via pyrolysis of polypropylene at an optimum pyrolysis temperature of 700°C. The pyrolysis temperature of 700°C produced better quality of liquid yield with appreciable amount of BTEX.

It is seen in the Fig. 4c that the liquid yield is higher for L-type/liquid phase catalytic pyrolysis in comparison to thermal and multiphase pyrolysis at a temperature of 700°C. The Maximum liquid yield of 86.3 wt. % is obtained for L-type/liquid phase catalytic pyrolysis using ZSM-5 catalyst. However, maximum liquid yield of 82 wt. % was obtained for M-type/multiphase catalytic pyrolysis at this temperature. The commercial ZSM-5 catalyst produced gaseous yield of 16.6 wt. % and 12.2 wt. % for M-type and L-type pyrolysis, respectively. It is clear from this observation that M-type/multiphase produced more gaseous yield than L-type/liquid phase pyrolysis and thus liquid yield is less for M-type/multiphase. It may be due to two stage catalytic pyrolysis in M-type arrangement, the further selective cracking at vapour phase of comparatively lighter hydrocarbons molecules which are formed by the catalytic pyrolysis at the bottom of the reactor (Fig. 2c). Lopez *et al*.[38] and Gaurh & Pramanik[2] reported that the use of catalyst improves the quality of liquid yield via aromatization when Si-Al based catalyst is used. The catalytic pyrolysis produced very low solid residue (1.1 wt. %) for M-type pyrolysis in comparison to L-type (1.5 wt. %) and thermal pyrolysis (12 wt. %). The reason behind low solid residue for M-type reactor arrangement may be due to the effective and selective two stages catalytic pyrolysis of hydrocarbons at liquid phase and vapor phase, respectively.

The GC-FID analysis of the liquid yield shows that the highest amount of aromatics BTEX is produced for the catalytic pyrolysis at a pyrolysis at a temperature of 700°C in M-type reactor arrangement. Thermal pyrolysis at the same temperature (700°C) produced lowest amount of liquid yield (80.56 wt. %), gaseous yield (7.44 wt. %) and highest amount of solid residue (12.05 wt. %).

Pyrolysis products analyses

FT-IR of the liquid fuel

Fourier Transform Infrared spectroscopy (FTIR) is an important analysis technique which detects various characteristic functional groups present in 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. The chemical composition of the pyrolysis oil in terms of the functional group were evaluated using FTIR in the wavelength range of 4000-600 cm^{-1}. Figure 5 shows the FTIR spectra of pyrolysis oil obtained at optimum condition by thermal and catalytic pyrolysis (M-type) of waste PP. The FTIR spectra were almost similar in nature for thermal and M-type pyrolysis oil. This may be due to the strong similarity among chemical structures of the hydrocarbons present in the pyrolysis oil. The FTIR spectra indicate that the pyrolysis oils are composed of aliphatic groups comprising carbon and hydrogen atoms. The alkanes is detected in the wavelength range of 2954-2913 cm^{-1} with C–H stretching vibrations. The stretching vibrations of C=C at 1782-1660 cm^{-1} indicates the presence of alkenes. This spectra range confirm the existence of olefinic compounds, also suggests the presence of vinyl, vinylidene or cis configurations. The presence of alkanes is detected by C–H scissoring and bending vibrations at 1453-1376 cm^{-1}, which verify the presence of benzene derivatives in the pyrolysis oil. The presence of alkenes is confirmed by the C–H bending vibrations at 968 cm^{-1}. The vinylidene functional group in the chemical composition of pyrolysis oil is also detected at the band 885 cm^{-1}. The phenyl ring substitution is also traced due to the C–H bending vibrations at frequency 738 cm^{-1}. The mono or ortho substitution of benzene ring occurs due to the presence of this region i.e., 738 cm^{-1}. The overall analysis of FTIR spectra for the pyrolysis oil confirm the presence of paraffinic, olefinic and aromatic compounds in the product oil[4,37]. The FT-IR data of pyrolysis oil is substantiated using GC-FID analysis of the oil obtained by the similar condition.

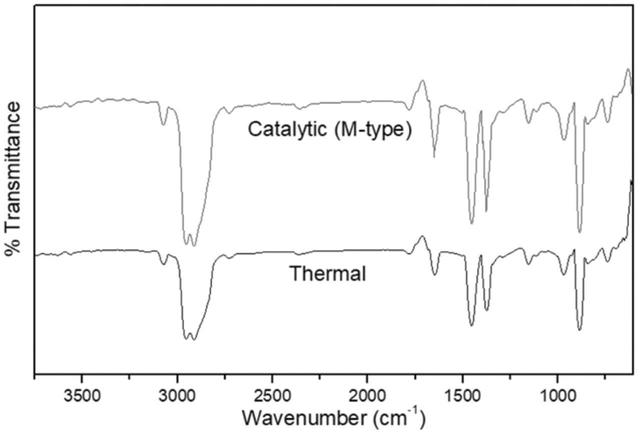


Fig. 5 —FT-IR spectrometry of pyrolysis oil obtained at optimized condition (700°C) by thermal and catalytic pyrolysis (M-type) of waste PP.

Gas Chromatography

Figure 6a-b show the comparison of GC-FID of the commercial kerosene oil, diesel oil and pyrolysis oil derived by the thermal and catalytic pyrolysis (L-type and M-type) of the waste polypropylene at 700°C. The important and prominent peaks obtained at identical retention time for the pyrolysis oil (700°C), commercial oils are grouped. The chromatograms of pyrolysis oil (700°C) are very close to kerosene and diesel oil in the retention time range between 4 min and 14 min for thermal pyrolysis and between 2 min and 16 min for L-type and M-type catalytic pyrolysis. In this range the pyrolysis oil (700°C) which consist of compounds, are similar as that of kerosene oil and diesel oil in terms of chemical structure of compounds and composition[2, 4].

Moreover, it is seen in Fig. 6 that the maximum numbers of peaks of L-type and M-type pyrolysis oil obtained by ZSM-5 catalyst are matched with diesel and kerosene. However, GC peaks of thermal pyrolysis are partially matched with diesel oil only. It may be due to presence of compounds of similar boiling point range.

The calibration characteristics between yield (wt.%) vs % area peaks under the curves were obtained by GC-FID analysis, making large number of mixtures of target compounds benzene, toluene, ethyl benzene and xylene (BTEX) of known concentration. High purity HPLC grade benzene, toluene, ethyl benzene and xylene were procured from Fisher Scientific, India to get the calibration characteristics. The GC-FID analysis of these mixtures were performed for the calibration characteristics of benzene, toluene, ethyl benzene and xylene as reported in our previous study elsewhere[2,4]. The amount (wt. %) of benzene, toluene, ethyl benzene and xylene in the liquid yield obtained via thermal and catalytic pyrolysis, were measured using these standard calibration characteristics.

It is clearly seen from Table 1 that the aromatic content in thermal pyrolysis of polypropylene was around 30.90 wt. %. Whereas, it is higher in the case of catalytic pyrolysis with respect to all types of reactor arrangement i.e., L-type and M-type in the study. The maximum aromatics/ BTEX content of 51.52 wt. % for L-type and 53.09 wt. % for M-type were found for the commercial catalyst ZSM-5. The

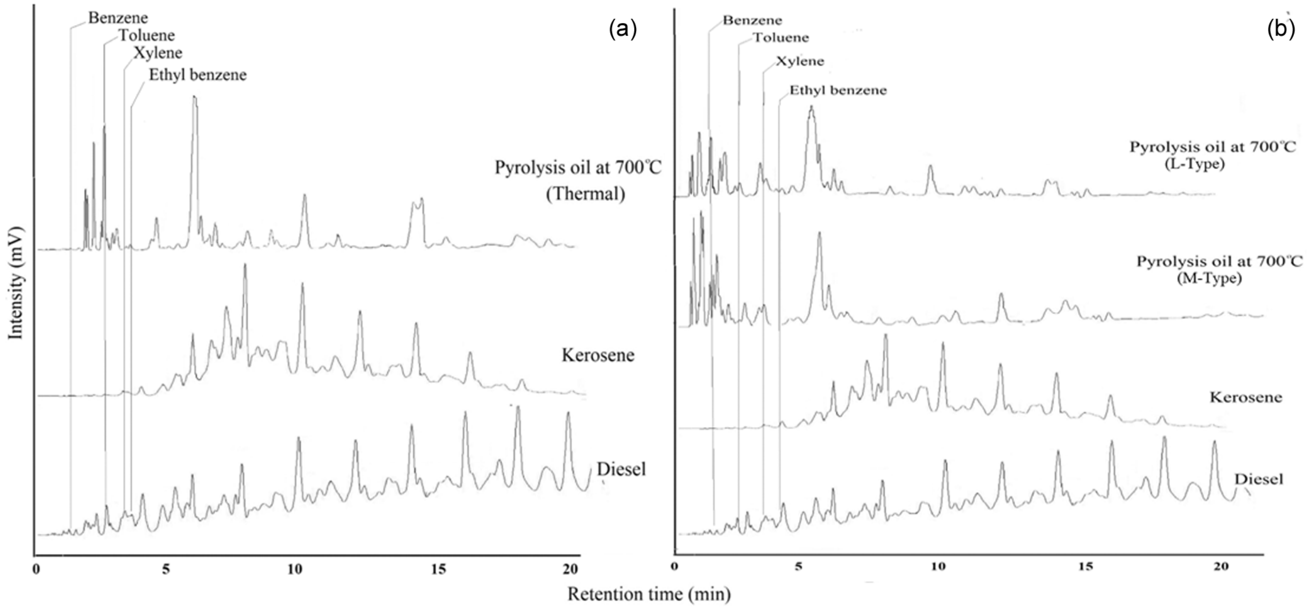


Fig. 6 — Gas chromatography characteristic of diesel oil (commercial), kerosene oil (commercial) and pyrolysis oil obtained from the polypropylene at a temperature of 700°C using (a) thermal pyrolysis and (b) catalytic pyrolysis on ZSM-5.

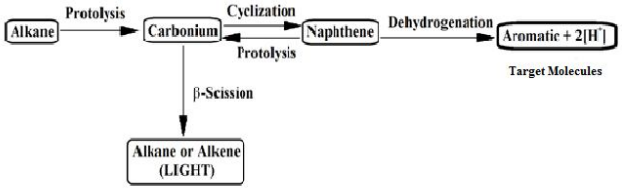
Table 1 — The aromatic content (BTEX) in pyrolysis oil obtained at 700°C for thermal and catalytic pyrolysis.

Sources of oil		Benzene (wt. %)	Toluene (wt. %)	Ethyl benzene (wt. %)	Xylene (wt. %)	Total (wt. %)
Thermal pyrolysis		3.55	1.5	2.34	23.52	30.90
Catalytic (ZSM-5)	L-type	13.76	3.474	5.34	28.95	51.52
	M-type	15.92	3.80	5.29	28.08	53.09
Commercial diesel		0.1485	0.54	4.38	4.26	9.33
Commercial kerosene		0.0144	0.0008	2.06	2.00	4.08
Commercial gasoline		0.8829	14.88	5.26	15.43	36.45

Table 2 — Physicochemical properties of pyrolysis oil/fuel obtained by thermal and catalytic pyrolysis of waste PP at optimized condition (700°C).

Physicochemical properties	Test method	Results obtained		
		Thermal pyrolysis	Catalytic pyrolysis (using ZSM-5)	
			(L-type)	(M-type)
Flash point (°C)	ASTM D 92	27	26	25
Fire point (°C)	ASTM D 92	32	30	30
Carbon residue (wt. %)	IP 14/65	0.28	0.25	0.23
Specific gravity	ASTM D 1298	0.78	0.77	0.74
API gravity (^{o})	API correlation	52.65	55.22	56.54
Calorific value (Cal/g)	IP 12/63 T	9015	9726	9914

results indicate that the performance of commercial ZSM-5 is excellent for PP pyrolysis in terms of liquid yield and aromatics/BTEX content. It may be due to the very high surface area and high Si to Al ratio (=30:1) provides more acidic sites with higher selectivity resulting in more aromatics (BTEX). For the M-type arrangement, liquid range hydrocarbon molecules and aromatics are formed in more amount, due to catalytic pyrolysis of PP at the liquid phase followed by the second stage selective catalytic pyrolysis of liquid range hydrocarbon molecules on ZSM-5 catalyst in the vapor phase (Fig. 2c). As per the proposed reaction schemes in the published literature, M-type/multiphase pyrolysis gives little higher aromatics (53.09 wt. %) than L-type (51.52 wt. %) for ZSM-5 catalyst, which is shown in Eq. (5) [2,4]. It is generally proposed that on acid catalysts the aromatization of alkanes occurs through protolysis of alkane, pyrolysis of carbonium ion to alkane and alkene, oligomerization of alkenes, cyclization of oligomerized products and formation or aromatics from cyclic rings by hydrogen transfer [2,4].



… (5)

Jung *et al.*[39] observed that the pyrolysis oil contained primarily aliphatic, mono aromatic and poly aromatic compounds. The aromatic/BTEX in PP pyrolysis oil were found higher (53 wt. %) than in the HDPE fraction (32 wt. %) at the same temperature (700°C). The most abundant compound comprised in the BTEX mixture was the benzene. The concentration of benzene, ethyl benzene and toluene increased with the temperature except xylene compound which slightly increased and did not have a significant difference with the temperature. The significant observations of the present study are that the M-type/multiphase catalytic process gives maximum amount of benzene, toluene, ethyl benzene and xylene (BTEX) in comparison to any other processes, as it is in-situ two stages catalytic pyrolysis.

Physicochemical properties of pyrolysis oil

Table 2 shows the physicochemical properties of liquid fuel obtained by thermal and catalytic pyrolysis of waste PP at optimum process condition. The appearance of the oil is light yellowish and free from visible sediments.

The flash point of the liquid product is in the comparable range with gasoline and lower than diesel which will not cause any trouble in most of the engines. Liquid fuel obtained by catalytic pyrolysis (M-type) of waste PP gives gross calorific value (GCV) of 9726 Cal/g for L-type/liquid phase and 9914 Cal/g for M-type/multi-phase which is in the range of gasoline and diesel and thus, it could perform relatively well in IC engines. The carbon residue for pyrolysis oil is <1 wt. % irrespective of process and catalyst used. This indicates very low cracking tendency for the derived pyrolysis oil due to presence of low molecular weight aromatics/BTEX which do not give carbon residue. Due to low flash point of pyrolysis oil, it could be recommended for IC engine during winter or cold climate region effectively. It is seen from the result that pyrolysis oil (L-type and M-type) could be possible feedstock for further upgrading to use in diesel engine besides recovery of BTEX as a valuable product.

Conclusion

The disposal problem of waste polypropylene could be addressed effectively using the developed process i.e., M-type/multiphase pyrolysis on commercial catalyst ZSM-5. The factors affecting the catalytic process are evaluated in detail to improve the product yield qualitatively and quantitatively. The experimental results on catalytic pyrolysis of PP and analyses of products show that the developed process M-type/multiphase pyrolysis could be a good option for production of aromatics BTEX. The commercial catalyst ZSM-5 produced BTEX of 53.09 wt. %. Physicochemical properties of the pyrolysis oil (M-type) show that it can be used as alternative fuels and as a source of valuable chemicals such as benzene, toluene, ethyl benzene or xylene. Gaseous product can also be used as fuel for process industry and the surplus may be used for domestic uses in place of LPG. Thus, the proposed process can reduce the waste polypropylene load to the environment and minimize disposal problem of plastic waste.

The flash point and fire point of pyrolysis oil are found to be very low irrespective of pyrolysis process used. Lower amount of carbon residue of pyrolysis oil indicates that the possibility of carbon soot formation is negligible in IC engine. The maximum gross calorific value of pyrolysis oil is 9914 Cal g^{-1} for M-type/multiphase catalytic pyrolysis at a temperature of 700°C on ZSM-5 catalyst. These results indicate that the commercial catalyst ZSM-5 is very effective for producing fuel range oil from waste PP. The developed process (M-type/multiphase pyrolysis) could be scaled up to handle large amount of municipal waste polypropylene to produce value added product BTEX.

References

1 Thongplang J, What is BTEX and why is it important? https://www.aeroqual.com/what-is-btex (2016).
2 Gaurh P & Pramanik H, *Waste Management*, 77 (2018b) 114.
3 Hamad K, Kaseem M & Deri F, *Polym Degrad Stabil*, 98 (2013) 2801.
4 Gaurh P & Pramanik H, *Waste Management*, 71 (2018a) 86.
5 Jung S H, Cho M H, Kang B S & Kim J S, *Fuel Process Technol*, 91 (2010) 277.
6 Ma C, Sun L, Jin L, Zhou C, Xiang J, Hu S & Su S, *Fuel Process Technol*, 135 (2015) 150.
7 Ahmad I, Khan M I, Khan H, Ishaq M, Tariq R & Gul K, *Int J Green Energy*, 12 (2014) 663.
8 Sakata Y, Uddin M A & Muto A, *J Anal Appl Pyrol*, 51 (1999) 135.
9 Fakhrhoseini S M & Dastanian M, *J Chem*, (2013) 1.
10 Demirbas A, *J Anal Appl Pyrol*, 72 (2004) 97.
11 Mordi R C & Fields R & Dwyer J, *J Chem Soc, Chem Commun*, 4 (1992) 374.
12 Aguado J, Sotelo J L, Serrano D P, Calles J A & Escola J M, *Energy Fuels*, 11 (1997) 1225.
13 Aguado J, Serrano D P, Escola J M, Garagorri E & Fernandez J A, *Polym Degrad Stab*, 69 (2000) 11.
14 Marcilla A, Gomez-Siurana A & Berenguer D, *Appl Catal A*, 301 (2006) 222.
15 Obali Z, Sezgi N A & Dogu T, *Chem Eng J*, 207 (2012) 421.
16 Park J H, Heo H S, Park Y K, Jeong K E, Chae H J, Sohn J M, Jeon J K & Kim S S, *Korean J Chem Eng*, 27 (2010) 1768.
17 Alyani M, Towfighi J & Sadrameli S M, *Korean J Chem Eng*, 28 (2011) 1351.
18 Kruse T M, Wong H W & Broadbelt L, *J Macromole*, 36 (2003) 9594.
19 Onu P, Vasile C, Ciocilteu S, Iojoiu E & Darie H, *J Anal Appl Pyrol*, 49 (1999) 145.
20 Luo G H, Suto T, Yasu S & Kato K, *Polym Degrad Stab*, 70 (2000) 97.
21 Lin Y H & Yen H Y, *Polym Degrad Stab*, 89 (2005) 101.
22 Tekin K, Akalin M K, Kadi C & Karagoz S, *J Energy Inst*, 85 (2012) 150.
23 Marcilla A, Gomez A, Reyes-Labarta J A & Giner A, *Polym Degrad Stab*, 80 (2003) 233.
24 Filho J G A P, Graciliano E C, Silva A O S, Souza M J B & Araujo A S, *Catal Today*, 107 (2005) 507.
25 Negelein D L, Lin R & White R L, *J Appl Polym Sci*, 67 (1998) 341.
26 Serrano D P, Aguado J, Escola J M, Rodriguez J M & Miguel S G, *J Anal Appl Pyrol*, 74 (2005) 370.
27 Zhao W, Hasegawa S, Fujita J, Yoshii F, Sasaki T, Makuuchi K, Sun J Z & Nishimoto S, *Polym Degrad Stab*, 53 (1996) 129.
28 Marcilla A, Gomez A, Reyes-Labarta J A, Giner A & Hernandez F, *J Anal Appl Pyrol*, 68 (2003) 467.
29 Durmus A, Koc S N, Pozan G S & Kasgoz A, *Appl Catal B*, 61 (2005) 316.
30 Saha B, Reddy P K, Chowlu A C K & Ghoshal A K, *Thermo chimica Acta*, 468 (2008) 94.
31 Hayashi J I, Nakahara T, Kusakabe K & Morooka S, *Fuel Process Technol*, 55 (1998) 265.
32 Sharuddin S D A, Abnisa F, Daud W M A W, Aroua M K, *Energy Conver Manage*, 115 (2006) 308.
33 Srivastava R, Krishna V & Sonkar I, *Int J Curr Res Acad Rev*, 2 (2014) 10.
34 Dan M, Shiburaj S, Sethuraman M G & George V, *Acta Pharm*, 55 (2005) 315.
35 Tiab D & Donaldson E C, *Petro Physics*, 7 (2004) 773.
36 Gaurh P & Pramanik H, *Indian J Chem Technol*, 25 (2018) 336.
37 Kung K H S & Hayes K F, *Langmuir*, 9 (1993) 263.
38 Lopez A, Marco I D, Caballero B M, Laresgoiti M F & Adrados A, *J Anal Appl Pyrol*, 96 (2012) 54.
39 Jung C H, Matsuto T & Tanaka N, *Waste Manage. (Amsterdam, Neth.)*, 25 (2005) 301.