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CO-PYROLYSIS OF SCRAP TIRE AND PLASTIC USING COAL DERIVED FLY-ASH

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ABSTRACT: Used automobile tires and thermoplastics (e.g. polypropylene) have become liability of modern societies and several avenues have been explored for their suitable disposal. Pyrolytic liquefaction of tires and plastics have attracted significant attention since the process can provide value-added products such as liquid transportation fuels and chemicals while mitigating the waste disposal issues. Pyrolysis can be done both in absence (thermal) or presence (catalytic) of a catalyst. Catalytic pyrolysis is favored by less demanding reaction conditions and better quality of product. Catalytic copyrolysis has the additional advantage in using a wider feedstock and a possible synergistic effects from different feeds during molecular transformations. This work investigates the effect of untreated fly-ash (class F) as catalyst for the copyrolysis of scrap tire and polypropylene at 300°C and atmospheric pressure using batch type pyrolysis reactor and also studied the effect of fly-ash during pyrolysis of scrap tire using Pyro-GC/MS. Copyrolysis was carried out using various ratio of scrap tire and polypropylene at 300°C, whereas the pyrolysis of scrap tire in pyro-GC/MS was carried out at 500°C. The maximum yield (23.33%) of oil was obtained at a ratio of 60:40 (w/w) of scrap tire and polypropylene in presence of 20wt% of fly ash catalyst. The oils were characterized by NMR, GC-MS, FT-IR and elemental analysis.

Keywords: Scrap tire, plastic, fly-ash, pyrolysis, pyro-GC/MS

1 INTRODUCTION

Value-addition of wastes generate alternative revenue streams while subduing the waste management issues. Environmental accumulation of non-biodegradable scrap tires and plastic wastes is a global problem and one way to control the problem is to convert them economically into fuels and chemicals. These tire pyrolysis industries mostly employ the thermal pyrolysis technique in absence of a catalyst for liquefaction. The resulting tire pyrolysis oil (TPO) consists of a host of aliphatic and aromatic hydrocarbons, oxygenates, and heterocyclic compounds of nitrogen and sulfur. The oil is unsuitable for direct use in engines due to higher sulfur content and inferior combustion properties and generally burnt in furnaces for process heat. The tire pyrolysis oil contains polar compounds and high amount of sulfur and not suitable for use in engines. It has been established that catalytic pyrolysis of scrap tire increases the amount of light oil including single ring aromatic hydrocarbons, and naphtha while decrease the sulfur content significantly. Needless to say, naphtha and simple aromatic hydrocarbons like benzene, toluene, and xylenes (BTX) have higher market value as chemical feedstock. Catalytic upgrading of TPO and downstream processing by distillation are also reported in the literature that furnishes light oil and diesel fuel of improved quality. Catalytic co-pyrolysis of scrap tire and plastic wastes are also reported and they provide produce better quality oil compared to that produced from the individual feedstock. Various catalysts ranging from alkaline earth metal oxides, silica, alumina, to zeolites have been examined. Hydro treating catalysts used in the petro-refinery operations have also been used. However, the catalysts listed above are relatively expensive. Hereby, we propose to use inexpensive fly-ash obtained from coal-fired power plants as catalyst and/or supporting material for the production of TPO. Fly-ash primarily contains silica (amorphous and crystalline), alumina, and calcium oxide. The potential of fly-ash as a catalyst has already been explored for the synthesis of bio-diesel and for

converting waste plastic into oil. However, use of fly-ash or its chemically-tailored varieties have never been used as catalyst for the pyrolysis of scrap tires or copyrolysis of scrap tire and plastic wastes.

Catalytic pyrolysis of scrap tires will lead to tire pyrolysis oil (TPO) which is a liquid mixture consisting of plethora of compounds including saturated straight chain and ring hydrocarbons of various carbon lengths, single ring aromatic hydrocarbons such as toluene and xylenes, polyromantic hydrocarbons, oxygenates, and a small amount of nitrogen and sulfur compounds. The mixture can be treated as crude petroleum and separated into valuable fractions following the steps followed in the petro-refineries. Although the mixture can be combusted directly in furnaces for process heat, more valuable fractions can be obtained if treated properly. The light naphtha and single chain aromatic hydrocarbons can be used as chemical feedstock and the straight chain hydrocarbons can be used as diesel-fuel. Chemically-modified fly-ash will be used as catalyst for catalytic pyrolysis of scrap tires or for the upgrading of oil obtained in thermal pyrolysis. Fly-ash contains significant amount of calcium oxide that has proved to be an efficient catalyst in lowering the sulfur content of pyrolysis oil. The silica and alumina in fly-ash will offer the acidic sites required for scission in carbon-carbon bond in polymers for their liquefaction. Use of an inexpensive catalyst like fly-ash while significantly improving the product quality and the fractions of higher market value will improve the process economy of the technology. The batch process will be optimized on various reaction parameters like temperature, loading of feedstock and catalyst, and the time of reaction. The optimized process will be scaled up to be demonstrated in the pilot scale. The intellectual property will be safeguarded by filing joint patents (NITK and Industrial partner) and then the research findings will be published in journal publications and technical reports.

Juan et al. [1] investigated the co- pyrolysis of forestry waste and waste tire using the different facilities and observed that co-pyrolysis of two feed stock like

forestry waste and waste tire significantly reduces the aldehydes and phenolic compounds. Kar [2] conducted the non-catalytic and catalytic pyrolysis of car tire waste and expanded perlite as an additive material and found that highest yield while using the catalyst to tire ratio as 0.05-0.25. Onay [3] studied the pyrolysis of waste tire and pistachio seed and their blends are carried out at 500°C in the absence and presence of catalyst. The result revealed that the hydrogen transfers and a synergic effect during the reaction improved the quality of pyrolytic oil. Jin et al. [4] studied the thermal behavior of co-pyrolysis of waste tires and rice husk using thermogravimetric analysis. They modelled kinetic equation for the evaporation of bio-oils by Achar's differential method and coal Redfern's integral method. Perondi et al. [5] characterized the pyrolysis products from co-pyrolysis of waste tires and spent foundry sand and experiment was conducted using bubbling fluidized bed reactor. The scanning electron microscope analysis showed that the removal of polymeric substance present in the core sand and the absence of phenol confirmed the polymeric resin degradation and the gas analysis showed that significant quantity of hydrogen, methane and ethane, which directly improves the calorific value of the fuel. OlgaBičáková et al. [6] studied the co-pyrolysis of waste tire/coal mixtures for smokeless fuel, maltenes and hydrogen-rich gas production and used the quartz reactor in a stationary bed at 5 °C/min up to the final temperature of 900 °C with a soaking time of 30 minutes. Beatriz Acevedo [7] studies the fuel-oils from co-pyrolysis of scrap tires with coal and a bituminous waste. Influence of oven configuration rotary oven were found to be more aromatic and to have lower oxygen contents. Lopez [8] studied the catalytic pyrolysis of plastic wastes with two different types of catalysts: zeolite ZSM-5 and Red Mud using semi batch reactor at 440-500°C. Muhammad Imran et al. [9] studies the production of fuels by co-pyrolysis of waste plastic and scrap tires at 350°C using rotary kiln. Walter

Kaminsky [10] studied the Pyrolysis of plastic waste and scrap tires in a fluid bed reactor. The results show that gaseous products like 40–60 wt.%, hydrogen, methane, ethylene, ethane) as well as liquid products (40–60 wt.%, mainly simple aromatics) are obtained.

Vatsala et al. [11] conducted the experiments on the pyrolysis of potato peel powder and polypropylene composite under identical conditions. They conclude that around 10% of pyrolysis oil with diesel exhibited the excellent fuel properties with improvement in cetane index, viscosity and density. Aparna Sarkar [12] conducted the experiments on copyrolysis of paper waste and mustard press cake in a semi-batch pyrolyzer in the temperature of 673-1173K. The optimization results shows that maximum bio-oil yield is 46.95% at 874. 75K. Ahamaruzzaman et al. [13] studied on co-cracking of petroleum vacuum residue with the Bakelite. They concluded that co-processing of petroleum residue with the coal, paper, biomass causes a synergistic interaction between them. Pradhan et al. [14] investigated the thermal pyrolysis of bicycle waste tire samples was carried out in a semi-batch reactor under 450-650°C. They observed that maximum liquid yield was obtained at 49% at 600°C and also proposed that the obtained pyrolytic oil has high calorific value and can be used in internal combustion engine. Kartikeyen et al. [15] reviewed the pyrolysis of scrap tires with a special focus to process parameters like temperature, gas flow rate, and

catalyst to tire ratio on yield. They concluded that the pyrolysis of scrap tires started at 250°C and completed at 550°C.

Post-consumer polymeric wastes like tires and plastics (e.g., polypropylene, polystyrene) can be used as inexpensive, alternative feedstock in producing fuels and chemicals. Catalytic pyrolysis has been an attractive strategy for a one-step, one-pot production of lighter hydrocarbons and fuel oil. Use of suitable catalysts markedly increase the fraction of naphtha, single ring aromatic compounds, and straight-chain diesel-range hydrocarbons in the pyrolysis oil when compared to that in the thermal pyrolysis oil in absence of a catalyst. The catalysts are generally pure inorganic compounds specifically tailored for this application and relatively expensive. Fly-ash, a waste product in the coal-driven thermal power plants, has the potential to be used as an inexpensive catalyst. Fly-ash has major components such as silica and calcium oxide which have separately been used as catalyst for catalytic pyrolysis and demonstrated marked improvement in the quality of pyrolysis oil. Fly-ash or its chemically-modified varieties have never been used as potential catalysts for catalytic pyrolysis of scrap tire or its copyrolysis with plastic waste. Successful application of fly-ash as a catalyst will not only lower the cost of pyrolysis oil but also develop a new market for fly-ash.

2 MATERIALS AND METHODS

The polypropylene was obtained from Sigma Aldrich. The scrap tire was purchased from Janata Tire, Udupi, Manipal. The raw materials were used as-received condition. The fly-ash used in the experiments are collected from Udupi Power Corporation limited. Table I shows the composition of coal derived fly-ash.

Table I: Composition of fly-ash

Fly-ash components	Composition (%)
SiO ₂	43.75
Al O _{2 3}	21.22
Fe O _{2 3}	11.90
CaO	8.64
MgO	4.58
SO ₃	1.12
Na O ₂	1.91
K O ₂	1.28
P O _{2 5}	0.321

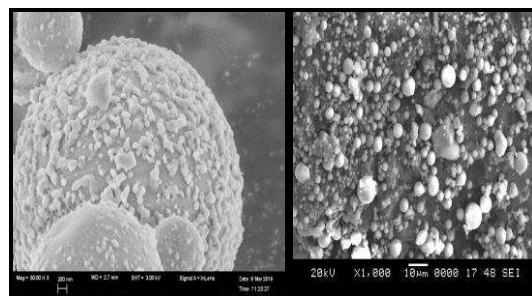


Figure 1: Scanning Electron microscopy of fly-ash at various magnification

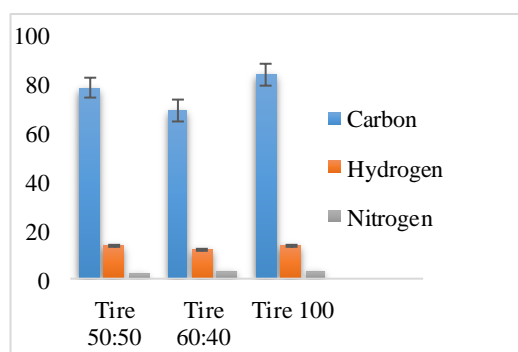


Figure 2: Elemental analysis of pyrolysis oil

3 EXPERIMENTAL

3.1 Pyrolysis using batch scale reactor facility

Pyrolysis is a thermochemical conversion process in the anaerobic conditions. The pyrolysis experiments were carried out using a laboratory batch scale reactor. The pyrolysis facility mainly consists of a 2L batch scale reactor, temperature controller, heating mantle, chiller, condenser etc. The pyrolysis temperature is maintained at 300°C during entire experiments at a rate of 10°C/min in absence of nitrogen atmosphere. The experiments were conducted using various ratio of tire: plastic ratio with 20% of raw fly-ash as catalyst. The samples were named as Tire 50 (Co-pyrolysis of 50 % tire with 50% plastic using 20 wt.% fly-ash), Tire 60 (Co-pyrolysis of 60% tire with 40% plastic using 20 wt.% fly-ash) and Tire 100 (Thermal pyrolysis of 100% tire).

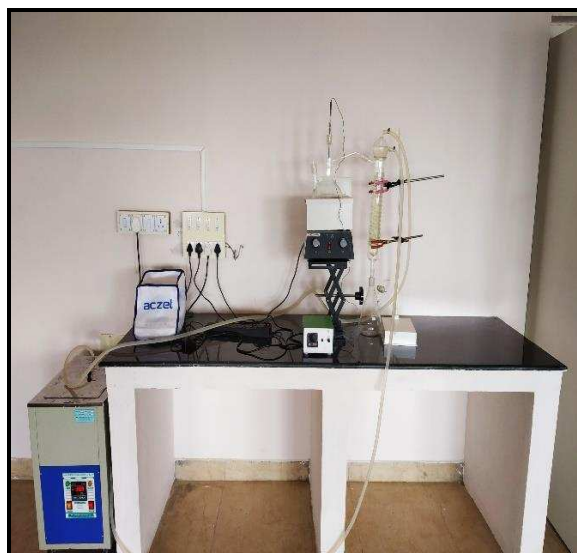


Figure 3: Schematic diagram of batch scale pyrolysis facility

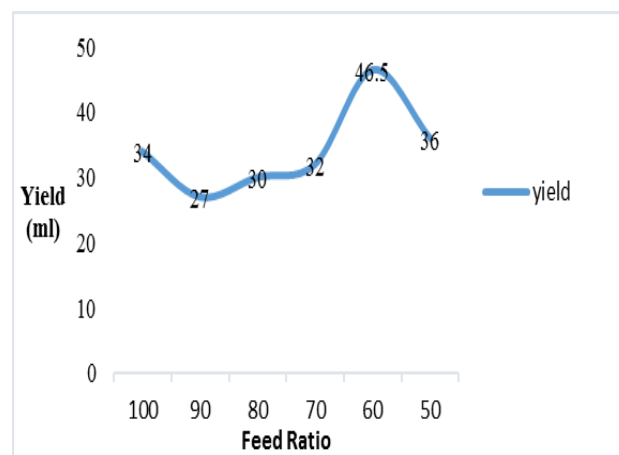


Figure 4: Yield of copyrolysis with tire: plastic feed ratio

3.2 Limitation of batch scale pyrolysis reactor

The major limitation during the pyrolysis of tire and plastic using fly-ash as a catalyst is the recovery and removal of tar fraction after the co-pyrolysis reaction. Thus we have focused the pyrolysis of scrap tire with fly-ash as catalyst using pyro-GC/MS facility at Indian Institute of Technology, Bombay are described in the next section.

3.3 Pyrolysis-Gas Chromatography/Mass Spectrometer (Py-GC/MS)

Fast pyrolysis experiments were performed in a single shot analytical micropyrolyzer (PY-3030S, Frontier Laboratories, Japan), and the products were analyzed in a Shimadzu GC/MS (Model: GC-2010 and QP2010). The pyrolysates were separated in a UA-5column (stationary phase: 5% diphenyl dimethyl polysiloxane, 30 m 0.25 mm i.d. 0.25 μ m thickness). Tire powder sample of c.a. 300 \pm 20 μ g was taken in a deactivated stainless steel cup, and dropped into the quartz tube surrounded by the micro pyrolyzer furnace. The pyrolysis temperature was set in the range of 350–800°C. The micropyrolyzer furnace was pre-calibrated to read the centerline temperature of the quartz tube. Experiments were performed in ultra-high pure helium (5.5grade) environment. Helium flow rate through the column was 2 mL min⁻¹ with a split ratio of 100:1. Prior to dropping the sample cup inside the quartz tube, helium gas was purged for a few minutes. The GC column oven was maintained at 40° C for 1 min, then heated at a rate of 20° C min to 300° C, and finally held at 500° C for 30 min. The pyrolysates were scanned in a mass range (m/z) of 28–300 Da. MS ion source temperature was maintained at 300° C. The products were identified by comparing the mass spectra with NIST mass spectral database [14].

3.4 Nuclear Magnetic Resonance Spectroscopy (NMR)

NMR studies are carried out using Bruker Advance III 500 MHz spectrometer and samples were dissolved in deuterated methanol [15]. Figure shows the H-NMR spectrum of 50% tire and 60% tire samples. The aliphatic fractions are significantly improved by the addition of more tire sample to plastic. However, the oxygenates are less in the 50% tire sample in comparison with 60% tire sample but the aromatics are reduced by adding more percentage of tire.

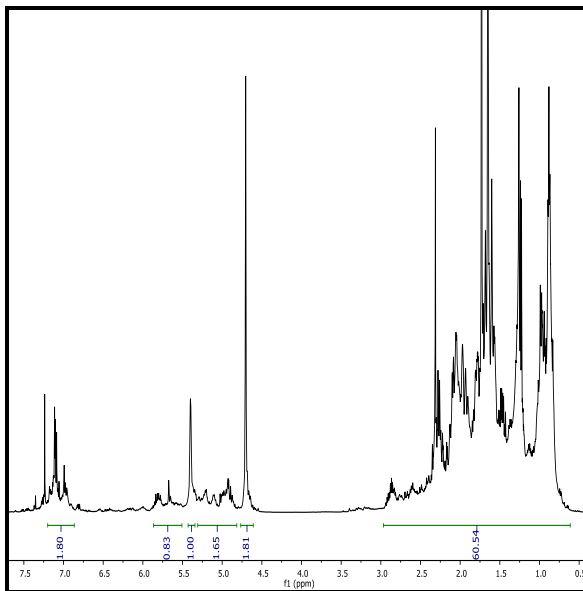
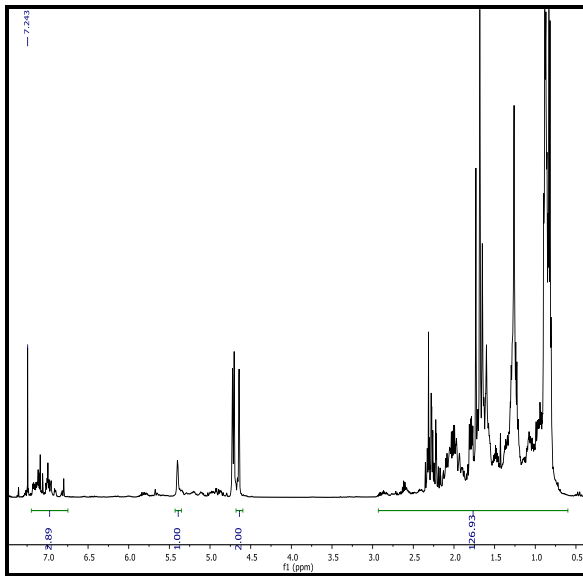


Figure 5: NMR spectra of Tire 50 and Tire 60

3.5 Fourier Transform Infrared Spectroscopy (FT-IR)

The compositional functional group analysis of the pyrolytic oil was carried out by using FTIR (Model:3000 Hyperion Microscope with Vertex 80 FTIR System) with data processing and library search facilities. The FT-IR spectra of the oil was collected in the range of 4000-400 cm^{-1} . The FTIR was done for 100% tyre, 60% tyre and 40% plastic, 50% tyre & 50% plastic oil samples. Table 2. shows the wavelength, functional group of various class of compounds present in co-pyrolysis oil produced from plastic and tire. The FT-IR spectra of all the samples seems straight forward.

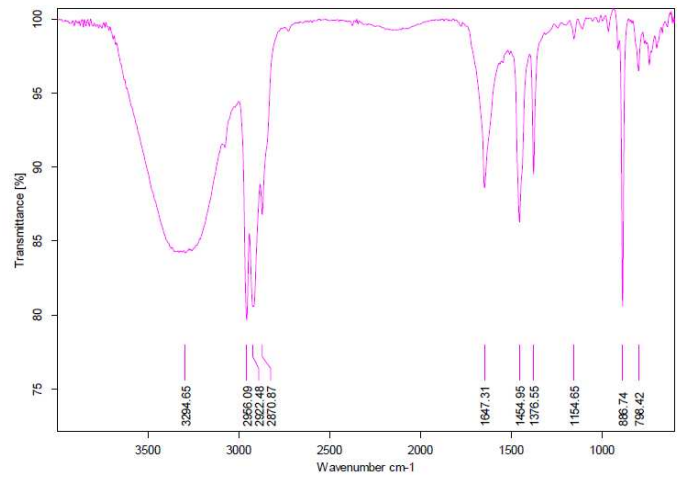


Figure 6: FTIR spectra of Tire 50

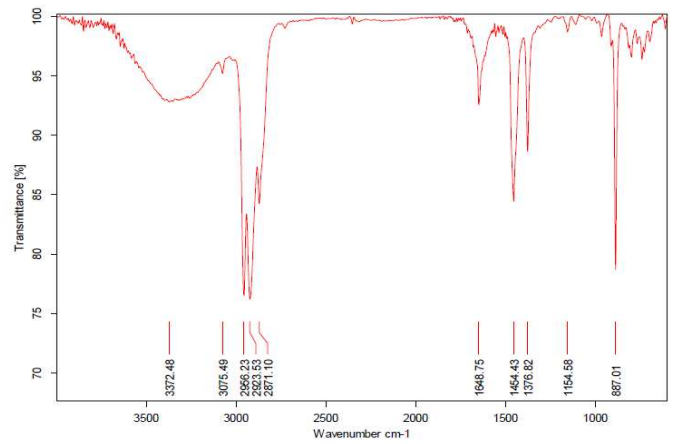


Figure 7: FTIR spectra of Tire 60

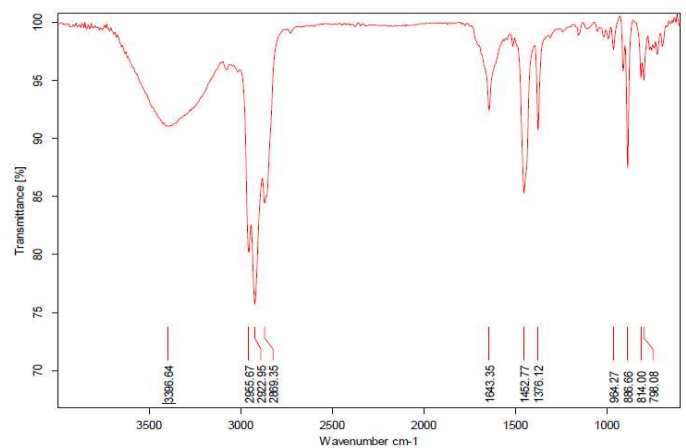


Figure 8: FTIR spectra of Tire 100

Table II: Functional group and classes of compounds

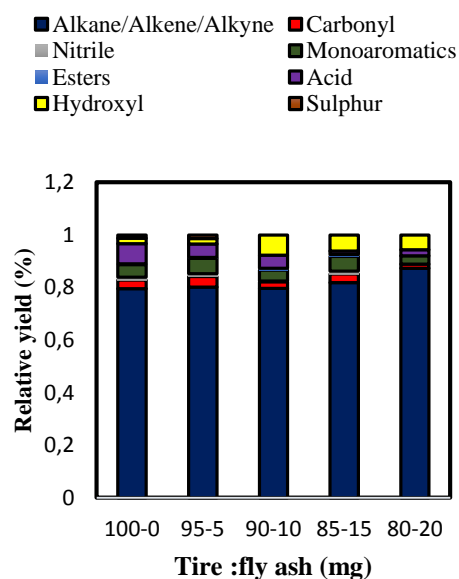
Wavelength Range	Functional Group	Class of Compounds
3400-3500	O-H	Alcohols
2900 – 3000	CH ₃ , CH ₂ & CH	Alkanes
2700-2900	H-C=O	Aldehyde
1550 – 1650	C ₆ H ₆	Benzene
1350 – 1470	CH ₂ & CH ₃	Alkanes
1330 – 1430	O-H bending (in-plane)	Phenols
970 – 1250	C-O	Phenols
880 – 925	=C-H & =CH ₂	Alkenes

3.6 Effect of fly-ash as catalyst during pyrolysis of scrap tires – Pyro-GC/MS study

The addition of fly-ash during the pyrolysis of scrap tire using raw fly-ash significantly improves the oil quality compared to thermal pyrolysis. Fly-ash is a multicomponent catalyst mainly composed of oxides of silica, alumina, iron, aluminum, magnesium and calcium. Due to the high quantity of silica in raw fly-ash derived from coal thermal power plants, accelerates the removal of nitrogenous and sulfurous compounds. Interestingly, the alkane fraction is increased with the addition of fly-ash in comparison with non-catalytic pyrolysis. Fig. 9. shows the relative yield or selectivity with the tire: fly-ash ratio for study the quality of oil after addition of fly-ash as a catalyst.

4 CONCLUSION

In this study, the effect of fly-ash during co-pyrolysis of tire and plastic are evaluated. The maximum oil yield was obtained during the co-pyrolysis of 60% of tire with 40% plastic due to the synergistic interaction of tire and plastic waste. The pyro-GC/MS studies showed that the addition of raw fly-ash in to scrap tire and plastic enhances the product quality by significant reduction in the nitrogen and sulfur containing compounds. However, there is a significant improvement in the composition of alkane with fly-ash addition due to presence of high quantity of silicon oxide.

**Figure 9:** Effect of fly-ash on pyrolysis of tire using pyro-GC/MS

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7 LOGO SPACE



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