Production of aliphatic-enriched pyrolytic oil from medical waste plastic as an alternative fuel

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ABSTRACT

A massive usage of plastic items resulted in a huge plastic waste generation. This creates adverse impacts to the environmental matrices if it not managed in an appropriate manner. Numerous plastic waste management practices have failed to accomplish environmentally friendly disposal/ management. However, pyrolysis creates more attention to the researches due to its possible reduction in plastic waste accumulation and simultaneously, generating hydro carbon fuels. This study investigated the pyrolysis experiments with plastic waste under various reaction conditions. The medically discarded polypropylene bottle (MDPB) was pyrolyzed in a reactor at 330-460 °C for 120 min. By conducting various experiments, the large quantity of liquid fuel (67.5%) yielded at 420 °C and 120 min. In addition, the pyrolytic oil was analysed using FTIR, GC-MS and physical property analytical methods. Hence, the obtained liquid yield is complied with commercial grade fuel and it may be suggested for using multi purposes such as fuel in boiler, and furnace.

Keywords: Pyrolysis, Thermolysis, Medically discarded polypropylene bottle (MDPB), Plastic waste, Hydrocarbon fuels, Liquid yield

1. INTRODUCTION

Due to the modern industrialization and urbanization, the usage of plastic has increased dramatically in the past few decades [1-3]. Plastic driven as one of most indispensable component and are used globally due to their distinctive characteristics such as cheap, low weight, durability, ease of production and energy efficiency [4-7]. Owing to their properties, which have increasingly become substantial economic benefits to various segments i.e. packaging, storage and handling, protective layer, pharmaceutical, insulation component, medical gadgets etc [8-10]. The high demand of plastic correspondingly increases the surge of plastic wastes being generated. Currently, the discarded plastic waste accumulation is around 359 million tons per year and it will be projected to reach more than 30000 million tons by 2050 [11]. In India, the generation trend was estimated as 9.47 million tons. Among these, the plastic wastes comprise 66.91% of polyethylene (LDPE & HDPE), 8.66% of Polyethylene Terephthalate (PET), 4.14% of Polyvinyl Chloride (PVC), 9.9% of Polypropylene (PP), 4.77% of Polystyrene and 5.62% of other plastics [12]. Of all these, about 50-70 % of waste plastics discarded from packaging material which are mainly composed of polyethylene, polypropylene and polystyrene [13]. Polypropylene is frequently used and recyclable plastic and which can be found in bottles, tubes, medical gadgets, computer accessories, etc [14-17]. The accumulation of plastic over a long period with an improper management practices pose serious threats to the mankind's health and environmental matrices such as hazardous PCBs emission, dioxin evolution, leachate fluid formation and some human health troubles i.e. neurological damage, asthma, child developmental disorders, birth imperfection and cancer etc [18-20]. Therefore, the safe disposal practices are becoming a big challenge to the contemporary society. Globally, about 60% of total generated plastic wastes are disposed off through landfill and only 10% is recycled [21].

Several methods were investigated for the perception of safe disposal of plastic wastes such as land filling, mechanical reprocessing, mechanical sorting, chemical recycling incineration, partial oxidation and chemical recovery [22-24]. Most of them pose severe environmental negativities eg. PCBs generation, yielded low-grade products, poisonous dioxins evolutions, etc. except chemical recycling; it can be significantly reduced operation cost [25,26]. Pyrolysis is one

of the categorization of chemical recycling, which is most prominent way to convert hydrocarbon based yield from discarded plastics. During process, the plastic waste undergoes thermal decomposition in an anaerobic condition. The resultants of this process are: liquid yield, residual char and non condensable gases [27-29]. The liquid yields formation heavily relies on process variables, such as types of reactor used, group of waste plastic, operating temperature, time consumption for entire process, etc [30]. Thus, the process optimization of temperature and time for effective productivity of liquid yield receives a significant attention. Also, the quality of liquid yield is more imperative to confirm their purity and assure to be used for commercial application. Analytical instruments identify the liquid yield quality. Hence, the optimization of pyrolysis of waste plastic (medically discarded polypropylene bottle) to yield a high quantity and quality liquid was investigated.

2. MATERIALS AND METHODS

2.1 MATERIAL COLLECTION

Plastic waste can be obtained in vast quantity from roadside dumping yards, households, industries etc. For this investigation, the plastic waste was obtained from roadside, Salem district, Tamil Nadu. The collected wastes sourced from medically discarded polypropylene bottle (MDPB).

2.2 MATERIAL PREPARATION

After collection, the polypropylene waste was cleaned by using deionised water to remove the impurities, which may affect the property of product yield. Then it was dried and shredded into size of 10 mm as shown in Fig.1.

2.3 ANALYSIS OF MDPB

Scanning Electron Microscopy (SEM) was used to examine the morphological structure of MDPB using Quanta FEG 250 SEM (FEI) with magnifications up to 5000 times. Proximate and ultimate analysis of investigated MDPB was performed by CHNS instrument using ASTM-D-4809 standards. Proximate analysis was performed to determine the moisture content, volatile matters, fixed carbon and ash contents in MDPB. While, ultimate analysis brings the information about elemental compositions. Thermal degradation of plastic material was analyzed by

Thermogravimetric technique (TGA) using Universal v4.7ATA instruments 0-600 °C with a 10 °C/ min increment. Test trial was conducted in an oven at 2 mL/ min of N₂ to know the temperature ranges for specified weight losses by degradation.



Fig.1. Medically Discarded Polypropylene Bottle (MDPB)

2.4 EXPERIMENTAL INVESTIGATION

The thermo-chemical conversion of MDPB was conducted to produce petroleum grade fuel in pyrolysis reactor. The main component of this system involves; reactor, thermostat, condenser, a heating mantle and water circulation system. The pyrolysis has designed simple, quite sensitive in quality of feedstock and good thermal efficiency. The setup of pyrolysis of MDPB to fuel is illustrated shown in Fig.2. The reactor has designed with 900 ml capacity with the series of shell-tube condenser connection. The reactor which holds up the temperature up to 550 °C and was heated by heating mantle and the condenser was fitted at reactor outlet section.



Fig.2. Experimental Setup of MDPB Pyrolysis Process

A 250 g of MDPB sample was kept in the reactor and the temperature was increased to attain 500 °C at a heating rate of 10 °C/min. Once the reacting temperature attained the degradation mechanism, the pyrolysis process was completed in 90 mins at low-temperature level. A liquid vapour due to thermo-chemical reaction in a reactor section was then condensed to produce petroleum-range fluid. The residual solid char was removed when it reaches the room temperature. Further, the mass balance of pyrolytic oil, residual solid char and producer gas were estimated using stoichiometric material balance method.

2.5 CHARACTERIZATION OF LIQUID YIELD

Physical analytical methods of viz. Density, viscosity, pour point, cloud point, flash point, fire point and gross calorific value (GCV) can be measured by ASTM methods. Moreover, the functional groups and hydrocarbon chain compounds with respect to retention time can be studied using Fourier Transform Infrared Spectroscopy and Gas chromatography with mass spectrometry (GC/MS) techniques.

3. RESULTS AND DISCUSSION

3.1 CHARACTERIZATION OF MDPB

The product distributions in a pyrolysis process heavily relies on feedstock composition, and degradation stages. High volatile matter resulted high liquid yield while high ash content

significantly reduced the liquid yield. According to the proximate analysis, the volatile matter was very high (100 wt. %), while the ash content is considerably too low (0.00 wt. %). The maximum quantity of hydrocarbon products can be maximized due to the presence of carbon and hydrogen contents. As observed from the results, the MDPB contains carbon and hydrogen levels as 81.03 wt. % and 13.17 wt. %, respectively.

Fig.3 reveals that the structural morphology of MDPB with 5 µm magnification is an undefined shape with an irregular morphological structure. There is some physical destruction has observed in their structure, which inferred the pre-treatment could eliminate some undesirable impurities.

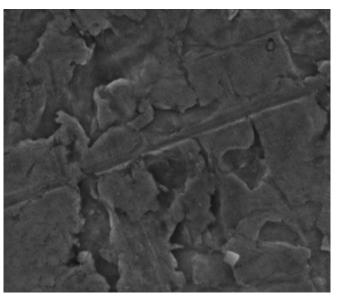


Fig.3. SEM analysis of MDPB

Fig.4 shows the thermal analysis of MDPB wherein the thermal decomposition began at 339.49 °C and degradation completed at 456.37 °C. A single-stage thermal degradation mechanism was observed during the polypropylene degradation process and achieved a complete conversion (T-100%) of MDPB until 456.37 °C. From this analysis, it could be observed that, the thermal degradation of MDPB performed between 330-460 °C.

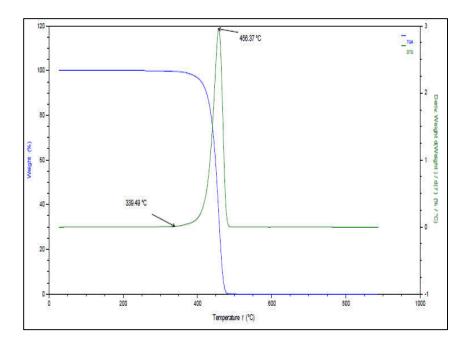


Fig.4. TGA curve of MDPB degradation at 10 °C/ min

3.2 FACTORS AFFECTING THE MDPB PYROLYSIS

Process optimization is vital of any thermal and chemical processes. In this experimentation, experimental temperature and operation time are most prevalent parameters so as to reach complete conversion and produces the maximum liquid yield with high quality. For this necessity, the temperature and time was optimized for the pyrolysis of MDPB in a prototype reactor at 330-460 °C and 60-120 min, respectively. Further, the effect of temperature on MDPB pyrolysis and effect of reaction time on polypropylene pyrolysis was shown in Fig.5.(a) and (b), respectively.

The reaction temperature plays an important role on liquid yield conversion in the pyrolysis of MDPB. The MDPB was pyrolyzed between 330-460 °C to identify the optimum temperature range for achieving a more amount of liquid. A 29.12% of liquid product was obtained at 330°C and yield was increased to 48.39% by increasing the temperature to 360 °C. A high liquid conversion (67.15 %) was obtained at 420 °C and which gets decreased beyond 420 °C. Thus, this condition was most preferable for non condensable gas or residual char yields.

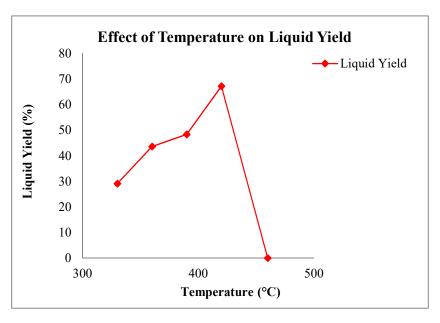


Fig.5. Effect of Temperature on MDPB Pyrolysis

The operation time can also mainly impacts the product distributions. Hence, the effect of operation time on MDPB pyrolysis was performed between 60-120 min at 420 °C. The results demonstrated that, the time (120 min) is as an optimum time for converting high liquid yield (67.5%). Above 120 min, there is no liquid drop was observed. In addition, the extreme low reaction time (<120 min) resulted more pyro gas production.

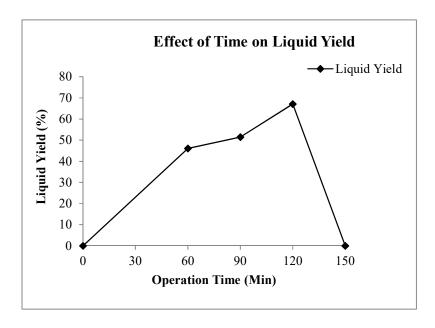


Fig.6. Effect of Reaction Time on Polypropylene pyrolysis

3.3 CHARACTERIZATION OF LIQUID YIELD

3.3.1 Physical property analytical methods

As shown in Fig.6(a), the density of MDPB pyrolyzed oil was demonstrated as 0.765 g/cm³, as compared to the density value of gasoline (0.780 g/cm³). The kinematic viscosity (1.2 cSt) also nearer to the gasoline fuel (1.17 cSt). The pour point and cloud point were +2 °C and +18.1°C respectively. Flashpoint examines the fuel hazards and the fuel has safe flash point (42°C). GCV found the fuel efficiency and GCV of MDPB liquid yield was 45.77 MJ/Kg, which is greater than the gasoline fuel (42.5 MJ/Kg). The properties were given in Table.1. All the properties shows that the produced liquid fuels have the advantage of easy handling and can be used all the geographical regions (Sharuddin et al.2016).

Table 1 Physical property analytical methods of MDPB liquid yield

| Properties | MDPB Pyrolyzed Oil | Commercial Fuels (Sharuddin et al.2016) | |
|------------------------------|-----------------------|--|---------|
| | | Gasoline | Diesel |
| Density (g/cm ³) | 0.765 | 0.780 | 0.807 |
| Kinematic Viscosity (CSt) | 1.2 | 1.17 | 1.9-4.1 |
| Pour point (°C) | +2 | - | 6 |
| Cloud point (°C) | +18.1 | - | - |
| Flash point (°C) | 40 | 42 | 52 |
| GCV (MJ/Kg) | 45.77 | 42.5 | 43.0 |



Fig.7.Liquid fuel obtained from PP Pyrolysis

3.3.2 FTIR analysis of MDPB pyrolyzed liquid yield

FTIR is a crucial analytical procedure to identify the functional group presence in liquid yield, which is portray in Fig. 6(b). From the FTIR spectra, the pyrolytic oil has aliphatic and aromatic compounds. The peaks with the presence of aliphatic groups (Alkanes: O-H stretch - 3025.25 cm⁻¹; \equiv C-H bend - 2920.34 cm⁻¹, C-H stretch - 2850.37 cm⁻¹, C-H bend - 1449.43 cm⁻¹, C-F stretch 1451.83 cm⁻¹ Aldehydes: C-H stretch - 1745.72 cm⁻¹. Cyclic alkene: N-H bend - 1492.62 cm⁻¹. Alkenes: C=C bend - 753.78 cm⁻¹, Alkyl Halides: C=C Strong - 695.83 cm⁻¹) and aromatic groups (Aromatic compound: C-H bend -1600.95 cm⁻¹). The spectra show that the liquid has high percentage of aliphatic groups without the presence of sulphur groups.

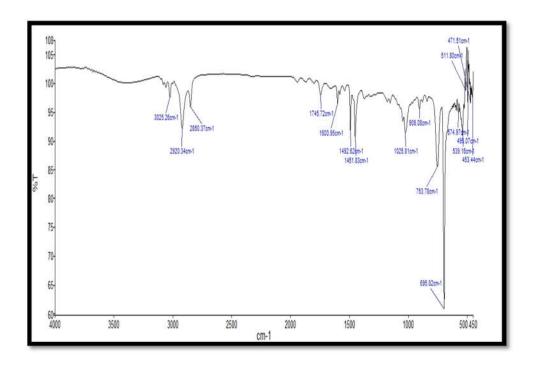


Fig.8. FTIR spectra of MDPB pyrolyzed liquid yield

3.3.3 GC/MS analysis of MDPB pyrolyzed liquid yield

GC/MS analysis examines the hydro carbon presence in the liquid yield, which is shown in Fig. 6(c). Table 2 shows the hydro carbon compounds of liquid yield analyzed with GCMS.

Table 2 GCMS analyses of MDPB liquid yield

| Retention time | Compound Name | Molecular |
|----------------|--|---------------------------------|
| | | Formula |
| 5.273 | AlphaMethylstyrene | C_4H_{10} |
| 5.920 | Benzene, 2-propenyl | C_5H_{10} |
| 6.357 | Benzene, butyl- | C ₆ H ₁₂ |
| 6.823 | Benzene, 2-methylcyclopropyl | C7H14 |
| 8.374 | Naphthalene | C ₇ H ₁₆ |
| 8.488 | Dodecane | C_8H_{16} |
| 9.919 | Tridecane | C_8H_{18} |
| 10.190 | Benzocycloheptatriene | C ₉ H ₁₈ |
| 12.473 | Benzene, 1,1'- ethylidenebis | $C_{10}H_{20}$ |
| 14.504 | Benzene, 1,1'- (1,3-propanediyl) bis | $C_{11}H_{22}$ |
| 14.908 | 1-Propene, 3- (2 - cyclopentenyl) – 2 – | $C_{12}H_{26}$ |
| | methyl - 1,1 - diphenyl | |
| 15.112 | 1-Propene, 3-(2-cyclopentenyl)-2-methyl- | $C_{13}H_{28}$ |
| | 1,1-diphenyl- | |
| 15.421 | 1,2-Diphenylcyclopropane | $C_{14}H_{28}$ |
| 15.854 | Benzene, 1,1'-(3-methyl-1-propene1,3- | C ₁₅ H ₃₀ |

| | diyl)bis | |
|--------|--|---------------------------------|
| 16.353 | Benzene, 1,1'- (1-butene - 1, 4-diyl) bis-, (Z)- | $C_{16}H_{32}$ |
| 17.928 | Naphthalene, 2-phenyl- | $C_{19}H_{40}$ |
| 19.135 | 4H-Benz[de]anthracene, 5,6-dihydro | $C_{20}H_{42}$ |
| 21.413 | 1-Propene, 3-(2-cyclopentenyl)-2-methyl- | C ₂₁ H ₄₄ |
| | 1,1-diphenyl | |
| 22.945 | 1-Propene, 3-(2-cyclopentenyl)-2-methyl- | C ₂₈ H ₅₈ |
| | 1,1-diphenyl- | |

After characterization of liquid yield sample by GCMS, the results demonstrate that the appeared hydrocarbon chain compounds resemble the mixed fractions of gasoline, kerosene and diesel range products in the carbon number regime from 4 to 28. Compared with Table 3, it can be observed that the liquid yield sample has mixed fractions of gasoline, kerosene and diesel range products were found abundant. This brings a good indication that the liquid yield has great potential to be replaced commercial fuels.

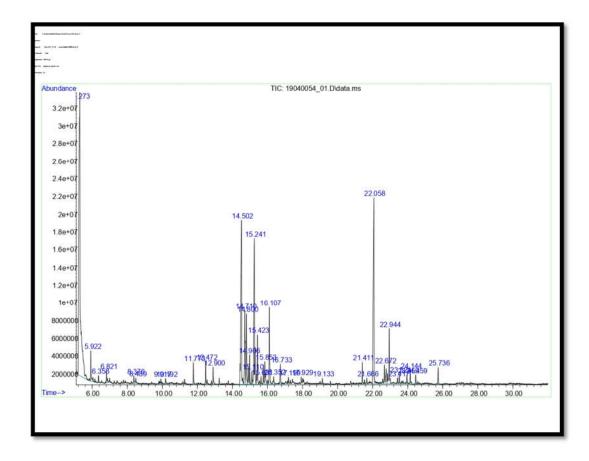


Fig.9. GCMS analysis of MDPB pyrolyzed liquid yield

4. CONCLUSIONS

From this study, it has been demonstrated that the medically discarded polypropylene bottle (MDPB) wastes can be converted to gasoline range fuel. The optimum operating temperature and experimental time were found as 420 °C and 120 min, for an extreme liquid yield 67.15%. The produced liquid fuel yield has similar properties of gasoline grade fuel and which resemble in the carbon number regime 4 to 28. Further, it was observed that the pyrolytic oil contained more aliphatic compounds than aromatic groups, which is most suitable to use as a fuel. Moreover, the liquid fuel obtained from MDPB pyrolysis have an advantageous of ease handlings and can be used in all the geographical regions.

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Conflict of interest

The authors declare that they have no competing interests relevant to the content of this article.

Ethical approval

This declaration is not applicable since this research work does not involve human and/or animal participants.

Author's contribution

Renuka Subramaniam: Writing — original draft, Investigation and Data curation; Nadachi Kumarasami: Investigation and Formal analysis; Jeyajothi Kalimuthu: Revised and proof read; Balakishore Lakshmanan, Keerthana Shivaji, and Jaffeer Ashraf Akbarshieak, are the graduate students who have performed the experiments and performed the analysis; Minar Mohamed Lebbai S, Writing — original draft, Project administration; Vinothkumar Natarajan, Project administration, Formal analysis, revision of the draft and Investigation.

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