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Effect of Fly Ash in Pyrolysis of HDPE, LDPE and PP Plastic Waste

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ABSTRACT

Fly ash is generally obtained as a by-product from the combustion of coal and other waste materials. It is used for making bricks, but it has few limitations. The fly ash consists of Silica, Alumina, and other metal oxide components in minor quantities. Fly ash particles are observed in the range of nanometers to micrometers and can act as a catalyst in various reactions. The use of low-cost catalysts in the pyrolysis of thermoplastic waste would achieve a high percentage of low molecular weight fractions in liquid form which increases its applicability in commercial sectors. Hence, there is a need to enhance these fractions to achieve a sustainable approach in the catalytic pyrolysis process. fly ash, being a side product, is very cheap, so its effect on the plastic waste pyrolysis process has been studied. In the present research paper, Physical & chemical characterization of fly ash has been carried out. As fly ash consists of different metal oxides in proportion, its applicability in the process of pyrolysis of HDPE, LDPE, and PP waste has been studied. The different weight percent of fly ash (i.e., 5, 10, 15, 20) have been tried in all pyrolysis experiments. It has been observed that 5 wt % fly ash is effective for enhancing the yield of liquid fuel as compared to that without a catalyst. Liquid fuel obtained from catalytic pyrolysis of HDPE, LDPE, and PP waste with Fly ash consists of a high percent of low molecular weight fractions as compared to that of liquid fuel without catalyst, which has been concluded by calorific values & GC-MS result.

INTRODUCTION

Fly ash is generally obtained as a by-product from the combustion of coal and other waste materials. In recent years, intensive research has been on fly ash due to the increasing demand for recycling industrial by-products to improve sustainability in manufacturing and infrastructure (Sarker et al. 2013, Hong et al. 2023, Joseph et al. 2020, Sonawane et al. 2017, 2015). Fly ash is generally used in making bricks and in construction activities with cement. It is also used as a fertilizer in agriculture. It consists of Silica and alumina as major components and some minor components like ferrous, calcium, etc. It has been used as a catalyst for biodiesel production by some researchers (Omotola et al. 2010), and fly ash-derived zeolite has also been used as a catalyst in catalytic cracking of crude oil from refineries (Ojha & Pradhan 2001) and for the production of carbon nanotubes (Oskar et al. 2009). Production of fatty acid methyl esters (FAME) from waste frying oil (WFO) was studied using fly ash as a heterogeneous catalyst by researchers (Robinson Muñoz et al. 2020). Researchers also focused on synthesizing modified catalysts by using fly ash with other catalysts (Zhang et al. 2020). In the present research, after the chemical characterization of fly ash, its effect as a catalyst on enhancing the yield in the pyrolysis of thermoplastic waste, including HDPE, LDPE, and PP, has been studied.

MATERIALS AND METHODS

The pyrolysis glass reactor has been designed and developed for treating plastic waste of 100 grams. The reactor consisted heating mantle of high quality insulation jacket and temperature controlling system with an energy regulator, Borosilicate glass reactor, Thermocouple and Temperature indicator (Nickel-Chromium), Condenser and Collection flask, etc.

Pyrolysis experiments on HDPE, LDPE and PP waste were carried out separately without catalyst and by using Fly ash as a catalyst. 100 grams of waste material was used for each experiment. The catalyst-to-feed ratios (1:5, 1:10, 1:20), i.e., 5, 10, 15 and 20 wt % of Fly ash were used. Experiments were carried out at a temperature range of 400-470°C, depending on the type of plastic waste material. The Plastic waste material (100g) was fed into a reactor flask of 500 mL capacity and attached with a connector consisting of a nitrogen inlet, thermocouple, temperature indicator, and outlet connected to the condenser. The mouth of the flask was then tightened with its lid and sealed with the help of Teflon tape to avoid any leakage of vapors.

Firstly, the nitrogen gas with a flow rate of 50 $mL.min^{-1}$ for 2-3 min and with pressure slightly above atm. The pressure was purged into the flask to make an inert atmosphere and then started heating waste plastic. Heating was supplied with the rise of temperature $20^oC.min^{-1}$. The melting temperature of each type of plastic was recorded. After melting and boiling of plastic waste, condensation of generated vapors produced liquid fuel in major quantities with wax and gases in minor quantities. The process required around 20-30 min to obtain liquid fuel in the collection flask and 1-2.5 hrs to complete the reaction. The quantity of liquid fuel was measured in milliliters, and wax was measured in grams. The generated gas was measured by using material balance. The required amount of energy was recorded with the help of an energy meter. All performed experiments were replicated twice to obtain statistically significant results.

RESULTS AND DISCUSSION

Characterization of Fly Ash

Fly ash (FA) (on dry basis) generally consists of SiO_2 50.91%, Al_2O_3 30.91%, Na_2O 0.10%, CaO 6.2%, Fe_2O_3 3.46%, MgO 1.48%, TiO_2 1.65%, MnO 0.02%, K_2O 0.60%, P_2O_5 0.56%. The average SiO_2/Al_2O_3 ratio of Fly ash was found to be 1.65 (Omotola et al. 2010). Grey-colored, amorphous fly ash was obtained for the study from the cement industry located near Pune and was ground to a fine powder before use.

Characterization of Fly ash has been done for SEM, XRD, XRF, and TGA-DTA to know the suitability as a catalyst for enhancing the yield and quality of liquid fuel in the pyrolysis process.

Scanning electron microscopic images of raw Fly ash at different magnifications of 5 and 40 KX are shown in Fig. 1. From the SEM image, the particle size of Fly ash was found to be 1.5 μm to 5 μm. Given Fly ash sample possesses a glossy and smooth surface, but due to spherical particles, the available surface area for the reaction was observed more.

From energy dispersion spectroscopy, it was observed that Fly ash consisted of SiO_2 Al_2O_3, CaO, Fe_2O_3, MgO, TiO_2, MnO, K_2O, P_2O_5, etc.

X-Ray Diffraction Study of Fly Ash

The XRD graph of Fly ash is shown in Fig. 2. Graph is plotted by considering 2Θ values on the X-axis and intensity on the Y-axis.

Fly ash has a major peak at 2Θ value of 26 with smaller peaks at 22.02, 30.94, 41.12, 50.52, 52.33, 61.23, 69.01 etc. The structure of Fly ash was observed to be monoclinic from 2Θ values and JCPDS reference. XRD pattern of Fly ash showed multiple numbers of small peaks, which represent the amorphous nature of Fly ash.

X-Ray Fluorescence Study of Fly Ash

From the XRF spectrum, the composition of Fly ash was found to be 66.50% SiO_2, 28.54% Al_2O_3, 1.64% CaO, 0.56% MgO, 4.081% Fe_2O_3, 2.36% TiO_2, 1.16% K_2O and 0.504% P_2O_5. The percentage of silica was found to be the highest. Alumina and iron were also found in

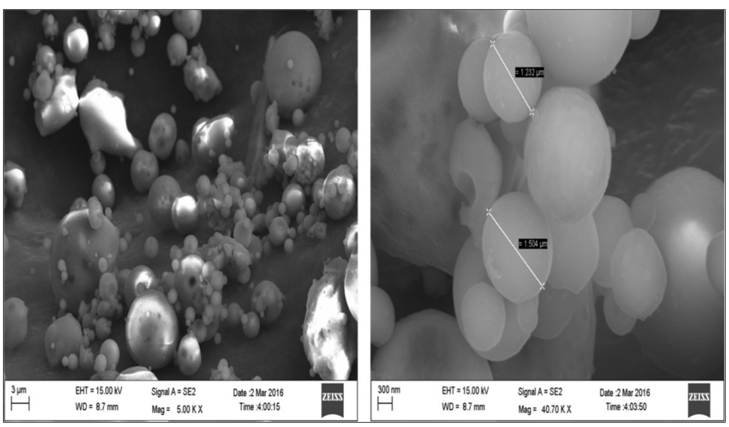


Fig. 1: SEM images of fly ash at different magnifications.

significant concentration with minor concentration of other elements.

Thermo Gravimetric Study of Fly Ash

A graphical representation of the TG and DTA of fly ash is shown in Fig. 3. The x-axis represents temperature in degrees Celsius, the Y-axis on the left side gives percent weight loss, and the Y-axis on the right side gives potential difference values. The black line represents the TG graph, and the blue line represents the DTA graph. Thermo gravimetric and differential thermal analysis study of Fly ash was done at the temperature range of 30 to 800°C.

From the graph, weight loss of Fly ash was observed around 0.9% at 450°C, which shows the thermal stability of fly ash at higher temperatures in pyrolysis.

The Percent Yield of Liquid Fuel

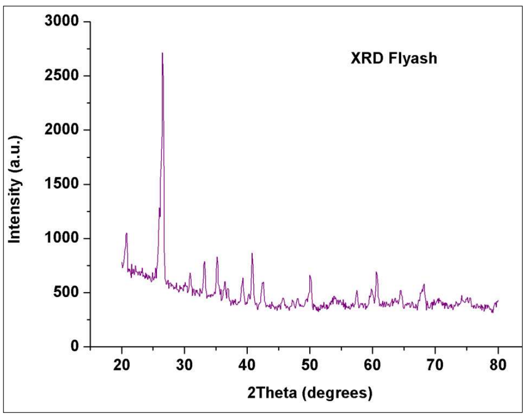


Fig. 2: XRD pattern of fly ash.

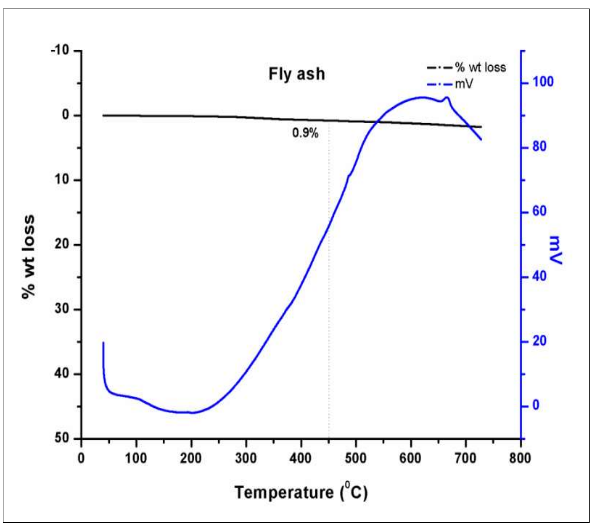


Fig. 3: TG-DTA graph of Fly ash.

The effect of Fly ash was studied in pyrolysis of HDPE, LDPE, PP, and mixed waste by conducting pyrolysis experiments at 450°C by using 5, 10 and 20% fly ash, and the yield of liquid fuel obtained was compared with that without catalyst, and displayed in Fig. 4.

The use of 5% fly ash enhanced the yield of liquid fuel in HDPE, LDPE while the use of 10% Fly ash enhanced the yield of liquid fuel for PP waste. The use of 20% fly ash reduced the yield of liquid fuel for all types of plastic wastes used as compared to that without catalysts.

FTIR Analysis of Liquid Fuel Obtained in Plastic Waste Pyrolysis Without Catalyst and By Using Fly ash Catalyst

Fourier Transform Infrared Spectroscopic (FTIR) analyses of liquid fuel samples obtained from HDPE, LDPE, PP, and mixed waste without catalysts and with fly ash were done to know functional groups or hydrocarbons and to detect the type of vibration in liquid fuel. Wave number range, type of vibrations, name of functional group observed in different liquid fuel samples

Fig. 5 represents FTIR spectra for liquid fuel samples obtained from pyrolysis of HDPE, LDPE, PP, and mixed waste without a catalyst and by using Fly ash as a catalyst. C-H bending vibrations were observed at wave numbers 721, 991, and 1080 $cm^{-1,}$ which proved the presence of alkenes, while peaks with wave numbers 1373 and 1462 cm^{-1} indicated C-H scissoring and bending vibrations which represent the presence of alkanes. C=C stretching was observed at wave number 1648 $cm^{-1,}$ which showed the presence of alkenes. The peak with carbonyl groups was found at 1736 cm^{-1} in liquid fuel samples obtained from pyrolysis of HDPE waste with fly ash.

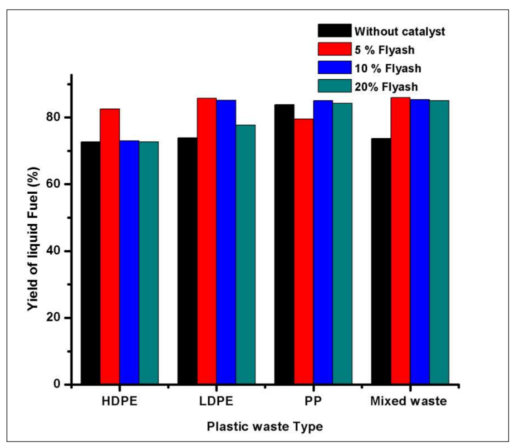


Fig. 4: Effect of fly ash on yield of liquid fuel in pyrolysis of plastic waste.

GC-MS Results of Liquid Fuel Obtained from Pyrolysis of HDPE Waste Without Catalyst and By Using Fly Ash

Fig. 6 & 7 show a gas chromatograph and mass spectrograph of liquid fuel obtained by using HDPE waste without a catalyst and by using a fly ash catalyst.

Liquid fuel obtained from HDPE waste consisted of hydrocarbons in the range of C-10 to C-27. From the GC-MS data, it was observed that the concentration of alcohol named 2 hexyl, 1-decanol was highest in liquid fuel obtained from HDPE waste as the total area percent of it was found to be maximum (44.07%). Low molecular weight fractions like Decene, Hexadecane, and Nonadecane were found in the sample but in lower concentrations. The area percent for Heptacosane was observed at about (20.56%) which represented a high percentage of it in the liquid fuel sample. As Heptacosane represents a high molecular weight fraction, its presence was found to be undesirable.

Gas chromatography of Pyrofuel (liquid fuel obtained from plastic waste pyrolysis) obtained with Fly ash consisted of C-9 to C-27 hydrocarbon fractions. The presence of low molecular weight alkenes and alcohols was found in significant amounts. The area percent of peaks for C-8 to C-15 fractions was observed to be around 78%, while the area percent for C-16 to C-19 fractions was around 15%. The peak area percent of Tetradecene was found highest i.e., 39%. A negligible amount of high molecular weight fraction of Heptacosane was observed in the fuel sample.

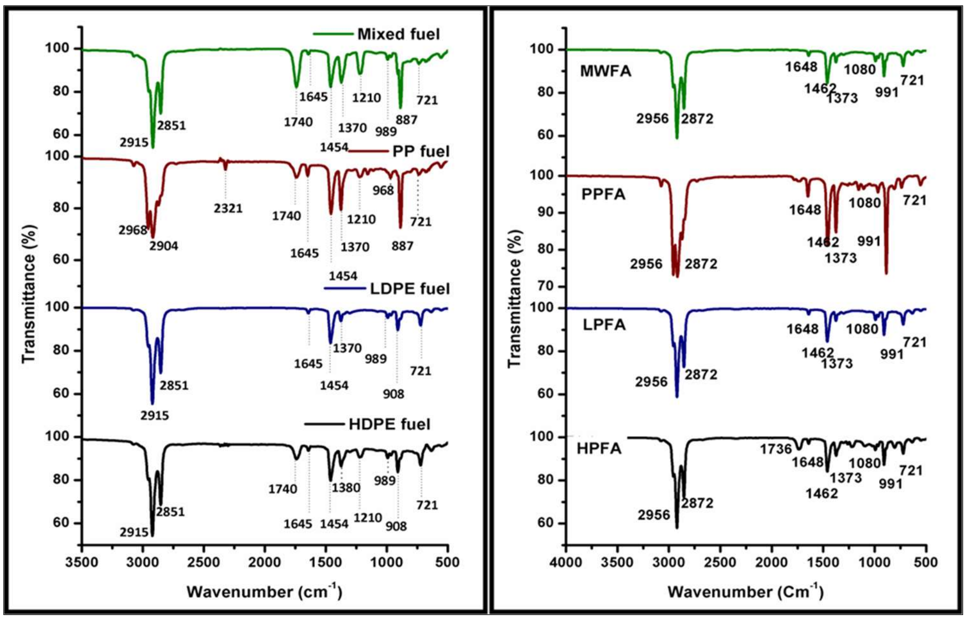
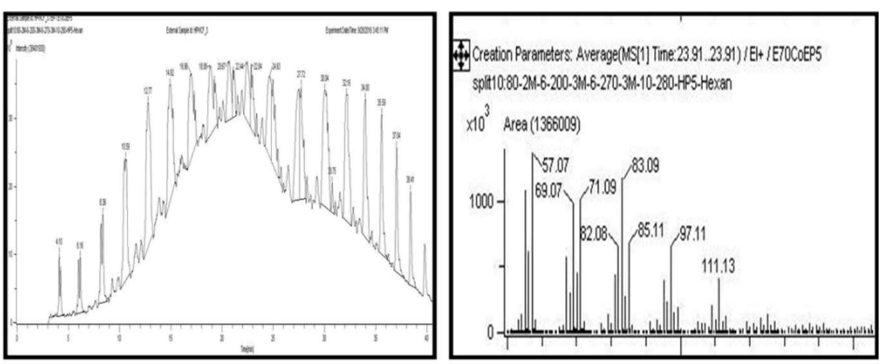


Fig. 5 (a & b): FTIR spectra for liquid fuel obtained without catalyst (a) and by using fly ash (b) in pyrolysis of HDPE, LDPE, PP, and mixed waste.



Gas chromotograph (Retention time Vs % area of a peak) Mass spectra

Fig. 6 (a & b): Gas chromatograph and mass spectrograph of liquid fuel sample-HPWC.

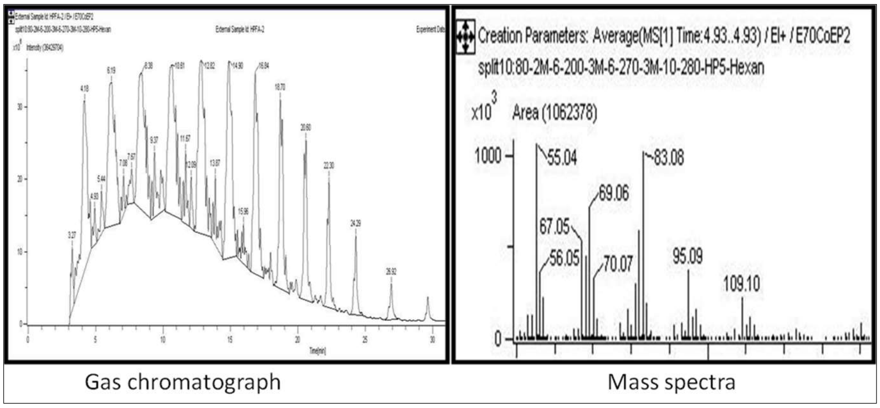


Fig. 7 (a & b): Gas chromatograph and mass spectrograph of liquid fuel sample-HPFA.

GC-MS Results of Liquid Fuel Obtained From Pyrolysis of LDPE Waste Without Catalyst & By Using Fly Ash

Fig. 8a & b show the gas chromatograph and mass spectra of liquid fuel obtained by using LDPE waste without a catalyst. From the chemical composition of liquid fuel obtained from pyrolysis of LDPE waste without a catalyst, it was observed that liquid fuel obtained from LDPE waste has hydrocarbons in the range of C-7 to C-44.

The area percent for the C-7 to C-15 hydrocarbons was observed to be around 55.3%. No significant amounts

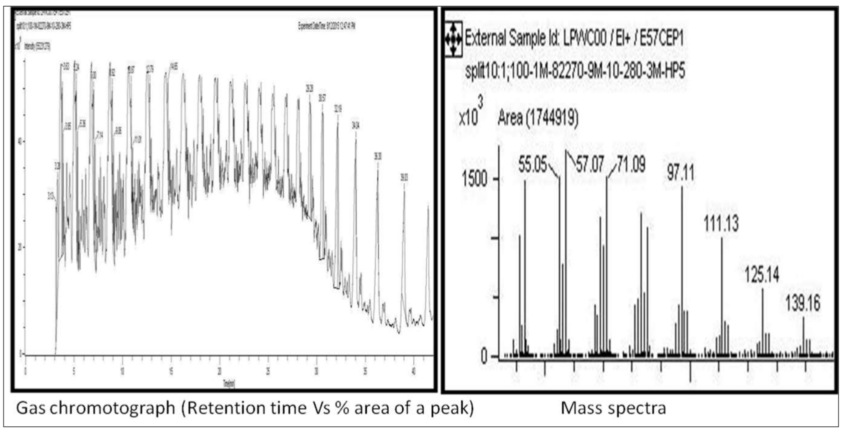


Fig. 8 (a & b): Gas chromatograph of liquid fuel sample-LPWC mass spectrograph of liquid fuel sample-LPWC.

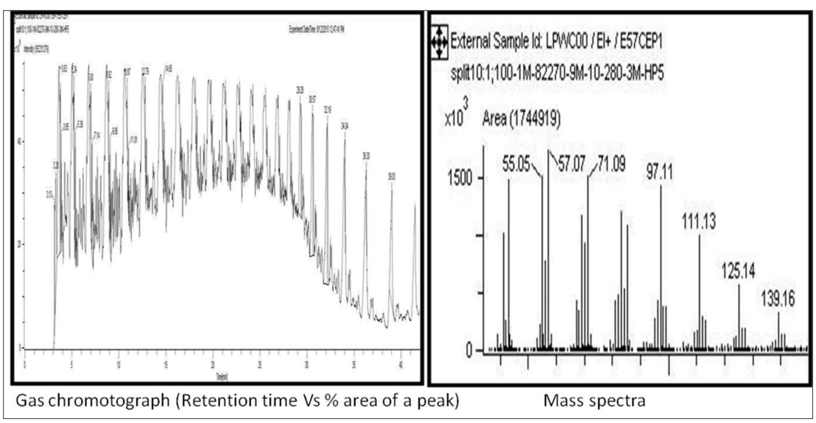


Fig. 9 (a & b): Gas chromatograph of liquid fuel sample-LPFA, mass spectrograph of liquid fuel sample-LPFA.

of hydrocarbons were observed from C-15 to C-25 in the liquid fuel. However, the presence of high molecular weight fractions like Nonacosane and Tetratetracontane with an area of peak of around 22% was found undesirable.

Fig. 9a and 9b show GC and mass spectrograph of liquid fuel obtained by using LDPE waste with fly ash catalyst. It was observed that liquid fuel obtained from LDPE waste with Fly ash has hydrocarbons in the range of C-9 to C-19. Various low molecular weight alkenes, Undecene, Dodecene, Tridecene, Tetradecene, Pentadecene, and alkanes butyl -Cyclopentane and Undecane were observed. Overall results showed high concentrations of low molecular weight hydrocarbons ranging from C-11 to C-15. The alcohol fraction Z-10-Pentadecenol was observed with a peak area of around 3.67%.

GC-MS Results of Liquid Fuel Obtained from Pyrolysis of PP Waste Without Catalyst and by Using Fly Ash

Fig. 10 shows the gas chromatograph and mass spectra of liquid fuel obtained by using PP waste without a catalyst.

GC-MS results obtained for liquid fuel with PP waste showed the presence of hydrocarbons from C-7 to C-29. Low molecular weight hydrocarbon fractions like 3-methyl-2 Hexene, Nonane, and 3-ethyl Heptane were observed. The total area of peaks in the hydrocarbon range C-7 to C-15 was found to be around 50.6%. The peak area for alcohol fractions, tridecanol and hexadecanol, was observed to be around 10.7%. The heavy oil fractions, nonacosane and heptacosane were also observed with a high peak area, i.e., 34.35%.

Fig. 11a and 11b show the GC and mass spectrograph of liquid fuel obtained by using PP waste with a fly ash catalyst. From the results, it was observed that fuel consisted of C-10 to C-22 hydrocarbon fractions. Significant amounts of various alcohol fractions like 2,7-dimethyl Octanol, 2-isopropyl, 5-methyl 1-Heptanol, 2-butyl 1-Octanol, 1-cyclopropanol, 2 hexyls, 1 Octanol, 2 hexyls, 1-Decanol,

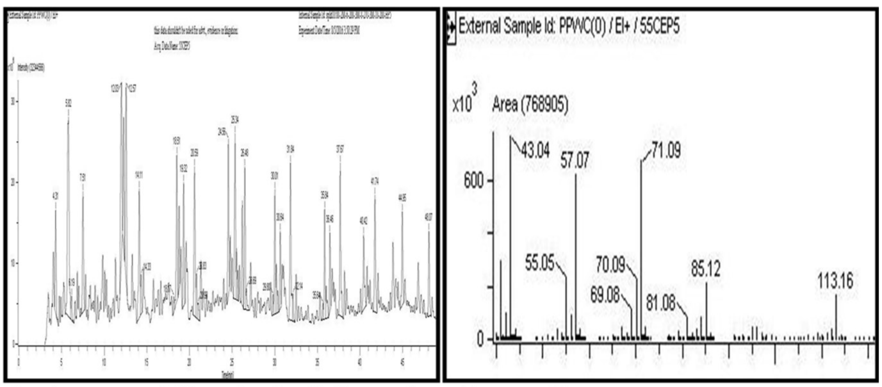


Fig. 10 (a & b): gas chromatograph and mass spectrograph of liquid fuel sample-PPWC.

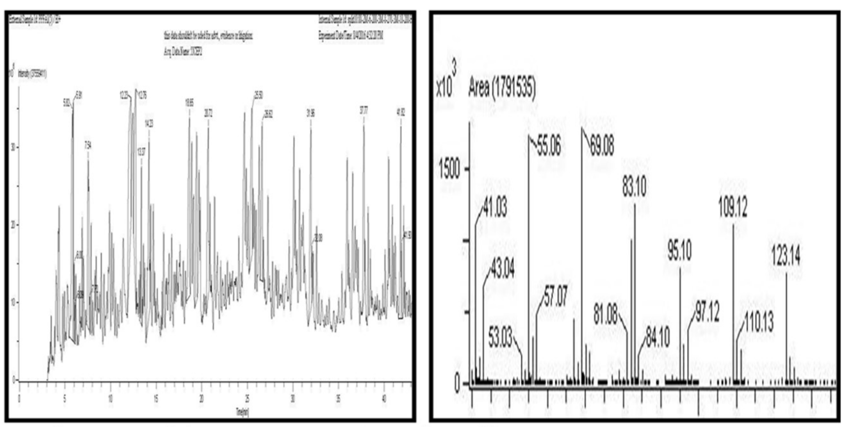


Fig. 11 (a & b): Gas chromatograph and Mass spectrograph of liquid fuel sample-PPFA.

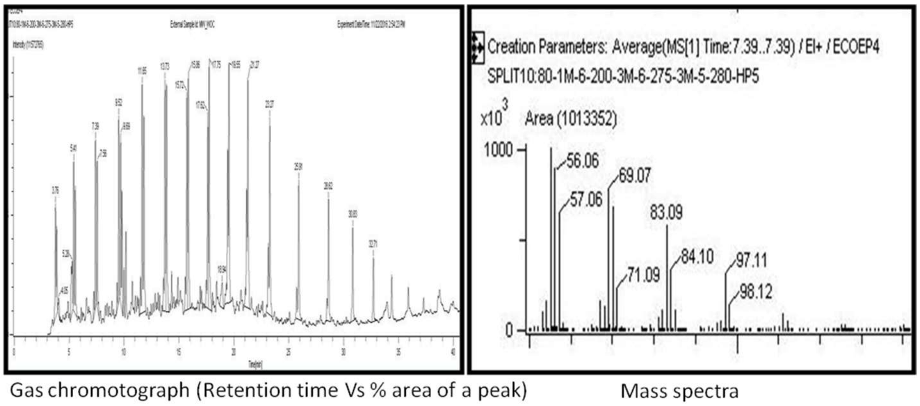


Fig. 12 (a & b): Gas chromatograph of liquid fuel sample-MWWC & Mass spectrograph of liquid fuel sample-MWWC.

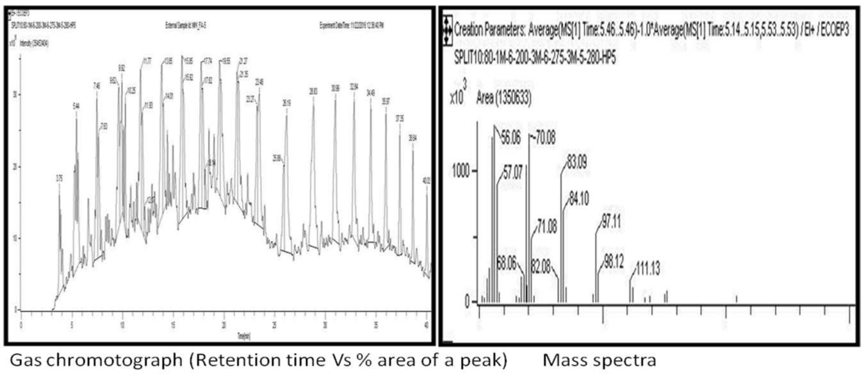


Fig. 13 (a & b): Gas chromatograph of liquid fuel sample-MWFA and mass spectrograph of liquid fuel sample-MWFA.

etc. were observed in the fuel. The area percent of alcohol peaks was found to be around 42%. Alkane fractions like Undecane, Dodecane, tetra isopropyl Cyclohexane, and alkenes like- Undecene and Dodecene were observed in the GC-MS graph. The presence of heavy oil fractions like Cyclotetradecane and 1-Docosene were also observed, with peak areas around 11.5% and 6.23%, respectively.

GC-MS Results of Liquid Fuel Obtained From Pyrolysis of Mixed Waste Without Catalyst & By Using Fly Ash

Fig. 12a and b show the gas chromatograph and mass spectra of liquid fuel obtained by using mixed waste without catalyst and with fly ash catalyst.

From the above data, it was found that liquid fuel obtained from the mixture of HDPE, LDPE, and PP waste without catalysts has hydrocarbons in the range of C-10 to C-27. Low molecular weight fractions like Decene,1-heptyl, 2 methyl cyclopropane, tridecene, tetradecane, and hexadecane were observed and found desirable. The highest area percent (i.e., 30.56%) was observed for 1-nonadecane fraction ($C_{19}H_{40}$), which showed that the concentration of 1-nonadecane is maximum in liquid fuel obtained from the mixture of HDPE, LDPE, and PP waste without catalyst. High molecular weight fractions like docosene and heptacosane were also observed in less concentration, but their presence was found to be undesirable in terms of quality.

Fig. 13b shows a mass spectrograph of liquid fuel obtained by using mixed waste with a fly ash catalyst. It was observed that fuel consisted of hydrocarbons ranging from C-11 to C-21. The presence of Hexadecane with a peak area of around 34% showed the maximum diesel component in the liquid fuel. The presence of high concentrations of low molecular weight alkanes, alkenes, and alcohols in the fuel was observed.

Calorific Values of Liquid Fuel Obtained From Pyrolysis of Plastic Waste by Using Fly Ash

Table 1. displays calorific values of liquid fuel obtained from pyrolysis of plastic waste with 5, 10, and 20% fly ash.

By using 5% fly ash in HDPE and LDPE, PP, and mixed waste pyrolysis, the calorific values of liquid fuel were significantly enhanced. In comparison, the use of 10 and

Table 1: Calorific values of liquid fuel obtained from plastic waste by using 5, 10, and 20 % fly ash.

Liquid fuel from Plastic waste	Calorific values [KJ.Kg^{-1}]			
	Without catalyst	5 % FA	10 % FA	20 % FA
Liquid fuel from HDPE waste	40614	49622	43034	43897
Liquid fuel from LDPE waste	41220	47858	42587	44811
Liquid fuel from PP waste	42200	49392	41675	44027
Liquid fuel from Mixed waste	44558	47578	42157	39857

20% fly ash reduced calorific values of liquid fuel for all plastic wastes used as compared to that without catalysts. The highest increase in calorific value was observed for liquid fuel obtained from HDPE waste with 5% Fly ash.

CONCLUSION

After a comparative study of liquid fuel yield and fuel characteristics without a catalyst and by using a fly ash catalyst, it was found that the use of fly ash enhanced the yield of liquid fuel in pyrolysis of HDPE, PP, and mixed plastic waste. The use of 5% fly ash showed enhanced calorific values of liquid fuel for HDPE, LDPE, PP, and mixed waste as compared to that of without catalysts due to the presence of low molecular weight fractions and alcohol in them. So, from all results obtained by using fly ash as a catalyst in the pyrolysis, it was concluded that fly ash enhanced the yield and low molecular weight fractions in liquid fuel in the pyrolysis of all plastic wastes used. GC-MS results and calorific values of the liquid fuel samples obtained in pyrolysis of HDPE, LDPE and PP waste give justification for improvement in the quality of liquid fuel. From the surface morphology, XRD, chemical composition, and thermal analysis of fly ash, it is proved that the Silica alumina ratio, surface morphology and nanoparticle size, and thermal stability of Fly ash can prove it as a better and cost-effective catalyst in catalytic pyrolysis of thermoplastic waste.

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