CHAPTER 4
RESULTS AND DISCUSSION

In this chapter, the results related to the thermal and catalytic pyrolysis of waste plastics like polyethylene, polypropylene and polystyrene are discussed in detail in two phases. In the first phase (Phase-I), thermal pyrolysis of waste plastic and the effect of different parameters are discussed. In second phase (Phase-II), the catalytic pyrolysis of waste plastics is discussed. The catalytic pyrolysis was performed using commercial ZSM-5 catalyst and fly ash derived synthesized catalyst. The synthesized catalyst was characterized by Fourier-Transformed Infra-Red spectroscopy (FTIR), Scanning Electron Microscope/Energy dispersive X-ray spectroscopy (SEM-EDX), Brunauer-Emmet-Teller surface area (BET). The effect of different parameters e.g., reaction time, reaction temperature, feed to catalyst ratio and calcination temperature of synthesized catalyst are discussed for the production of BTEX. The product yield was characterized by ASTM distillation, flash and fire point, carbon residue, American Petroleum Institute (API) gravity, calorific value, FTIR analysis and GC analysis. Finally, the catalyst regeneration, performance of used and regenerated catalyst and stability of catalyst for pyrolysis of waste plastics are discussed at the end of this chapter. It should be noted that the thermal pyrolysis of waste plastics were performed for the comparison of performance between thermal and catalytic process and to obtain percentage enhancement in liquid yield and BTEX content for catalytic process.

4.1 Thermal Pyrolysis of Waste Plastics: Phase I

The thermal pyrolysis of waste plastic polyethylene, polypropylene and polystyrene, effect of different parameters and characterization of product yield are described in the following section.

4.1.1 Effect of parameters on pyrolysis yield

4.1.1.1 Effect of reaction time

The effect of reaction time on the conversion for thermal pyrolysis of polyethylene, polypropylene and polystyrene at a temperature of 700 ^{o}C are shown in Fig (4.1a), Fig (4.1b) and Fig (4.1c), respectively. It is clearly seen in the figure that the conversion rate decreases with the increase in reaction time for all three feed materials. 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 PE, PP and PS, respectively. The Fig (4.1a) to Fig (4.1c) show that there is no conversion after 25 min of reaction time. Thus, to ensure complete conversion and achieve maximum product yield, the thermal pyrolysis of PE, PP and PS were performed for 30 min.

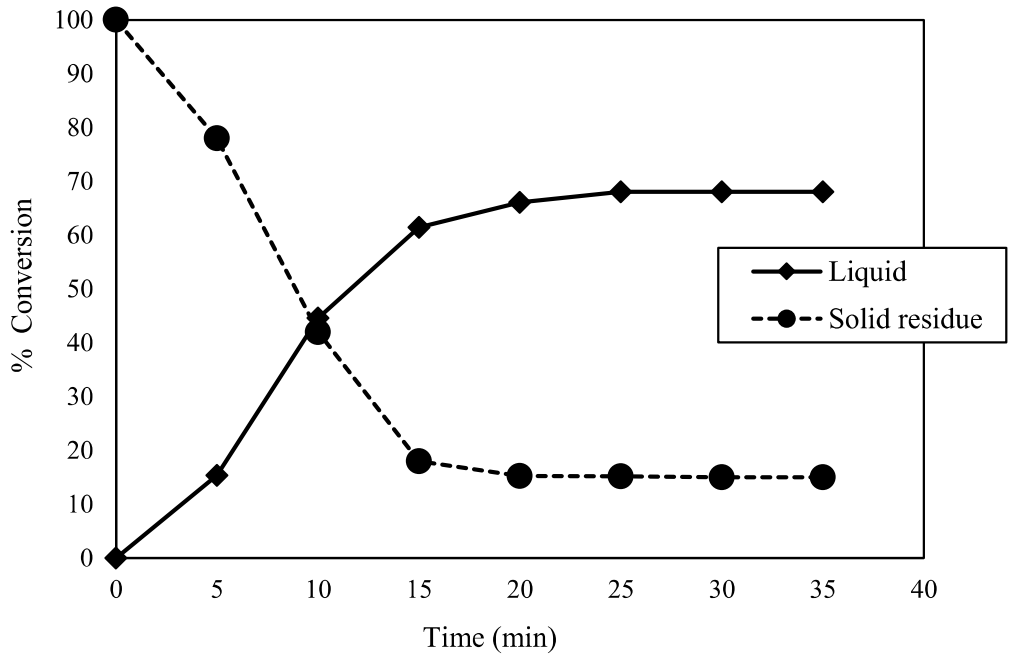

Figure 4.1a Time vs. percentage conversion of liquid and solid residue for thermal pyrolysis of polyethylene at the temperature of 700 °C.

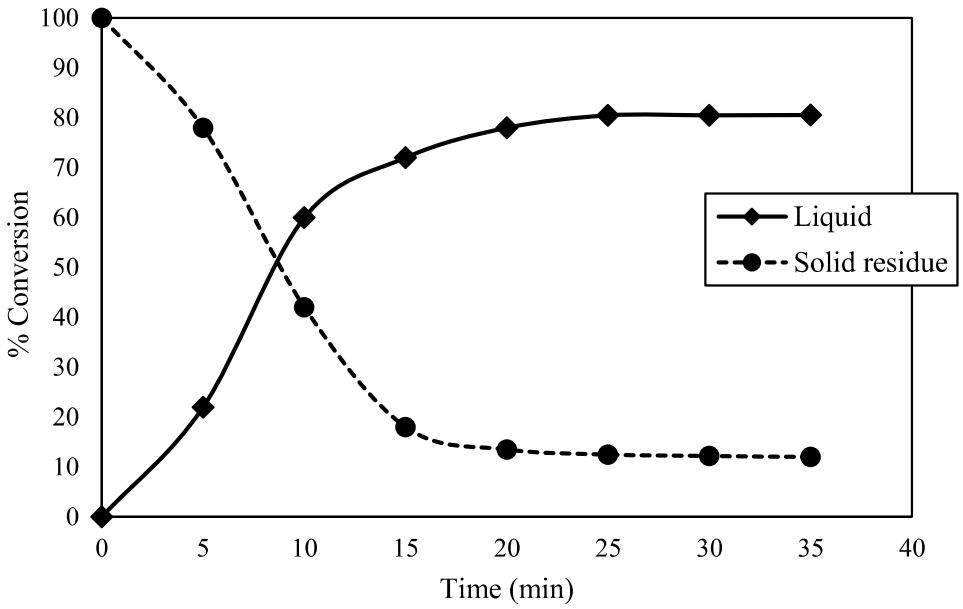

Figure 4.1b Time vs. percentage conversion of liquid and solid residue for thermal pyrolysis of polypropylene at the temperature of 700 °C.

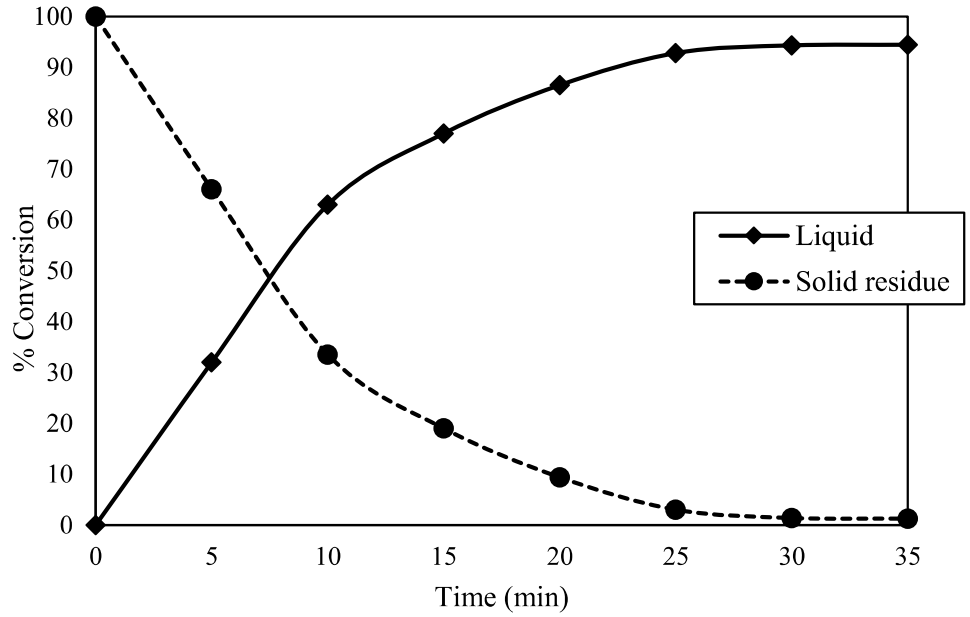

Figure 4.1c Time vs. percentage conversion of liquid and solid residue for thermal pyrolysis of polystyrene at the temperature of 700 °C.

4.1.1.2 Effect of reaction temperature

Fig (4.2a) to Fig (4.2c) show the effect of temperature on liquid, gaseous and solid residue yield for thermal pyrolysis of polyethylene, polypropylene and polystyrene, respectively.

The thermal pyrolysis of waste plastics PE, PP and PS were performed at the temperature ranging from 500 ^{o}C to 800 ^{o}C. Fig (4.2a) shows the thermal pyrolysis of waste plastic polyethylene at different temperature. It is seen in the Fig (4.2a) that liquid yield increases and solid residue decreases with the increase in temperature. The maximum liquid yield of 68.02 wt. % was obtained at a temperature of 700 ^{o}C. However, at a temperature of 800 ^{o}C, the obtained liquid yield (72.66 wt.%) was waxy at room temperature. It may be due to the high reaction temperature which does not allow the high molecular weight hydrocarbon to remain in the reactor for longer time and did not participate in further cracking process. Thus, they enter in the condenser and collected as pyrolysis oil which becomes waxy at room temperature. The maximum solid residue of 20 wt.% was obtained at a temperature of 500 ^{o}C for polyethylene. Whereas, it was only 9.4 wt.% at highest temperature of 800 ^{o}C (Fig 4.2a). It implies that more decomposition of higher molecular weight solid residue takes place at high temperature resulting in more liquid yield and non-condensable gases. Thus, obtained coke is less at high temperature.

The similar pattern is observed for thermal pyrolysis of polypropylene (Fig 4.2b) and polystyrene (Fig 4.2c) also. The liquid yield increases and solid residue decreases with the increase in temperature. The maximum liquid yield of 86.34 wt. % obtained at a temperature of 700 ^{o}C for the thermal pyrolysis of polypropylene as seen in Fig (4.2b). The liquid yield of 87.62 wt.% was obtained at a temperature of 800 ^{o}C and it solidifies at room temperature. The polypropylene feed showed similar trend as that of polyethylene. The highest solid residue of 19.6 wt.% was obtained at a temperature of 500 ^{o}C. However, solid residue decreased to 4.52 wt.% at the temperature of 800 ^{o}C for polypropylene (Fig 4.2b). Similar results have been reported by Abbas-Abadi et al., 2014. They performed PP pyrolysis in semi batch reactor at 450 ^{o}C and obtained liquid yield of 92.4 wt. %, gas yield of 3.6 wt. % and solid residue of 4.1 wt. % (Abbas-Abadi et al., 2014).

It is seen in Fig (4.2c) that the maximum liquid yield of 96 wt.% was obtained for the thermal pyrolysis of polystyrene at the temperature of 700 ^{o}C. There was about 5.5 wt.% increase in the pyrolysis oil when temperature was increased from 500 ^{o}C to 700 ^{o}C. Beyond the temperature 700 ^{o}C, the liquid yield decreased to 91.5 wt.% and gets solidify at the temperature of 800 ^{o}C. The solid residue coke keeps on decreasing from 7.32 wt.% to 2.27 wt.% up to the pyrolysis temperature 800 ^{o}C for polystyrene. As temperature increases the gaseous product increases and solid char decreases irrespective of feed materials polyethylene, polypropylene and polystyrene used in the pyrolysis process. At high temperature the lower molecular weight hydrocarbon (mainly liquid range) converts into gaseous range hydrocarbons. Lee et al., 2002 obtained similar results from pyrolysis of PS at 400 ^{o}C and obtained liquid yield of 90 wt. %, gas yield of 4 wt. % and solid residue of 6 wt. %.

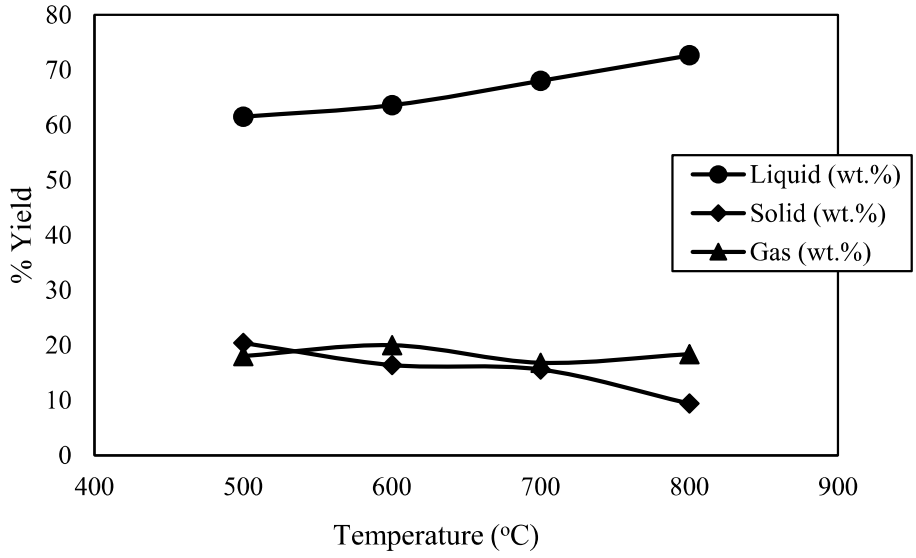

Figure 4.2a Temperature vs. % yield of pyrolysis product obtained from thermal pyrolysis of polyethylene.

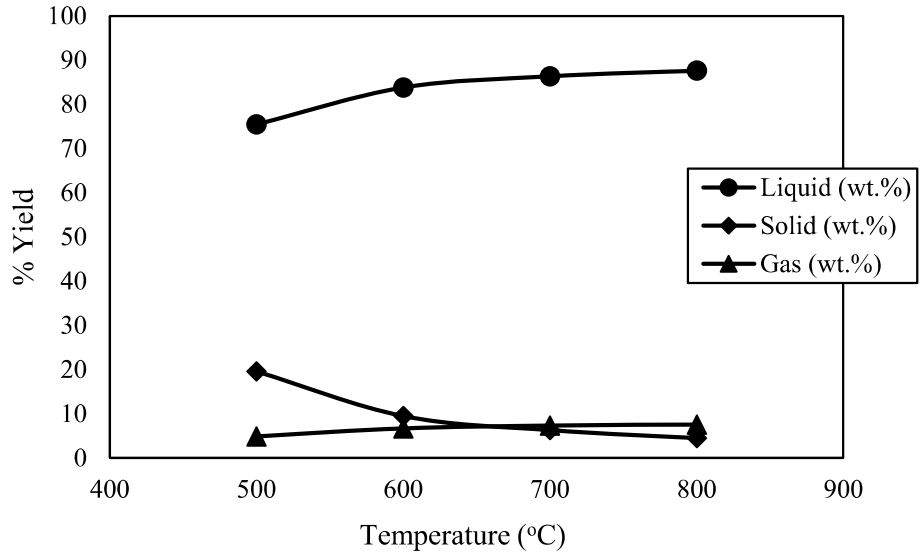

Figure 4.2b Temperature vs. % yield of pyrolysis product obtained from thermal pyrolysis of polypropylene.

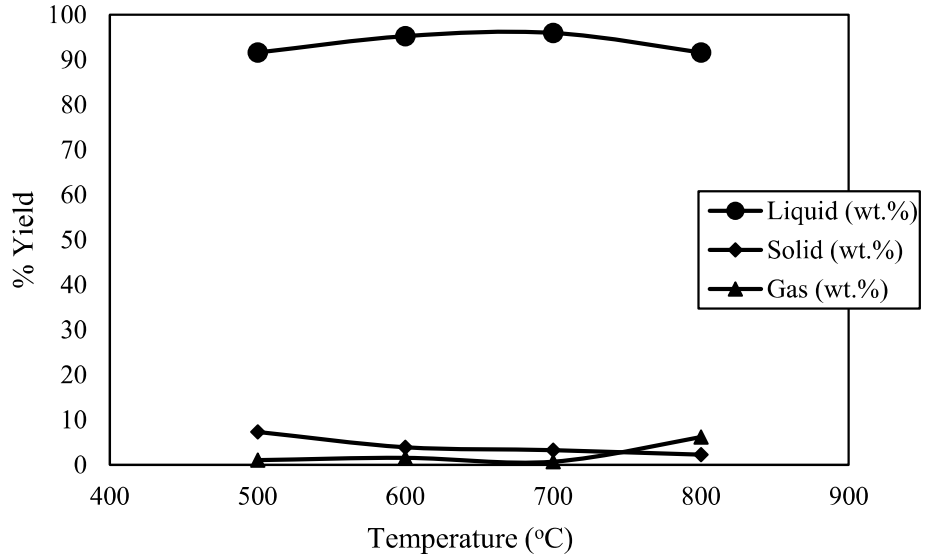

Figure 4.2c Temperature vs. % yield of pyrolysis product obtained from thermal pyrolysis of polystyrene.

The Table 4.1 shows the BTEX yield in commercial diesel, kerosene and gasoline obtained by GC-FID analysis. The effect of temperature on BTEX yield obtained by the pyrolysis of PE, PP and PS are presented in Table (4.2a) to Table (4.2c). The BTEX yield was evaluated in the pyrolysis oil, commercial diesel, kerosene and gasoline using calibration characteristics (Fig 3.9) as described in chapter 3 experimental section (Page no. 47). The

aromatics BTEX of commercial fuel oil was evaluated for comparison with the BTEX content in the pyrolysis oil of PE, PP and PS, respectively.

Table 4.1 The aromatic content (BTEX) of commercial diesel, kerosene and gasoline oil.

Sources of oil	Benzene (wt. %)	Toluene (wt. %)	Ethylbenzene (wt.%)	Xylene (wt. %)	Total BTEX (wt. %)
Commercial diesel	0.15	0.54	4.38	4.26	9.33
Commercial kerosene	0.01	0.0008	2.06	2.00	4.08
Commercial gasoline	0.88	14.88	5.26	15.43	36.45

It is seen in the Table (4.2a) that the maximum BTEX yield for polyethylene was 10.75 wt. % at the temperature of 700 ^{o}C. Whereas, maximum BTEX yield for polypropylene and polystyrene are found to be 30.91 wt. % and 13.58 wt. %, respectively. From these results it is clear that the optimum temperature is 700 ^{o}C for the production of BTEX using thermal pyrolysis of PE, PP and PS, respectively.

Table 4.2a The aromatic content (BTEX) in pyrolysis oil obtained from thermal pyrolysis of polyethylene at different temperature.

Pyrolysis temperature (^{o}C)	Benzene (wt. %)	Toluene (wt. %)	Ethylbenzene (wt.%)	Xylene (wt. %)	Total BTEX (wt. %)
500	0.001	0.24	3.93	5.93	10.10
600	0.002	0.28	4.12	6.11	10.51
700	0.003	0.32	4.21	6.22	10.75
800	0.002	0.22	4.01	6.03	10.45

Table 4.2b The aromatic content (BTEX) in pyrolysis oil obtained from thermal pyrolysis of polypropylene at different temperature.

Pyrolysis temperature (°C)	Benzene (wt. %)	Toluene (wt. %)	Ethylbenzene (wt.%)	Xylene (wt. %)	Total BTEX (wt. %)
500	3.26	1.1	2.16	20.63	27.15
600	3.41	1.4	2.27	22.09	29.17
700	3.55	1.5	2.34	23.52	30.91
800	3.43	1.2	2.19	21.34	28.16

Table 4.2c The aromatic content (BTEX) in pyrolysis oil obtained from thermal pyrolysis of polystyrene at different temperature.

Pyrolysis temperature (°C)	Benzene (wt. %)	Toluene (wt. %)	Ethylbenzene (wt.%)	Xylene (wt. %)	Total BTEX (wt. %)
500	0.21	7.13	2.90	0.93	11.17
600	0.28	7.93	3.06	1.36	12.63
700	0.31	8.57	3.23	1.47	13.58
800	0.22	7.22	2.81	1.18	11.43

4.1.2 Characterization of pyrolysis oil

The oil samples are characterized using ASTM distillation, flash and fire point, carbon residue, American Petroleum Institute (API) gravity, calorific value, FTIR analysis and GC-FID analysis for detail composition and fuel properties to check its usability as fuel in IC engine. The photographs of pyrolysis oil and solid residue obtained from thermal pyrolysis of polyethylene, polypropylene and polystyrene are shown in Appendix-A2**.**

4.1.2.1 Gas chromatography (GC) of pyrolysis oil

Fig (4.3a) to Fig (4.3c) show the GC-FID of the pyrolysis oil derived by the pyrolysis of the polyethylene, polypropylene and polystyrene at the optimum temperature of 700 °C,

commercial kerosene oil and diesel oil, respectively. It is seen in the Fig (4.3a) the chromatogram peaks for pyrolysis oil obtained at 700 ^{o}C from polyethylene are very close to kerosene and diesel oil in the range between 7 and 18 min of retention time. This range may be specifically interesting for the pyrolysis oil (700 ^{o}C) containing major compounds, which are similar as that of kerosene oil and diesel oil in terms of chemical structure (Nicholas, 1998). However, within the retention time range 1 to 7 min and 18 to 20 min GC peaks are found for pyrolysis oil and diesel oil only and it may be because of compounds of similar boiling point range (Fig 4.3a).

The similar trends were also observed for polypropylene (Fig 4.3b) and polystyrene (Fig 4.3c) as it was seen for polyethylene (PE) in (Fig 4.3a). The GC peaks in both PP and PS matches with the commercial kerosene and diesel oil. The GC-FID of standard/pure benzene, toluene, ethylbenzene and xylene were done to get retention time of individual compounds. 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. Fig (4.3a) to Fig (4.3c) shows the prominent peaks at the corresponding retention time for benzene, toluene, ethylbenzene and xylene (BTEX) in the pyrolysis oil obtained from thermal pyrolysis of polyethylene, polypropylene and polystyrene, respectively. A comparison between pyrolysis oil and commercial oils is shown to check the suitability of the use of pyrolysis oil in diesel engine and confirm its composition.

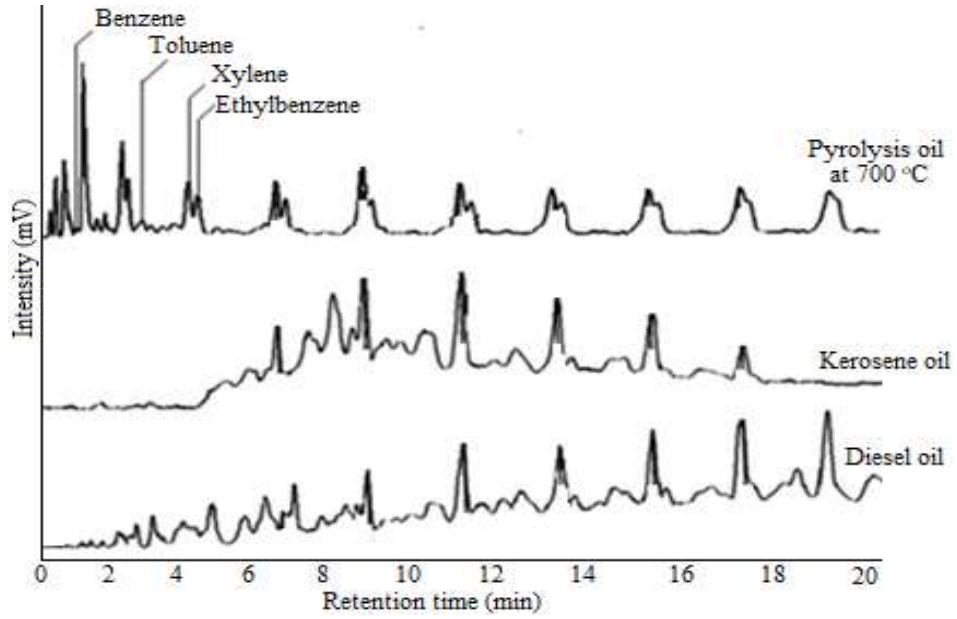

Figure 4.3a GC-FID of pyrolysis oil obtained at a temperature of 700 ºC for polyethylene, kerosene oil and diesel oil.

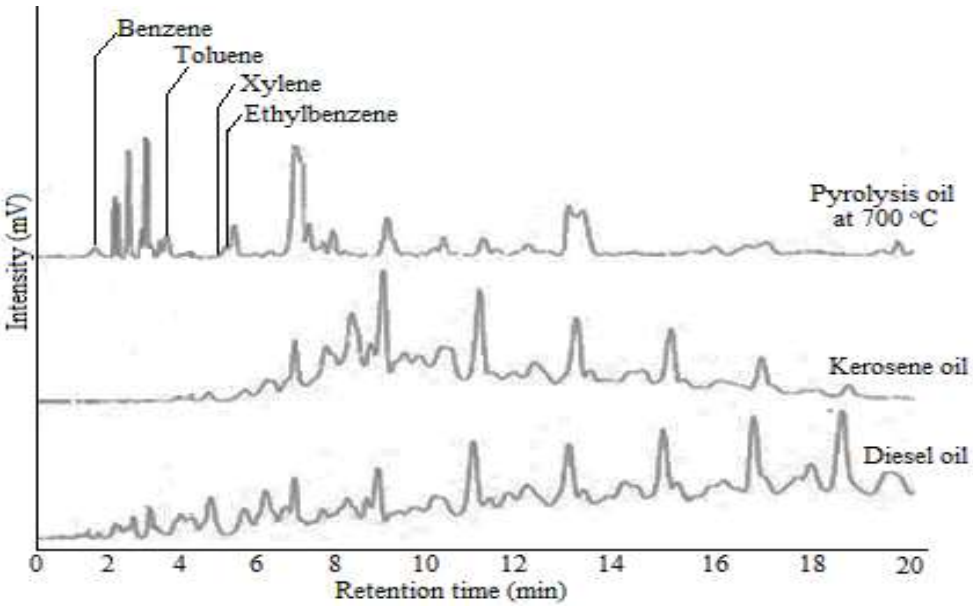

Figure 4.3b GC-FID of pyrolysis oil obtained at a temperature of 700 ºC for polypropylene, kerosene oil and diesel oil.

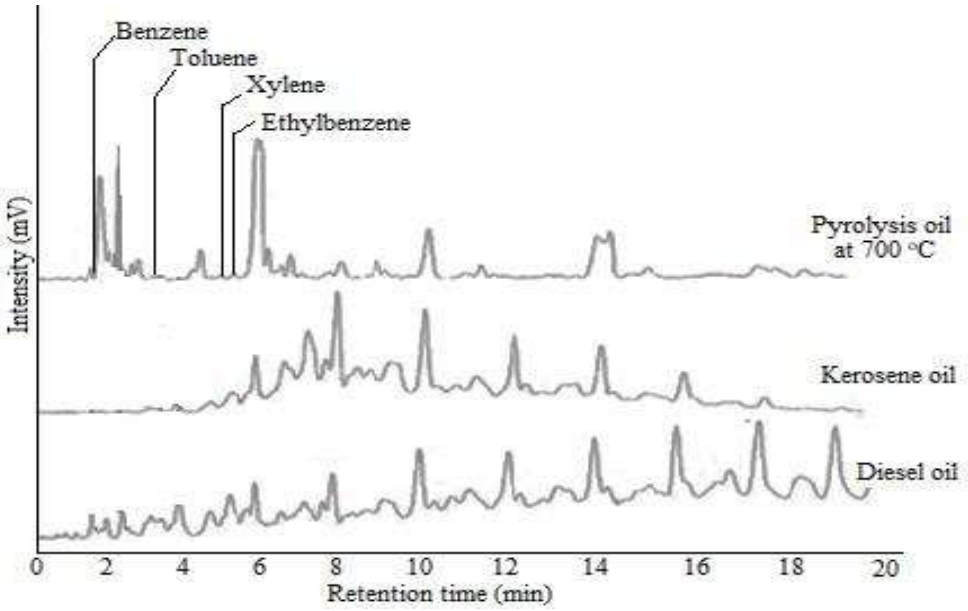

Figure 4.3c GC-FID of pyrolysis oil obtained at a temperature of 700 °C for polystyrene, kerosene oil and diesel oil.

4.1.2.2 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 vapours (Gaurh and Pramanik, 2018c). The distillation characteristics are critically important for both automotive and aviation gasolines affecting start-up of engine, warm-up and tendency to vapour lock at high operating temperature or at high altitude, or both. Fig (4.4a) to Fig (4.4c) show comparison between standard fuel (Perry and Green, 2007) and pyrolysis oil obtained from polyethylene, polypropylene and polystyrene at different temperature. The boiling point range of pyrolysis oil obtained from polyethylene (Fig 4.4a) at temperature of 500 °C, 600 °C and 700 °C lies in between gasoline and kerosene for the recovery of distillate 0-30 %. Similarly, the boiling point range of pyrolysis oil obtained at the temperature of 500 °C lies in between JP-4 and kerosene for the recovery

of distillate 30-95 % for polyethylene. In addition, the pyrolysis oil obtained at 500 ^{o}C tends to behaves as kerosene above 60 % recovery. Whereas, interestingly pyrolysis oil obtained at the temperature of 600 ^{o}C and 700 ^{o}C behave similar to diesel oil above 50 % of distillate recovery.

It is seen from Fig (4.4b) that the trend of ASTM curve for polypropylene is slightly different from ASTM characteristics of PE. The boiling point range of pyrolysis oil obtained from polypropylene (Fig 4.4b) at the temperature of 500 ^{o}C, 600 ^{o}C, 700 ^{o}C and 800 ^{o}C are almost same as gasoline for the recovery of distillate 0-30%. Pyrolysis oil lies in between gasoline and diesel for the recovery of distillate 30-55 % and it tends to behaves as diesel oil above 55 % recovery.

Fig (4.4c) shows the comparison between standard fuel and pyrolysis oil obtained from polystyrene at the temperatures of 500 ^{o}C, 600 ^{o}C, 700 ^{o}C and 800 ^{o}C, respectively. The boiling point range of pyrolysis oil obtained at temperature of 700 ^{o}C for thermal pyrolysis lies in between heavy naphtha and paint 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 above 75 % of distillate recovery for thermal and catalytic pyrolysis.

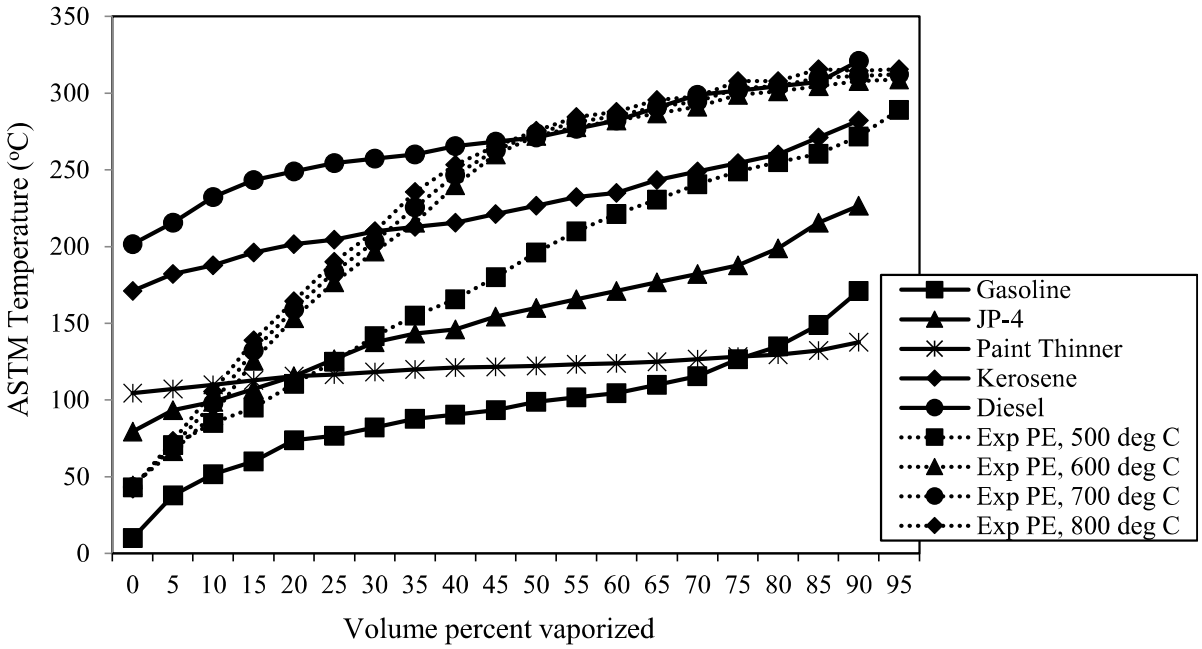

Figure 4.4a Volume percent vaporized vs. ASTM temperature characteristics of standard fuel and pyrolysis oil obtained from polyethylene.

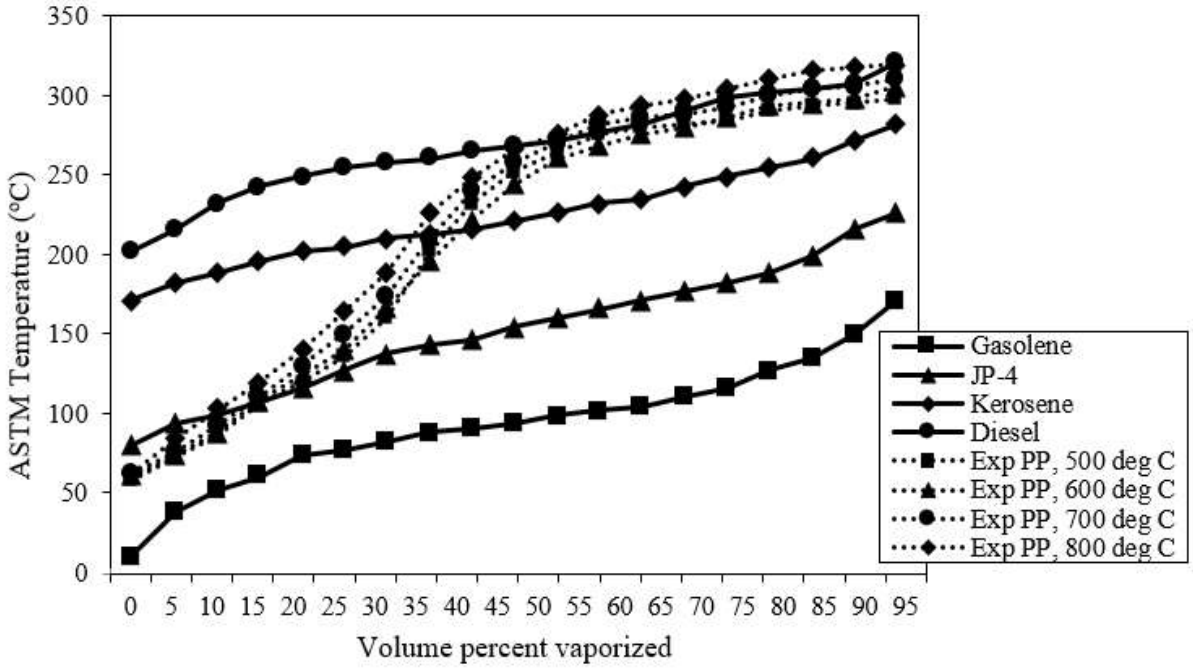

Figure 4.4b Volume percent vaporized vs. ASTM temperature characteristics of standard fuel and pyrolysis oil obtained from polypropylene.

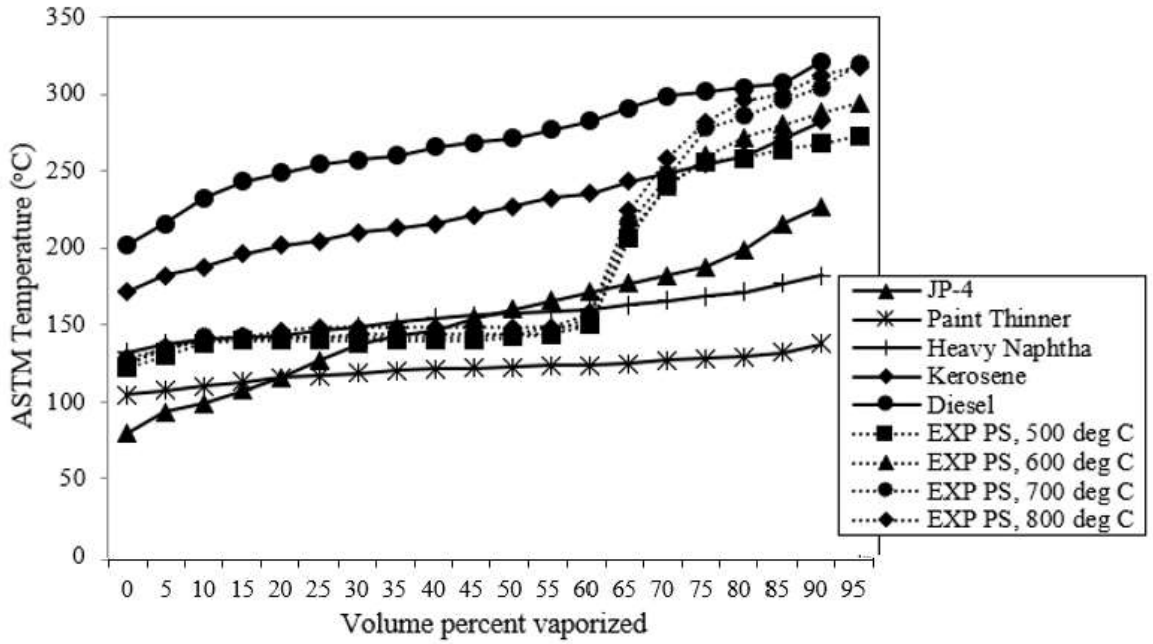

Figure 4.4c Volume percent vaporized vs. ASTM temperature characteristics of standard fuel and pyrolysis oil obtained from polystyrene.

4.1.2.3 FTIR analysis

The 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. In order to gather systematic information about the chemical composition of the pyrolysis oil, the resultant fuels were examined using FTIR in the wavelength range of 3200-600 cm^{-1}. Fig (4.5) shows the FTIR spectra of liquid fuel obtained at optimized condition by thermal pyrolysis of waste PE, PP and PS. As expected, there are only slight differences among the first two spectra. This is due to the strong resemblance among polymeric structures. The spectra confirm that these fuels are composed of aliphatic groups comprising carbon and hydrogen atoms. The presence of alkanes is detected at 2954 cm^{-1} for PE, 2944 cm^{-1} for PP and 3024 cm^{-1} for PS with C–H stretching vibrations. C=C stretching vibrations at 1645 cm^{-1} for PE, 1768 cm^{-1} for PP and 1662 cm^{-1} for PS indicates

the presence of alkenes/fingerprint region. This band 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 1454 cm^{-1} for PE, 1415 cm^{-1} for PP and 1461 cm^{-1} for PS which verify the presence of benzene derivatives in the pyrolysis oil. C–H bending vibrations at 976 cm^{-1} for PE, 968 cm^{-1} for PP and 966 cm^{-1} for PS indicates the presence of alkenes. The 890-886 cm^{-1} band certified the presence of vinylidene functional group in the chemical composition of pyrolysis oil. The C–H bending vibrations at frequency 732 cm^{-1} for PE, 722 cm^{-1} for PP and 738 cm^{-1} for PS indicates the presence of phenyl ring substitution bands. This region confirms mono or ortho substitution of benzene ring. Thus, it can be summarized that pyrolysis oil is a complex mixture of paraffinic, olefinic and aromatic compounds (Djebara et al., 2012; Fernández et al., 2012; Heydariaraghi et al., 2016; Jin et al., 2016; Kumar et al., 2013; Williams and Williams, 1997). The FT-IR data of pyrolysis oil is substituted using GC-FID analysis of the oil obtained by the similar condition.

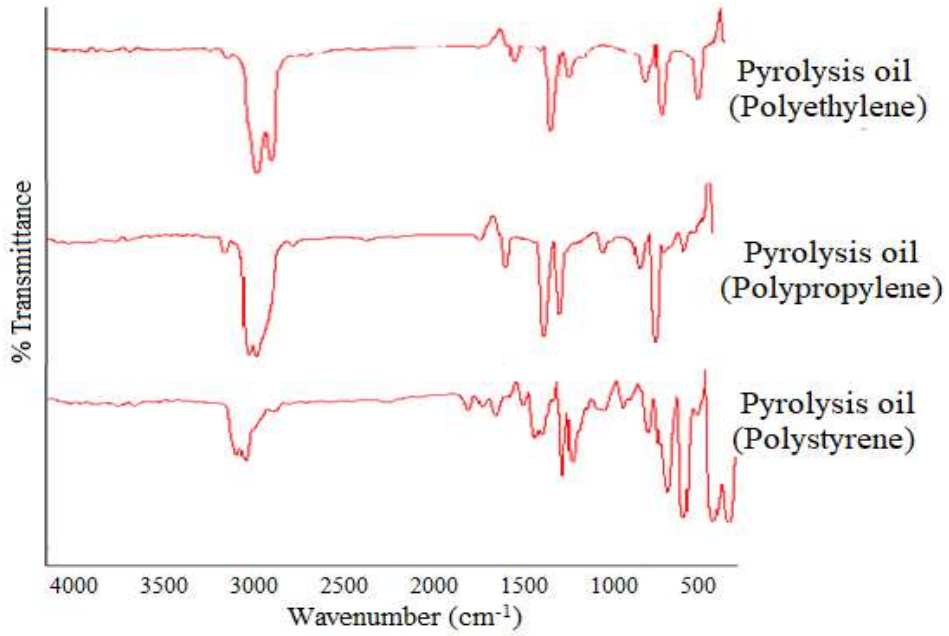

Figure 4.5 FT-IR spectrometry of liquid fuel obtained at optimized condition (700 °C) by thermal pyrolysis of waste polyethylene, polypropylene and polystyrene.

4.1.2.4 Physicochemical properties of pyrolysis oil

Table (4.3a) to Table (4.3c) show the results of physicochemical property analysis of liquid fuel obtained at optimized condition from thermal pyrolysis of waste PE, PP and PS, respectively. The appearance of the all pyrolysis oil were dark yellowish free from visible sediments. The flash point of the liquid product obtained from waste PE, PP and PS were found in a comparable range and thus, it is expected not to cause any trouble in most of the engines. The gross calorific value (GCV) for liquid fuel obtained by thermal pyrolysis of waste PE was 10982 Cal/g which is in the range of gasoline and diesel. Thus, this liquid product would perform relatively well in IC engines. However, GCV of pyrolysis oil obtained from waste PP and PS were 9015.48 Cal/g and 7073.37 Cal/g, which are lower in comparison to waste PE. The PE, PP and PS produced very low carbon residue of 0.28 wt. %, 0.24 wt. % and 0.86 wt. %, respectively at a temperature of 700 ^{o}C. This indicates good fuel property as carbon residue is less than 1 wt. % in all pyrolysis oil at a temperature 700 ^{o}C. This also confirms that pyrolysis oil contains very low amount of aromatics. From these studies, it is observed that the product oil from all three waste plastics could be possible feedstock for further upgrading to use in diesel engine besides recovery of BTEX as a valuable product.

Table 4.3a Physicochemical properties of pyrolysis oil obtained at different temperatures for polyethylene.

Physicochemical Properties	**Test method**	**Pyrolysis Temperature**			
		500 ^{o}C	**600 ^{o}C**	**700 ^{o}C**	**800 ^{o}C**
Flash point (^{o}C)	ASTM D 92	31	29	27	26
Fire point (^{o}C)	ASTM D 92	35	34	32	30
Carbon residue (wt. %)	IP 14/65	0.39	0.32	0.28	0.33
Specific gravity	ASTM D 1298	0.793	0.782	0.768	0.787
API gravity (^{o})	API correlation	46.95	49.91	52.65	48.30
Calorific value (Cal/g)	IP 12/63 T	9965	10512	10982	10090

Table 4.3b Physicochemical properties of pyrolysis oil obtained at different temperatures for polypropylene.

Physicochemical Properties	**Test method**	**Pyrolysis Temperature**			
		500 °C	**600 °C**	**700 °C**	**800 °C**
Flash point (°C)	ASTM D 92	33	31	28	30
Fire point (°C)	ASTM D 92	36	34	31	33
Carbon residue (wt. %)	IP 14/65	0.38	0.29	0.24	0.32
Specific gravity	ASTM D 1298	0.806	0.793	0.781	0.788
API gravity (°)	API correlation	44.06	46.94	49.68	48.06
Calorific value (Cal/g)	IP 12/63 T	8674.2	8883.1	9015.48	8612.3

Table 4.3c Physicochemical properties of pyrolysis oil obtained at different temperatures for polystyrene.

Physicochemical Properties	**Test method**	**Pyrolysis Temperature**			
		500 °C	**600 °C**	**700 °C**	**800 °C**
Flash point (°C)	ASTM D 92	32	33	35	39
Fire point (°C)	ASTM D 92	36	38	39	43
Carbon residue (wt. %)	IP 14/65	0.99	0.92	0.86	0.93
Specific gravity	ASTM D 1298	0.873	0.852	0.847	0.887
API gravity (°)	API correlation	30.58	34.58	35.56	28.03
Calorific value (Cal/g)	IP 12/63 T	6865.7	6993.20	7073.37	6735.4

4.2 Catalytic Pyrolysis of Waste Plastics: Phase II

The catalytic pyrolysis of waste plastics like polyethylene, polypropylene and polystyrene were performed on commercial catalyst ZSM-5 and synthesized natural catalyst derived from fly ash. The effect of different parameters, characterization of product yield and suitability of catalysts for the catalytic pyrolysis of waste plastics viz polyethylene, polypropylene and polystyrene are described in the following section.

4.2.1 Pyrolysis of waste plastics on ZSM-5 catalyst

4.2.1.1 Effect of parameters on pyrolysis yield

4.2.1.1.1 Effect of feed to catalyst ratio

The catalytic pyrolysis of waste polyethylene, polypropylene and polystyrene were performed at different feed to catalyst ratio of 10:1, 20:1 and 30:1 for A-type (vapor phase), B-type (liquid phase) and C-type (vapor and liquid/multiphase) reactor arrangements, respectively. The detailed reactor arrangement is shown in the experimental section (page no. 39). Fig (4.6a) to Fig (4.6c) show the comparison of liquid yield, gas yield and solid residue of catalytic pyrolysis of waste PE, PP and PS at a temperature of 700 ^{o}C for A-type reactor arrangement. The effect of feed to catalyst ratio is presented here for A-type reactor arrangement as A-type gives maximum liquid yield irrespective of types of waste plastics used. Although not shown here, the effect of feed to catalyst ratio for B-type and C-type reactor arrangements are presented in Appendix-A3. It is seen form Fig (4.6a) that the feed to catalyst ratio of 20:1 (PE to ZSM-5) gives maximum liquid yield of 72.72 wt. % because of the large number of active 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 70.34 wt. % with maximum solid residue of 9.25 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 in 10:1 feed to catalyst ratio, the process would be less feasible as compared to 20:1 feed to catalyst ratio.

Similar results were obtained for polypropylene and polystyrene as shown in Fig (4.6b) and Fig (4.6c), respectively. The maximum liquid yield for polypropylene of 86.3 wt. % was obtained at feed to catalyst ratio of 20:1 as shown in Fig (4.6b). For polystyrene, maximum liquid yield of 88 wt. % was obtained at 20:1 feed to catalyst ratio. However, feed to catalyst ratio of 30:1 produced liquid yield of 83.97 wt. % and 85.84 wt. % for polypropylene and polystyrene, respectively. Thus, all the catalytic pyrolysis of polyethylene, polypropylene and polystyrene were carried out using feed to catalyst ratio of 20:1, irrespective of the reactor arrangements and all other process parameters used.

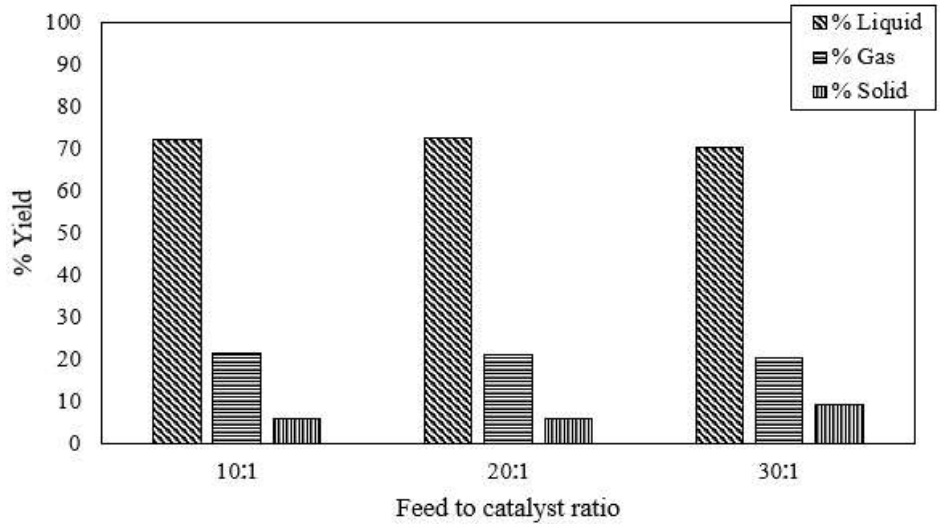

Figure 4.6a Comparison of liquid yield, gaseous yield and solid residue at 700 ^{o}C for A-type (Vapor phase) arrangement using ZSM-5 for 50 g of polyethylene.

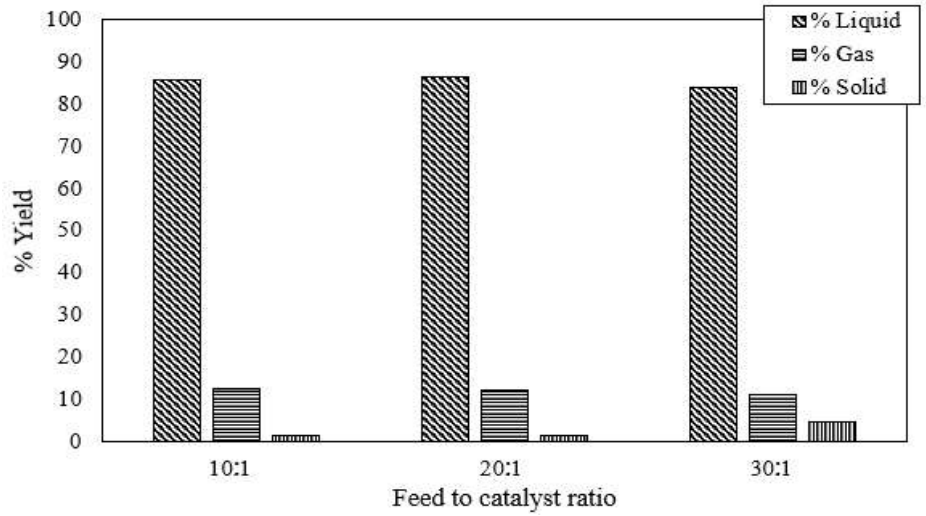

Figure 4.6b Comparison of liquid yield, gaseous yield and solid residue at 700 ºC for A-type (Vapor phase) arrangement using ZSM-5 for 50 g of polypropylene.

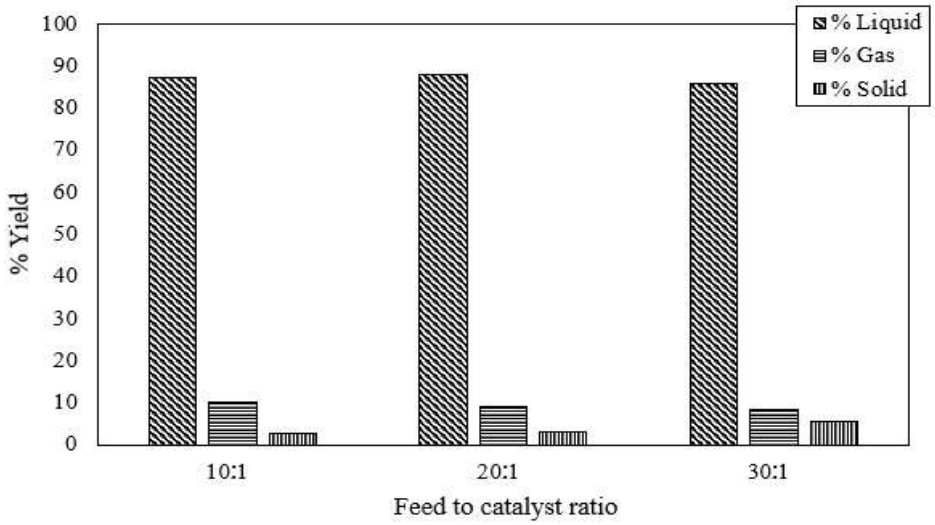

Figure 4.6c Comparison of liquid yield, gaseous yield and solid residue at 700 ºC for A-type (Vapor phase) arrangement using ZSM-5 for 50 g of polystyrene.

4.2.1.1.2 Effect of reaction time

The effect of reaction time on the conversion for catalytic pyrolysis of polyethylene, polypropylene and polystyrene using ZSM-5 at a temperature of 700 ºC is shown in Fig (4.7a) to Fig (4.7c) for A-type reactor arrangement. The effect of reaction time for A-type and C-type are presented in Appendix-A4. The percentage conversion increases with the increase in reaction time for all three waste plastics, polyethylene, polypropylene and

polystyrene, respectively. This indicates that the reaction time plays vital role for the conversion of waste plastic and achieving product yield. After 25 min, the percentage conversion becomes constant for PE, PP and PS. The Fig (4.7a), Fig (4.7b) and Fig (4.7c) shows that there is no conversion after 25 min of reaction time. Thus, to ensure complete conversion and achieve maximum product yield, catalytic pyrolysis of PE, PP and PS were performed for 30 min for all three A-type, B-type and C-type reactor arrangements.

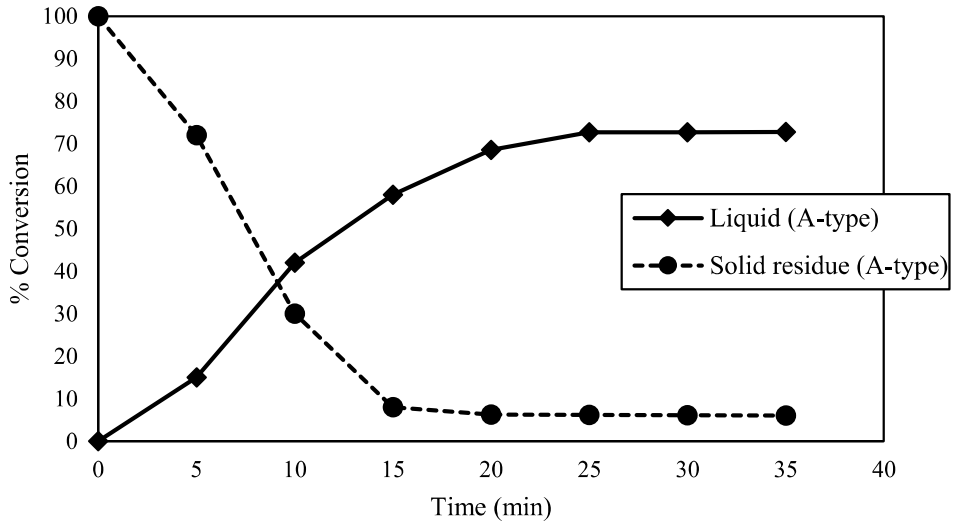

Figure 4.7a Time vs. percentage conversion of liquid and solid residue for catalytic pyrolysis of polyethylene using ZSM-5 catalyst at the temperature of 700 °C in A-type reactor arrangement (Vapor phase).

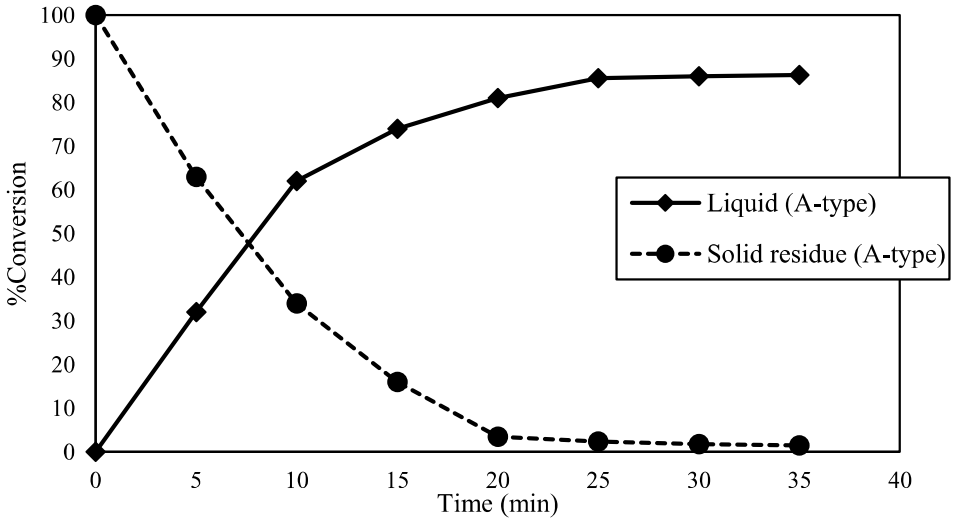

Figure 4.7b Time vs. percentage conversion of liquid and solid residue for catalytic pyrolysis of polypropylene using ZSM-5 catalyst at the temperature of 700 °C in A-type reactor arrangement (Vapor phase).

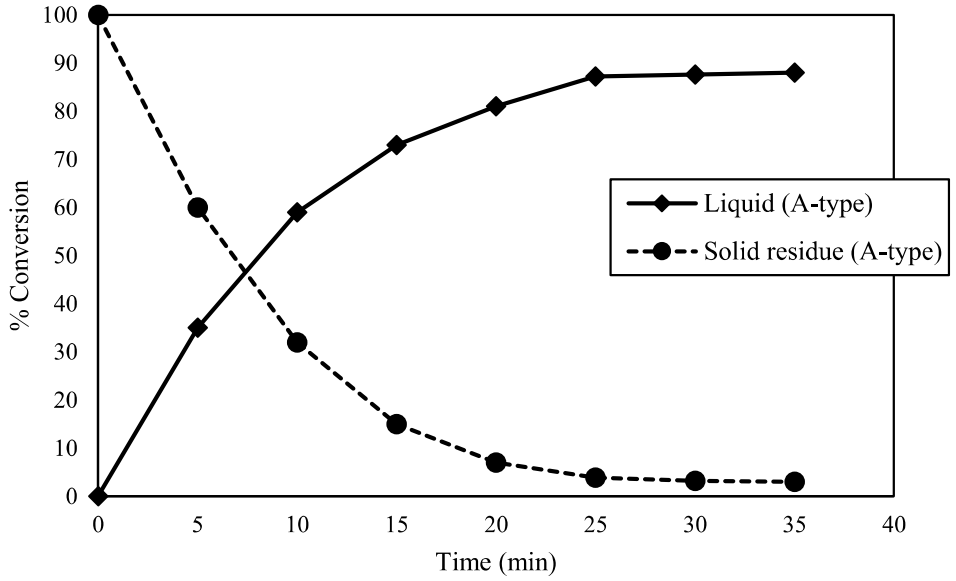

Figure 4.7c Time vs. percentage conversion of liquid and solid residue for catalytic pyrolysis of polystyrene using ZSM-5 catalyst at the temperature of 700 °C in A-type reactor arrangement (Vapor phase).

4.2.1.1.3 Effect of reaction temperature

4.2.1.1.3.1 Polyethylene as feed

Fig (4.8a) to Fig (4.8c) show the product yield obtained for A-type, B-type and C-type reactor arrangements using catalytic pyrolysis of polyethylene at the temperature of 500 ^{o}C, 600 ^{o}C, 700 ^{o}C and 800 ^{o}C, respectively. The optimum feed to catalyst ratio of 20:1 and reaction time 30 min were maintained for the reaction process. The product yield obtained are compared for different reactor arrangements to show the improvement in product qualitatively and quantitatively for the liquid yield, gaseous yield and solid residue, respectively. The maximum liquid yield of 72.72 wt. %, 58.68 wt. % and 46.36 wt. % at a temperature of 700 ^{o}C were obtained for catalytic pyrolysis in the reactor arrangement A-type, B-type and C-type respectively (Fig 4.7a). The use of catalyst decreases the quantity of liquid yield in comparison to thermal process, but increases the quality of liquid oil in terms of aromatics BTEX, which is discussed later on (page no. 76). The catalyst affects the pyrolysis mechanism and converts the heteroatoms into a gaseous range hydrocarbon.

It is clearly seen in Fig (4.8b) that the gaseous yield obtained was maximum (49.46 wt. %) for C-type/multiphase reactor arrangement, irrespective of temperature. Thus, the liquid yield obtained is minimum (46.36 wt. %) for C-type reactor arrangement. The gaseous yield for catalytic pyrolysis increases, when catalyst interacts with cracked molecule within the reactor, as shown in Fig (3.3b-d) of experimental section chapter 3.

The reaction takes place in a recognized pyrolysis process of polyethylene [$(C_2H_4)n.H_2$] can be expressed as:

$(C_2H_4)n.H_2 + Q \longrightarrow$ Liquid hydrocarbon+ Gas hydrocarbon + Solid residue (4.1)

Where Q is the heat that needs to be input to the reactor for the reactions to take place (Castano et al., 2011) .

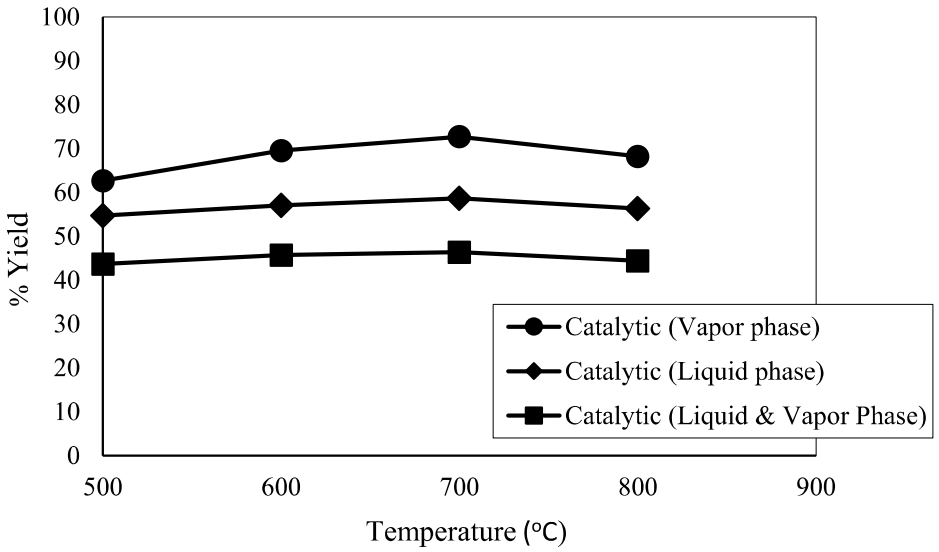

Figure 4.8a Temperature vs. % liquid yield obtained from the catalytic pyrolysis of polyethylene using A-type, B-type and C-type reactor arrangements.

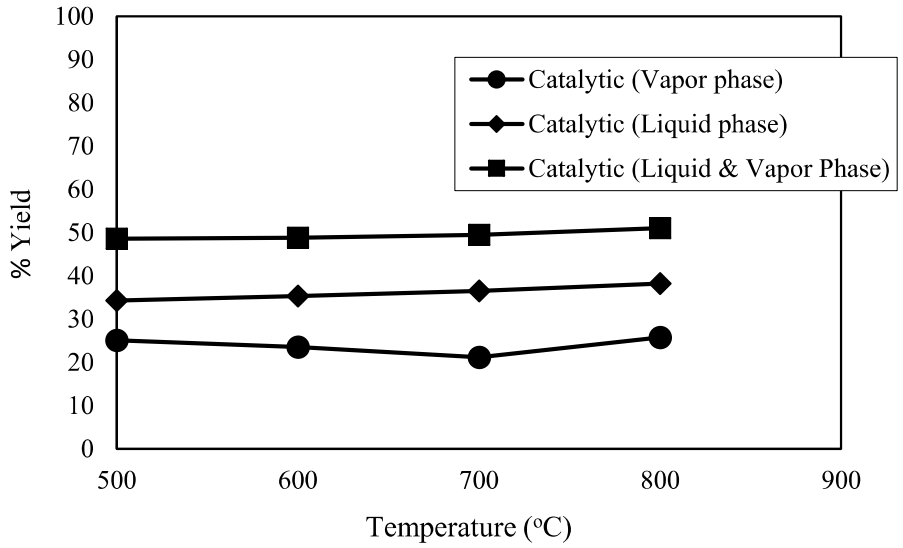

Figure 4.8b Temperature vs. % gas yield obtained from the catalytic pyrolysis of polyethylene using A-type, B-type and C-type reactor arrangements.

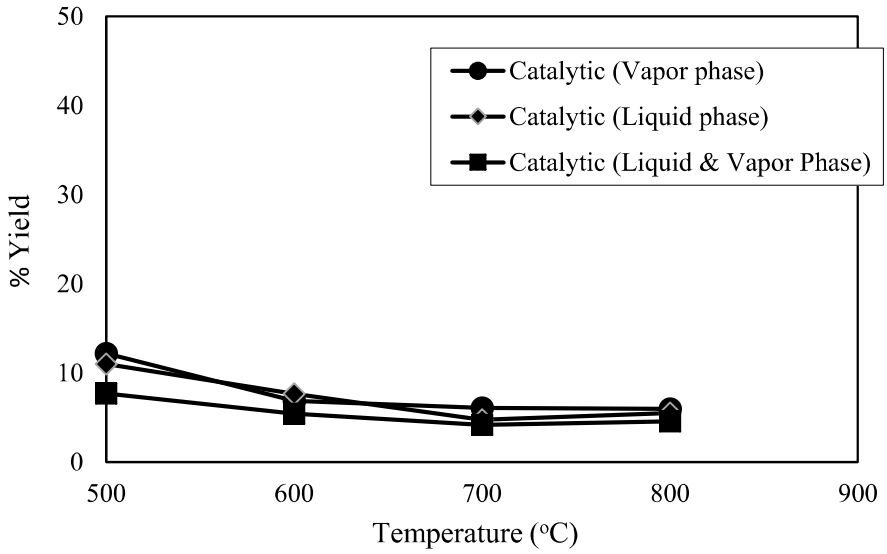

Figure 4.8c Temperature vs. % solid residue obtained from the catalytic pyrolysis of polyethylene using A-type, B-type and C-type reactor arrangements.

It is seen in the Fig (4.8c) that solid residue gets reduced for catalytic pyrolysis in the reactor arrangements in the order A-type (vapor phase) > B-type (liquid phase) > C-type (liquid and vapor/multiphase). Moreover, solid residue decreases for catalytic pyrolysis in the reactor arrangements A-type, B-type and C-type in comparison to that of thermal pyrolysis. The gaseous yield for catalytic pyrolysis increases, when catalyst interacts with cracked molecule within the reactor, as shown in Fig (3.3b–d). The catalyst in vapor phase (A-type)

results in maximum liquid yield of 72.72 wt.% and solid residue of 6.06 wt.%. It may be due to selective cracking at vapor phase of comparatively higher molecular weight hydrocarbon which are produced via thermal cracking at the bottom of reactor. According to Lopez-Urionabarrenechea et al., 2012 and Miskolczi et al., 2006, the use of catalyst increases the quality of liquid oil. The catalyst presences reduced the liquid fraction and increased the gaseous fraction (Syamsiro et al., 2014). In the catalytic cracking using B-type reactor arrangement, liquid yield further decreases (58.68 wt.%), gaseous yield increases (36.56 wt.%) and solid residue decreases (4.76 wt.%). In the arrangement B, the ZSM-5 catalyst is in contact with polyethylene from the beginning of the reaction. Thus, largest to smallest hydrocarbon molecules may interact with the ZSM-5, which results in more aromatics and gaseous hydrocarbon.

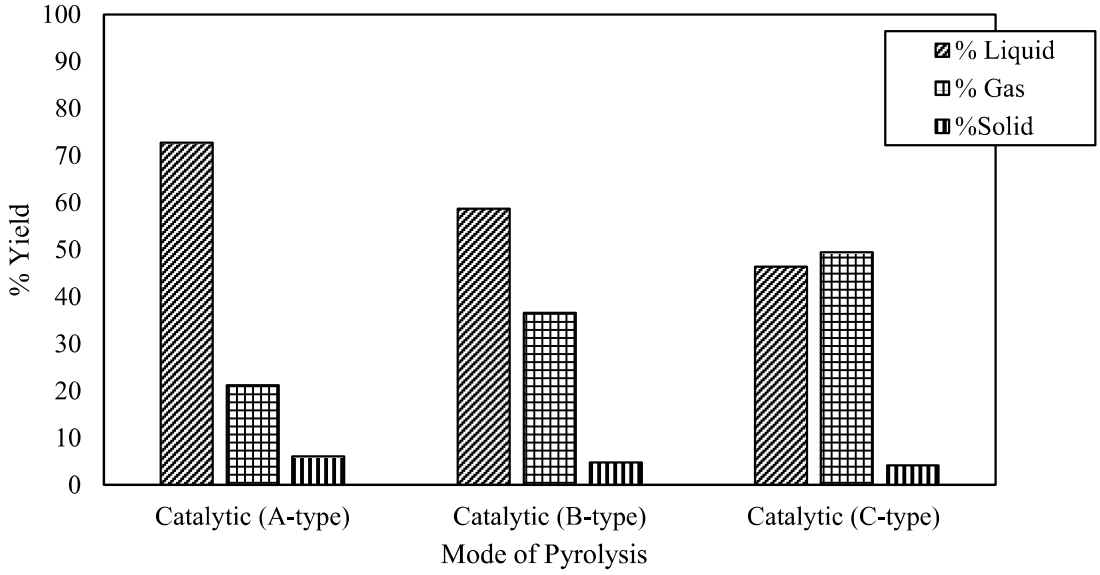

Figure 4.9 Comparison between liquid, gaseous and solid residue obtained at optimum temperature of 700 ^{o}C for polyethylene.

It is seen in the Fig (4.9) that the C- type (multiphase) produced lowest liquid yield of 46.36 wt. % and maximum gaseous yield of 49.46 wt. % at the optimum temperature of 700 ^{o}C. Higher gaseous yield for multiphase reaction may be due to the catalyst is in both liquid and vapor phase helps in two stage catalytic reaction of alkanes. In the first stage, the

catalytic pyrolysis is same as that of B type arrangement (liquid phase) followed by a second stage pyrolysis in the vapor phase of lighter alkanes which escapes from first stage. Thus, C arrangements behaves as a multiphase catalytic pyrolysis with more production of aromatics/BTEX and gaseous hydrocarbons.

Evaluation of BTEX yield in the pyrolysis oil/liquid yield is main aim of the thesis work. Thus, the calibration characteristics (Fig 3.9) were developed for the evaluation of BTEX in the pyrolysis oil obtained by the catalytic pyrolysis of PE, PP and PS using ZSM-5 catalyst as described in chapter 3 experimental section (Page no. 47). Table (4.4) shows the aromatic content (BTEX) in pyrolysis oil obtained from the catalytic pyrolysis of waste plastic polyethylene at different temperatures.

Table 4.4 The aromatic content (BTEX) in pyrolysis oil obtained from polyethylene at different temperatures.

Pyrolysis temperature (°C)		**Benzene (wt. %)**	**Toluene (wt. %)**	**Ethylbenzene (wt.%)**	**Xylene (wt. %)**	**Total BTEX (wt. %)**
500	A-type	0.21	2.37	3.86	6.13	12.57
	B-type	8.53	0.31	4.17	11.94	24.95
	C-type	12.92	2.38	4.21	15.24	34.75
600	A-type	0.25	3.18	3.98	6.94	14.35
	B-type	10.19	0.36	4.28	12.72	27.55
	C-type	14.21	2.51	4.39	16.54	37.65
700	A-type	0.27	3.54	4.23	7.11	15.15
	B-type	12.35	0.40	4.32	13.14	30.21
	C-type	15.36	2.66	4.42	17.03	39.47
800	A-type	0.22	2.58	3.88	6.37	13.05
	B-type	9.27	0.31	4.23	12.09	25.9
	C-type	12.56	2.41	4.27	15.63	34.87

It is seen from Table (4.4) that the highest amount of aromatic content i.e., 39.47 wt.% was found in the pyrolysis oil at a temperature of 700 ^{o}C using catalyst in multiphase/C-type reactor arrangement. It may be due to the ZSM-5 catalyst, having smaller pore size provides higher selectivity for lower alkanes. Thus, for the C-type pyrolysis, smaller molecules in the liquid and vapor phase both comes in contact with ZSM-5. This gives maximum BTEX yield of 39.47 wt. % as per the reaction schemes shown in the Fig (4.10). The C-type/ multiphase pyrolysis produced benzene, toluene, ethylbenzene and xylene are in maximum quantity irrespective of temperatures and reactor arrangements. It is generally proposed that on acid catalysts the aromatization of alkanes occurs through protolysis of alkane, cracking of carbonium ion to alkane and alkene, oligomerization of alkenes, cyclization of oligomerized products and formation or aromatics from cyclic rings by hydrogen transfer. However, catalyst in vapor phase (A) only interacts with the molecules which comes from thermal pyrolysis in the liquid phase. Thermal pyrolysis is non-selective, which gives the product may not be suitable for aromatization in vapor phase. Thus, catalytic pyrolysis (A-type) gives lower BTEX (15.15 wt.%) than C-type at a temperature of 700 ^{o}C. For the B-type catalytic pyrolysis, the catalyst is in contact with PE from the beginning, resulting in selective cracking of wide range of molecules. Thus, B-type arrangement gives BTEX yield of 30.21 wt. % which is more than A-type (15.16 wt. %) at the same temperature. As discussed earlier, among all pyrolysis, C-type (vapor and liquid phase) catalytic reactor arrangement gives highest BTEX yield of 39.47 wt. %. Thus, C-type reactor arrangement could be recommended as suitable design to convert polyethylene into BTEX which is value added upgraded product. It is seen in Table (4.1) that commercial gasoline also contains about 36.45 wt. % BTEX to improve octane rating of fuel. It should be noted that the thermal pyrolysis of polyethylene produced very low BTEX yield of 10.75 wt.% at the same temperature of 700 ^{o}C (Table 4.2a, page no. 57).

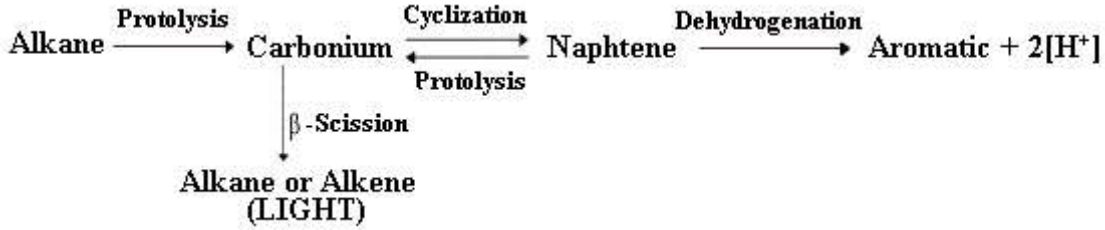

Figure 4.10 Reaction scheme of aromatization

4.2.1.1.3.2 Polypropylene as feed

Fig (4.11a) to Fig (4.11c) show the product yield obtained for A-type, B-type and C-type reactor arrangements using catalytic pyrolysis of polypropylene at the temperature of 500 ^{o}C, 600 ^{o}C, 700 ^{o}C and 800 ^{o}C, respectively. The optimum feed to catalyst ratio of 20:1 and reaction time 30 min were maintained for the reaction process. The product yield obtained are compared for different reactor arrangements to show the improvement in product qualitatively and quantitatively for the liquid yield, gaseous yield and solid residue, respectively. The maximum liquid yield of 86.3 wt. %, 82.2 wt. % and 82.0 wt. % at a temperature of 700 ^{o}C were obtained for catalytic pyrolysis in the reactor arrangement A-type, B-type and C-type respectively (Fig 4.11a). The use of catalyst decreases the quantity of liquid yield in comparison to thermal process but increases the quality of liquid oil in terms of aromatics BTEX, which is discussed later on (page no. 81). The catalyst affects the pyrolysis mechanism and converts the heteroatoms into a gaseous range hydrocarbon. It is clearly seen in Fig (4.11b) that the gaseous yield obtained was maximum (16.8 wt.%) for C-type/multiphase reactor arrangement, irrespective of temperature. Thus, the liquid yield obtained was minimum (82.0 wt.%) for C-type reactor arrangement.

As discussed for the polyethylene in the previous section, the similar trend for solid residue was also found in the case of polypropylene. It is seen in the Fig (4.11c) that solid residue get decreases for catalytic pyrolysis in the reactor arrangements in the order B-type (liquid

phase) > A-type (vapor phase) > C-type (liquid and vapor/multiphase). Moreover, solid residue gets reduced for catalytic pyrolysis using the reactor arrangements A-type, B-type and C-type in comparison to that of thermal pyrolysis. The gaseous yield for catalytic pyrolysis increases, as the catalyst interacts with cracked molecule within the reactor, which is shown in Fig (3.3b–d). The catalyst in vapor phase (A-type) results in maximum liquid yield of 86.3 wt.% and solid residue of 1.5 wt.%. It may be due to selective cracking at vapor phase of comparatively higher molecular weight hydrocarbon which are produced via thermal cracking at the bottom of reactor. In the catalytic cracking (B-type), liquid yield further decreases (82.2 wt.%), gaseous yield increases (12.6 wt.%) and solid residue increases (5.2 wt.%). In the arrangement B, the ZSM-5 catalyst is in contact with polypropylene from the beginning of the reaction. Thus, largest to smallest hydrocarbon molecules may interact with the ZSM-5, which results in more aromatics and gaseous hydrocarbon.

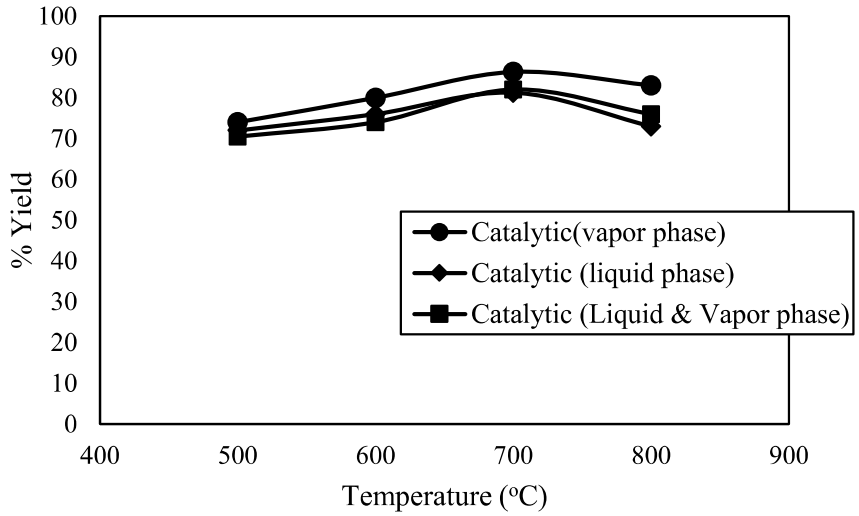

Figure 4.11a Temperature vs. % liquid yield obtained from the catalytic pyrolysis of polypropylene using A-type, B-type and C-type reactor arrangements.

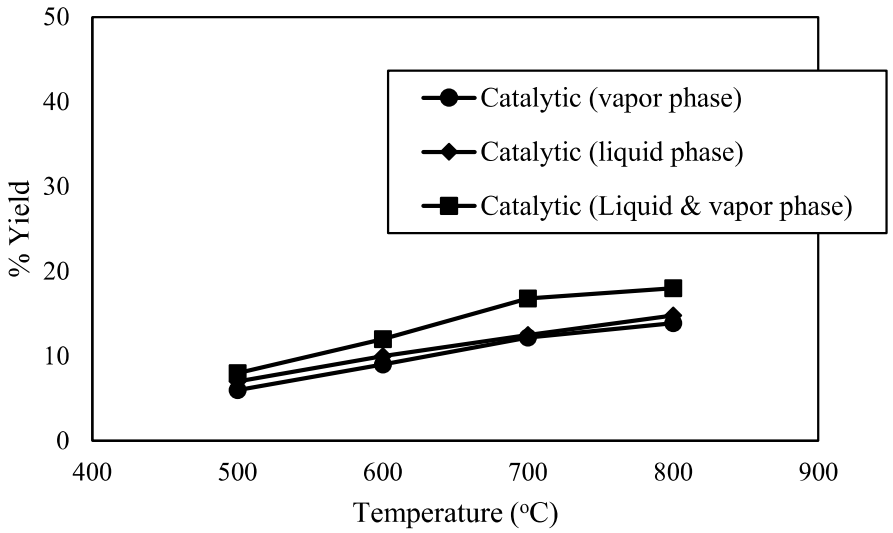

Figure 4.11b Temperature vs. % gas yield obtained from the catalytic pyrolysis of polypropylene using A-type, B-type and C-type reactor arrangements.

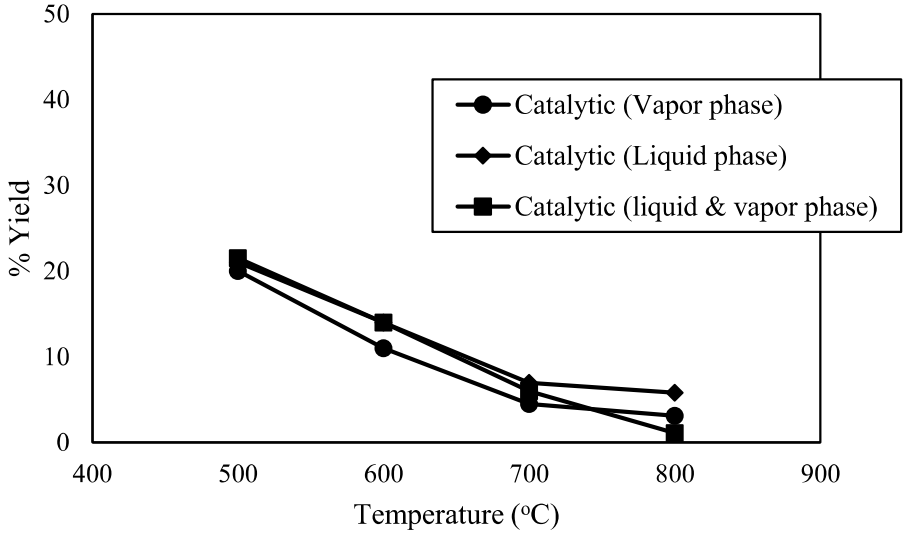

Figure 4.11c Temperature vs. % solid residue obtained from the catalytic pyrolysis of polypropylene using A-type, B-type and C-type reactor arrangements.

It is seen in the Fig (4.12) that the C- type (multiphase) produced lowest liquid yield of 82.0 wt. % and maximum gaseous yield of 16.8 wt. % at the optimum temperature of 700 °C (Fig 4.12). higher gaseous yield for multiphase reaction may be due to the catalyst is in both liquid and vapor phase helps in two stage catalytic reaction of alkanes. In the first stage, the catalytic pyrolysis is same as that of B type arrangement (liquid phase) followed

by a second stage pyrolysis in the vapor phase of lighter alkanes which escapes from first stage. Thus, C arrangements behaves as a multiphase catalytic pyrolysis with more production of aromatics/BTEX and gaseous hydrocarbons.

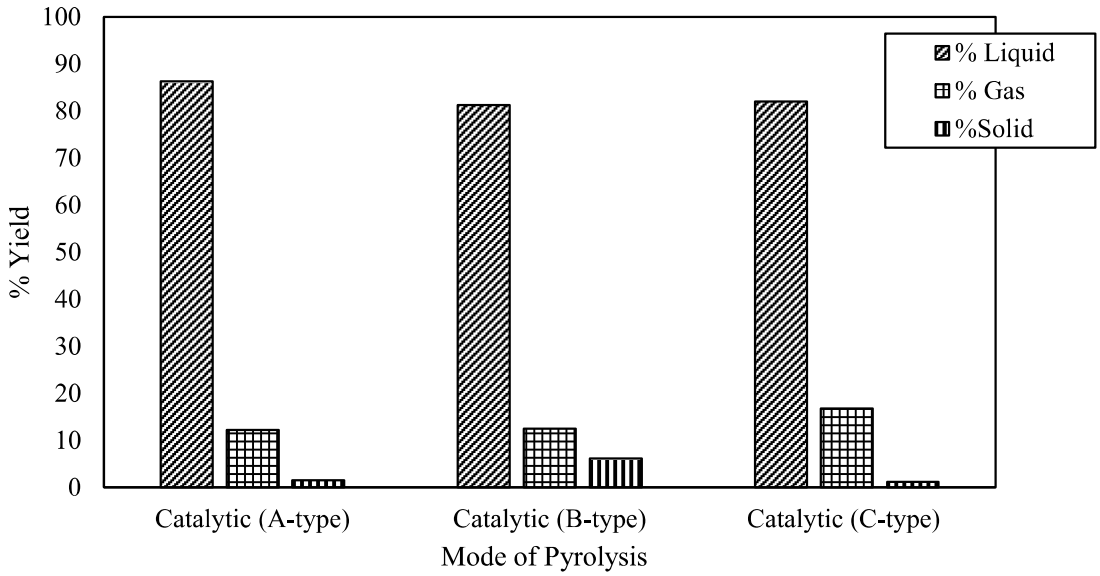

Figure 4.12 Comparison between liquid, gaseous and solid residue obtained at optimum temperature of 700 ^{o}C for polypropylene.

It is seen from Table (4.5) that the highest amount of aromatic content i.e., 53.12 wt. % was found in the pyrolysis oil at a temperature of 700 ^{o}C using catalyst in multiphase/C-type reactor arrangement. It may be due to the ZSM-5 catalyst, having smaller pore size provides higher selectivity for lower alkanes. Thus, for the C-type pyrolysis smaller molecules in the liquid and vapor phase both comes in contact with ZSM-5. This gives maximum BTEX of 53.12 wt. % as per the reaction schemes shown in the Fig (4.10) (page no. 78). The C-type/multiphase pyrolysis produced benzene, toluene, ethylbenzene and xylene are in maximum quantity irrespective of temperatures and reactor arrangements. It is generally proposed that on acid catalysts the aromatization of alkanes occurs through protolysis of alkane, cracking of carbonium ion to alkane and alkene, oligomerization of alkenes, cyclization of oligomerized products and formation or aromatics from cyclic rings by hydrogen transfer. However, catalyst in vapor phase (A) only interacts with the molecules

which comes from thermal pyrolysis in the liquid phase. Thus, catalytic pyrolysis (A-type) gives lower BTEX (51.52 wt.%) than C-type at a temperature of 700 ^{o}C. For the B-type catalytic pyrolysis, the catalyst is in contact with PE from the beginning, resulting in selective cracking of wide range of molecules. Thus, B-type arrangement gives BTEX (50.19 wt. %) at the same temperature.

Table 4.5 The Aromatic content (BTEX) in pyrolysis oil obtained from polypropylene at optimum temperature 700 ^{o}C.

Pyrolysis temperature (^{o}C)		**Benzene (wt. %)**	**Toluene (wt. %)**	**Ethylbenzene (wt.%)**	**Xylene (wt. %)**	**Total BTEX (wt. %)**
500	A-type	12.86	2.73	4.84	23.85	44.28
	B-type	12.43	2.83	4.91	23.48	43.65
	C-type	14.91	2.86	4.96	23.92	46.65
600	A-type	13.51	3.08	5.08	26.71	48.38
	B-type	13.19	3.18	5.18	26.11	47.66
	C-type	15.41	3.21	5.15	26.53	50.3
700	A-type	13.76	3.47	5.34	28.95	51.52
	B-type	13.35	3.60	5.40	27.84	50.19
	C-type	15.92	3.80	5.30	28.10	53.12
800	A-type	12.97	2.78	4.88	22.46	43.09
	B-type	12.64	2.89	4.95	23.12	43.6
	C-type	15.07	2.94	5.03	24.53	47.57

As discussed earlier, among all pyrolysis, C-type (multiphase) catalytic reactor arrangement gives highest BTEX yield (53.12 wt. %). Jung et al. 2005 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 PE fraction (39 wt. %) at the same temperature (700 ^{o}C) (Jung et al., 2005). 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 C-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. It is seen in Table (4.1) that commercial gasoline also contains about 36.45 wt. % BTEX to improve octane rating of fuel. It should be noted that the thermal pyrolysis of polypropylene produced very low BTEX yield of 30.91 wt.% at the same temperature of 700 ^{o}C (Table 4.5).

4.2.1.1.3.3 Polystyrene as feed

Fig (4.13a) to Fig (4.13c) show the product yield obtained for A-type, B-type and C-type reactor arrangements using catalytic pyrolysis of polystyrene at the temperature of 500 ^{o}C, 600 ^{o}C, 700 ^{o}C and 800 ^{o}C, respectively. The optimum feed to catalyst ratio of 20:1 and reaction time 30 min were maintained for the reaction process as used in the case of polyethylene and polypropylene. The product yield obtained are compared for different reactor arrangements to show the improvement in product qualitatively and quantitatively for the liquid yield, gaseous yield and solid residue, respectively. The maximum liquid yield of 88 wt. %, 86.2 wt. % and 83.0 wt. % at a temperature of 700 ^{o}C were obtained for catalytic pyrolysis in the reactor arrangement A-type, B-type and C-type respectively (Fig 4.13a). The use of catalyst decreases the quantity of liquid yield in comparison to thermal process but increases the quality of liquid oil in terms of aromatics BTEX, which is discussed later on (page no. 86). This pattern is similar as that of polyethylene and polystyrene. It is clearly seen in Fig (4.13b) that the gaseous yield obtained was highest (16.3 wt.%) for C-type/multiphase reactor arrangement, irrespective of temperature. The

liquid yield obtained was minimum (83.0 wt.%) for C-type reactor arrangement. The reason behind the increase in gaseous yield has already been discuss for polyethylene (page no. 73) and polypropylene (page no. 78).

It is seen in the Fig (4.13c) that solid residue gets reduced for catalytic pyrolysis in the reactor arrangements in the order A-type (vapor phase) > C-type (liquid and vapor/multiphase) > B-type (liquid phase). The catalyst in vapor phase (A-type) results in maximum liquid yield of 88 wt.% and solid residue of 3 wt.%. It may be due to selective cracking at vapor phase of comparatively higher molecular weight hydrocarbon which are produced via thermal cracking at the bottom of reactor. It is seen in the Fig (4.14) that the catalytic cracking (B-type), liquid yield of 86.2 wt. % which is lower than A-type. Whereas, gaseous yield increases from 9 wt. % (A-type) to 13.5 wt.% (B-type) at the same temperature (700 ^{o}C) (Fig 4.14). In the arrangement B, the ZSM-5 catalyst is in contact with polystyrene from the beginning of the reaction. Thus, largest to smallest hydrocarbon molecules may interact with the ZSM-5, which results in more aromatics and gaseous hydrocarbon.

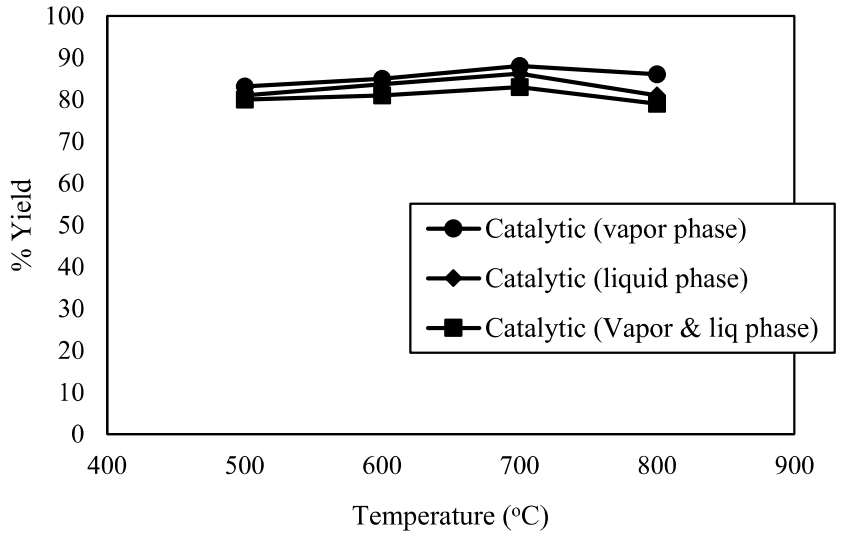

Figure 4.13a Temperature vs. % liquid yield obtained from the catalytic pyrolysis of polystyrene using A-type, B-type and C-type reactor arrangements.

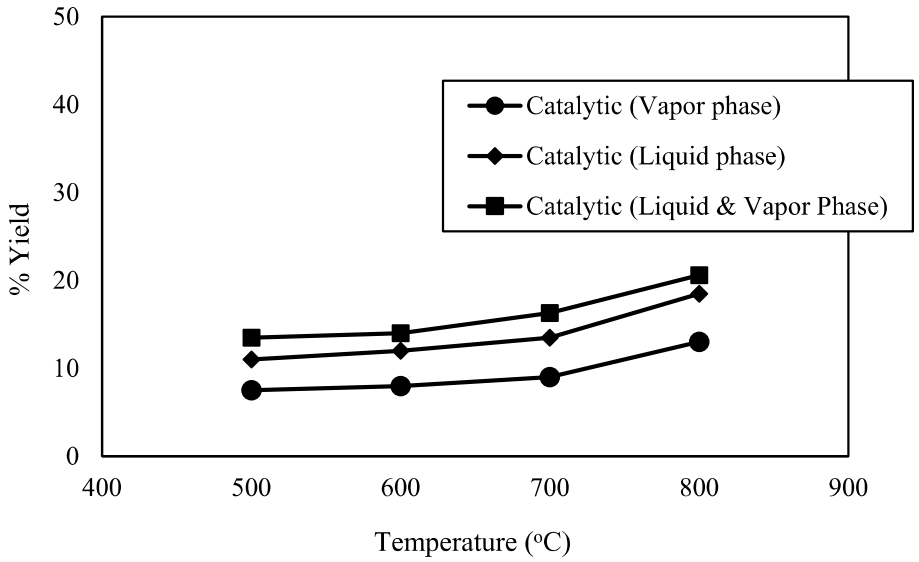

Figure 4.13b Temperature vs. % gas yield obtained from the catalytic pyrolysis of polystyrene using A-type, B-type and C-type reactor arrangements.

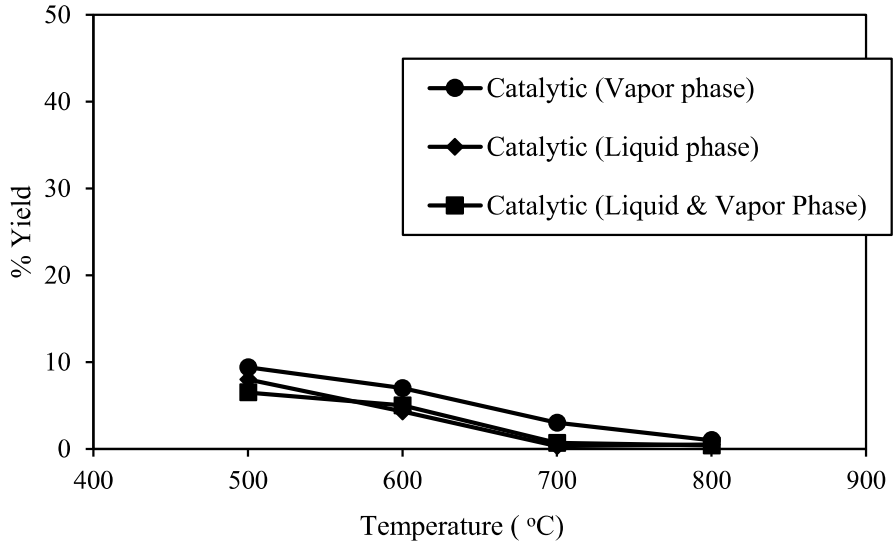

Figure 4.13c Temperature vs. % Solid residue obtained from the catalytic pyrolysis of polystyrene using A-type, B-type and C-type reactor arrangements.

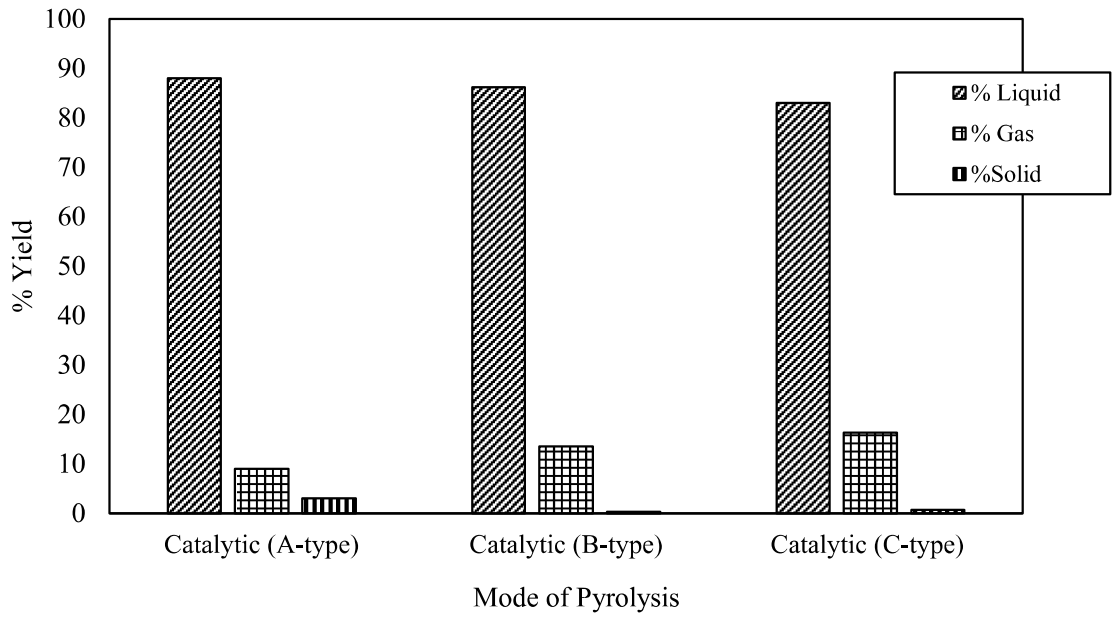

Figure 4.14 Comparison between liquid, gaseous and solid residue obtained at optimum temperature of 700 ^{o}C for polystyrene.

The aromatic content BTEX was also evaluated using similar method as discussed earlier (page no. 47) The similar trend for BTEX was observed for polystyrene pyrolysis as it was seen for polyethylene (page no. 76) and polypropylene (page no. 81) at the optimum temperature of 700 ^{o}C. It is seen from Table (4.6) that the maximum aromatic content/BTEX of 26.86 wt.% was obtained for C-type reactor arrangement. The BTEX yield was significantly increased for catalytic pyrolysis (C-type) i.e., about 95 % in comparison to thermal pyrolysis (13.58 wt.%). The reactor arrangements A-type and B-type gives BTEX yield of 18.68 wt.% and 23.72 wt.%, respectively at the same temperature. The aromatic/BTEX in PS pyrolysis oil were found lowest i.e., 26.86 wt. % than found in the PE (39.47 wt. %) and PP (53.12 wt. %) at the same temperature (700 ^{o}C) for C-type reactor arrangement. The reason for lowest BTEX in polystyrene (PS), may be due to the presence of high amount of styrene monomer in pyrolysis oil obtained from PS pyrolysis.

Table 4.6 The aromatic content (BTEX) in pyrolysis oil obtained from polystyrene at optimum temperature 700 ^{o}C.

Pyrolysis temperature (^{o}C)		Benzene (wt. %)	Toluene (wt. %)	Ethylbenzene (wt.%)	Xylene (wt. %)	Total BTEX (wt. %)
500	A-type	0.48	11.48	3.20	2.16	17.32
	B-type	0.71	14.61	3.39	2.57	21.28
	C-type	0.78	17.84	3.43	2.83	24.88
600	A-type	0.54	12.18	3.28	2.21	18.21
	B-type	0.73	15.24	3.47	2.64	22.08
	C-type	0.82	18.75	3.52	3.04	26.13
700	A-type	0.57	12.37	3.37	2.37	18.68
	B-type	0.80	16.57	3.57	2.78	23.72
	C-type	0.89	19.27	3.60	3.10	26.86
800	A-type	0.49	11.53	3.27	2.19	17.48
	B-type	0.68	14.76	3.32	2.63	21.39
	C-type	0.81	17.89	3.46	2.85	25.01

4.2.1.2 Characterization of product yield

4.2.1.2.1 Gas chromatography (GC) analysis of pyrolysis oil

The GC-FID of standard/pure benzene, toluene, ethylbenzene and xylene were done to get retention time of individual compounds. 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. Fig (4.15a) to Fig (4.15c) show the prominent peaks for benzene, toluene, ethylbenzene and xylene (BTEX) in the pyrolysis oil obtained from pyrolysis of polyethylene, polypropylene and polystyrene, respectively. A comparison between pyrolysis oil and commercial oils is shown to check the suitability of the use of pyrolysis oil in diesel engine and confirm its composition.

Fig (4.15a) to Fig (4.15c) show the GC-FID of the pyrolysis oil derived by the pyrolysis of the polyethylene, polypropylene and polystyrene at the optimum temperature of 700 ^{o}C, commercial kerosene oil and diesel oil, respectively. The important and prominent peaks obtained at same retention time for the pyrolysis oil obtained from PE, PP and PS pyrolysis (700 ^{o}C), commercial kerosene oil and diesel oil is shown in Fig (4.15a) to Fig (4.15c). It is seen from the Fig (4.15a) that the chromatogram peaks for pyrolysis oil obtained from polyethylene at a temperature of 700 ^{o}C are very close to kerosene and diesel oil in the retention time range between 2 and 18 min for A-type and B-type catalytic pyrolysis, and between 5 and 18 min for C-type/multiphase pyrolysis. This range may be specifically interesting for the pyrolysis oil (700 ^{o}C) which consist of compounds, are similar as that of kerosene oil and diesel oil in terms of chemical structure of compounds and composition (Nicholas, 1998). Moreover, the maximum numbers of peaks of A-type and C-type pyrolysis oil are matched with diesel and kerosene.

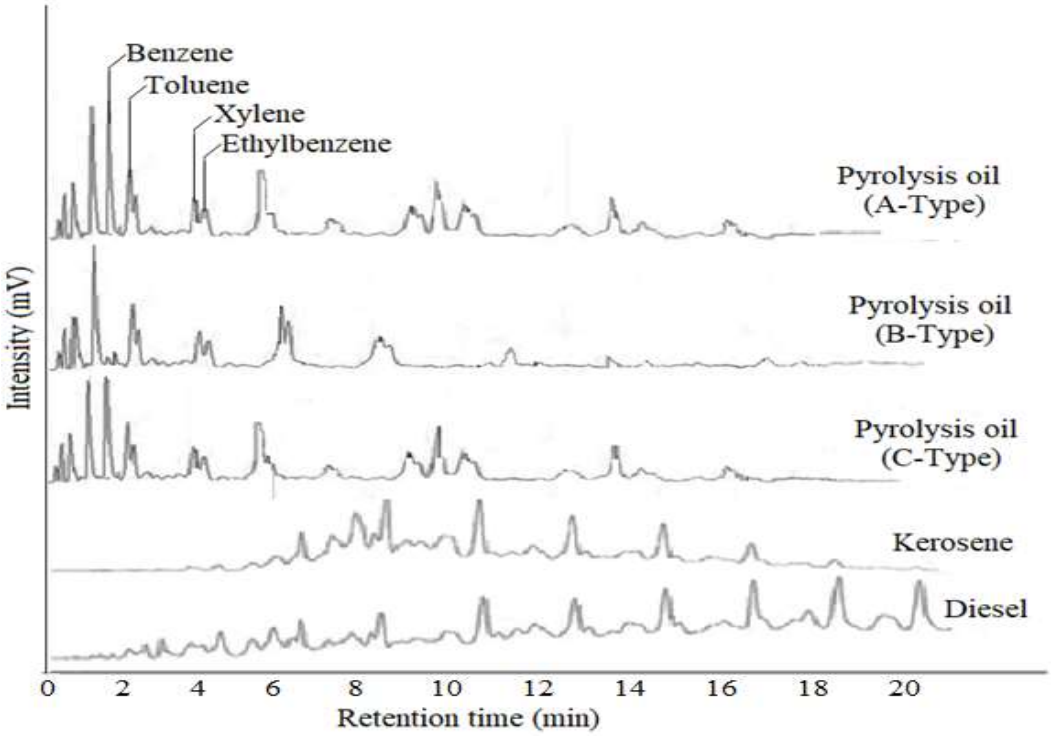

Figure 4.15a Gas chromatography characteristic of kerosene oil (commercial), diesel oil (commercial) and pyrolysis oil obtained from the catalytic pyrolysis of polyethylene at a temperature of 700 ^{o}C for A-type (vapor phase), B-type (liquid phase) and C-type (both liquid and vapor phase) reactor arrangements.

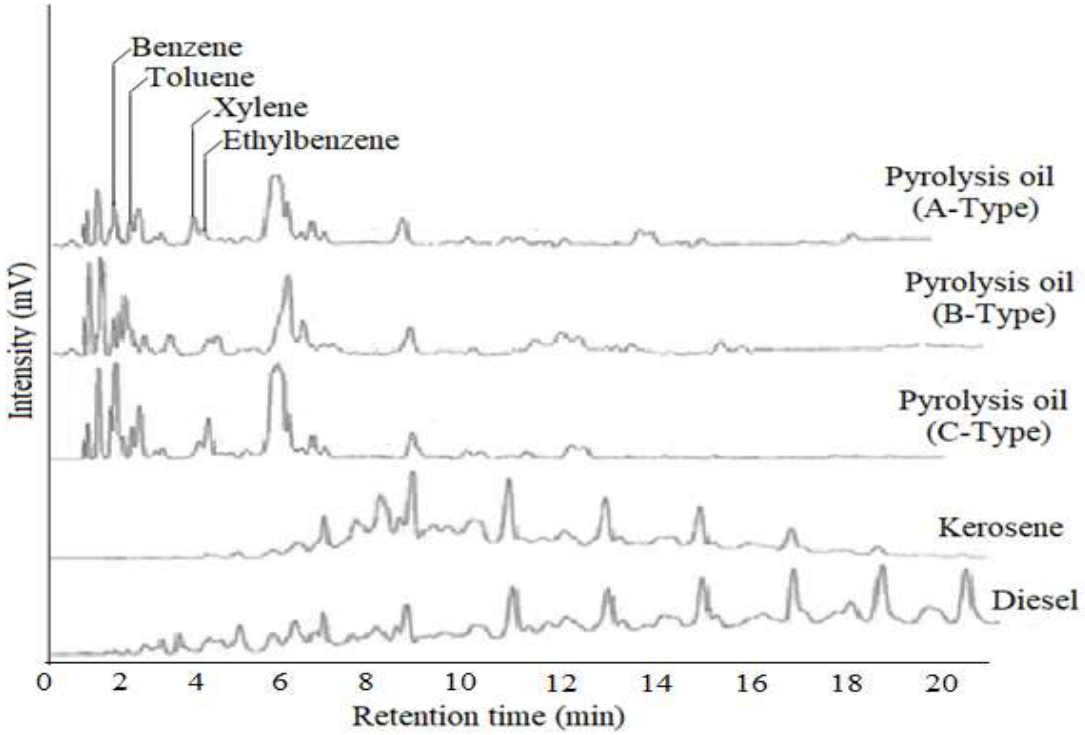

Figure 4.15b Gas chromatography characteristic of kerosene oil (commercial), diesel oil (commercial) and pyrolysis oil obtained from the catalytic pyrolysis of polypropylene at a temperature of 700 ^{o}C for A-type (vapor phase), B-type (liquid phase) and C-type (both liquid and vapor phase) reactor arrangements.

It is seen from the Fig (4.15b) that the chromatogram peaks for pyrolysis oil obtained from polypropylene at a temperature of 700 ^{o}C are very close to kerosene and diesel oil in the retention time range between 4 and 15 min for A-type and B-type catalytic pyrolysis, and between 6 and 12 min for C-type/multiphase pyrolysis. This range may be specifically interesting for the pyrolysis oil (700 ^{o}C) which consist of compounds, are similar as that of kerosene oil and diesel oil in terms of chemical structure of compounds and composition (Nicholas, 1998). Moreover, the maximum numbers of peaks of A-type and B-type pyrolysis oil are matched with commercial diesel.

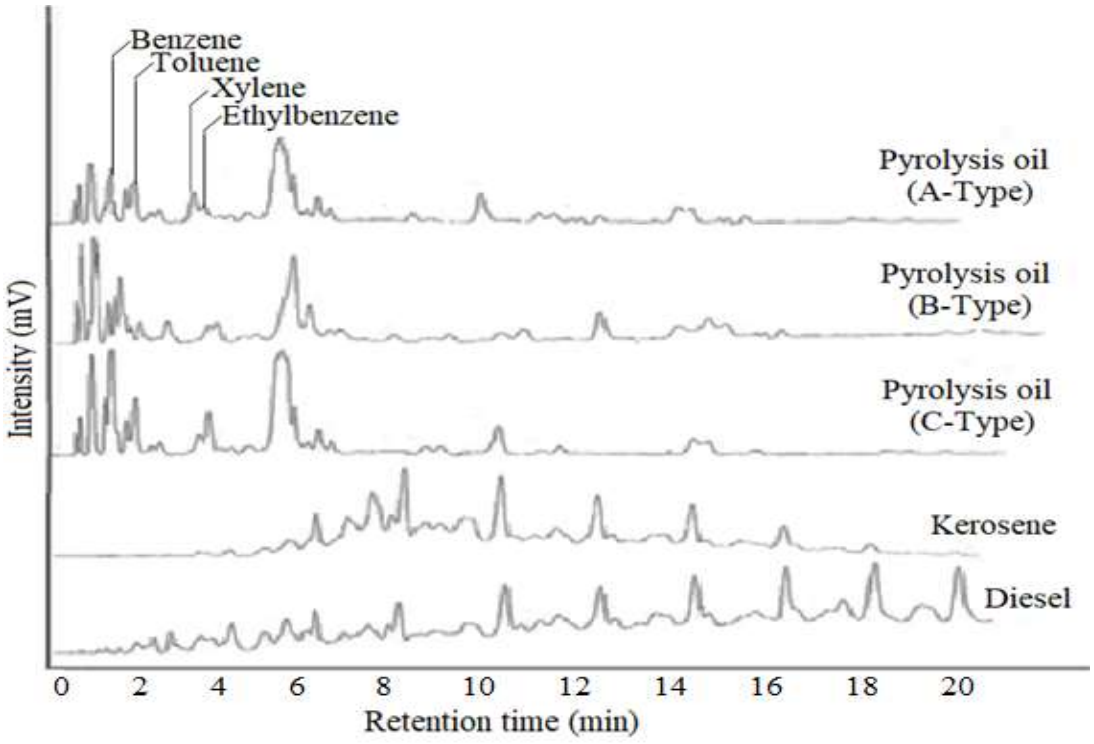

Figure 4.15c Gas chromatography characteristic of kerosene oil (commercial), diesel oil (commercial) and pyrolysis oil obtained from the catalytic pyrolysis of polystyrene at a temperature of 700 ^{o}C for A-type (vapor phase), B-type (liquid phase) and C-type (both liquid and vapor phase) reactor arrangements.

It is seen from the Fig (4.15c) that the chromatogram peaks for pyrolysis oil obtained from polystyrene at a temperature of 700 ^{o}C are very close to kerosene and diesel oil in the retention time range between 7 and 16 min for A-type and B-type catalytic pyrolysis, and between 5 and 15 min for C-type/multiphase pyrolysis. This range may be specifically interesting for the pyrolysis oil (700 ^{o}C) which consist of compounds, are similar as that of kerosene oil and diesel oil in terms of chemical structure of compounds and composition (Nicholas, 1998). Moreover, the maximum numbers of peaks of pyrolysis oil for A-type and B-type reactor arrangements are matched with commercial diesel.

4.2.1.2.2 ASTM distillation of pyrolysis oil

Fig (4.16a) to Fig (4.16c) shows comparison between standard fuel (Perry and Green, 2007) and pyrolysis oil obtained from polyethylene, polypropylene and polystyrene for different

types of reactor arrangements at a temperature of 700 ^{o}C. The boiling point range of pyrolysis oil obtained from catalytic pyrolysis of polyethylene using A-type, B-type and C-type reactor arrangements (Fig 4.16a) at the optimum temperature of 700 ^{o}C lies in between gasoline and kerosene for the recovery of distillate 0-30%. The boiling point range of pyrolysis oil obtained from catalytic pyrolysis using A-type, B-type and C-type reactor arrangements tend to behave as kerosene for the recovery of distillate range 30-60 %. In addition, pyrolysis oil obtained from catalytic pyrolysis (A-type, B-type and C-type) of PE lies in the range of kerosene and diesel oil above 60 % of distillate recovery.

The trend of ASTM curve for polypropylene is little different from polyethylene. The boiling point range of pyrolysis oil obtained from catalytic pyrolysis of polypropylene are almost same as JP-4 for the recovery of distillate 0-30% using A-type, B-type and C-type reactor arrangements, respectively (Fig 4.16b). Pyrolysis oil obtained from catalytic pyrolysis for A-type, B-type and C-type lies in between JP-4 and kerosene for the recovery of distillate 30-55 % and it tends to behaves as diesel oil above 70 % recovery.

Fig (4.16c) shows the comparison between standard fuel and pyrolysis oil obtained from polystyrene at a temperature of 700 ^{o}C. The boiling point range of pyrolysis oil obtained at temperature of 700 ^{o}C for catalytic pyrolysis (A-type, B-type and C-type) tends to behave as heavy naphtha for the recovery of distillate 0-60% recovery. In addition, all the pyrolysis oil obtained lies between heavy naphtha and diesel for 60-80 % recovery. Whereas, interestingly pyrolysis oil tends to behaves as diesel oil above 80 % of distillate recovery for catalytic pyrolysis using A-type, B-type and C-type reactor arrangements, respectively.

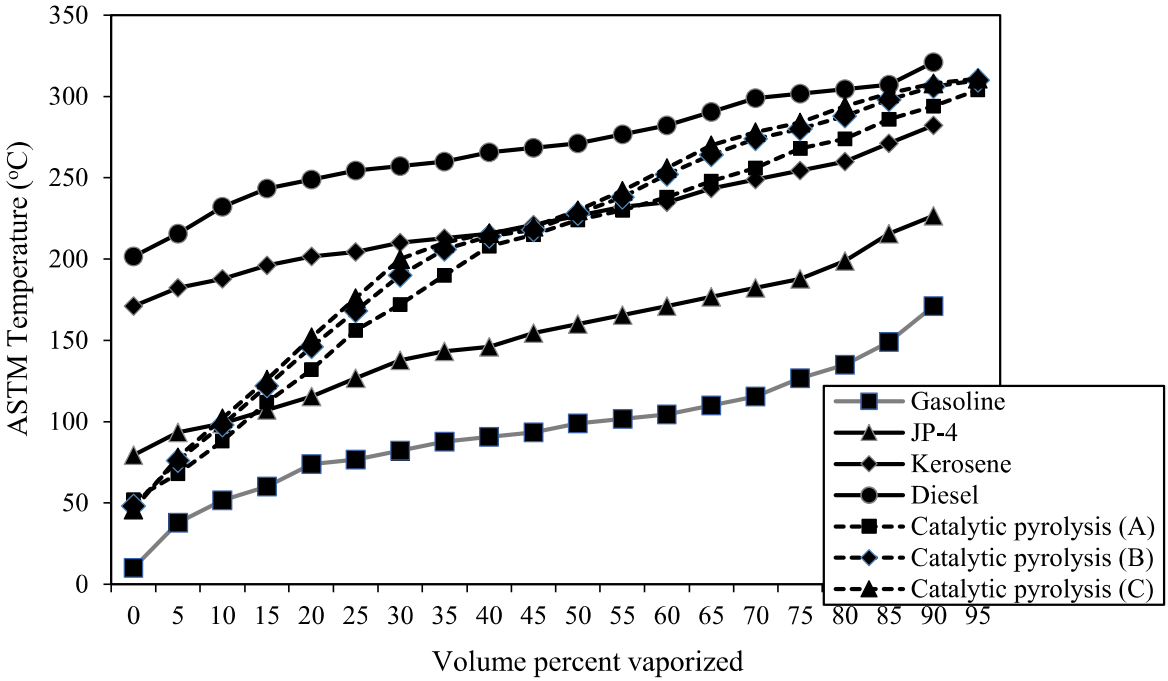

Figure 4.16a Volume percent vaporized vs. ASTM temperature characteristics of standard fuel and pyrolysis oil obtained from polyethylene.

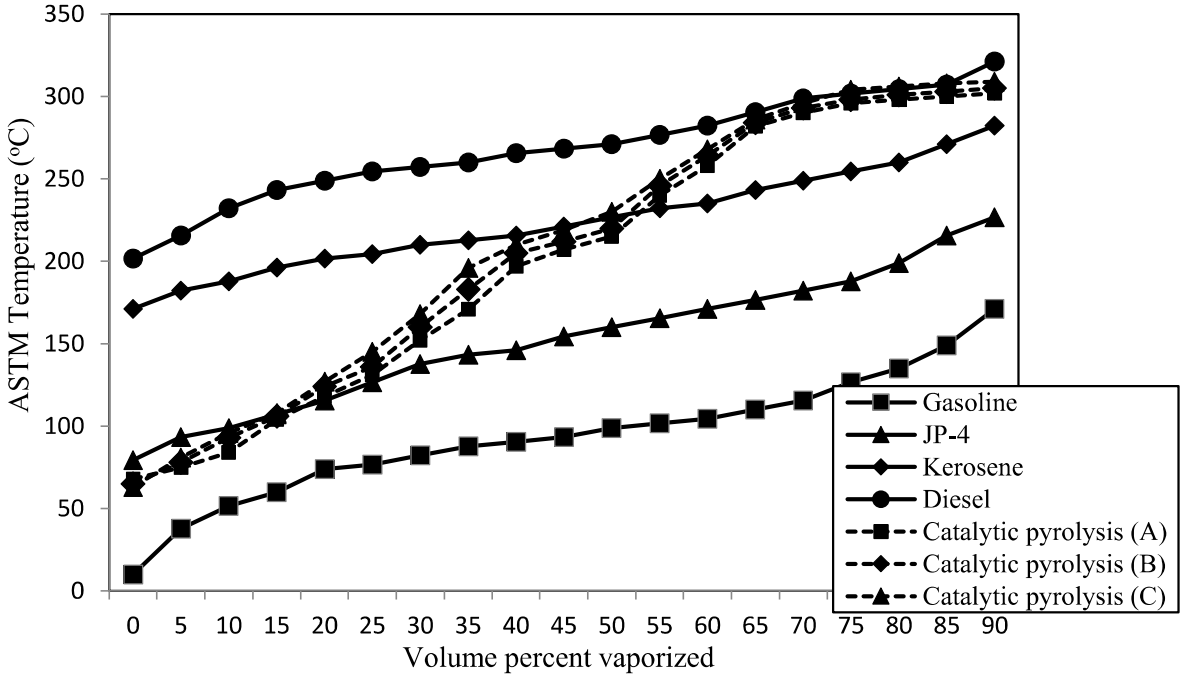

Figure 4.16b Volume percent vaporized vs. ASTM temperature characteristics of standard fuel and pyrolysis oil obtained from polypropylene.

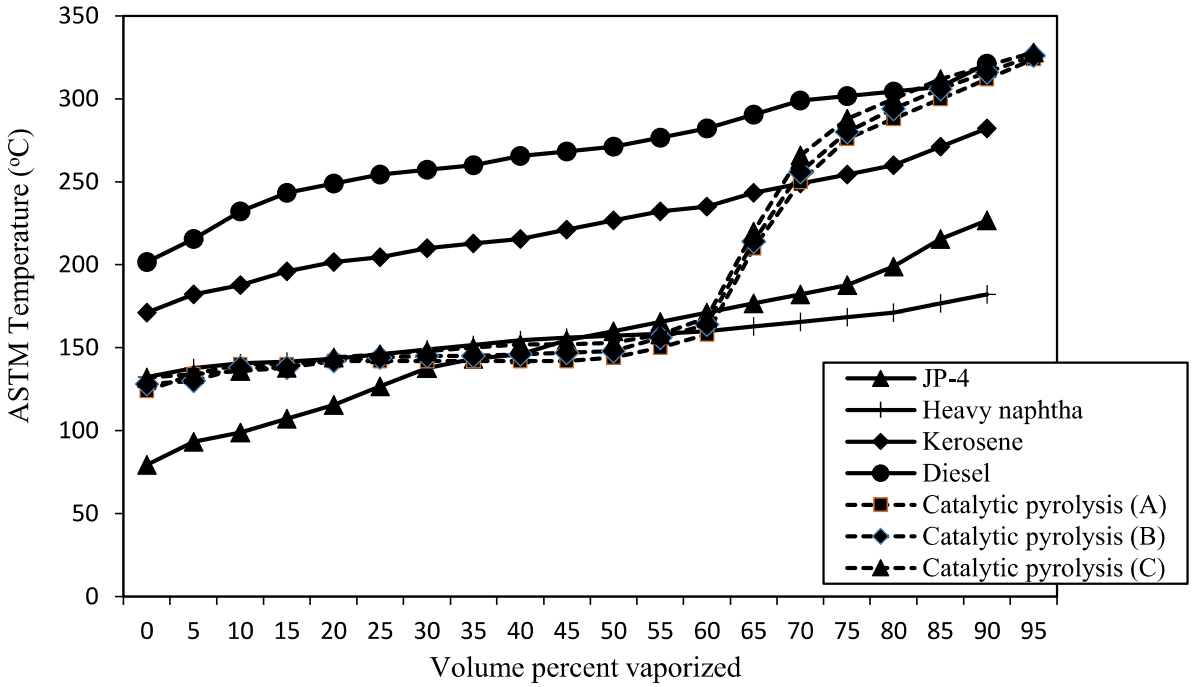

Figure 4.16c Volume percent vaporized vs. ASTM temperature characteristics of standard fuel and pyrolysis oil obtained from polystyrene.

4.2.1.2.3 FTIR analysis of pyrolysis oil

The 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. In order to gather systematic information about the chemical composition of the pyrolysis oil, the resultant fuels were examined using FTIR in the wavelength range of 3200-600 cm^{-1}. Fig (4.17a) shows the FTIR spectra of liquid fuel obtained at optimized condition by catalytic pyrolysis of waste polyethylene using A-type, B-type and C-type reactor arrangements. As expected, there are only slight differences among the first two spectra. This is due to the strong resemblance among polymeric structures. The spectra confirm that these fuels are composed of aliphatic groups comprising carbon and hydrogen atoms. The presence of alkanes is detected at 2959-2919 cm^{-1} with C–H stretching

vibrations. C=C stretching vibrations at 1660-1630 cm^{-1} indicates the presence of alkenes/fingerprint region. This band 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 1457-53 cm^{-1}, which verify the presence of benzene derivatives in the pyrolysis oil. C–H bending vibrations at 990-966 cm^{-1} indicate the presence of alkenes. The 890-886 cm^{-1} band certified the presence of vinylidene functional group in the chemical composition of pyrolysis oil. The C–H bending vibrations at frequency 739-722 cm^{-1} indicates the presence of phenyl ring substitution bands. This region confirms mono or ortho substitution of benzene ring. Thus, it can be summarized that pyrolysis oil is a complex mixture of paraffinic, olefinic and aromatic compounds (Djebara et al., 2012; Fernández et al., 2012; Heydariaraghi et al., 2016; Jin et al., 2016; Kumar et al., 2013; Williams and Williams, 1997). The FT-IR data of pyrolysis oil is substituted using GC-FID analysis of the oil obtained by the similar condition.

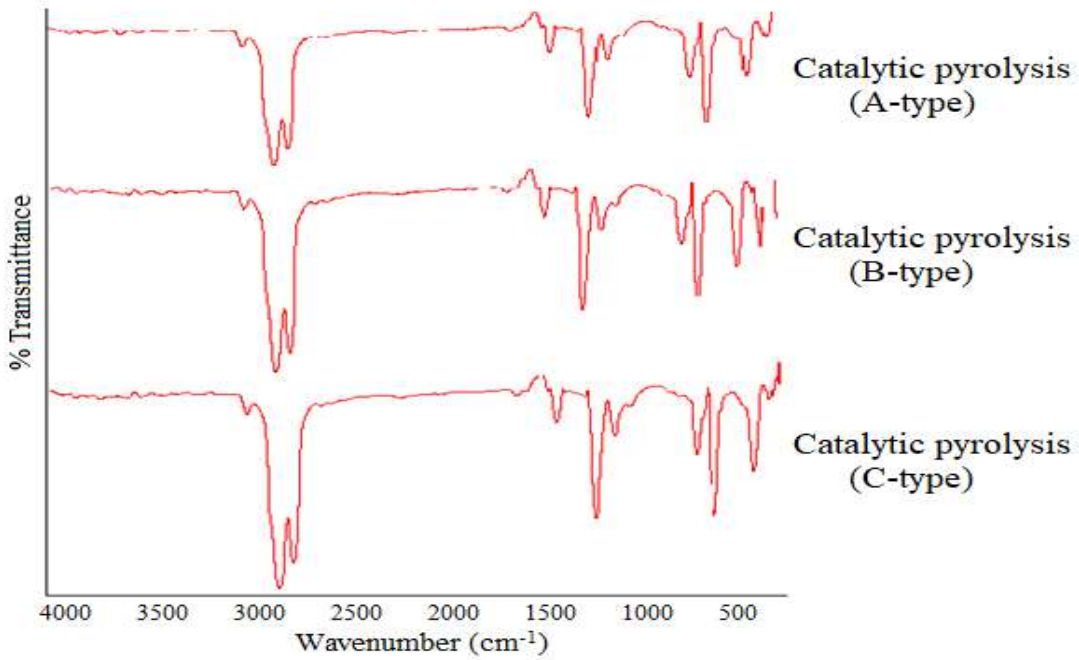

Figure 4.17a FT-IR spectrometry of liquid fuel obtained at optimized condition (700 °C) by catalytic pyrolysis of waste polyethylene for A-type, B-type and C-type reactor arrangements.

Fig (4.17b) shows the FTIR spectra of pyrolysis oil obtained at optimum condition by catalytic pyrolysis of waste polypropylene using A-type, B-type and C-type reactor arrangements. 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. 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 overall analysis of FTIR spectra for the pyrolysis oil confirm the presence of paraffinic, olefinic and aromatic compounds in the product oil.

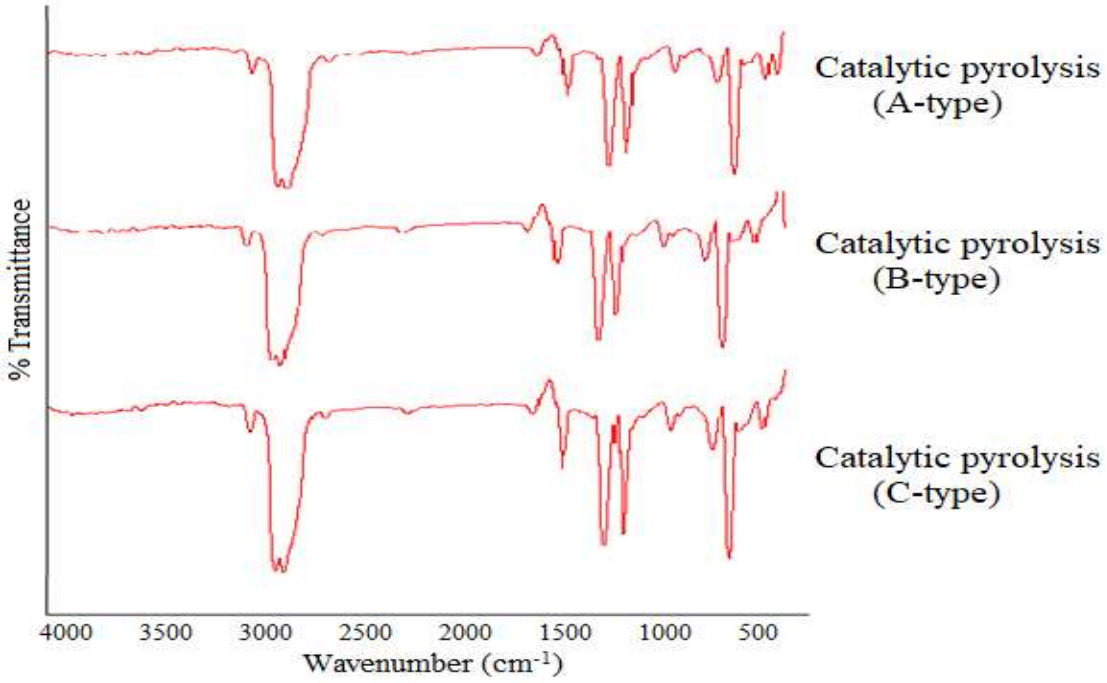

Figure 4.17b FT-IR spectrometry of liquid fuel obtained at optimized condition (700 °C) by catalytic pyrolysis of waste polypropylene for A-type, B-type and C-type reactor arrangements.

Fig (4.17c) shows the FTIR spectra of liquid fuel obtained at optimized condition by catalytic pyrolysis of waste polystyrene using A-type, B-type and C-type reactor arrangements. 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.

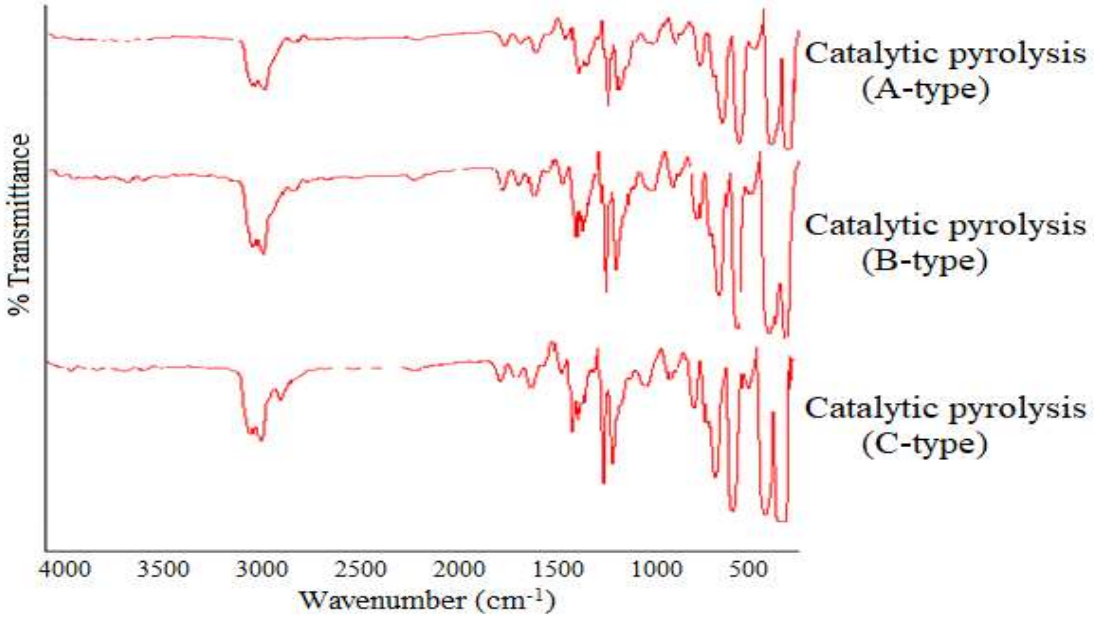

Figure 4.17c FT-IR spectrometry of liquid fuel obtained at optimized condition (700 ^{o}C) by catalytic pyrolysis of waste polystyrene for A-type, B-type and C-type reactor arrangements.

4.2.1.2.4 Physicochemical properties of pyrolysis oil

Table (4.7a) to (4.7c) shows the results of physicochemical property analysis of liquid fuel obtained at optimized condition from catalytic pyrolysis of waste PE, PP and PS, respectively. The appearance of the all pyrolysis oil were light yellowish free from visible sediments. The flash point of the liquid product obtained from waste PE, PP and PS were

found in a comparable range and thus, it is expected not cause any trouble in most of the engines. The gross calorific value (GCV) for liquid fuel obtained by catalytic pyrolysis of waste PE using A-type, B-type and C-type reactor arrangements were 10996 Cal/g, 11090 Cal/g and 11230 Cal/g, respectively which is in the range of gasoline and diesel. Thus, this liquid product would perform relatively well in IC engines. However, GCV of pyrolysis oil obtained from catalytic pyrolysis of waste PP and PS using C-type reactor arrangement were 9914 Cal/g and 9268 Cal/g, respectively which are lower in comparison to waste PE. As discussed earlier in the phase-I, the GCV of pyrolysis oil obtained from thermal pyrolysis of PE (10982 Cal/g), PP (9015.48 Cal/g) and PS (7073.37 Cal/g) are found to be low as compared to catalytic pyrolysis at a temperature of a temperature of 700 ^{o}C. The PE, PP and PS produced very low carbon residue of 0.234 wt. %, 0.23 wt. % and 0.64 wt. %, respectively at a temperature of 700 ^{o}C. This indicates good fuel property as carbon residue is less than 1 wt. % in all pyrolysis oil at a temperature 700 ^{o}C. This confirms the presence of low molecular weight aromatics in the oil. From these studies, it is observed that the product oil from all three waste plastics could be possible feedstock for further upgrading to use in diesel engine besides recovery of BTEX as a valuable product.

Table 4.7a Physicochemical properties of pyrolysis oil obtained at 700 ^{o}C for polyethylene using ZSM-5 catalyst.

Physicochemical Properties	**Test method**	**Results obtained**		
		Catalytic Pyrolysis		
		A-Type	**B-Type**	**C-Type**
Flash point (^{o}C)	ASTM D 92	27	26	25
Fire point (^{o}C)	ASTM D 92	31	30	30
Carbon residue (wt. %)	IP 14/65	0.264	0.252	0.234
Specific gravity	ASTM D 1298	0.7624	0.7578	0.7525
API gravity (^{o})	API correlation	54.10	55.22	56.54
Calorific value (Cal/g)	IP 12/63 T	10996	11090	11230

Table 4.7b Physicochemical properties of pyrolysis oil obtained at 700 °C for polypropylene using ZSM-5 catalyst.

Physicochemical Properties	**Test method**	**Results obtained**		
		Catalytic Pyrolysis		
		A-Type	**B-Type**	**C-Type**
Flash point (°C)	ASTM D 92	28	26	25
Fire point (°C)	ASTM D 92	31	30	30
Carbon residue (wt. %)	IP 14/65	0.264	0.25	0.23
Specific gravity	ASTM D 1298	0.76	0.77	0.74
API gravity (°)	API correlation	54.10	55.22	56.54
Calorific value (Cal/g)	IP 12/63 T	9568.20	9726.10	9914

Table 4.7c Physicochemical properties of pyrolysis oil obtained at 700 °C for polystyrene using ZSM-5 catalyst.

Physicochemical Properties	**Test method**	**Results obtained**		
		Catalytic Pyrolysis		
		A-Type	**B-Type**	**C-Type**
Flash point (°C)	ASTM D 92	28	26	25
Fire point (°C)	ASTM D 92	31	30	30
Carbon residue (wt. %)	IP 14/65	0.78	0.72	0.64
Specific gravity	ASTM D 1298	0.8484	0.8567	0.8618
API gravity (°)	API correlation	35.28	33.68	32.69
Calorific value (Cal/g)	IP 12/63 T	8568.2	8726.1	9268

4.2.2 Pyrolysis of Waste Plastics on Fly Ash Derived Catalyst

The catalytic pyrolysis of waste plastics e.g., polyethylene, polypropylene and polystyrene using fly ash derived catalyst, catalyst characterization, effect of different parameters and characterization of product yield are described in the following section.

4.2.2.1 Characterization of fly ash derived catalyst

4.2.2.1.1 SEM-EDX Analysis

The surface morphology of the treated (calcined) and untreated fly ash samples are shown in Fig (4.18a) to Fig (4.18e). It is evident from the SEM images that most of the particles were spherical in shape with high porosity. The fly ash consists of spherical, vitreous particles of different sizes. These particles are usually porous in nature and some pores may contain other smaller particles in their interior. The surface texture of fly ash particles appears to be smooth and also some vitreous, unshaped fragments or quartz particles can be seen. The average size of these particles is in the range of 0.1023 to 3.61μm. The SEM and EDX analysis of FA particles was performed to determine the ratio of silicon (Si) and aluminium (Al) in these samples. Silica (Si) to Alumina (Al) ratio in these samples are significantly increased from 3.32 to 16.03 i.e., 3.32 for FA-600, 5.22 for FA-700 and 16.03 for FA-800, when they were treated at different temperatures ranging from 600 ^{o}C to 800 ^{o}C. However, calcined fly ash at 900 ^{o}C (FA-900) gives Si/Al ration of 1.43 (Table 4.8, page no. 103). This may be due to degradation of FA particles, micropores get collapse at such very high temperature, resulting in very low surface area of 5.78 m^2/g (Table 4.8) and low surface concentration of (Si/Al) (Fig 4.18e). Whereas, untreated fly ash gives Si/Al ratio of 2.18 due to low surface area, lesser amount of micropores and very high impurities get deposited on the surface of the FA particles. The morphological changes in the fly ash during calcination process at the temperature range of 600 ^{o}C to 900 ^{o}C is clearly noticed

in the Fig 4.18a-e. The spheres of fly ash were covered by precipitates and complexes formed by the heavy metal ions when calcined at high temperatures (Gaurh and Pramanik, 2018b; Musapatika et al., 2010).

SEM-EDX analyses show that the particles of fly ash calcined at 900 ^{o}C (Fig. 4.18e), contain large pore diameter compared to the fly ash particles calcined between 600 ^{o}C to 800 ^{o}C. Surface concentration of (Si/Al) also get decreased for the calcination temperature of 900 ^{o}C, due to availability of low surface area. The maximum (Si/Al) ratio was obtained at the calcination temperature of 800 ^{o}C due to the availability of large surface area (310 m^2/g) (Table 4.8). It implies that calcination temperature plays an important role to achieve maximum surface area with maximum surface concentration of active component silica (Si) and alumina (Al).

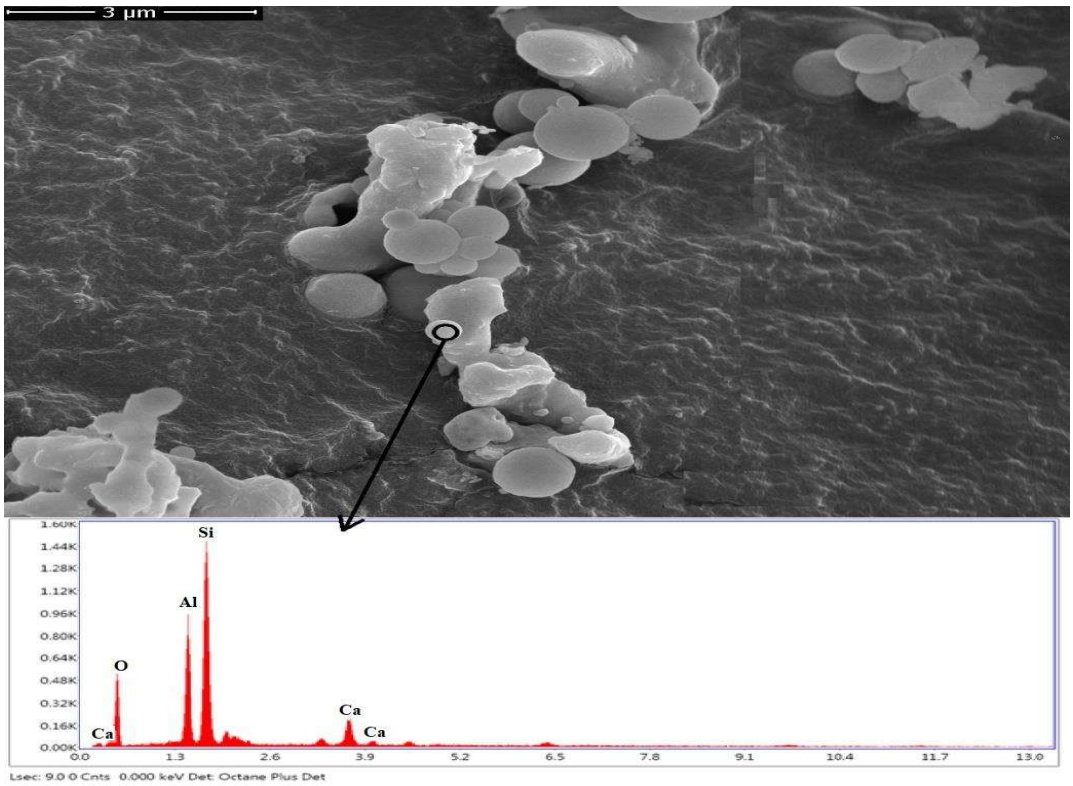

Figure 4.18a SEM-EDX images of Fly ash in natural form(FAN).

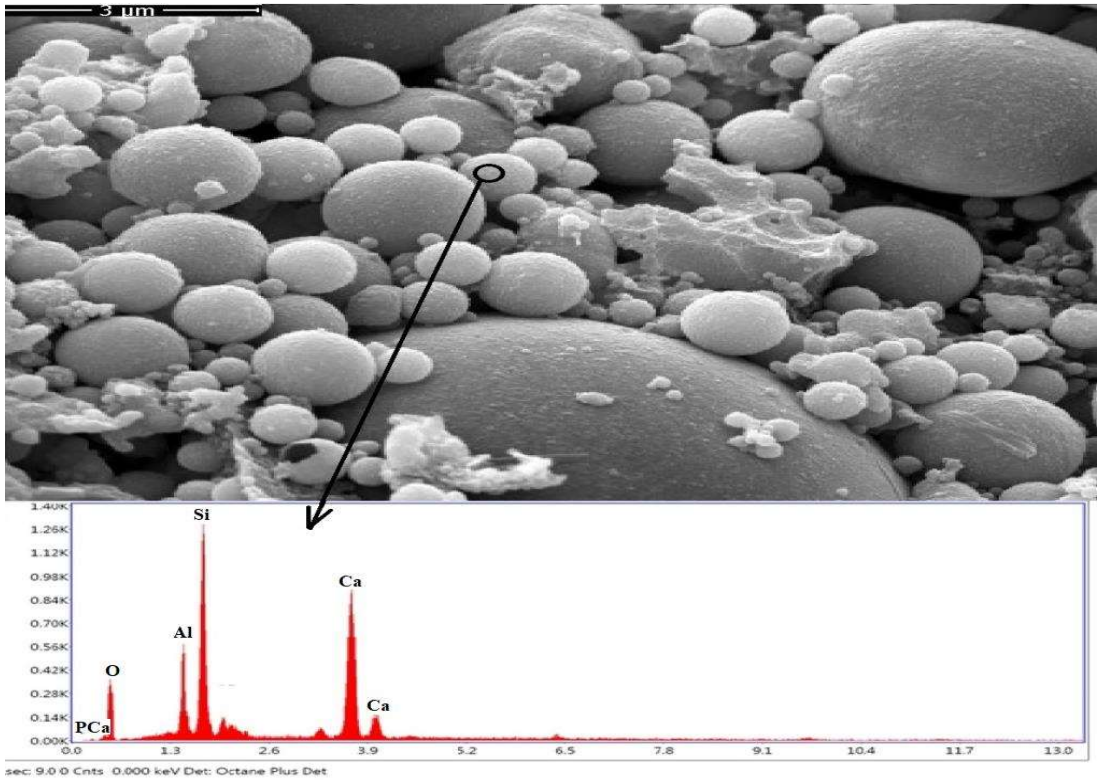

Figure 4.18b SEM-EDX images of FA synthesized catalyst FA-600 (fly ash calcined at 600 ^{o}C).

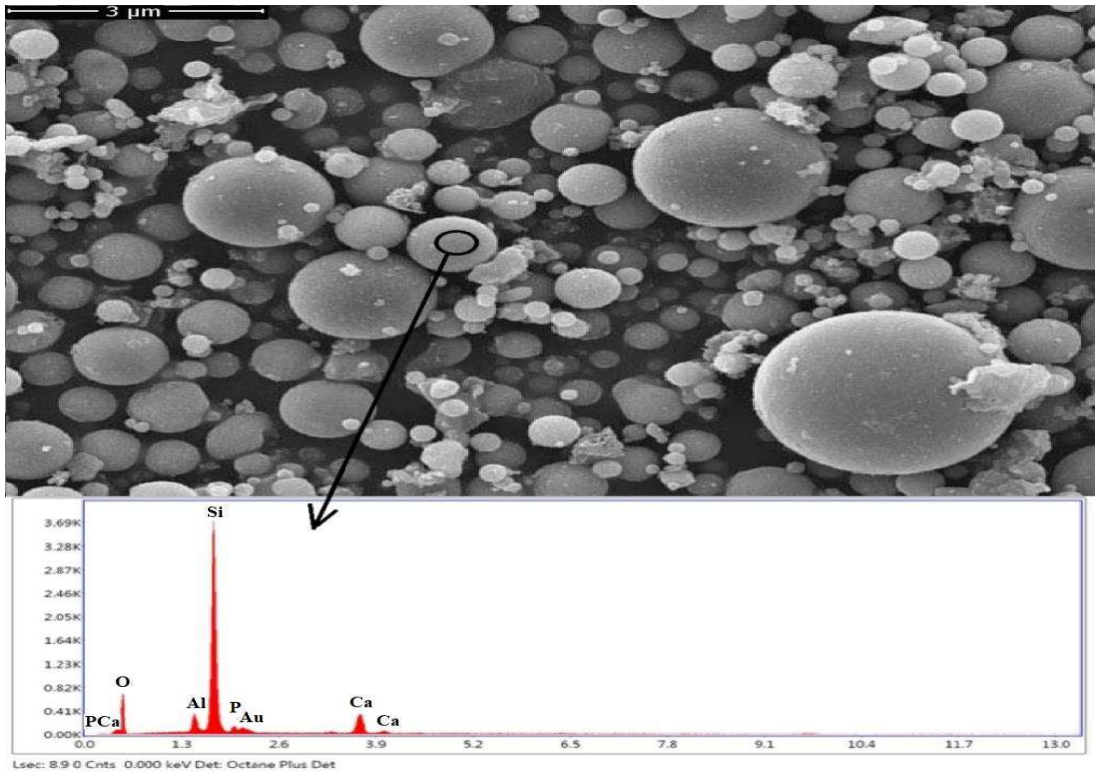

Figure 4.18c SEM-EDX images of FA synthesized catalyst FA-700 (fly ash calcined at 700 ^{o}C).

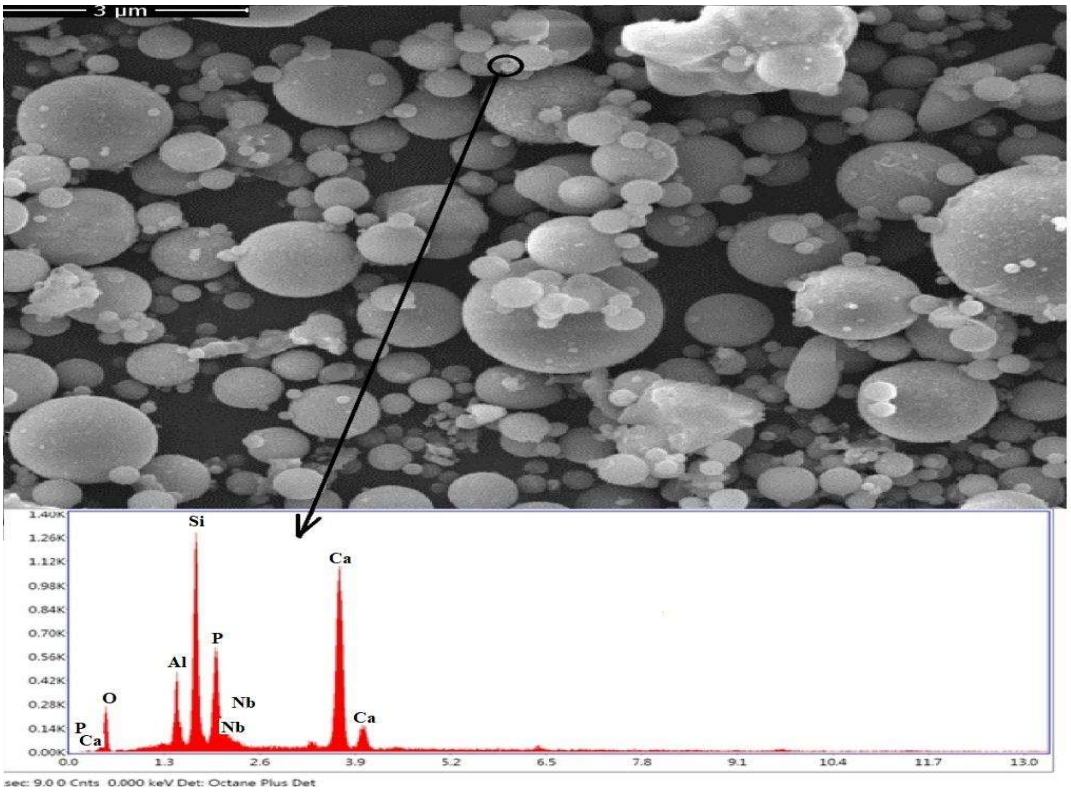

Figure 4.18d SEM-EDX images of FA synthesized catalyst FA-800 (fly ash calcined at 800 ºC).

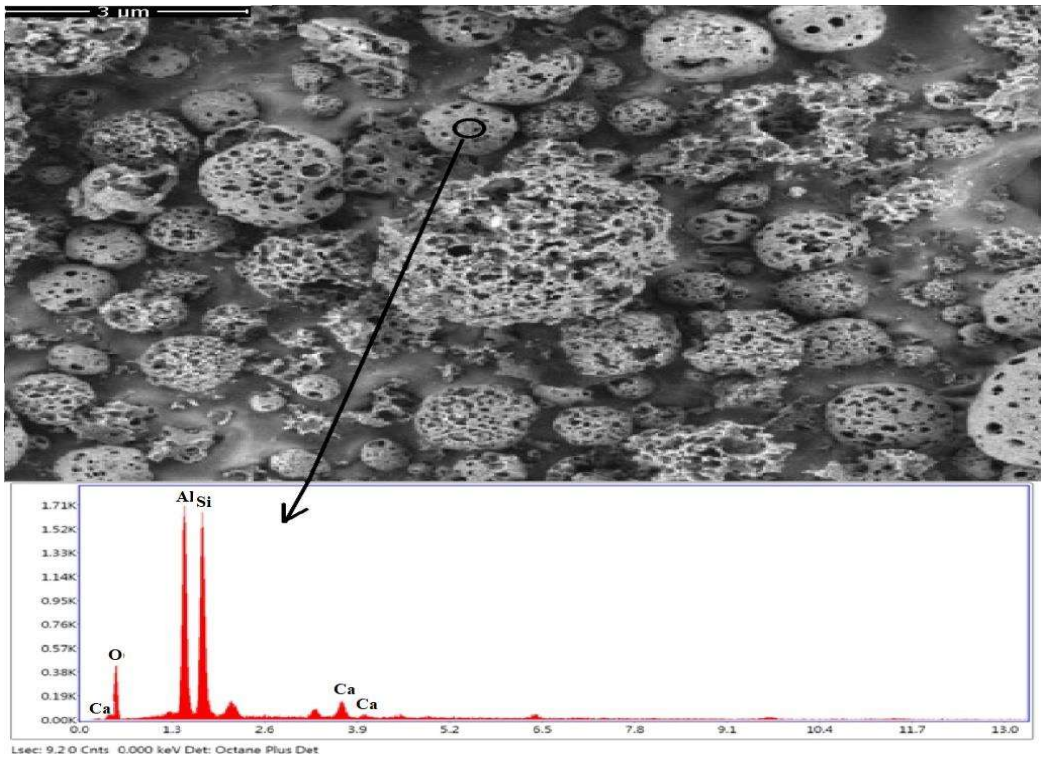

Figure 4.18e SEM-EDX images of FA synthesized catalyst FA-900 (fly ash calcined at 900 ºC).

4.2.2.1.2 BET surface area analysis

Table (4.8) shows that surface area and pore volume both increases with the increase in calcination temperature from 600 ^{o}C to 800 ^{o}C. Whereas, further increase in temperature to 900 ^{o}C, surface area gets decreased. The uncalcined or fresh fly ash (FAN) shows surface area of 1.74 m^2/g and pore volume of 2.25 ml/g. The maximum surface area of 310.40 m^2/g is obtained when the fly ash is calcined at a temperature of 800 ^{o}C (FA-800). However, catalyst surface area decreased to 5.78 m^2/g when calcination temperature is raised to 900 ^{o}C. The increase in temperature upto 800 ^{o}C, raised the surface area 177.4 times (310.40 m^2/g). It may be due to increase in temperature, the micropores get opened up which increases pore volume and surface area both upto heating of 800 ^{o}C. Beyond the calcination temperature 800 ^{o}C, the wall of micropores get collapsed resulting in low surface area. Thus, the study on catalytic pyrolysis of polyethylene using the catalyst FA-800 shows excellent performance in term of quantity and quality of liquid yield with higher BTEX production.

Table 4.8 Surface area, pore volume and (Si/Al) ratio of FA catalyst.

Name of catalysts	Surface area (m^2/g)	Pore volume (ml/g)	(Si/Al) ratio
FAN	1.74	2.25	2.18
FA-600	10.98	14.19	3.32
FA-700	25.95	19.34	5.22
FA-800	310.40	43.95	16.03
FA-900	5.78	59.28	1.43

4.2.2.1.3 FTIR Analysis

The Fourier Transform Infrared spectroscopy (FTIR) is an important analysis technique which detects various characteristic functional groups present in synthesized catalyst. In

order to collect systematic information about the chemical composition of the fly ash, all the catalysts were examined using FTIR in the wavelength range of 500-4000 cm^{-1}. Fig (4.19) shows the FTIR spectra of fly ash catalyst obtained at different calcination temperatures and fresh fly ash, respectively.

The sharp peak at 450 cm^{-1} and also the bands at 545 cm^{-1}, 585 cm^{-1}, and 600 cm^{-1} could be assigned to the structurally sensitive double five-member ring tetrahedral vibrations, and it is typical for the crystalline ZSM-5 zeolite. The characteristic bands between 850 and 1250 cm^{-1} can be assigned to the symmetric and asymmetric stretching vibrations of the Si–O–Si linkages of the zeolite framework. The vibration modes between 700 and 580 cm^{-1} are assigned to the internal vibration of SiO_4 and AlO_4 tetrahedra symmetric stretching vibration. The H–OH bending vibrations of the adsorbed water molecules are observed between 1700-1400 cm^{-1}. The IR spectroscopy carefully observes the acidic hydroxyl OH groups of solid catalysts. The IR band at 3700-3300 cm^{-1} is a characteristic of protonated form of zeolite and its intensity is correlated with framework aluminium (FAL). The IR band at 3619 cm^{-1} corresponds to bridging hydroxyl groups of the Bronsted acid sites that are found responsible for catalyzing cracking.

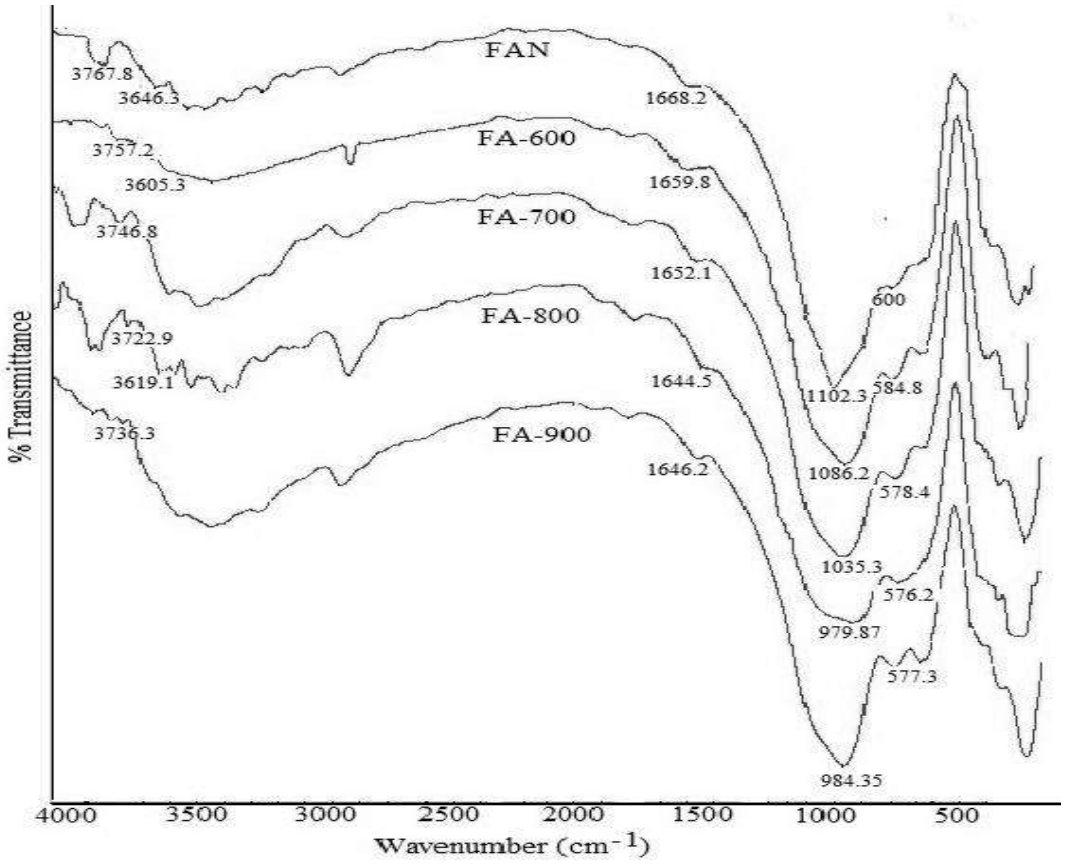

Figure 4.19 FT-IR spectrometry of synthesized fly ash catalyst; FAN, FA-600, FA-700, FA-800 and FA-900.

Formation of silicoaluminate crystalline material in FA-800 was confirmed by the shift of the band from 1102.3 cm^{-1} for FA to 979.87 cm^{-1} for FA-800 on Fourier transformed infrared (FTIR) spectra (Fig 4.18 and Table 4.9). An increase in tetrahedral Al (formation of zeolitic phases) would induce a shift of the band within the range of 1180–950 cm^{-1} (which is assigned to the asymmetric internal T-O stretching vibration mode of the TO_4 tetrahedra, where T = Si or Al) to a lower wave number (Agarwal and Rani, 2017; Xie et al., 2012). The four bands at 577, 612, 687 and 789 cm^{-1} confirm the formation of zeolitic material on synthesized fly ash catalyst (Gougazeh and Buhl, 2014). The FTIR absorption bands at 2856 and 2926 cm^{-1}, which are attributed to the symmetric and asymmetric stretching vibrations of C-H of FA-800, and it indicates that FA-800 formed a bilayer micelle, rather than monolayer coverage (Kung and Hayes, 1993).

Table 4.9 Comparison and shifting of bands data for FAN, FA-600, FA-700, FA-800 and FA-900 in FTIR spectroscopy.

Wave number (cm^{-1})	**Possible assignment**	**Observed value (cm^{-1})**				
		FAN	FA-600	FA-700	FA-800	FA-900
3700-3300	Stretching vibration of -OH group and Silanol (Si-OH)	3767.8 3646.3	3757.2 3605.3	3746.8 -	3722.9 3619.1	3736.3 -
1700-1400	-OH deformation & bending vibration of interstitial water	1668.2	1659.8	1652.1	1644.5	1646.2
1250-850	Asymmetric stretching of internal tetrachedral TO_4, Si-O-Si (T = Si, Al)	1102.3	1086.2	1035.3	979.87	984.35
700-580	Symmetric stretching of internal tetrachedral TO_4 (T=Si, Al)	- 600	- 584.8	- 578.4	668.2 576.2	- 577.3

4.2.2.2 Effect of parameters on pyrolysis yield

4.2.2.2.1 Effect of feed to catalyst ratio

The catalytic pyrolysis of waste polyethylene, polypropylene and polystyrene were performed using fly ash derived catalyst FA-800 at different feed to catalyst ratio of 10:1, 20:1 and 30:1 for A-type (vapor phase), B-type (liquid phase) and C-type (vapor and liquid/multiphase) reactor arrangements, respectively. The detailed reactor arrangement is shown in the experimental section (page no. 39). Fig (4.20a) to Fig (4.20c) show the comparison of liquid yield, gas yield and solid residue of catalytic pyrolysis of waste PE, PP and PS at a temperature of 700 ^{o}C for A-type reactor arrangement. The effect of feed to catalyst ratio is presented here for A-type reactor arrangement as A-type (vapor phase) gives maximum liquid yield irrespective of waste plastics used. Although it is not shown here, the effect of feed to catalyst ratio for B-type and C-type reactor arrangements are presented in Appendix-A5. It is seen form Fig (4.20a) that the feed to catalyst ratio of 20:1

(polyethylene to FA-800) gives maximum liquid yield of 78.2 wt. % and it may be because of the large number of active 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 76.1 wt. % with maximum solid residue of 2.4 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 in 10:1 feed to catalyst ratio, the process would be less feasible as compared to 20:1 feed to catalyst ratio.

Similar results were obtained for polypropylene and polystyrene as shown in Fig (4.20b) and Fig (4.20c), respectively. The maximum liquid yield for polypropylene of 83.2 wt. % was obtained at feed to catalyst ratio of 20:1 as shown in Fig (4.20b). For polystyrene, maximum liquid yield of 84.36 wt. % was obtained at 20:1 feed to catalyst ratio. However, feed to catalyst ratio of 30:1 produced liquid yield of 80.97 wt. % and 82.41 wt. % for polypropylene and polystyrene, respectively. Thus, all the catalytic pyrolysis of polyethylene, polypropylene and polystyrene were carried out using feed to catalyst ratio of 20:1, irrespective of the reactor arrangements and all other process parameters used.

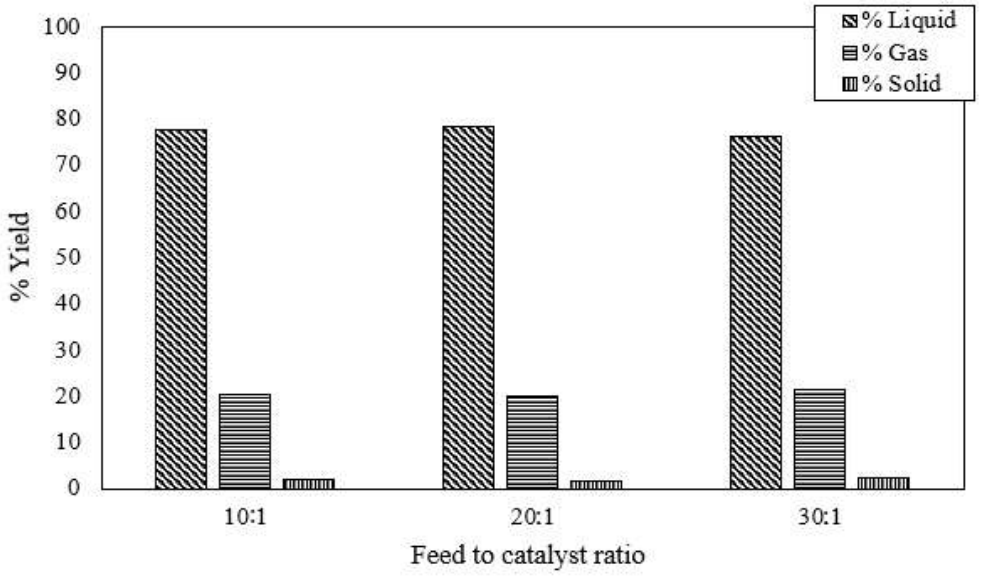

Figure 4.20a Comparison of liquid yield, gaseous yield and solid residue at 700 ^{o}C for A-type (Vapor phase) arrangement using FA-800 for 50 g of polyethylene.

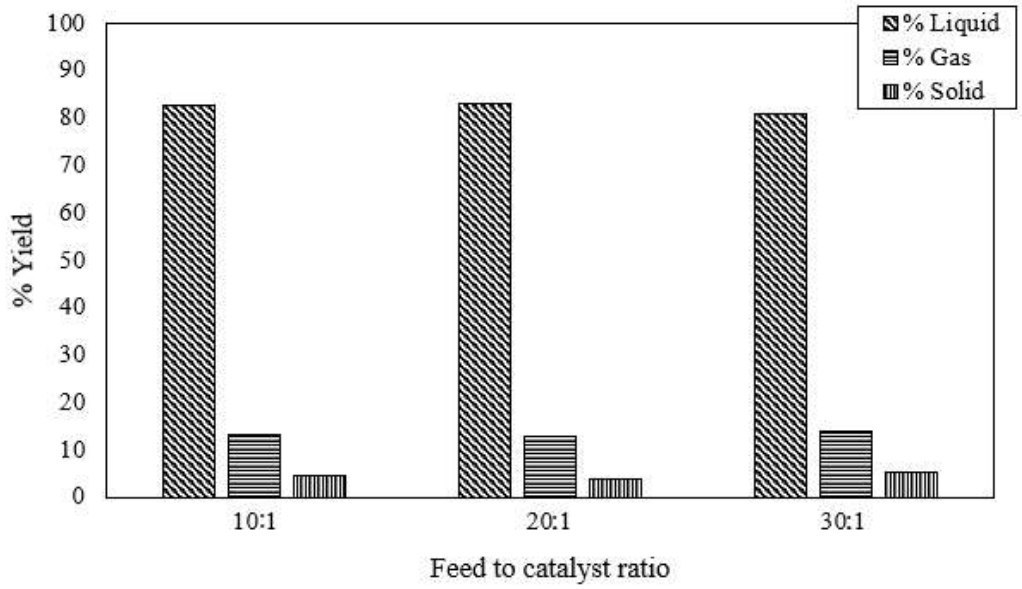

Figure 4.20b Comparison of liquid yield, gaseous yield and solid residue at 700 ^{o}C for A-type (Vapor phase) arrangement using FA-800 for 50 g of polypropylene.

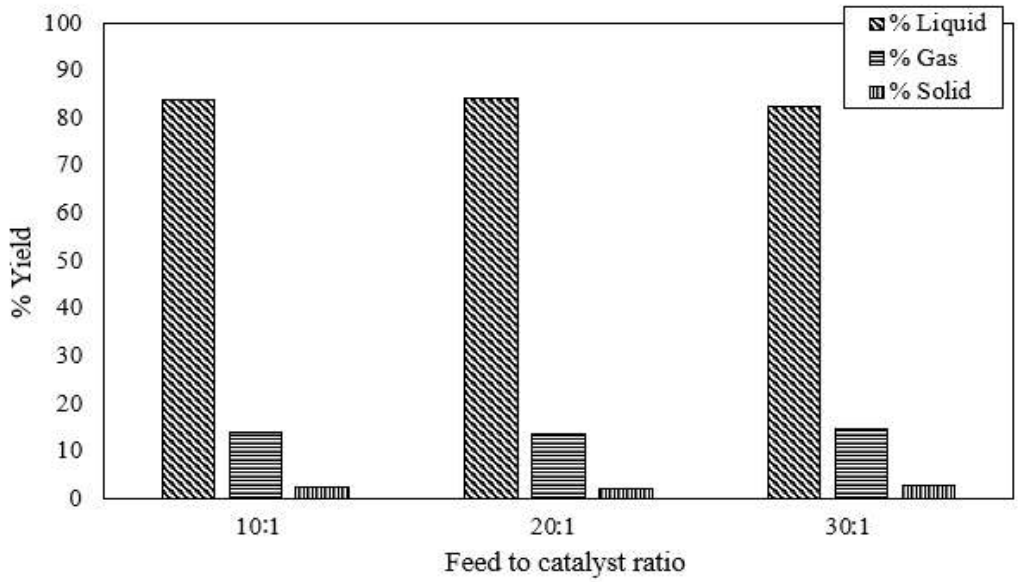

Figure 4.20c Comparison of liquid yield, gaseous yield and solid residue at 700 ^{o}C for A-type (Vapor phase) arrangement using FA-800 for 50 g of polystyrene.

4.2.2.2.2 Effect of reaction time

The effect of reaction time on the conversion for catalytic pyrolysis of polyethylene, polypropylene and polystyrene using fly ash derived catalyst FA-800 at a temperature of 700 ^{o}C is shown in Fig (4.21a) to Fig (4.21c) for A-type reactor arrangement. The effect of

reaction time for B-type and C-type reactor arrangements are presented in Appendix-A6. It is seen from Fig (4.21a) to Fig (4.21c) that the percentage conversion increases with the increase in reaction time for all three waste plastics, polyethylene, polypropylene and polystyrene, respectively. This indicates that the reaction time plays vital role for the conversion of waste plastic and achieving product yield. After 25 min, the percentage conversion becomes constant for PE, PP and PS. The Fig (4.21a), Fig (4.21b) and Fig (4.21c) show that there is no conversion after 25 min of reaction time. Thus, to ensure complete conversion and achieve maximum product yield, catalytic pyrolysis of PE, PP and PS were performed for 30 min for all three A-type, B-type and C-type reactor arrangements.

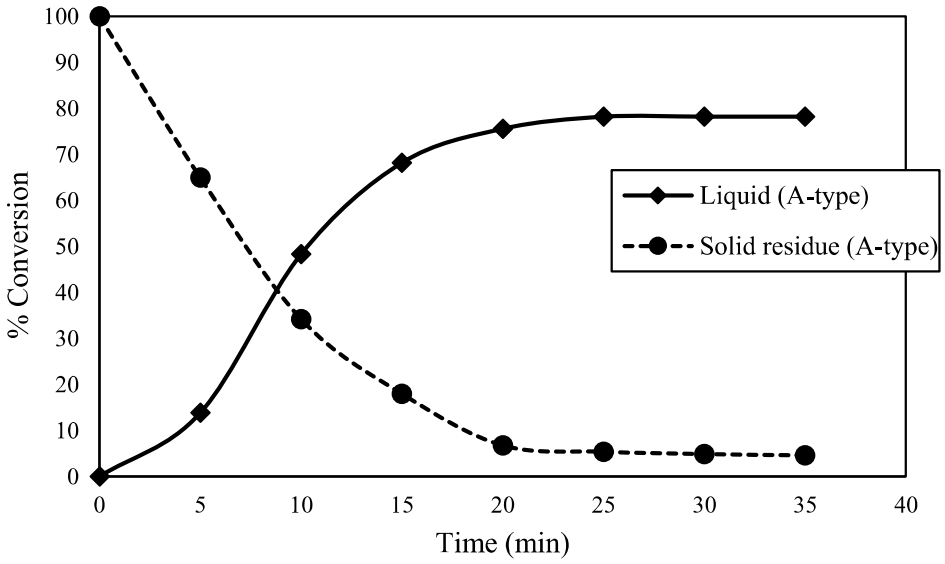

Figure 4.21a Time vs. percentage conversion of liquid and solid residue for catalytic pyrolysis of polyethylene using FA-800 catalyst at the temperature of 700 °C in A-type reactor arrangement (vapor phase).

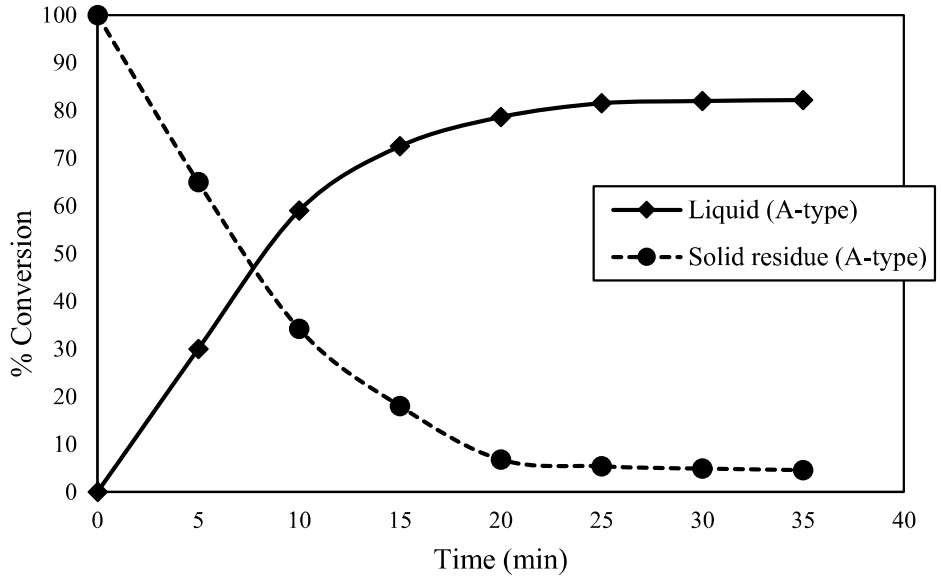

Figure 4.21b Time vs. percentage conversion of liquid and solid residue for catalytic pyrolysis of polypropylene using FA-800 catalyst at the temperature of 700 °C in A-type reactor arrangement (vapor phase).

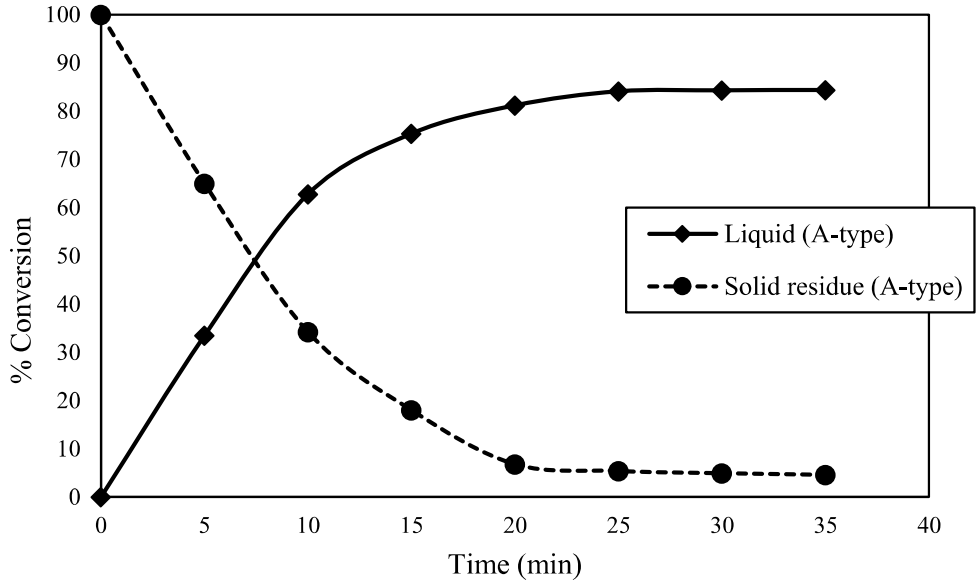

Figure 4.21c Time vs. percentage conversion of liquid and solid residue for catalytic pyrolysis of polystyrene using FA-800 catalyst at the temperature of 700 °C in A-type reactor arrangement (Vapor phase).

4.2.2.2.3 Effect of calcination temperature

Fig (4.22a) shows effect of calcination temperature for the catalytic pyrolysis of polyethylene at a temperature of 700 ^{o}C on synthesized natural catalysts derived from fly ash. As the pyrolysis temperature of 700 ^{o}C resulting in better quality of liquid yield with

appreciable amount of liquid and gaseous hydrocarbon, the effect of calcination temperatures on product yields are presented in Fig (4.22a) for this temperature (700 °C) only. However, other pyrolysis temperature 500 °C, 600 °C and 800 °C were also studied for the effect of calcination temperatures on product yield and those are shown in Appendix-A7.

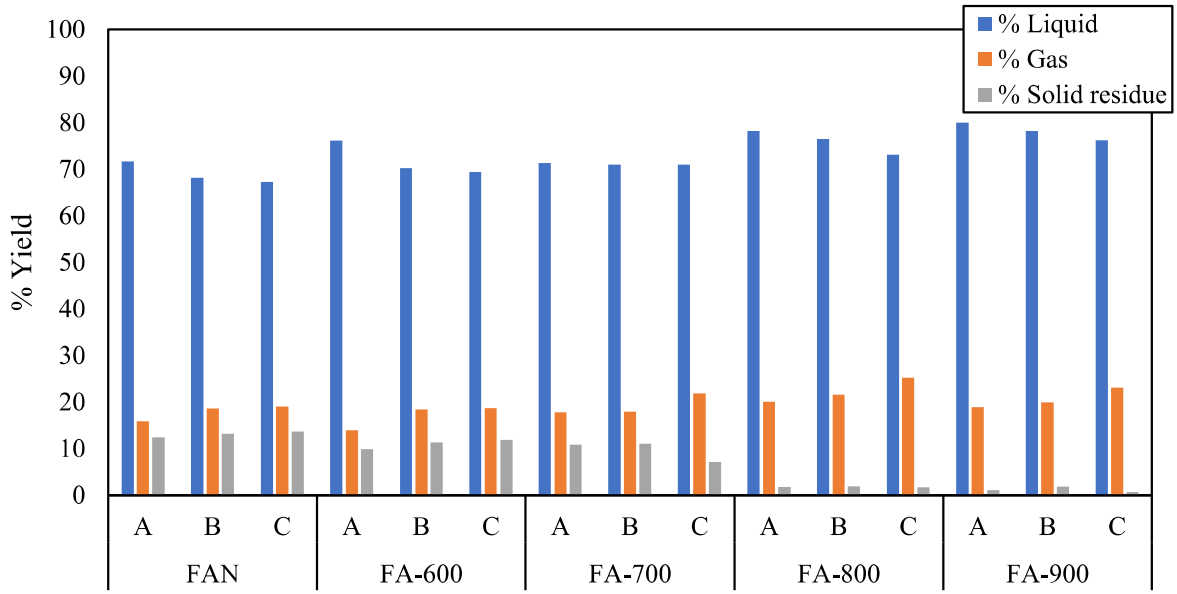

Figure 4.22a Product yield obtained from catalytic pyrolysis of polyethylene using A-type, B-type and C-type reactor arrangements at the temperature of 700 °C.

It is seen from the Fig (4.22a) that the liquid yield increases with the increase in calcination temperature up to 800 °C. FA-800 catalyst resulting in maximum liquid yield of 78.2 wt.%, 76.5 wt. % and 73.12 wt. % for A-type, B-type and C-type/multiphase reactor arrangements, respectively. Although, at the same temperature catalyst FA-900 produced liquid yield of 80.02 wt. %, 78.25 wt. % and 76.22 wt. % for A-type, B-type and C-type reactor arrangements, which becomes waxy at room temperature. It may be due to poor quality of catalyst with very low surface area (5.78 m^2/g) of FA-900 as shown in Table (4.8) (page no. 103). The use of catalyst FA-800 reduces the solid residue and improves the liquid yield quantitatively and qualitatively in terms of aromatics BTEX at a temperature of 700 °C irrespective of reactor arrangements. The gaseous yield also increased

dramatically for FA-800 catalyst in C-type/multiphase arrangement at the same temperature. The catalyst affects the pyrolysis mechanism and converts the heteroatoms into gaseous range hydrocarbons.

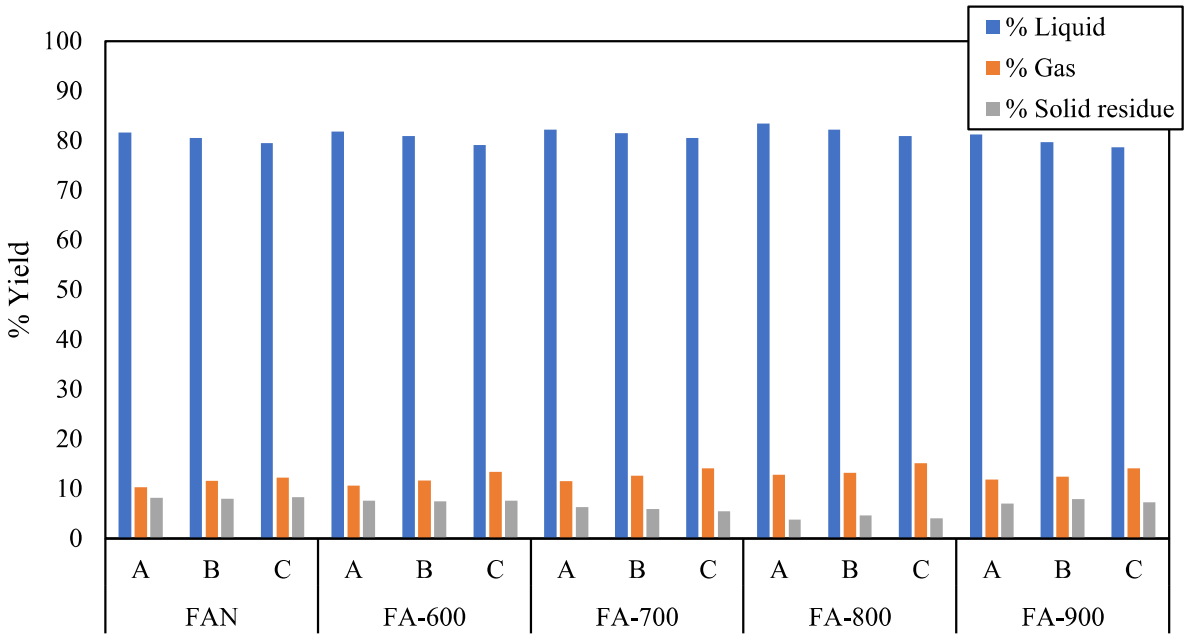

Figure 4.22b Product yield obtained from catalytic pyrolysis of polypropylene using A-type, B-type and C-type reactor arrangements at the temperature of 700 ºC.

Fig (4.22b) shows the comparison of liquid yield, gas yield and solid residue obtained from catalytic pyrolysis of polypropylene using fly ash derived catalyst at different temperatures. The maximum liquid yield of 83.4 wt. %, 82.2 wt. % and 80.9 wt. % were obtained for FA-800 catalyst in A-type, B-type and C-type reactor arrangements, respectively. However, FA-900 catalyst at the same temperature produced liquid yield of 81.23 wt. %, 79.68 wt. % and 78.67 wt. % for A-type, B-type and C-type reactor arrangements, respectively which is waxy at room temperature. It may be due to poor quality of catalyst with very low surface area (5.78 m^2/g) of FA-900 as shown in Table (4.8). Use of catalyst FA-800 reduced the solid residue and improved the liquid yield quantitatively and qualitatively in terms of aromatics BTEX at 700 ºC irrespective of reactor arrangements. The gaseous yield also increased dramatically for FA-800 catalyst in C-type/multiphase

arrangement at the same temperature. It may be due to selective cracking of comparatively higher molecular weight hydrocarbon at both liquid and vapor phase in C-type arrangement.

Fig (4.22c) shows the comparison of liquid yield, gas yield and solid residue obtained from catalytic pyrolysis of polystyrene using fly ash derived catalyst at different temperatures. The maximum liquid of 84.36 wt. %, 83.65 wt. % and 82.36 wt. % were obtained for FA-800 catalyst in A-type, B-type and C-type reactor arrangements, respectively. Polystyrene also showed similar trend as found for the polyethylene and polypropylene. At the temperature of 700 °C, FA-900 catalyst produced liquid yield of 76.26 wt. %, 75.24 wt. % and 74.32 wt. % for A-type, B-type and C-type reactor arrangements, respectively which is waxy at room temperature. The gaseous yield also increased dramatically for FA-800 catalyst in C-type/multiphase arrangement at the same temperature. It may be due to selective cracking of comparatively higher molecular weight hydrocarbon at both liquid and vapor phase in C-type arrangement.

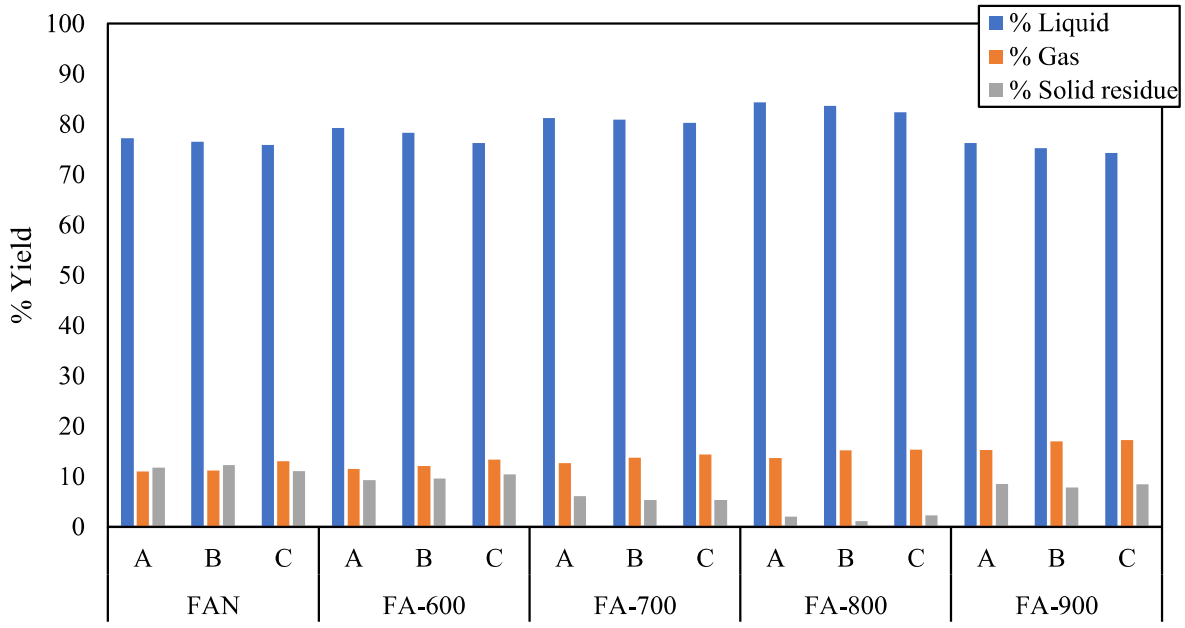

Figure 4.22c Product yield obtained from catalytic pyrolysis of polystyrene using A-type, B-type and C-type reactor arrangements at the temperature of 700 °C.

As discussed earlier, calcination temperature plays a crucial role during the synthesis of FA catalyst resulting in the formation of superior quality FA-800 catalyst at a calcination temperature of 800 ^{o}C. Thus, the FA-800 catalyst could effectively convert waste plastic PE, PP and PS to valuable aromatics BTEX with better quality of liquid and gaseous yield at a pyrolysis temperature of 700 ^{o}C.

4.2.2.2.4 Effect of reaction temperature

Fig (4.23) to Fig (4.25) show the comparison of product yield obtained from catalytic pyrolysis of waste PE, PP and PS at different temperatures in A-type, B-type and C-type reactor arrangements. The catalytic pyrolysis using reactor arrangements A-type, B-type and C-type were carried out at the temperature of 500 ^{o}C, 600 ^{o}C, 700 ^{o}C and 800 ^{o}C, respectively. The product yields obtained by the catalytic pyrolysis were compared to show the improvement in product, qualitatively and quantitatively for the liquid yield, gaseous yield and solid residue, respectively. As already mentioned, “A” refers to the catalytic pyrolysis of waste plastic in vapor phase only, “B” refers to the catalytic pyrolysis of waste plastic in liquid phase only and “C” refers to the both liquid and vapor phase/multiphase catalytic pyrolysis. In the A-type reactor arrangement produced gases interacts with FA catalyst particles in vapor phase, while B-type reactor arrangement melted liquid waste plastic interacts with FA catalyst particles and leaving relatively smaller hydrocarbon molecules. Whereas, C-type/multiphase reactor arrangement provides opportunities for catalyst and waste plastic interaction in the bottom of the reactor (liquid phase) followed by interaction of smaller hydrocarbon molecules with FA catalyst in vapor phase resulting in more aromatics in comparison to A-type/vapor phase and B-type/liquid phase reactor arrangement.

As discussed earlier in effect of calcination temperature section, the superior quality of FA-800 catalyst gives better results in comparison to other fly ash derived catalyst FAN, FA-600, FA-700 and FA-900. The effect of reaction temperature on product yield and BTEX obtained from waste PE, PP and PS are shown only for FA-800 catalyst in following section. Although, it is not shown here, the effect of reaction temperature on waste PE, PP and PS using FAN, FA-600, FA-700 and FA-900 catalysts are shown in Appendix-A8.

4.2.2.2.4.1 Polyethylene as feed

It is seen in the Fig (4.23) that the catalyst FA-800 produced more liquid yield for A-type (vapor phase) than the B-type (liquid phase) and C-type/multiphase reactor arrangement irrespective of pyrolysis temperature used. The optimum feed to catalyst ratio of 20:1 and reaction time 30 min were maintained for the pyrolysis process. The maximum liquid yield of 78.2 wt.%, 76.5 wt. % and 73.12 wt. % were obtained for catalytic pyrolysis at a temperature of 700 ^{o}C using the reactor arrangement A-type, B-type and C-type, respectively. The use of catalyst decreases the quantity of liquid yield in comparison to thermal process, but increases the quality of liquid oil in terms of aromatics BTEX, which is discussed later on (page no. 118). However, gaseous yield (25.2 wt. %) for C-type/ multiphase was always high for all temperatures in comparison to B-type (21.6 wt. %) and A-type (20.04 wt. %). The catalyst affects the pyrolysis mechanism and converts the heteroatoms into a gaseous range hydrocarbon. The catalyst in vapor phase (A-type) results in maximum liquid yield of 78.2 wt.% and solid residue of 1.76 wt.%. It may be due to selective cracking at vapor phase of comparatively higher molecular weight hydrocarbon which are produced via thermal cracking at the bottom of reactor. In the catalytic cracking using B-type reactor arrangement, liquid yield further decreases (76.5 wt.%), gaseous yield increases (21.6 wt.%) and solid residue decreases (1.9 wt.%). In the arrangement B-type,

the FA-800 catalyst is in contact with polyethylene from the beginning of the reaction. Thus, largest to smallest hydrocarbon molecules may interact with the FA-800, which results in more aromatics and gaseous hydrocarbon.

The solid residue gets decreased in the order B-type (liquid phase) > A-type (vapor phase) > C-type (multiphase). The solid residue (1.66 wt.%) is also very low for C-type reactor arrangement. It may be due to the presence of catalyst in both phases (C-type/liquid and vapor phase) the higher hydrocarbon molecules which are produced at the bottom of the reactor (liquid phase) will move through the vapor phase catalyst bed, which helps in further selective cracking of the higher hydrocarbon molecule to lower aromatic and gaseous range hydrocarbon.

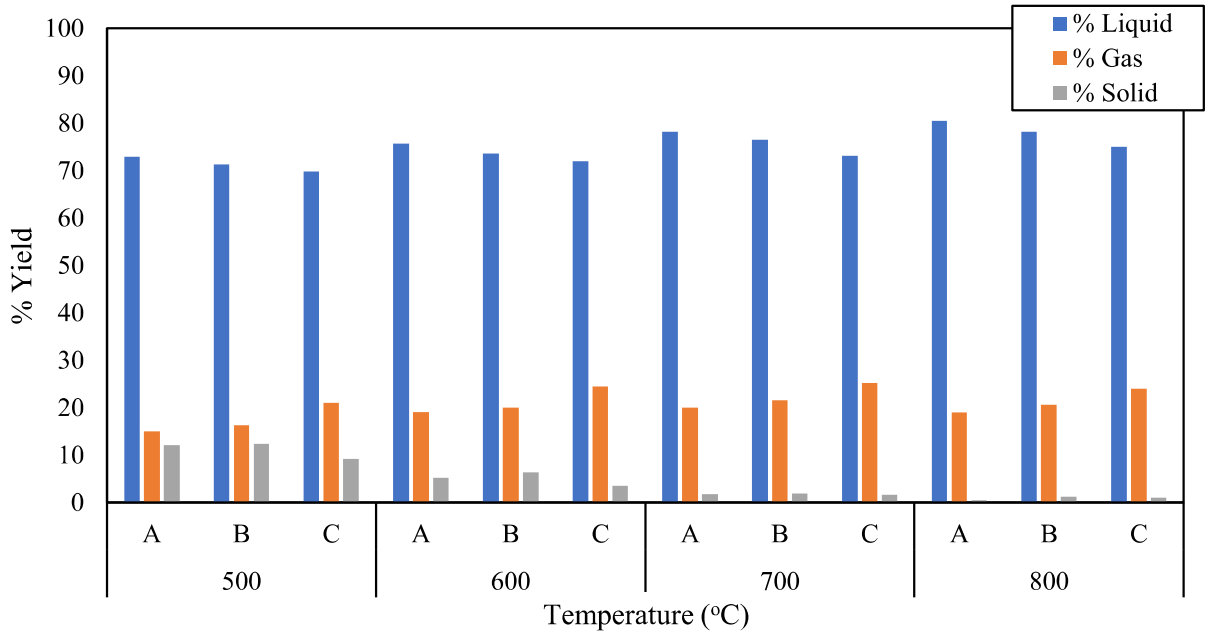

Figure 4.23 Comparison of liquid, gas and solid yield obtained from catalytic pyrolysis of polyethylene for reactor arrangements A-type, B-type and C-type using catalyst FA-800.

It is clearly seen in the Fig (4.23) that the gaseous yield obtained was maximum (25.2 wt.%) for C-type/multiphase reactor arrangement, irrespective of temperature. Thus, the liquid yield obtained is minimum (73.12 wt.%) for C-type reactor arrangement. The aromatic content, mainly BTEX was found to be highest amount for C-type/multiphase reactor

arrangement in comparison to A-type, B-type reactor arrangement and thermal pyrolysis at the same temperature. The FA-800 affects the pyrolysis mechanism and converts heteroatoms into gaseous hydrocarbons. As BET surface area analysis and SEM-EDX suggest that FA-800 catalyst could be the superior catalyst due to its maximum surface area 310.10 m^2/g and (Si/Al) ratio of 16.03.

The liquid yield is always high for the temperature ranging from 500 ^oC to 800 ^oC for A-type reactor arrangement. On the other hand, gaseous yield is always higher for C-type/ multiphase pyrolysis at this temperature range. It implies that the A-type only converts waste polyethylene to liquid range hydrocarbons due to its shorter duration of interaction between cracked hydrocarbons and FA-800 catalyst particles. However, C-type/multiphase pyrolysis converts the cracked liquid range hydrocarbons to lighter hydrocarbon molecules in two stages when hydrocarbon vapors from the bottom of the reactor/liquid escapes and passes through the catalyst bed in the vapor phase. In addition, multiphase (C-type) gives more aromatics BTEX in comparison to A-type and B-type reactor arrangements. Thus, probably the use of FA-800 resulting in slightly low quantity of liquid yield but improved the quality of liquid oil in terms of aromatics BTEX.

Evaluation of BTEX yield in the pyrolysis oil/liquid yield is main aim of the thesis work, as already mentioned. Thus, the calibration characteristics (Fig 3.9) were developed for the evaluation of BTEX in the pyrolysis oil obtained by the catalytic pyrolysis of PE, PP and PS using FA-800 catalyst as described in chapter 3 experimental section (Page no. 39). Table (4.10) shows the aromatic content (BTEX) in pyrolysis oil obtained from the catalytic pyrolysis of waste plastic polyethylene at different temperatures.

Table 4.10 The aromatic content (BTEX) in pyrolysis oil obtained from polyethylene at different temperatures using FA-800 catalyst.

Pyrolysis temperature (°C)		Benzene (wt. %)	Toluene (wt. %)	Ethylbenzene (wt.%)	Xylene (wt. %)	Total BTEX (wt. %)
500	A-type	4.43	7.35	5.17	1.82	18.77
	B-type	5.19	7.41	5.23	1.93	19.76
	C-type	5.28	7.48	5.28	1.98	20.02
600	A-type	5.64	7.72	5.41	2.11	20.88
	B-type	6.07	7.76	5.46	2.14	21.43
	C-type	6.18	7.83	5.49	2.17	21.67
700	A-type	5.78	7.87	5.53	2.16	21.34
	B-type	6.16	7.90	5.54	2.21	21.81
	C-type	6.36	7.95	5.57	2.22	22.10
800	A-type	4.49	7.40	5.21	1.89	18.99
	B-type	5.26	7.46	5.29	1.97	19.98
	C-type	5.31	7.53	5.36	2.05	20.25

It is seen from Table (4.10) that the highest amount of aromatic content i.e., 22.10 wt.% was found in the pyrolysis oil at a temperature of 700 °C using FA-800 catalyst in multiphase/C-type reactor arrangement. It may be due to the very high surface area 310.40 m^2/g of FA-800 catalyst, high Si to Al ratio (=16.03) could provide more acidic sites with higher selectivity which produces maximum amount of more aromatics (BTEX). Moreover, vapor-liquid phase/multiphase (C-type) produced more BTEX (22.11 wt. %) than that of vapor phase (A-type) catalytic pyrolysis (21.34 wt. %) and liquid phase (B-type) catalytic pyrolysis (21.81 wt. %). For the C-type pyrolysis, smaller hydrocarbon molecules are formed due to catalytic pyrolysis of PE at the liquid phase followed by the second stage selective catalytic cracking of liquid range hydrocarbon molecules on FA-800 catalyst in the vapor phase. The catalyst in vapor phase (A) only interacts with the

molecules which comes from thermal pyrolysis in the liquid phase. Thermal pyrolysis is non-selective, which gives the product may not be suitable for aromatization in vapor phase. Thus, catalytic pyrolysis (A-type) gives lower BTEX (21.34 wt.%) than C-type at a temperature of 700 ^{o}C. For the B-type catalytic pyrolysis, the catalyst is in contact with PE from the beginning, resulting in selective cracking of wide range of molecules. Thus, B-type arrangement gives BTEX yield of 21.81 wt. % which is more than A-type (21.34 wt. %) at the same temperature. As discussed earlier, among all pyrolysis, C-type (vapor and liquid phase) catalytic reactor arrangement gives highest BTEX yield of 22.11 wt. %. Thus, C-type reactor arrangement could be recommended as suitable design to convert polyethylene into BTEX which is value added upgraded product. It should be noted that the thermal pyrolysis of polyethylene produced very low BTEX yield of 10.75 wt.% at the same temperature of 700 ^{o}C (Table 4.2a, page no. 57).

4.2.2.2.4.2 Polypropylene as feed

Fig (4.24) shows the product yield obtained from catalytic pyrolysis of polystyrene using FA-800 catalyst in A-type, B-type and C-type reactor arrangements at the temperature of 500 ^{o}C, 600 ^{o}C, 700 ^{o}C and 800 ^{o}C, respectively. The optimum feed to catalyst ratio of 20:1 and reaction time 30 min were maintained for the pyrolysis process as used in the case of polyethylene and polypropylene. The maximum liquid yield of 83.4 wt. %, 82.2 wt. % and 80.9 wt. % were obtained at the temperature of 700 ^{o}C for FA-800 catalyst in A-type, B-type and C-type reactor arrangements, respectively. The liquid yield is always high for the temperature ranging from 500 ^{o}C to 800 ^{o}C for A-type reactor arrangement.

The solid residue gets reduced and gas yield increases for catalytic pyrolysis in the reactor arrangements A, B and C in comparison to that of thermal pyrolysis. The solid residue gets decreased in the order B-type (liquid phase) > C-type (multiphase) > A-type (vapor phase).

C-type/multiphase reactor arrangement produced maximum gas yield of 15.1 wt. % and solid residue of 4 wt. % for the catalytic pyrolysis of PP using FA-800. The reason has already been discussed for polyethylene (page no. 115). The selective cracking of comparatively higher molecular weight hydrocarbon at both liquid and vapor phase in C-type arrangement. However, gaseous yield (15.1 wt. %) for C-type/multiphase was always high for all temperatures in comparison to B-type (13.2 wt. %) and A-type (12.8 wt. %). The aromatic content, mainly BTEX was found to be highest amount for C-type/multiphase reactor arrangement in comparison to A-type, B-type reactor arrangement and thermal pyrolysis at the same temperature. The catalyst in vapor phase (A-type) results in maximum liquid yield of 83.4 wt.% and solid residue of 3.8 wt.%. It may be due to selective cracking at vapor phase of comparatively higher molecular weight hydrocarbon which are produced via thermal cracking at the bottom of reactor.

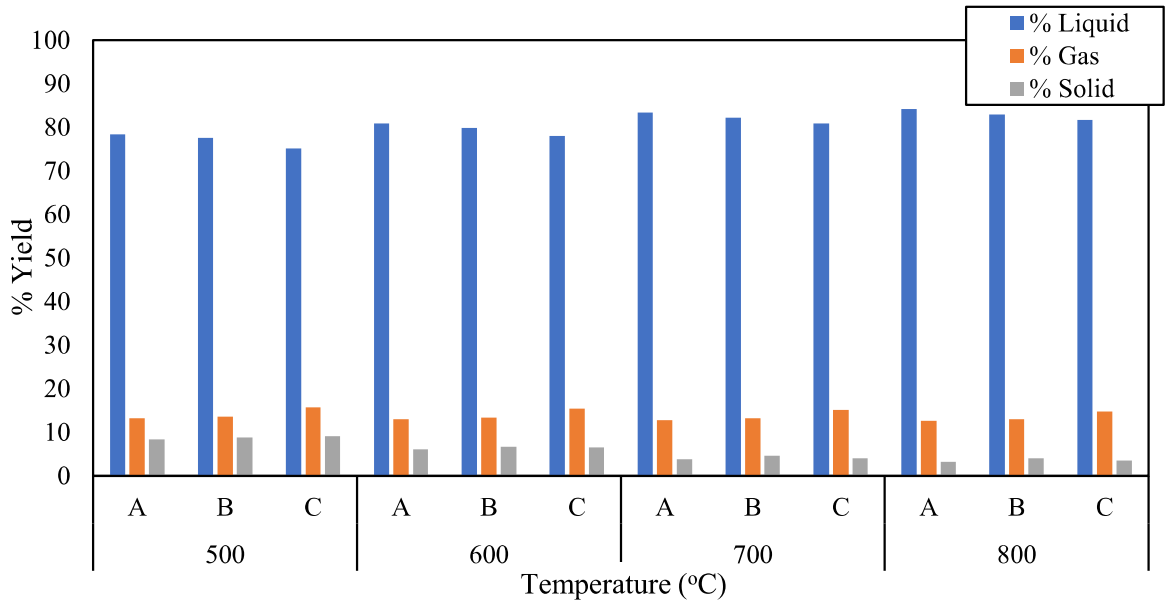

Figure 4.24 Comparison of liquid, gas and solid yield obtained from catalytic pyrolysis of polypropylene for reactor arrangements A-type, B-type and C-type using catalyst FA-800.

It is seen in the Fig (4.24) that the liquid yield (82.2 wt. %) for B-type is lower than A-type (83.4 wt. %). Whereas, gaseous yield increases from 12.8 wt. % (A-type) to 13.2 wt.% (B-type) at the same temperature (700 °C). In the reactor arrangement B, the FA-800

catalyst is in contact with polypropylene from the beginning of the reaction. Thus, largest to smallest hydrocarbon molecules may interact with the FA-800, which results in more aromatics and gaseous hydrocarbon.

It is seen from Table (4.11) that the highest amount of aromatic content i.e., 43.43 wt.% was found in the pyrolysis oil at a temperature of 700 ^{o}C using catalyst in multiphase/C-type reactor arrangement. It may be due to the FA-800 catalyst, having smaller pore size provides higher selectivity for lower alkanes. Thus, for the C-type pyrolysis smaller molecules in the liquid and vapor phase both comes in contact with FA-800. This gives maximum BTEX of 43.43 wt. % as per the reaction schemes shown in the Fig (4.10) (page no. 78). The C-type/multiphase pyrolysis produced benzene, toluene, ethylbenzene and xylene are in maximum quantity irrespective of temperatures and reactor arrangements. The reason has already been discussed for ZSM-5 (page no. 81) and FA-800 for PE pyrolysis (page no.118). It is generally proposed that on acid catalysts the aromatization of alkanes occurs through protolysis of alkane, cracking of carbonium ion to alkane and alkene, oligomerization of alkenes, cyclization of oligomerized products and formation or aromatics from cyclic rings by hydrogen transfer. However, catalyst in vapor phase (A) only interacts with the molecules which comes from thermal pyrolysis in the liquid phase. Thus, catalytic pyrolysis (A-type) gives lower BTEX (42.21 wt.%) than C-type at a temperature of 700 ^{o}C. For the B-type catalytic pyrolysis, the catalyst is in contact with PP from the beginning, resulting in selective cracking of wide range of molecules. Thus, B-type arrangement gives BTEX (42.63 wt. %) at the same temperature (700 ^{o}C). As discussed earlier, among all pyrolysis, C-type (vapor and liquid phase) catalytic reactor arrangement gives highest BTEX yield (43.43 wt. %).

Table 4.11 The Aromatic content (BTEX) in pyrolysis oil obtained from polypropylene at different temperatures using FA-800 catalyst.

Pyrolysis temperature (°C)		**Benzene (wt. %)**	**Toluene (wt. %)**	**Ethylbenzene (wt.%)**	**Xylene (wt. %)**	**Total BTEX (wt. %)**
500	A-type	8.73	2.63	2.54	20.93	34.83
	B-type	8.89	2.78	2.65	21.15	35.47
	C-type	9.15	2.93	2.71	21.32	36.11
600	A-type	9.62	2.81	2.76	24.03	39.22
	B-type	9.73	2.96	2.87	24.48	40.04
	C-type	10.03	3.15	2.93	24.75	40.86
700	A-type	9.85	3.10	2.92	26.34	42.21
	B-type	9.95	3.26	3.01	26.41	42.63
	C-type	10.34	3.45	3.12	26.52	43.43
800	A-type	8.76	2.68	2.55	21.07	35.06
	B-type	8.93	2.89	2.73	21.19	35.74
	C-type	9.29	3.01	2.77	21.54	36.61

The significant observations of the present study are that the C-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. As already discussed, the commercial gasoline also contains about 36.45 wt. % BTEX to improve octane rating of fuel (Table 4.1). It should be noted that the thermal pyrolysis of polypropylene produced low BTEX yield of 30.91 wt.% at the same temperature of 700 °C (Table 4.5). The results indicate that the performance of FA-800 catalyst is comparable to commercial ZSM-5 in terms of liquid yield and aromatics/BTEX content.

4.2.2.2.4.3 Polystyrene as feed

Fig (4.25) shows the product yield obtained for A-type, B-type and C-type reactor arrangements using catalytic pyrolysis of polystyrene using FA-800 at the temperature of 500 ^{o}C, 600 ^{o}C, 700 ^{o}C and 800 ^{o}C, respectively. The optimum feed to catalyst ratio of 20:1 and reaction time 30 min were maintained for the pyrolysis process. Similar to polyethylene and polypropylene, the product yield obtained are compared for different reactor arrangements to show the improvement in product qualitatively and quantitatively for the liquid yield, gaseous yield and solid residue, respectively. The maximum liquid yield of 84.36 wt. %, 83.65 wt. % and 82.36 wt. % were obtained at 700 ^{o}C for FA-800 catalyst in A-type, B-type and C-type reactor arrangements, respectively. The liquid yield is always high for the temperature ranging from 500 ^{o}C to 800 ^{o}C for A-type reactor arrangement. The solid residue gets reduced and gas yield increases for catalytic pyrolysis in the reactor arrangements A-type, B-type and C-type in comparison to that of thermal pyrolysis.

The solid residue gets decreased in the order C-type (multiphase) > A-type (vapor phase) > B-type (liquid phase). C-type/multiphase reactor arrangement produced maximum gas yield of 15.35 wt. % and solid residue of 2.29 wt. % for the catalytic pyrolysis of PP using FA-800. It may be due to selective cracking of comparatively higher molecular weight hydrocarbon at both liquid and vapor phase in C-type arrangement. The gaseous yield (15.35 wt. %) for C-type/multiphase was always high for all temperatures in comparison to B-type (15.2 wt. %) and A-type (13.65 wt. %). Higher gaseous yield for multiphase reaction may be due to the catalyst is in both liquid and vapor phase helps in two stage catalytic reaction of alkanes. In the first stage, the catalytic pyrolysis is same as that of B type arrangement (liquid phase) followed by a second stage pyrolysis in the vapor phase of lighter alkanes which escapes from first stage. Thus, C arrangements behaves as a multiphase catalytic pyrolysis with more production of aromatics/BTEX and gaseous

hydrocarbons in comparison to catalytic pyrolysis using A-type and B-type reactor arrangement. The catalyst in vapor phase (A-type) results in maximum liquid yield of 84.36 wt. % and solid residue of 1.99 wt. %. It may be due to selective cracking at vapor phase of comparatively higher molecular weight hydrocarbon which are produced via thermal cracking at the bottom of reactor. In the reactor arrangement B-type, the FA-800 catalyst is in contact with polystyrene from the beginning of the reaction. Thus, largest to smallest hydrocarbon molecules may interact with the FA-800, which results in more aromatics and gaseous hydrocarbon.

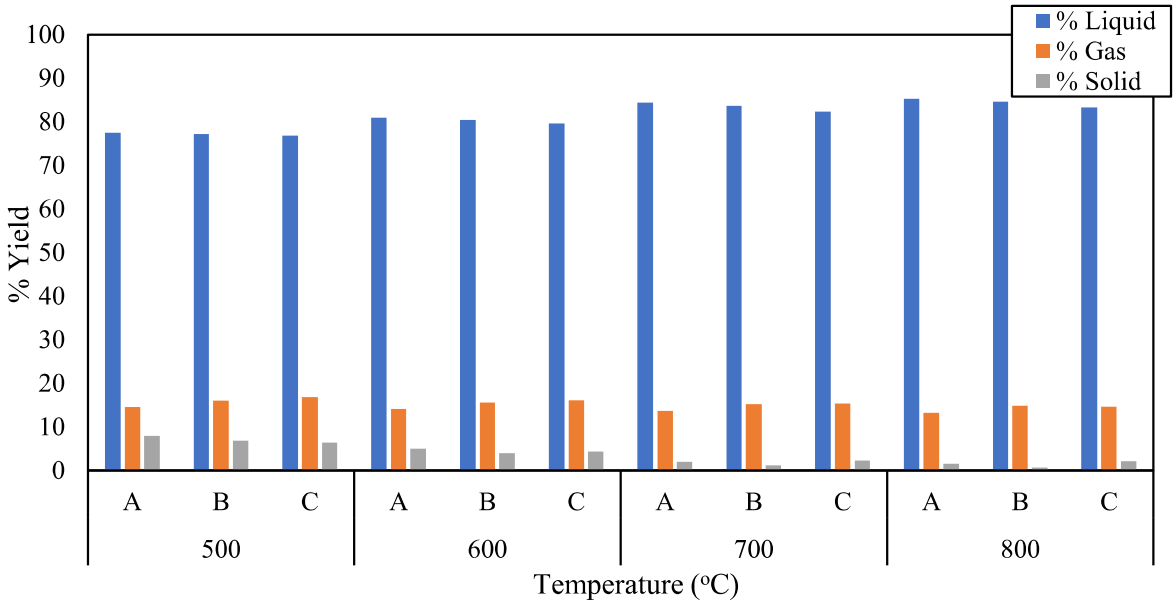

Figure 4.25 Comparison of liquid, gas and solid yield obtained from catalytic pyrolysis of polystyrene for reactor arrangements A-type, B-type and C-type using catalyst FA-800.

The aromatic content BTEX was also evaluated using similar method as discussed earlier (page no. 47) The similar trend for BTEX was observed for polystyrene pyrolysis as it was seen for polyethylene (page no. 118) and polypropylene (page no.121) at the optimum temperature of 700 °C. It is seen from Table (4.12) that the maximum aromatic content/BTEX of 20.93 wt.% was obtained for C-type reactor arrangement. The reactor arrangements A-type and B-type gives BTEX yield of 17.38 wt.% and 19.32 wt.%, respectively at the same temperature. The aromatic/BTEX in PS pyrolysis oil were found

lowest i.e., 20.93 wt. % than found in the PE (22.10 wt. %) and PP (43.43 wt. %) at the same temperature (700 ^{o}C) for C-type reactor arrangement. The reason for lowest BTEX in polystyrene (PS), may be due to the presence of high amount of styrene monomer in pyrolysis oil obtained from PS pyrolysis. However, the maximum aromatics/ BTEX content of 18.67 wt. % for A-type, 23.71 wt. % for B-type and 26.86 wt. % for C-type were found for ZSM-5 catalyst, which is little higher the FA-800 catalyst. This result also indicates that the FA-800 shows excellent catalytic performance and gives comparable result as of commercial ZSM-5.

Table 4.12 The Aromatic content (BTEX) in pyrolysis oil obtained from polystyrene at different temperatures using FA-800 catalyst.

Pyrolysis temperature (^{o}C)		**Benzene (wt. %)**	**Toluene (wt. %)**	**Ethylbenzene (wt.%)**	**Xylene (wt. %)**	**Total BTEX (wt. %)**
500	A-type	0.32	10.13	2.37	1.78	14.60
	B-type	0.38	10.91	2.46	2.27	16.02
	C-type	0.43	11.76	2.61	2.34	17.14
600	A-type	0.51	10.56	2.64	1.93	15.64
	B-type	0.64	12.08	2.81	2.43	17.96
	C-type	0.68	13.21	2.84	2.58	19.31
700	A-type	0.55	11.89	2.78	2.15	17.37
	B-type	0.69	13.25	2.92	2.45	19.31
	C-type	0.73	14.56	2.98	2.65	20.92
800	A-type	0.33	10.27	2.41	1.81	14.82
	B-type	0.41	10.98	2.52	2.29	16.20
	C-type	0.45	11.83	2.63	2.36	17.27

Thus, C-type/multiphase catalytic pyrolysis on FA-800 can be recommended as a suitable process design to convert waste polyethylene into BTEX which is value added upgraded

product. However, it is proposed that benzene should be removed before the pyrolysis oil (C-type) is used as an alternative fuel. Moreover, recovered benzene could also be used as raw material for many chemicals manufacturing. Thus, it can be seen from above discussion that effect of temperature plays main role for the production of valuable hydrocarbon BTEX. The optimum temperature for BTEX production from polyethylene, polypropylene and polystyrene was found to be 700 ^{o}C.

4.2.2.3 Characterization of product yield

4.2.2.3.1 Gas chromatography (GC) analysis of pyrolysis oil

The GC-FID of standard/pure benzene, toluene, ethylbenzene and xylene were done to get retention time of individual compounds. 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. Fig (4.26a) to Fig (4.26c) show the prominent peaks for benzene, toluene, ethylbenzene and xylene (BTEX) in the pyrolysis oil obtained from pyrolysis of polyethylene, polypropylene and polystyrene, respectively. A comparison between pyrolysis oil and commercial oils is shown to check the suitability of the use of pyrolysis oil in diesel engine and confirm its composition.

Fig (4.26a) to Fig (4.26c) show the GC-FID of the pyrolysis oil derived by the pyrolysis of the polyethylene, polypropylene and polystyrene at the optimum temperature of 700 ^{o}C, commercial kerosene oil and diesel oil, respectively. The important and prominent peaks obtained at same retention time for the pyrolysis oil obtained from PE, PP and PS pyrolysis (700 ^{o}C), commercial kerosene oil and diesel oil is shown in Fig (4.26a) to Fig (4.26c).

It is seen in the Fig (4.26a) that the chromatogram peaks for pyrolysis oil obtained from polyethylene at the temperature of 700 ^{o}C are very close to kerosene and diesel oil in the retention time range between 3 and 16 min for A-type and B-type catalytic pyrolysis, and

between 5 and 14 min for C-type/multiphase pyrolysis. This range may be specifically interesting for the pyrolysis oil (700 ^{o}C) which consist of compounds, are similar as that of kerosene oil and diesel oil in terms of chemical structure of compounds and composition (Nicholas, 1998). Moreover, the maximum numbers of peaks of A-type and C-type pyrolysis oil are matched with diesel and kerosene.

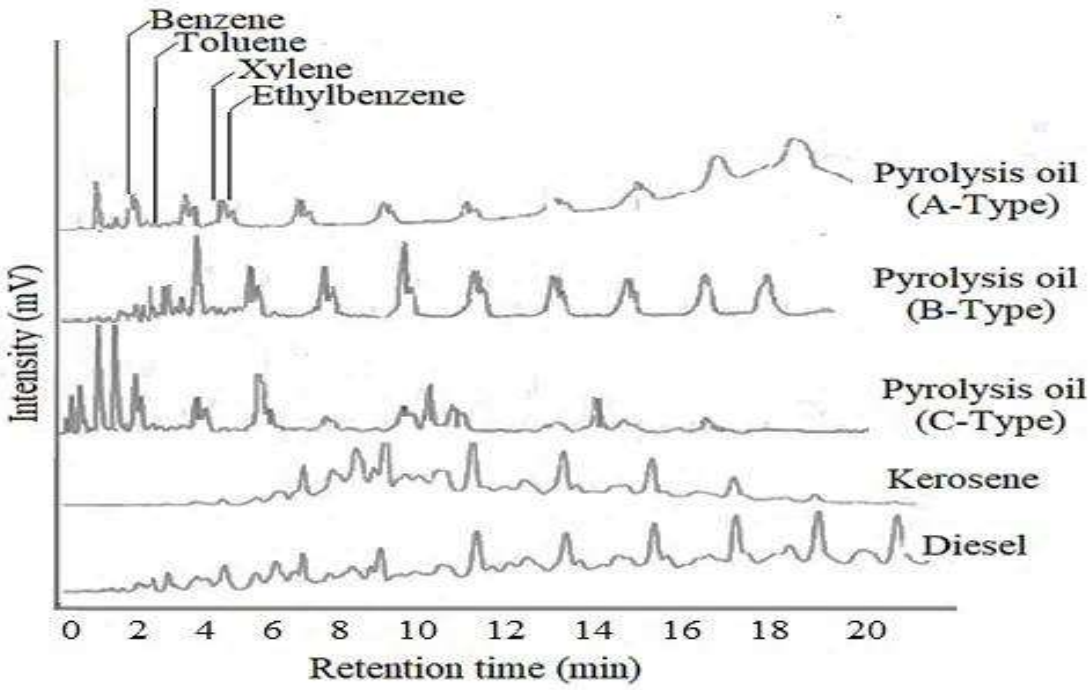

Figure 4.26a Gas chromatography characteristic of kerosene oil (commercial), diesel oil (commercial) and pyrolysis oil obtained from the catalytic pyrolysis of polyethylene at a temperature of 700 ^{o}C using fly ash synthesized catalyst FA-800 for A-type (vapor phase), B-type (liquid phase) and C-type (both liquid and vapor phase) reactor arrangements.

It is seen from the Fig (4.26b) that the chromatogram peaks for pyrolysis oil obtained from polypropylene at a temperature of 700 ^{o}C are very close to kerosene and diesel oil in the retention time range between 5 and 15 min for A-type catalytic pyrolysis, and between 6 and 18 min for B-type and C-type/multiphase pyrolysis. This range may be specifically interesting for the pyrolysis oil (700 ^{o}C) which consist of compounds, are similar as that of kerosene oil and diesel oil in terms of chemical structure of compounds and composition (Nicholas, 1998). Moreover, the maximum numbers of peaks of A-type and B-type pyrolysis oil are matched with commercial diesel.

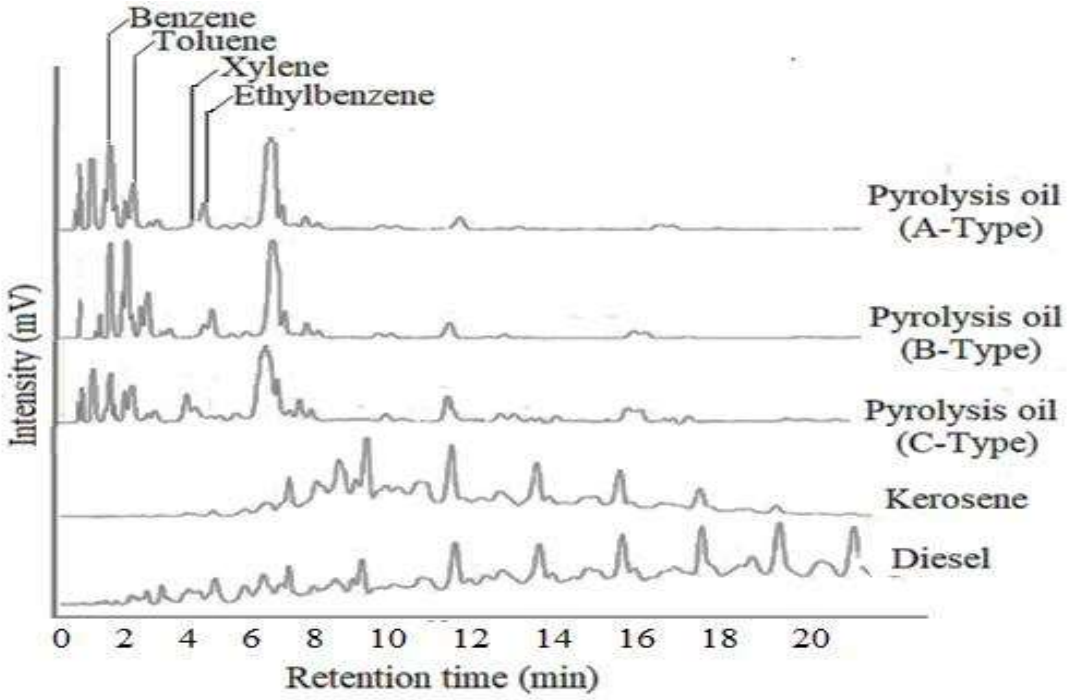

Figure 4.26b Gas chromatography characteristic of kerosene oil (commercial), diesel oil (commercial) and pyrolysis oil obtained from the catalytic pyrolysis of polypropylene at a temperature of 700 ^{o}C using fly ash synthesized catalyst FA-800 for A-type (vapor phase), B-type (liquid phase) and C-type (both liquid and vapor phase) reactor arrangements.

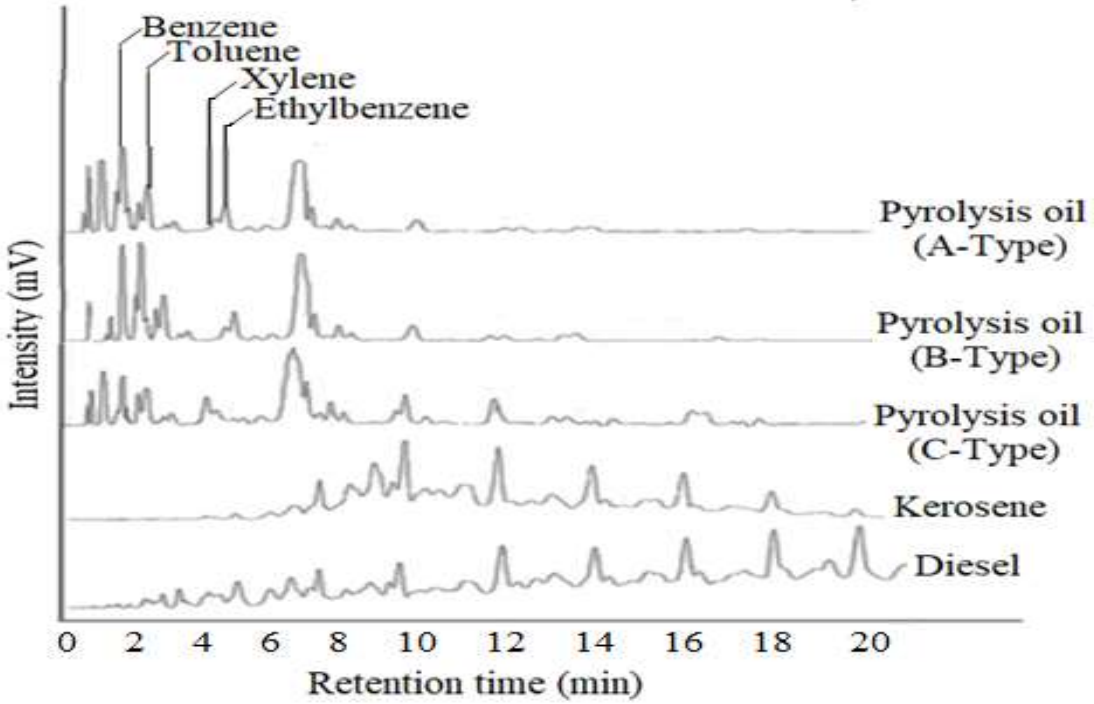

Figure 4.26c Gas chromatography characteristic of kerosene oil (commercial), diesel oil (commercial) and pyrolysis oil obtained from the catalytic pyrolysis of polystyrene at a temperature of 700 ^{o}C using fly ash synthesized catalyst FA-800 for A-type (vapor phase), B-type (liquid phase) and C-type (both liquid and vapor phase) reactor arrangements.

Similarly, the chromatogram peaks for pyrolysis oil obtained from polystyrene at a temperature of 700 ^{o}C are very close to kerosene and diesel oil in the retention time range between 5 and 14 min for A-type and B-type catalytic pyrolysis, and between 5 and 18 min for C-type/multiphase pyrolysis (Fig 4.26c). This range may be specifically interesting for the pyrolysis oil (700 ^{o}C) which consist of compounds, are similar as that of kerosene oil and diesel oil in terms of chemical structure of compounds and composition (Nicholas, 1998). Moreover, the maximum numbers of peaks of pyrolysis oil for A-type and B-type reactor arrangements are matched with commercial diesel.

4.2.2.3.2 ASTM distillation of pyrolysis oil

Fig (4.27a) to Fig (4.27c) shows comparison between standard fuel (Perry and Green, 2007) and pyrolysis oil obtained from polyethylene, polypropylene and polystyrene for different types of reactor arrangements at the temperature of 700 ^{o}C. Similar pattern of ASTM distillation curve for pyrolysis oil obtained by the catalytic pyrolysis using FA-800 as it was seen for ZSM-5 (Fig 4.16a-c, page no. 90). The boiling point range of pyrolysis oil obtained from catalytic pyrolysis of polyethylene using A-type, B-type and C-type reactor arrangements (Fig 4.27a) at the optimum temperature of 700 ^{o}C lies in between gasoline and kerosene for the recovery of distillate 0-30 %. The boiling point range of pyrolysis oil obtained from catalytic pyrolysis using A-type, B-type and C-type reactor arrangements tend to behave as kerosene for recovery of distillate, in the range of 30-60 %. In addition, the pyrolysis oil obtained from catalytic pyrolysis (A-type, B-type and C-type) of PE lies in the range of kerosene and diesel oil above 60 % of distillate recovery.

The trend of ASTM curve for polypropylene is little different from polyethylene. The boiling point range of pyrolysis oil obtained from catalytic pyrolysis of polypropylene are almost same as JP-4 for the recovery of distillate 0-30 % using A-type, B-type and C-type

reactor arrangements, respectively (Fig 4.27b). Pyrolysis oil obtained from catalytic pyrolysis for A-type, B-type and C-type lies in between JP-4 and kerosene for the recovery of distillate, in the range of 30-60 % and it tends to behaves as diesel oil above 70 % recovery.

Fig (4.27c) shows the comparison between standard fuel and pyrolysis oil obtained from polystyrene at the temperatures of 700 ^{o}C. The boiling point range of pyrolysis oil obtained at temperature of 700 ^{o}C catalytic pyrolysis (A-type, B-type and C-type) tends to behave as heavy naphtha for the recovery of distillate 0-60 % recovery. In addition, all the pyrolysis oil obtained lies between heavy naphtha and diesel for 60-85 % recovery. Whereas, interestingly pyrolysis oil tends to behaves as diesel oil above 85 % of distillate recovery and catalytic pyrolysis using A-type, B-type and C-type reactor arrangements, respectively.

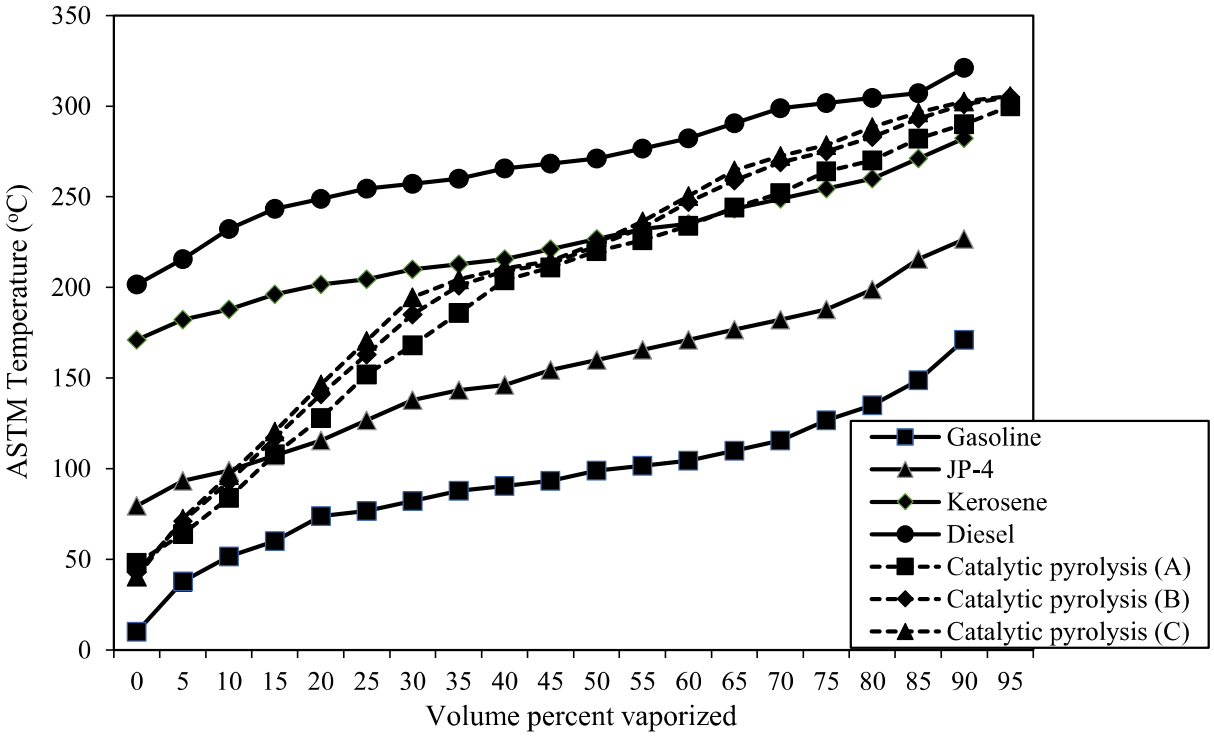

Figure 4.27a Volume percent vaporized vs. ASTM temperature characteristics of standard fuel and pyrolysis oil obtained from polyethylene using FA-800 catalyst.

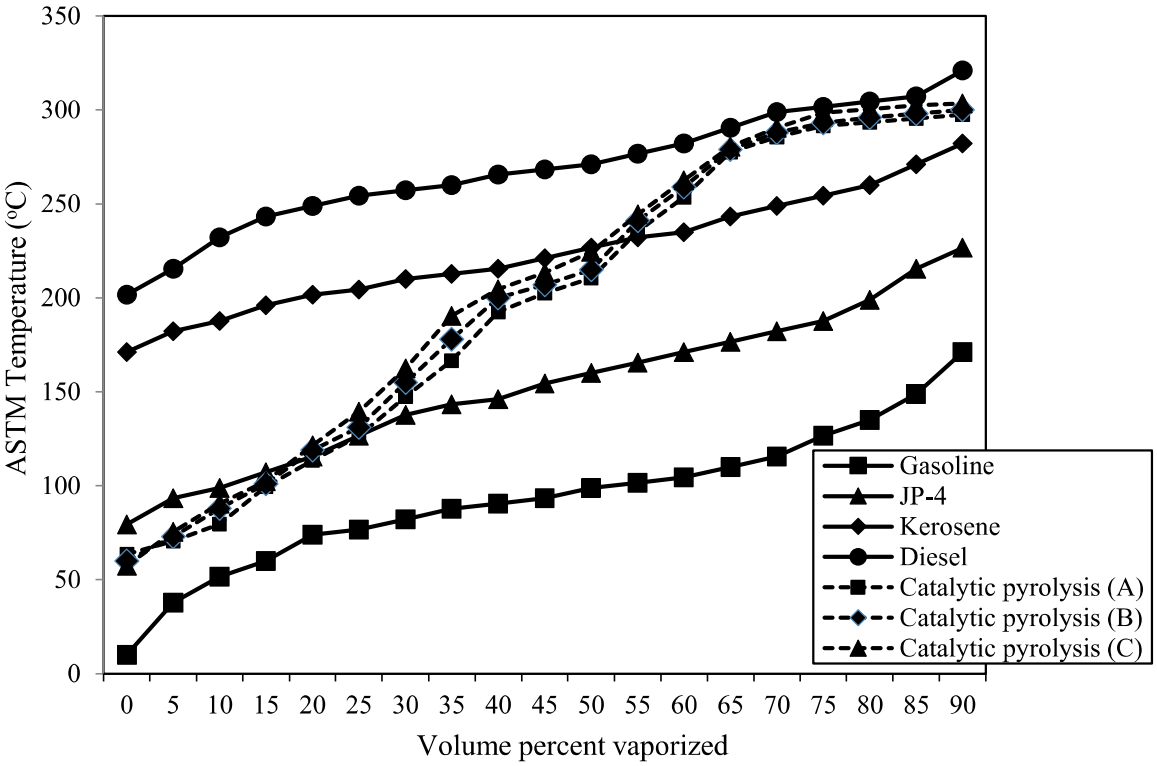

Figure 4.27b Volume percent vaporized vs. ASTM temperature characteristics of standard fuel and pyrolysis oil obtained from polypropylene using FA-800 catalyst.

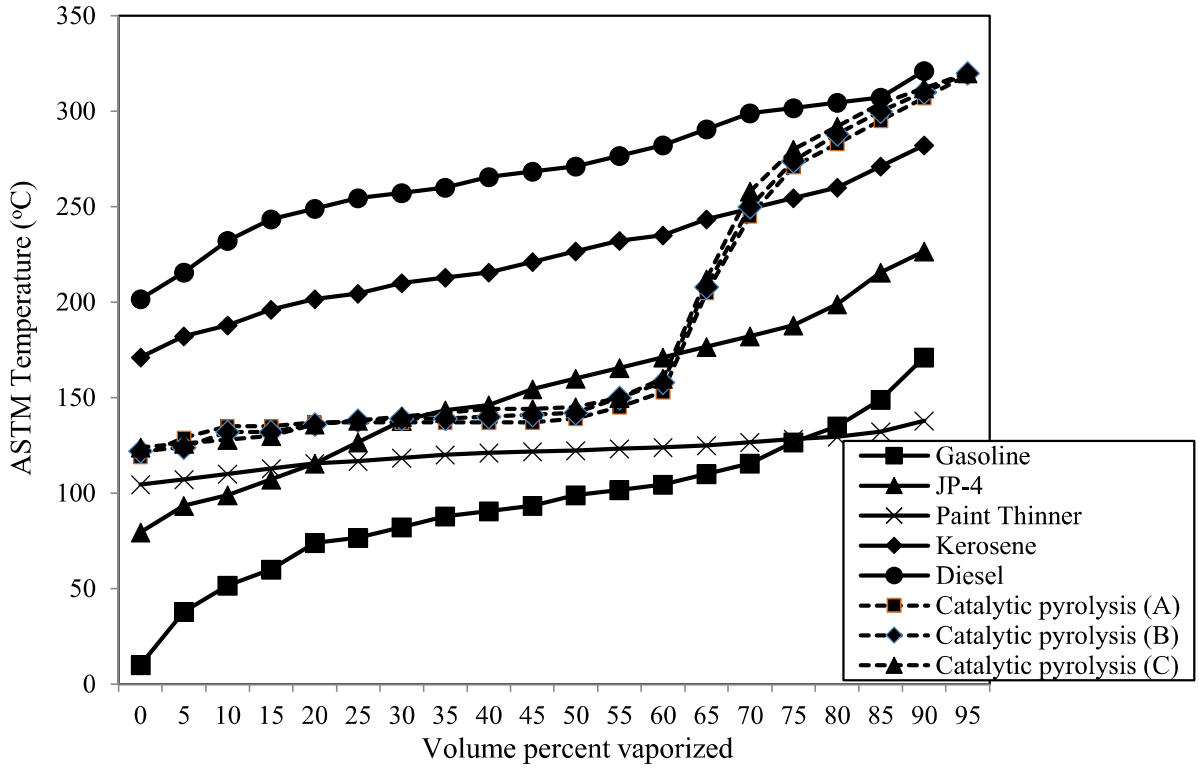

Figure 4.27c Volume percent vaporized vs. ASTM temperature characteristics of standard fuel and pyrolysis oil obtained from polystyrene using FA-800 catalyst.

4.2.2.3.3 FTIR analysis of pyrolysis oil

The Fourier Transform Infrared spectroscopy (FTIR) is an important analysis technique which detects various characteristic functional groups present in pyrolysis oil. In order to gather systematic information about the chemical composition of the pyrolysis oil, the resultant fuels were examined using FTIR in the wavelength range of 3200-600 cm^{-1}. Fig (4.28a) shows the FTIR spectra of liquid fuel obtained at optimized condition by catalytic pyrolysis of waste polyethylene on Fa-800 catalyst at a temperature of 700 ^oC using A-type, B-type and C-type reactor arrangements. As expected, there are only slight differences among the first two spectra. This is due to the strong resemblance among polymeric structures. The spectra confirm that these fuels are composed of aliphatic groups comprising carbon and hydrogen atoms. The presence of alkanes is detected at 2950-2935 cm^{-1} with C–H stretching vibrations. C=C stretching vibrations at 1660-1630 cm^{-1} indicates the presence of alkenes/fingerprint region. This band 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 1451-59 cm^{-1}, which verify the presence of benzene derivatives in the pyrolysis oil. C–H bending vibrations at 986-961 cm^{-1} indicate the presence of alkenes. The 893-887 cm^{-1} band certified the presence of vinylidene functional group in the chemical composition of pyrolysis oil. The C–H bending vibrations at frequency 732-718 cm^{-1} indicates the presence of phenyl ring substitution bands. This region confirms mono or ortho substitution of benzene ring. Thus, it can be summarized that pyrolysis oil is a complex mixture of paraffinic, olefinic and aromatic compounds (Djebara et al., 2012; Fernández et al., 2012; Heydariaraghi et al., 2016; Jin et al., 2016; Kumar et al., 2013; Williams and Williams, 1997). The FT-IR data of pyrolysis oil is substituted using GC-FID analysis of the oil obtained by the similar condition.

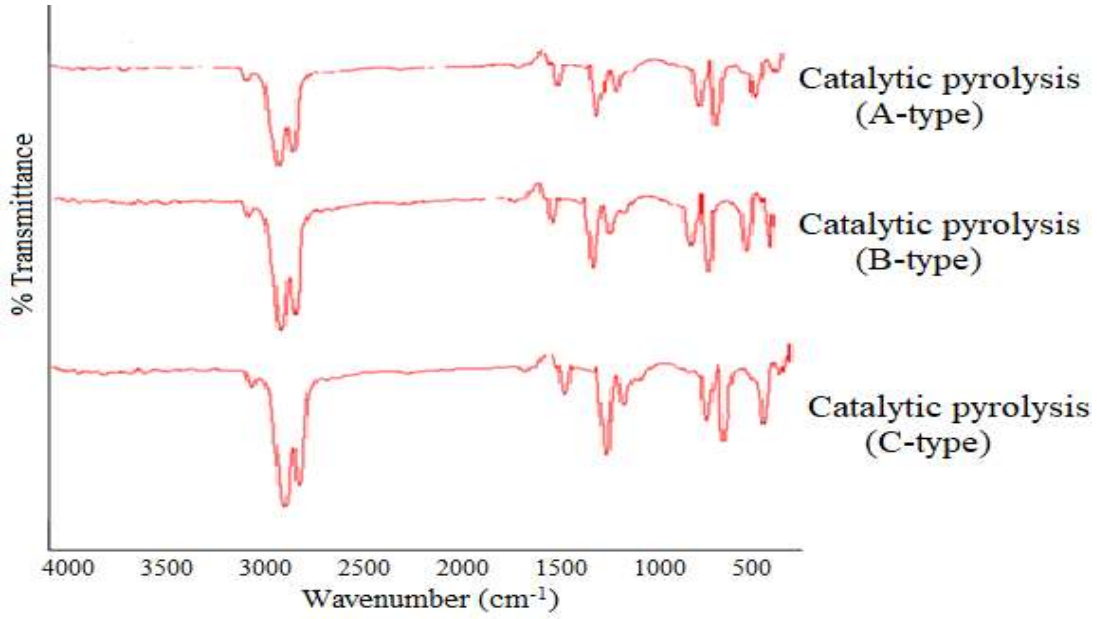

Figure 4.28a FT-IR spectrometry of liquid fuel obtained at optimized condition (700 ºC) by catalytic pyrolysis of waste polyethylene for A-type, B-type and C-type reactor arrangements.

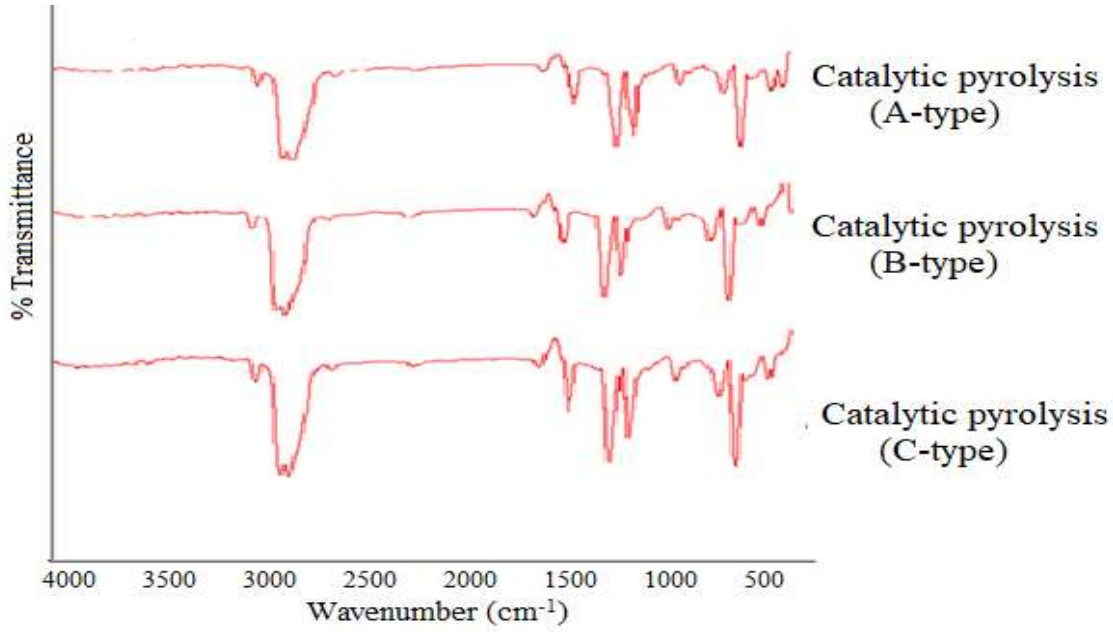

Figure 4.28b FT-IR spectrometry of liquid fuel obtained at optimized condition (700 ºC) by catalytic pyrolysis of waste polypropylene for A-type, B-type and C-type reactor arrangements.

Fig (4.28b) shows the FTIR spectra of pyrolysis oil obtained at optimum condition by catalytic pyrolysis of waste polypropylene on FA-800 catalyst using A-type, B-type and C-

type reactor arrangements. The FTIR spectra were almost similar in nature for catalytic pyrolysis oil. This may be due to the strong similarity among chemical structures of the hydrocarbons present in the pyrolysis oil. The alkanes is detected in the wavelength range of 2950-2923 cm^{-1} with C–H stretching vibrations. The stretching vibrations of C=C at 1763-1668 cm^{-1} indicates the presence of alkenes. The presence of alkanes is detected by C–H scissoring and bending vibrations at 1456-1379 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 963 cm^{-1}. The vinylidene functional group in the chemical composition of pyrolysis oil is also detected at the band 879 cm^{-1}. The phenyl ring substitution is also traced due to the C–H bending vibrations at frequency 746 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.

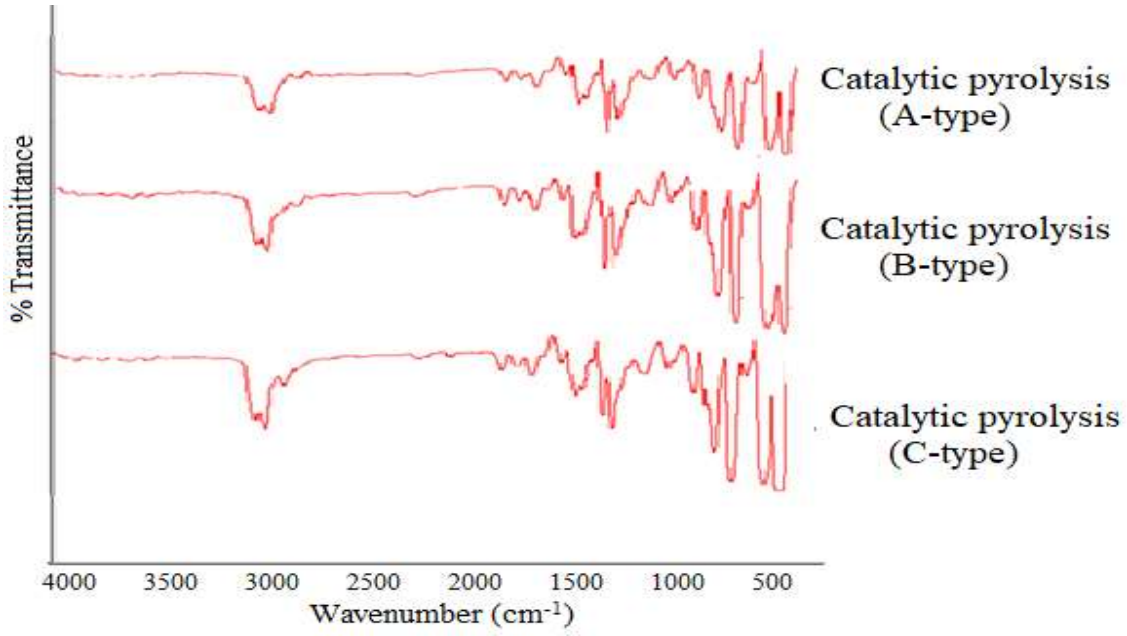

Figure 4.28c FT-IR spectrometry of liquid fuel obtained at optimized condition (700 ^{o}C) by catalytic pyrolysis of waste polystyrene for A-type, B-type and C-type reactor arrangements.

Fig (4.28c) shows the FTIR spectra of liquid fuel obtained at optimized condition by catalytic pyrolysis of waste polystyrene using A-type, B-type and C-type reactor arrangements. The presence of alkanes is detected at 3021 cm^{-1} with C–H stretching vibrations. C=C stretching vibrations at 1662-1597 cm^{-1} indicates the presence of alkenes/fingerprint region. The presence of alkanes is detected by C–H scissoring and bending vibrations at 1463 cm^{-1}. C–H bending vibrations at 966 cm^{-1} indicate the presence of alkenes and the C–H bending vibrations at frequency 725 cm^{-1} indicates the presence of phenyl ring substitution bands.

4.2.2.3.4 Physicochemical properties of pyrolysis oil

Table (4.13a) to (4.13c) shows the results of physicochemical property analysis of liquid yield obtained at optimized temperature (700 ^{o}C) from catalytic pyrolysis (C-type) of waste PE, PP and PS, respectively. The appearance of the all pyrolysis oil were light yellowish free from visible sediments. The flash point of the liquid product obtained from waste PE, PP and PS were found in a comparable range and thus, it is expected that it would not cause any trouble in most of the IC engines. The gross calorific value (GCV) for liquid fuel obtained by catalytic pyrolysis of waste PE using C-type reactor arrangements was 111786 Cal/g for FA-800 catalyst, which is in the range of gasoline and diesel. Thus, this liquid product would perform relatively well in IC engines. However, GCV of pyrolysis oil obtained from catalytic pyrolysis of waste PP and PS using C-type reactor arrangement were 9625 Cal/g and 8953 Cal/g, respectively which are lower in comparison to waste PE. As discussed earlier in the phase-I, the GCV of pyrolysis oil obtained from thermal pyrolysis of PE (10982 Cal/g), PP (9015.48 Cal/g) and PS (7073.37 Cal/g) are found to be low as compared to catalytic pyrolysis at a temperature of a temperature of 700 ^{o}C. The PE, PP and PS produced very low carbon residue of 0.38 wt. %, 0.24 wt. % and 0.69 wt. %,

respectively at a temperature of 700 ^{o}C on FA-800 catalyst. This indicates good fuel property as carbon residue is less than 1 wt. % in all pyrolysis oil at a temperature 700 ^{o}C. This also confirms the presence of low molecular weight aromatics in the oil. As already mentioned, that FA-900 catalyst gives liquid yield which is waxy at room temperature. The waxy liquid yield might contain high molecular weight aromatics which gives very high carbon residue of 1.6 wt. % for PE, 1.06 wt.% for PP and 1.14 wt. % for PS, when tested by the Rams bottom carbon residue method. From these studies, it is observed that the product oil from all three waste plastics could be possible feedstock for further upgrading to use in diesel engine besides recovery of BTEX as a valuable product.

Table 4.13a Physicochemical properties of pyrolysis oil obtained from catalytic pyrolysis of polyethylene using FA-800 in C-type reactor arrangement at 700 ^{o}C.

Physicochemical Properties	**Test method**	**Results obtained**				
		Catalytic Pyrolysis				
		FAN	**FA-600**	**FA-700**	**FA-800**	**FA-900**
Flash point (^{o}C)	ASTM D 92	27	27	27	26	28
Fire point (^{o}C)	ASTM D 92	33	33	32	31	33
Carbon residue (wt.%)	IP 14/65	0.52	0.45	0.41	0.38	1.62
Specific gravity	ASTM D 1298	0.759	0.754	0.748	0.731	0.769
API gravity (^{o})	API correlation	54.93	56.17	57.67	62.07	52.50
Calorific value (Cal/g)	IP 12/63 T	11037	11196	11238	11786	8914

Table 4.13b Physicochemical properties of pyrolysis oil obtained from catalytic pyrolysis of polypropylene using FA-800 in C-type reactor arrangement at 700 °C.

Physicochemical Properties	Test method	Results obtained				
		Catalytic Pyrolysis				
		FAN	FA-600	FA-700	FA-800	FA-900
Flash point (°C)	ASTM D 92	27	27	27	26	28
Fire point (°C)	ASTM D 92	33	33	32	31	33
Carbon residue (wt.%)	IP 14/65	0.275	0.26	0.255	0.24	1.06
Specific gravity	ASTM D 1298	0.759	0.754	0.748	0.731	0.769
API gravity (°)	API correlation	54.93	56.17	57.67	62.07	52.50
Calorific value (Cal/g)	IP 12/63 T	9445.2	9537.23	9598.19	9625	8914

Table 4.13c Physicochemical properties of pyrolysis oil obtained from catalytic pyrolysis of polystyrene using FA-800 in C-type reactor arrangement at 700 °C.

Physicochemical Properties	Test method	Results obtained				
		Catalytic Pyrolysis				
		FAN	FA-600	FA-700	FA-800	FA-900
Flash point (°C)	ASTM D 92	29	28	28	26	28
Fire point (°C)	ASTM D 92	33	33	32	31	33
Carbon residue (wt.%)	IP 14/65	0.78	0.765	0.745	0.69	1.14
Specific gravity	ASTM D 1298	0.8468	0.8454	0.8372	0.8221	0.8691
API gravity (°)	API correlation	35.78	35.88	37.52	40.62	31.31
Calorific value (Cal/g)	IP 12/63 T	7945.2	8337.23	8698.19	8953	8214

4.2.3 Catalyst regeneration for pyrolysis process

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.

4.2.3.1 Regenerated catalyst ZSM-5

4.2.3.1.1 Characterization of regenerated catalyst ZSM-5

4.2.3.1.1.1 SEM analysis

Fig (4.29a) to Fig (4.29c) show the surface morphology of fresh, used and regenerated ZSM-5 catalyst. It is seen in the Fig (4.29a) that most of the particles were spherical in shape with high porosity. The SEM image of Fig (4.29b) 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. The Fig (4.29c) shows the SEM image of regenerated ZSM-5 which is similar to fresh ZSM-5 (Fig 4.29a).

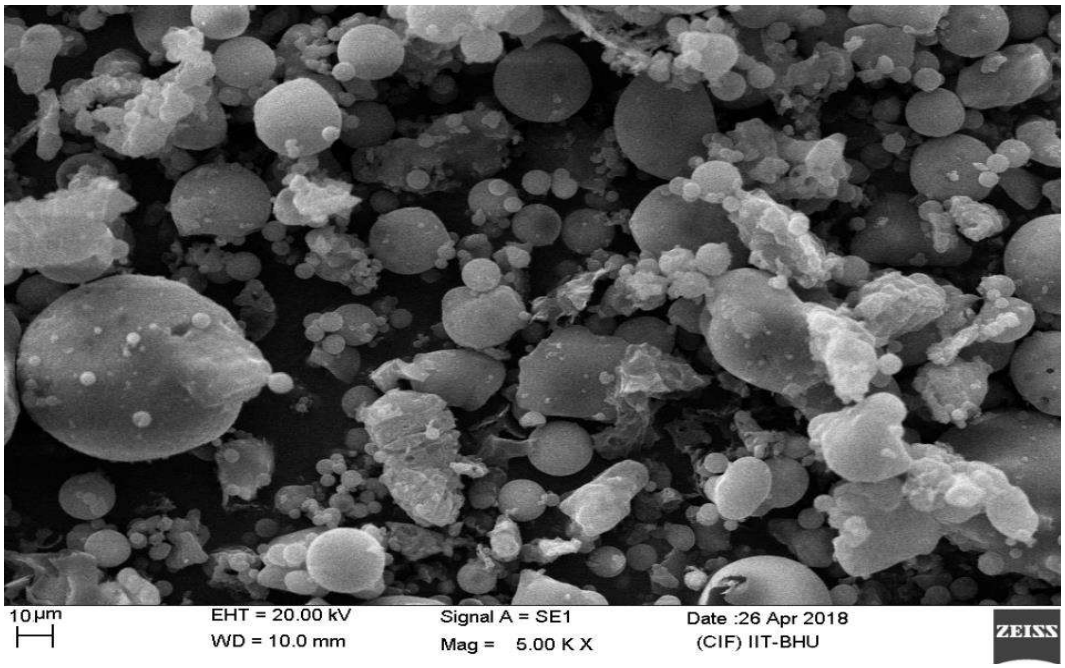

Figure 4.29a SEM images of fresh ZSM-5 catalyst

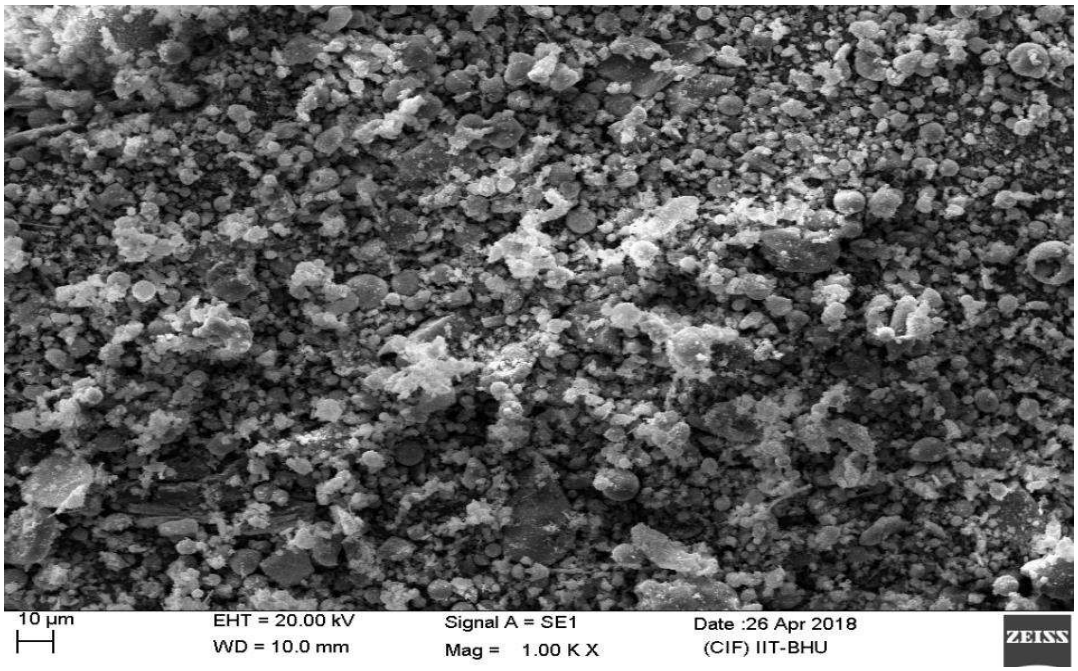

Figure 4.29b SEM images of used ZSM-5 catalyst

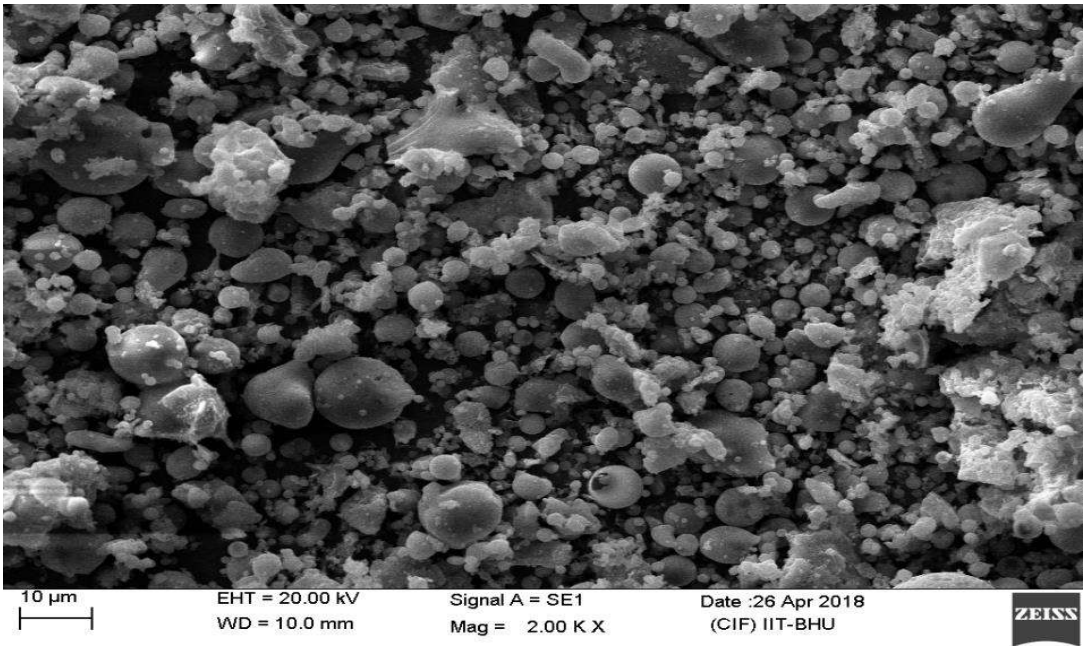

Figure 4.29c SEM images of regenerated ZSM-5 catalyst

4.2.3.1.1.2 BET analysis

Table (4.14) shows the surface area and pore volume of fresh, used and regenerated ZSM-5 catalyst. It is seen in the Table (4.14) 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 that ZSM-5 catalyst can be reused after regeneration process, which is economical.

Table 4.14 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

4.2.3.1.2 Product yield on regenerated catalyst ZSM-5

Fig (4.30) 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 PE, PP and PS using C-type (liquid and vapor phase) reactor arrangement at the optimum temperature of 700 °C. Although it is not shown here, the comparison of liquid yield and BTEX for catalytic pyrolysis of waste PE, PP and PS using fresh, used and regenerated ZSM-5 catalyst for A-type (vapor phase) and B-type (liquid phase) reactor arrangements is shown in Appendix-A9. It is seen from Fig (4.30) that the liquid yield and BTEX decreases to noticeable amount after 2nd run for all the cases. Table 4.15 shows the comparison of liquid, gaseous, solid residue and BTEX yield for catalytic pyrolysis of PE, PP and PS using C-type reactor arrangement for ZSM-5 upto 3rd run and regenerated 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.

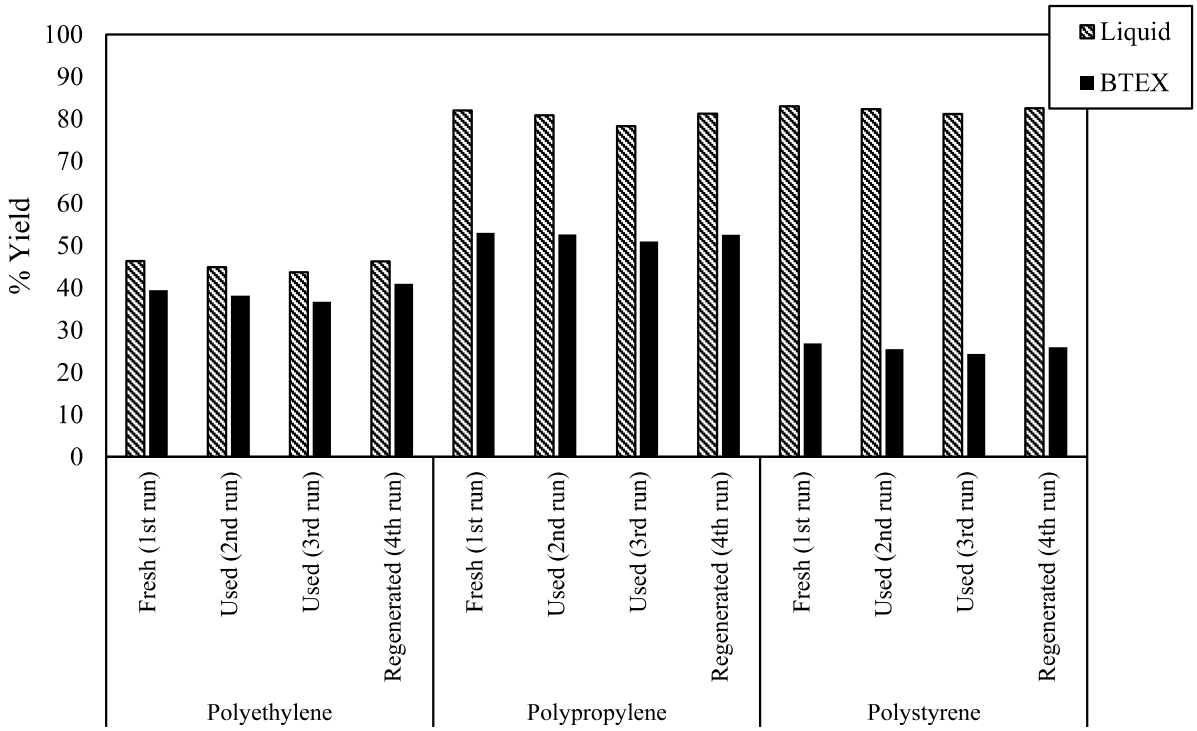

Figure 4.30 Comparison of liquid and BTEX yield for catalytic pyrolysis of PE, PP and PS using C-type reactor arrangement at the temperature of 700 ºC for ZSM-5 upto 3rd run and regenerated catalyst.

Table 4.15 Comparison of liquid, gaseous, solid residue and BTEX yield for catalytic pyrolysis of PE, PP and PS using C-type reactor arrangement for ZSM-5 upto 3rd run and regenerated catalyst.

Feed	Catalyst run	Liquid (wt. %)	Gas (wt. %)	Solid (wt. %)	BTEX (wt. %)
PE	Fresh (1st run)	46.36	49.46	4.18	39.47
	Used (2nd run)	44.97	49.05	5.98	38.16
	Used (3rd run)	43.72	48.56	7.72	36.37
	Regenerated (4th run)	46.31	49.21	4.48	38.97
PP	Fresh (1st run)	82	16.8	1.2	53.12
	Used (2nd run)	80.9	15.2	3.9	52.67
	Used (3rd run)	78.3	14.9	6.8	51.02
	Regenerated (4th run)	81.3	16.3	2.4	52.57
PS	Fresh (1st run)	83	16.3	0.7	26.86
	Used (2nd run)	82.3	15.27	2.43	25.54
	Used (3rd run)	81.23	14.92	3.85	24.36
	Regenerated (4th run)	82.6	15.98	1.42	25.98

4.2.3.2 Regenerated fly ash synthesized catalyst FA-800

4.2.3.2.1 Characterization of regenerated catalyst FA-800

4.2.3.2.1.1 SEM Analysis

Fig (4.31a) to Fig (4.31c) show the surface morphology of fresh, used and regenerated FA-800 catalyst. It is seen in the Fig (4.31a) that most of the particles were spherical in shape with high porosity. The SEM image of Fig (4.31b) shows that the particles of used FA-800 catalyst are covered with pyrolysis residue/coke which is formed during the pyrolysis and

aromatization within the reactor. The Fig (4.31c) shows the SEM image of regenerated FA-800 which is similar to fresh FA-800 (Fig 4.31a).

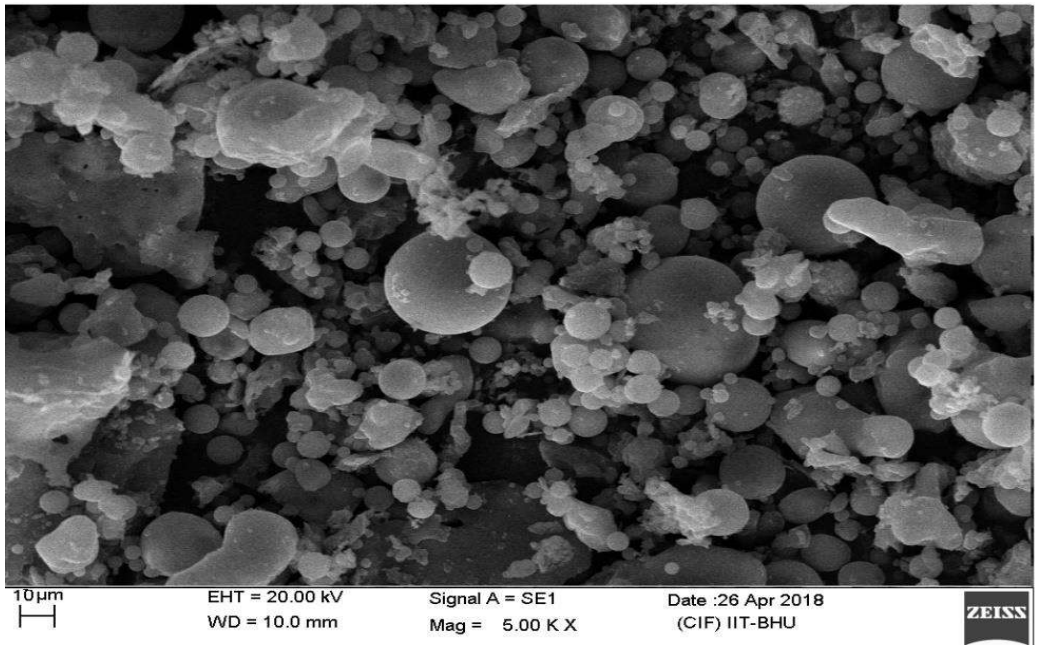

Figure 4.31a SEM images of fresh FA-800 catalyst

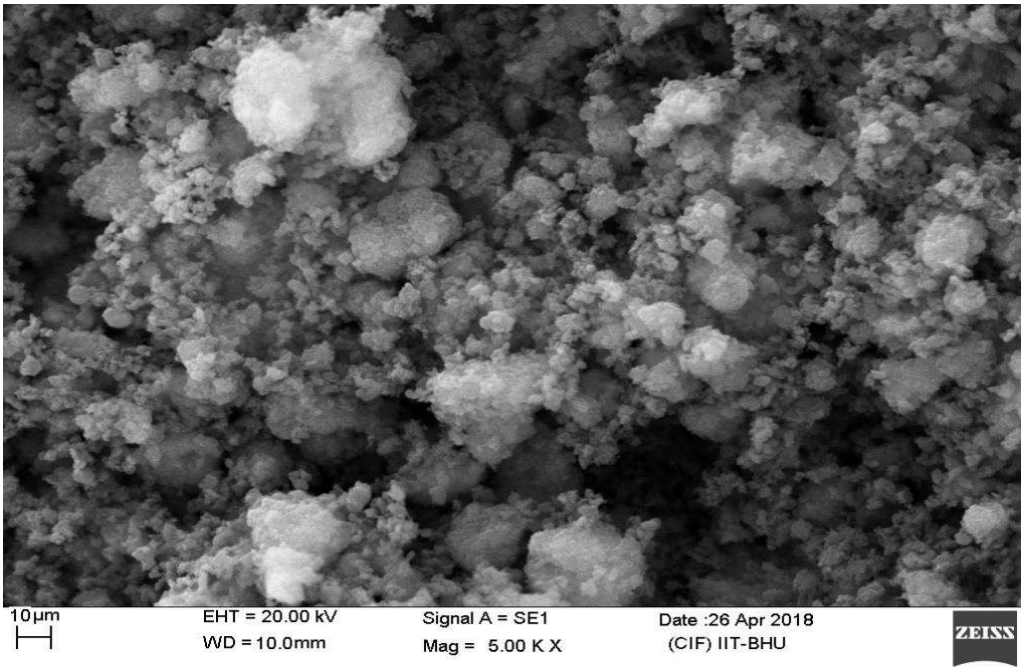

Figure 4.31b SEM images of used FA-800 catalyst

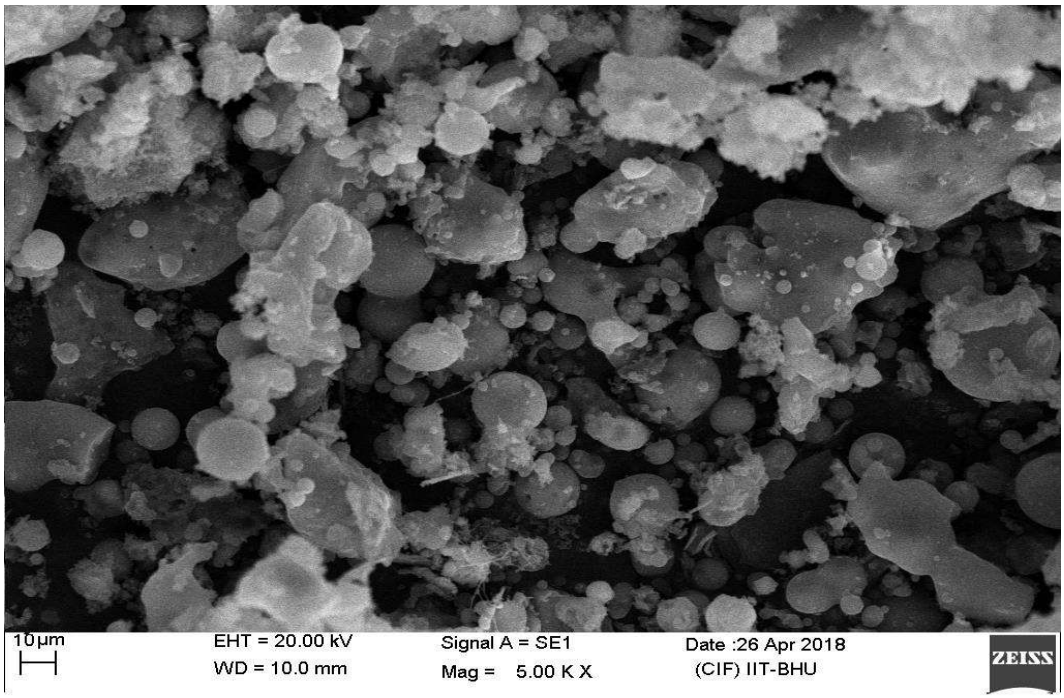

Figure 4.31c SEM images of regenerated Fly ash derived FA-800 catalyst

4.2.3.2.1.2 BET analysis

Table (4.16) shows the surface area and pore volume of fresh, used and regenerated FA-800 catalyst. It is seen in the Table (4.16) that the used FA-800 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 FA-800 (310.40 m^2/g) and regenerated FA-800 (305 m^2/g) are almost same. The pore volume for fresh and regenerated catalyst is also same. This result indicates that FA-800 catalyst can be reused after regeneration process, which is economical.

Table 4.16 Surface area and pore volume of fresh, used and regenerated catalyst FA-800.

Name of catalysts		**Surface area (m^2/g)**	**Pore volume (ml/g)**
FA-800	Fresh	310.40	43.95
	Used	215	39.45
	Regenerated	305	42.62

4.2.3.2.2 Product yield on regenerated catalyst FA-800

Fig (4.32) 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 pyrolysis of waste PE, PP and PS using C-type (liquid and vapor phase) reactor arrangement at the temperature of 700 °C. Although it is not shown here, the comparison of liquid yield and BTEX for catalytic pyrolysis of waste PE, PP and PS using fresh, used and regenerated FA-800 catalyst for A-type (vapor phase) and B-type (liquid phase) reactor arrangements is shown in Appendix-A9. The Fig (4.32) shows that the liquid yield decreases to noticeable amount after 2nd run for A-type, B-type and C-type. Table 4.17 shows the comparison of liquid, gaseous, solid residue and BTEX yield for catalytic pyrolysis of PE, PP and PS using C-type reactor arrangement for FA-800 upto 3rd run and regenerated catalyst. The regenerated catalyst gives comparable result as that of fresh catalyst. This shows the stability, suitability and reusuability of FA-800 catalyst for pyrolysis process.

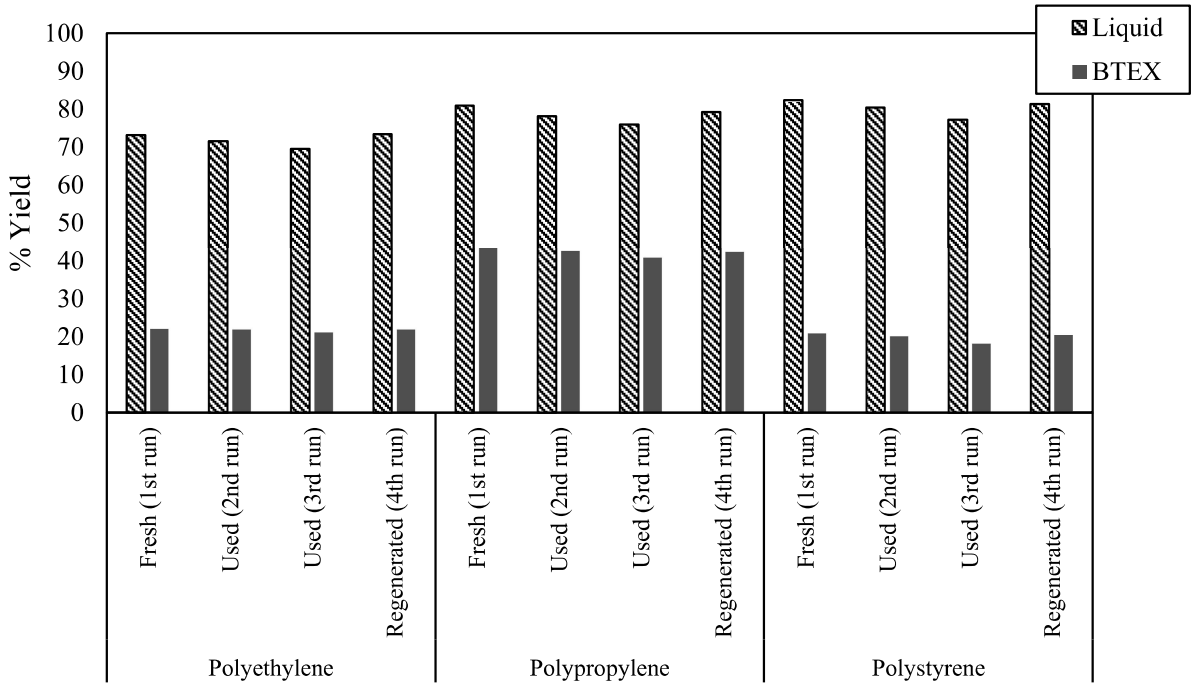

Figure 4.32 Comparison of liquid and BTEX yield for catalytic pyrolysis of PE, PP and PS using C-type reactor arrangement at the temperature of 700 °C for FA-800 upto 3rd run and regenerated catalyst.

Table 4.17 Comparison of liquid, gaseous, solid residue and BTEX yield for catalytic pyrolysis of PE, PP and PS using C-type reactor arrangement at the temperature of 700 ^{o}C for FA-800 upto 3rd run and regenerated catalyst.

Feed	**Catalyst**	**Liquid (wt. %)**	**Gas (wt. %)**	**Solid (wt. %)**	**BTEX (wt. %)**
PE	Fresh (1st run)	73.12	25.22	1.66	22.11
	Used (2nd run)	71.54	26.57	1.89	21.89
	Used (3rd run)	69.54	26.48	3.98	21.2
	Regenerated (4th run)	73.35	24.97	1.68	21.9
PP	Fresh (1st run)	80.9	15.1	4.0	43.43
	Used (2nd run)	78.1	14.8	7.1	42.65
	Used (3rd run)	75.9	14.4	9.7	40.84
	Regenerated (4th run)	79.25	14.8	5.95	42.41
PS	Fresh (1st run)	82.36	15.35	2.29	20.93
	Used (2nd run)	80.43	15.1	4.47	20.17
	Used (3rd run)	77.19	14.89	7.92	18.2
	Regenerated (4th run)	81.34	15.08	3.58	20.51

4.3 Comparison of pyrolysis product and BTEX yield for different reactor arrangements

Fig (4.33) and Table (4.18) show the comparison of liquid, gas, solid and BTEX yield of pyrolysis oil obtained from polyethylene, polypropylene and polystyrene for different type of catalyst and reactor arrangements at the optimum temperature of 700 °C.

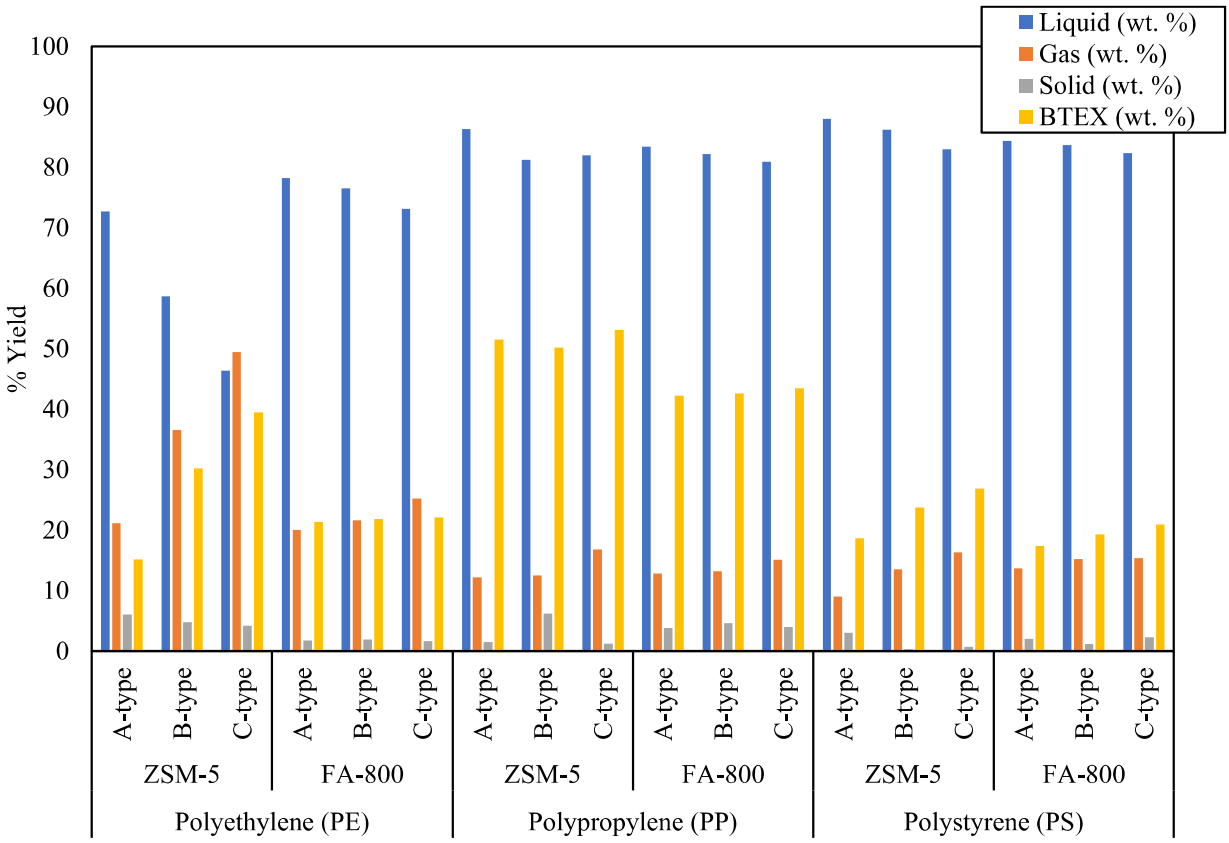

Figure 4.33 Comparison of liquid, gas, solid and BTEX yield of pyrolysis oil obtained from polyethylene, polypropylene and polystyrene for different type of catalyst and reactor arrangements at the optimum temperature of 700 °C.

It is seen from the Fig (4.33) and Table (4.18) that the maximum liquid yield of 72.72 wt. % was obtained for A-type reactor arrangement using waste polyethylene (PE) as feed and commercial ZSM-5 catalyst. However, B-type and C-type reactor arrangements resulted in the liquid yield of 58.68 wt. % and 46.36 wt. % respectively. Although, liquid yield was

maximum (72.72 wt. %) for A-type reactor arrangement, the maximum BTEX yield of 39.47 wt. % was found for C-type/multiphase reactor arrangement using similar condition. Nevertheless, A-type and B-type reactor arrangements produced BTEX yield of 15.15 wt. % and 30.21 wt. % on ZSM-5 at the temperature of 700 ^{o}C. The similar trend was observed for pyrolysis of waste PE using synthesized catalyst FA-800 which resulted in maximum liquid yield of 78.2 wt. % for A-type reactor arrangement at the optimum temperature (700 ^{o}C). The highest BTEX yield of 22.1 wt. % was found for C-type reactor arrangement.

The pyrolysis of polypropylene (PP) on commercial ZSM-5 produced maximum liquid yield of 86.3 wt. % for A-type reactor arrangement at the optimum temperature of 700 ^{o}C. Whereas, B-type and C-type reactor arrangements resulted in the lower liquid yield of 81.23 wt. % and 82.0 wt. % respectively. As seen in earlier for PE feed, the maximum BTEX yield of 53.12 wt. % was obtained for the pyrolysis of polypropylene on commercial ZSM-5 catalyst using C-type/multiphase reactor arrangement. The similar trend was found for waste PP pyrolysis on fly ash synthesized catalyst FA-800 which resulted in maximum liquid yield of 83.4 wt. % for A-type reactor arrangement at the optimum temperature of 700 ^{o}C. Whereas, B-type and C-type produced liquid yield of 82.2 wt. % and 80.9 wt. %, respectively. The maximum BTEX yield of 43.43 wt. % was obtained for C-type/ multiphase reactor arrangement using similar conditions.

Table 4.18 Comparison of liquid, gas, solid and BTEX of pyrolysis oil obtained from polyethylene, polypropylene and polystyrene for different type of catalyst and reactor arrangements.

Type of feed	Catalyst	Reactor arrangement	Liquid (wt. %)	Gas (wt. %)	Solid (wt. %)	BTEX (wt. %)
Polyethylene (PE)	ZSM-5	A-type	72.72	21.12	6.06	15.15
		B-type	58.68	36.56	4.76	30.21
		C-type	46.36	49.46	4.18	39.47
	FA-800	A-type	78.2	20.04	1.76	21.34
		B-type	76.5	21.6	1.9	21.81
		C-type	73.12	25.22	1.66	22.1
Polypropylene (PP)	ZSM-5	A-type	86.3	12.2	1.5	51.52
		B-type	81.23	12.5	6.19	50.19
		C-type	82.0	16.8	1.2	53.12
	FA-800	A-type	83.4	12.8	3.8	42.21
		B-type	82.2	13.2	4.6	42.63
		C-type	80.9	15.1	4.0	43.43
Polystyrene (PS)	ZSM-5	A-type	88.0	9.0	3.0	18.68
		B-type	86.2	13.5	0.3	23.72
		C-type	83.0	16.3	0.7	26.86
	FA-800	A-type	84.36	13.65	1.99	17.37
		B-type	83.65	15.2	1.15	19.31
		C-type	82.36	15.35	2.29	20.92

The pyrolysis of polystyrene (PS) using commercial ZSM-5 produced maximum liquid yield of 88 wt. % for the reactor arrangement of A-type/vapor phase at the optimum temperature of 700 ^{o}C. Whereas, B-type/liquid phase and C-type/multiphase produced liquid yield of 86.2 wt. % and 83.0 wt. % respectively. The maximum BTEX yield of 26.86 wt. % was obtained for C-type/multiphase reactor arrangement on ZSM-5 catalyst using same temperature (700 ^{o}C). The pyrolysis of PS on fly ash synthesized catalyst FA-800 resulted in maximum liquid yield of 84.36 wt. % for the reactor arrangement

A-type/vapor phase at a temperature of 700 ^{o}C. As seen in the case of PE and PP pyrolysis, similar trend was observed for BTEX production using polystyrene as feed on synthesized catalyst FA-800 which resulted in maximum BTEX yield of 20.92 wt. % for C-type/ multiphase reactor arrangement at a temperature of 700 ^{o}C. Whereas, A-type and B-type produced BTEX yield of 17.37 wt. % and 19.31 wt. % respectively.