Pyrolysis of Waste Polyolefins into Liquid Petrochemicals Using Metal Carbonate Catalyst

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Abstract

Currently, demand of liquid hydrocarbons is continuously growing because of the uncertain supply of fossil fuels. The current advanced technology will contribute to our societies (Swachh Bharat Mission) because the aim of the research is to provide alternative energy, and it will minimize waste plastics. The liquid petrochemicals were obtained from sustainable waste polyolefins. TGA (thermogravimetric analysis) was analyzed to find the thermal stability of all polyolefin’s wastes. The pyrolysis process was started at 22°C and then completed at 390°C. Recoveries as liquids, gases, and residues were obtained from pyrolysis of 16 gm LD-PE (low-density polyethylene), 64 gm HD-PE (high-density polyethylene) and 15 gm PP (polypolypropylene) plastic waste polyolefins with 5 gm magnesium carbonate (MgCO₃). The conversion ratio of waste polyolefins (LD-PE, HD-PE, and PP plastics) to liquid hydrocarbons was 92%, 7.52% to light gases, and 0.48% residue. A mixture of hydrocarbons such as aliphatic, aromatics, alcohol, acetate, and aster were found in liquid hydrocarbons through GC-MS-MS (triple quadrupole gas chromatography-mass spectrometry), and functional groups were observed through FT-IR (Fourier transform infrared spectroscopy). The alternative fraction recovery from waste plastic materials was excellent. Liquid hydrocarbons could be used in petrochemical industries as a raw material, in automobiles as an alternative fuel, and in diesel furnace.

Keywords: Waste polyolefins; Liquid petrochemicals; Pyrolysis; MgCO₃.

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1. Introduction

People are using plastic products in considerable quantities in their lifetimes. Plastic demand is continually increasing globally and their use leads to reduced consumption of other materials such as metals. Some advantageous properties of plastics are high durability, resistance to chemicals and moisture, lightweight, and high strength. Zang et al. have recorded high thermal properties of polypropylene (PP). And globally, plastic cultures have developed since 1940. Plastic products are made from hydrocarbons, therefore it can serve as an alternative source for hydrocarbon fuels. Many countries have been working on alternative energy sources to meet the increasingly green, clean, and sustainable energy requirements. Some researches have been focused on pyrolysis products from certain plastics such as PE (polyethylene), PS (polystyrene), and PP because pyrolysis studies are limited. Since 1950, plastic productions have also been increasing on an average by 10% every year around the globe. Plastic production growth in 2007 was around 245 million tons. In 1998, 60% (approximately 800,000 tons) plastics-waste rose in India, and their recycly rate was maximum in the world, and it was recycled by 2000 recycle units. Globally, plastic consumption was around 150 million tions in 2000, and approximately 258 million tons in 2010. The estimated plastic per capita consumption is 9.7 kg from 2012 to 2013 in India, lower than that in the United States and China. According to Plastindia Foundation, 16.5 million tons of plastics demand was reached from 2016 to 2017, while it was 11 million tons between from 2012 to 2013. The annual growth rate of the solid plastics was 8.1%. In 1960, there was a total of 7 million tons of plastics produced in the world. The estimate of plastic production will be reaching over 530 million tons in 2020. Globally, the plastic production has increased since it was initially commercially manufactured, from 1.5 million tons in 1950 to 260 million tons in 2007. Globally, Europe consumes approximately 25% of the total plastic production, equal to 60 million tons per year. Annually, large amounts of mixed plastic wastes are collected from agriculture, feed bags, fertilizer bags, silage, films, etc. Plastic wastes were 32 million tons in 2011, representing 12.7% of total municipal plastic wastes. Approximately 500 billion plastic bags have been used annually around the globe.
Waste plastics and tires are slow biodegradable materials. So, these materials are unpleasant for the environmental and health. Waste materials help the growth of insects, mosquito-breeding, and the continuously release of harmful gases. In urban India, plastic waste is comprised of 51% organic municipal plastic waste, 31% inert products, and 17.5% recyclable products. The mixed waste plastics require separation during the recycling process. Plastic waste can be converted into valuable chemicals through pyrolysis so as to potentially reduce the volume of plastic waste. Pyrolysis studies of various fuels are vital understanding for the combustion and gasification of hydrocarbons.[24]

The present study aims to analyze waste plastics (LD-PE, HD-PE, and PP) through TGA (thermogravimetric analysis), and whether the produced materials are suitable as pyrolysis feedstock. Sample preparation includes blending of waste plastic materials with catalyst magnesium carbonate (MgCO₃). The pyrolysis process is started at 22°C (room temperature) and completed at 390°C. The fuel fraction recovery from waste plastic materials is excellent. The present pyrolysis recycling technology will also help the lifestyles of the villages and cities and their developments because plastic waste occupies landfills, releases harmful gases to the environment.

Plastic wastes were collected as municipal and industrial origins. There are different properties subject to different management strategies.[25-26] Mixed plastic waste can be separated into two groups based on their density. In the first group, waste plastics [PT-ET (polyethylene terephthalate), PVC (polyvinyl chloride) and PS] have a density greater than water and settle to bottom when put in water. In the second group, waste plastics (LD-PE, HD-PE, and PP) have a density lower than water and will float on water surface.[27] Globally, 78% of thermostatic out of total plastic waste has been used.[28] Plastic identification code helps for reuse, pyrolysis, and recycling manufacturing. Thermoplastics are polyolefins and polystyrene able to be recycled;[29-30] while thermosets plastics cannot be able to recycled in petrochemicals.[28] Plastics have physical properties required to be measured when processing any product, as shown in Table S1 supporting materials.[8] The Kissinger method has provided by Homer E. Kissinger in 1957 for thermal analysis in DTA (Differential thermal analytical) and DSC (Differential scanning calorimetry) instruments.[10]

The purpose of the tables has been summarized here in Fig. 1; Table S1 supporting materials shows the physical properties of plastics as thermal properties, strength, and density. These properties are required for the pyrolysis process. In the Table S2 supporting materials, calorific values of plastics have compared to petroleum fractions. The basis of calorific values can define the range of petroleum fractions as light gases, petrol, kerosene, and diesel. In the Table S3 supporting materials, it is classified which plastics are suitable for pyrolysis feedstock or not. In the Table S4 supporting materials, pyrolysis feedstock can allow to pyrolysis process only basis on a higher percentage of carbon and hydrogen. In the Table S5 supporting materials, obtained petrochemicals have analyzed through GC-MS-MS and FT-IR (Fourier transform infrared spectroscopy) for confirmation of petrochemicals.

All plastic (Polyolefins, polystyrenes, and synthetic/natural butyl rubber) are mostly hydrocarbons consisting of material, therefore, it has equal property to liquid hydrocarbons fuels.[16,31-32] Waste plastics are chemically compared to petroleum. Hydrocarbons are naturally available in petroleum also such as paraffins are 15-60%, Nepthenes are 30-60%, Aromatics are 3-30%, Asphaltic are remainder while the elemental composition of petroleum such as 83-87% C, 10-14% C, 0.1-2% N, 0.05-6% Sulfur and most common metals are Fe, Cu, and V 0.1%. Manually percentages of C and H in plastics are calculated by the following Equation 1.[34]

\[
\text{Percentage composition} = \frac{n \times \text{molar mass of the element}}{100\%} = \frac{\text{molar mass of the compound}}{(1)}
\]

A hydrocarbon fuel can define a combustible material that has carbon containing in the main chain, which provides a high calorific value after combustion process. Therefore, this can be used for industrial and domestic purposes. The calorific value (the better is the quality of fuel) of a hydrocarbons fuel depends upon the carbon content. Hence the more excellent the percentage of carbon, the more significant is the calorific value of the fuel. A high rate of hydrogen also increases the calorific value of the fuel. The primary sources of hydrocarbon fuels are coal, petroleum oils, and natural gas. The non-combustible substance as nitrogen and sulfur is available in fuel, and it will reduce the calorific value of fuel and releases the SO₂ and NO₂ flue gases after the combustion.[35] Plastics derived from fossil fuels have a calorific value equal to petrol, diesel, and LPG (Liquid petroleum gas), as given in Table S2 supporting materials.[33] After characterization of waste, plastic material is proofing that waste is wealth. Calorific values of plastics are closely similar to petroleum products. Therefore, petroleum products (petrochemicals) can get from waste.
plastics. The higher percentage of carbon and hydrogen in thermoplastics make excellent pyrolysis feedstock for fuel production, as shown in Table S2 supporting materials. [8,16,17]

Business pyrolysis treatment plants have been in the process of mixing plastics. Hydrochloride scrubber requires polyvinyl chloride treatment because of chlorine in polyvinyl chloride, which is not desirable in the fuel. [36-37] Small plants are not suitable for small production. [36] In plants, catalysis improves the quality of pyrolysis fuel in many existing types of equipment. [38] To understand and optimize the pyrolysis of various kinds of certain plastics study has been completed in the earlier period as Kaminsky et al. and Scheirs et al. and their colleagues. [36,39-40] observed the special effects of the pyrolysis reaction conditions on the product. Suhanya et al. used the pyrolysis method of waste tires. [41] M. Sarker et al. used the pyrolysis method of polypropylene (PP). [42] S. L. Low et al. have observed the use of the pyrolysis method of mixed plastic wastes. [43] Z. Zeynep Obli et al. have stated the pyrolysis method of catalytic deformation of PP with alumina mesoporous catalyst at 400 °C temperature. [44] N. Miskoleczi et al. have reported thermal cracking to HD-PE and LD-PE. [45] D. P. Serrano et al. used to develop superior catalysts in the conversions of polyolefins wastes plastic into chemicals. [46] S. L. Wong et al. have been used plastic waste as the source of fuel. [47] M. A. Hazrat et al. have used plastic waste as a recent development alternative fuel resource. [48] In these researchers, pyrolysis reactions are completed in the laboratory as batch type or semi-batch type instead of reactors. Most research focused on the effects of the product yield controlled through the catalyst, heating rate, and temperature. Various investigations have focused on specific pyrolysis parameters, cracking, and obtained chemicals as saturated, unsaturated, aromatics, naphthalene, and their isomers. [49-52]

2. Materials and methods

2.1 Materials

Waste PP (sample size < 3-4 mm², melting point = 160 °C, and ρ=0.92 g/cm³), HD-PE and LD-PE plastics collected from the near at Dev Bhumi Uttarakhand University, Dehradun, Uttarakhand. Waste PP, LD-PE, and HD-PE plastic separated with the help of the identification 5, 2, and 4 numbers, and their contents were white and transparent. Collected waste PP, LD-PE, and HD-PE plastic were washed with liquid soap to remove dirt then and then dried in the sunlight. Dried all waste plastics were ground into small pieces using a grinder machine. In the first experiment, 16 gm waste LD-PE + 64 gm HD-PE and 15 gm PP plastic were incorporated with 5 gm MgCO₃ (CDH make). In the second experiment, 54 gm waste HD-PE and 36 gm PP plastics were blended with 10 gm MgCO₃ (CDH make). In the third experiment, 15 gm waste LD-PE + 55 gm HD-PE and 15gm PP plastic incorporated with 15 gm MgCO₃ (CDH make) before the experiment process.

2.2 Thermogravimetric analysis (TGA)

Waste polyolefins plastic was characterized through TGA 4000, as shown in Fig. 2. Heat ranges were 30 °C to 515 °C, 30 °C to 510 °C, 30 °C to 475 °C and 30 °C to 500 °C at 20 °C/m for degradation of waste LD-PE, HD-PE, and PP plastic. Thermal stability is found suitable for pyrolysis feedstock that is required for pyrolysis temperature.

![Fig. 2](image)

**Fig. 2** Analyzed of waste LD-PE, HD-PE, and PP through TGA.

2.3 Pyrolysis experimental method

The giant molecular weights of polymer are cracking into simple molecules without oxygen through pyrolysis process. [8,17,53-57] Old plastic treatment was land-filling, which is a create health and environmental problems. [58] Pyrolysis process diagram as shown in Fig. 3. Separately, samples were placed into a glass reactor. Reactor vessels kept into furnace then furnace started at 22 °C. Pyrolysis reactions were completed at 22 °C to 370 °C. Waste plastics have liquefied inside the reactor then came into the vapors phase. Vapors have condensed at 22 °C (room temperature) then collected as liquid hydrocarbons (organic compounds/petrochemicals)—the gases filled in the Teflon bag. Residues contents obtained from inside the reactor.

![Fig. 3](image)

**Fig. 3** Pyrolysis process diagrams of waste olefins to petrochemicals.

3. Results and discussions

3.1 Recoveries from waste polyolefins

The experiments process was run in three batches. The liquids, gases, and residues collected from wastes 16 gm LD-PE and 64 gm HD-PE and 15 gm PP plastic with 5 gm MgCO₃, as
shown in Fig. 4. Meanwhile, their conversions were waste LD-PE, HD-PE, and PP plastics whose conversion rate in pyrolysis was 92%, gases 7.52%, and residue 0.48%. Liquids, gases, and residues from waste 54 gm HD-PE and 36 gm PP plastics with 10 gm MgCO₃ collected, whose conversion rate in liquid chemicals was 92%, light gases 7.55%, and residue 0.45%. Liquids, gases, and residues from 15 gm LD-PE and 55 gm HD-PE and 15gm PP plastic whose conversion rate in liquid chemicals was 90%, 9.64% gases, and 0.36% residue.

![Fig. 4 Liquids, Gases, Residues from waste LD-PE, HD-PE, and PP with MgCO₃.](image)

Eze et al. obtained 66.9% liquid yield from mixed plastics through thermal pyrolysis process and 46.7% liquid yield from mixed plastics through catalytic pyrolysis process.[91] Liu et al. recovered 4.21-34.35% energy from polyethylene terephthalate plastics by microwave pyrolysis.[92]

### 3.2 Factors affecting pyrolysis

The most important factors affecting the molecular distribution of plastic pyrolysis and pyrolysis yield are the chemical composition of the raw materials, the cracking temperature and heating rate, and the operating pressure.

#### 3.2.1 Chemical composition of the feedstock for liquid petrochemicals

The quality of pyrolysis fractions is dependent upon waste plastics’ structure and chemical composition. The pyrolysis process is affected by the chemical composition of the plastic wastes. Foreign particles typically contaminate waste plastics before plastic recycling which might jeopardize the pyrolysis process. Polyethylene is formed frommonomer ethylene molecules by polymerization, as shown in the following chemical reaction 2.[27]

\[ \text{n CH}_2\text{CH}_2 \text{ Polymerization } \rightarrow [\text{CH}_2\text{CH}_2]_{\text{n}} \]

Based on their polymeric structure, the polymer can be classified as linear, branched, or cross-linked. Continued repeating side groups are calculated to be part of the unit, but branches are not calculated. Branches, structure, and the functional groups of plastics have a significant effect on the pyrolysis product. For example, the dominant component in polyolefins pyrolysis products is olefin molecule that is the side groups that come off from polyolefin carbon backbone chain.[27,63] The relationship is between the density and the branching intensity of the polymer. According to McMurry’s study, polyethylene has more branches and lower density.[63]

### 3.2.2 Cracking temperature/heating rate of pyrolysis

Cracking of the plastics varies upon various temperature ranges. Molecules are bound together by Vander Waals force, and this type of attraction reduces the cracking of molecules. When the vibration of molecules is adequate, the molecules will easily vaporize.[58,64] Giant plastic molecules are decomposed rather than boiled when heated. Bond dissociation temperatures of C-C in plastics should be the same, but it is found to differ by researches.[65] These differences also are found through TGA, where the temperature sensors are located.[59] According to A. Karaduman et al., there is a difference in the temperature on the surface in making contact with plastics and the temperature of the plastics close up to the surface. This research study measured the relatively minor and constant temperature of the reaction where the surface was selected to monitor the cracking. Shah et al. researched the blend of polyolefins and PS plastics pyrolyzed in a fixed-bed reactor at various temperatures.[66] It is found that a high temperature reaction favors to the yields due to lower gas molecules in the liquid yield [67,68] The influence of the heating rate on the plastics pyrolysis and product distribution varies in various researches because of differences in the pyrolysis reactor, operation conditions (pressure and temperature), and temperature measurement location. Normally, in a fast or flash pyrolysis, heating rate refers to the temperature change of the polymer when it is dropped on the hot surface when decomposed and vaporized.[69-70] Once again, waste plastics are heated to the cracking; the temperature remains relatively stable until all waste plastics have pyrolyzed. Therefore, the heating rate is ordinarily applied as the temperature indicator instead of the reaction temperature in a prolonged pyrolysis process.[71-74] The dAlpha/dT explained the reaction rate (K-1) and plotted as a function of absolute temperature for different heating rates from 10 to 25 K/m.[75-78]

### 4. Petrochemicals from waste polyolefins analyzed by FT-IR and GC-MS-MS

The liquid petrochemicals are obtained from the pyrolysis of waste LD-PE and HD-PE and PP with 5% MgCO₃ catalyst, and they are analyzed through a triple quadrupole GC-MS-MS system. It has shown in Fig. 5 and Table S5 supporting materials. Liquid petrochemical consists of aliphatic, aromatics, alcohols, acetates, and asters hydrocarbons. Petrochemicals can be used as a rich source of raw materials
for petrochemical industries and refineries. During GC-MS analysis of liquid petrochemicals, the compound appeared at retention time (RT) 4.84 was assigned as cyclobutane, 1-butyl-2-ethyl-, RT 6.35 as 1-undecene, RT 7.84 as 1-dodecene, RT 9.27 as 1-tridecene, RT 10.60 as 1-tetradecene, RT 11.87 as E-14-hexadecenal, RT 15.26 as eicosane, RT 16.26 as eicosane, respectively. The functional groups of liquid petrochemicals collected from plastic wastes of LD-PE, HD-PE, and PP using 5% MgCO₂ catalyst were analyzed through FT-IR. The energy calculated by above describes equation $E=\hbar\nu$. The energies values are calculated by their wave number.¹,³,⁶,¹⁶-¹⁷ The spectrum provided 2921.67 cm⁻¹ frequency provides methylene CH₂asymsym. stretch had its calculated energy, 2855.38 cm⁻¹ frequency provide methyl CH₃asymsym. stretch group, 1643.21 cm⁻¹ frequency provide alkenyl C=C stretch functional, 1457.88 cm⁻¹ frequency provide methylene C-C bends group, 1374.84 cm⁻¹ frequency provide gem dimethyl CH₃ group, 992.24 cm⁻¹ frequency provide C-H bend group, 905.31 cm⁻¹ frequency provide vinyl C-H out of plan bends group, 724.11 cm⁻¹ aromatic frequency provide C-H out of plane bend group, 633.79 cm⁻¹ frequency provide alkyne C-H bend group.

Fig. 5 Chromatogram of liquid petrochemicals from waste LD-PE and HD-PE and PP with 5% MgCO₂.

5. Economic values to the society

Regular energy demand is required for our existence as a way of improving human improvement leading to monetary boom and productivity. Save lots of land recourses through pyrolysis technology when it utilizes waste plastics into valuable energy and petrochemicals. Presently, the bulk of the waste plastics have been landfilled that requires a long time for the complete decay.⁸⁰-⁹⁰ Plastic usage is steadily increasing in various areas like automobiles, consumer packaging, in infrastructure because of the steadily growing population, urbanization, and economic development. Estimated, India is among the top 10 packaging consumers globally in 2016, and the value will reach 24 billion dollars.⁸¹ The Indian plastic industries are likely to double its twenty million metric tons of plastic consumption in 2020.⁸² Chemical recycling technology helps to conversions of plastic waste to get valuable energy rather than being dumped elsewhere. Plastic waste can be minimized through recycling processes. A plastic recycling system can create vast employment opportunities for millions of people. It can further develop to ensure the safety of the environment.⁸³ Recycling process is the act of reusing something as plastics, cardboard, and glass. Recycling benefits explain in the following points, economically various benefits for those who recycle. According to 2011, it had been calculable that over 2.3 million people worked in the recycling business industries. Manufacturers can reuse materials instead of creating new, more energy-efficient ones. Recycling minimizes pollution because it is not being burned and dumped.⁸⁴ Paper packing applications are very important for savings plastic materials and fossil fuel energy.⁸⁵ The economic growth rate is indefensible devoid of the conservation of energies.⁸⁶-⁸⁸ Recycling will create a significant quantity of energy and can be an alternative fuel resource. Therefore, this technology is environment-friendly and provides a positive impact on the community. We can obtain sulfur-free or low sulfur content liquid hydrocarbons by pyrolysis process because of the absence of sulfur in the waste plastic. This is a benefit for fuel from plastics if compared with fossil fuels like diesel, petrol because the sulfur content in the fuel releases SO₂ after combustion.

6. Conclusion

The pyrolysis process was applied to convert waste polyolefins into petrochemicals using MgCO₂. 92% maximum liquid yield was obtained using 5% MgCO₂ catalyst. Aliphatic, aromatic, acetic, ester, and alcohol hydrocarbons were obtained from waste polyolefins through GC-MS-MS; therefore, waste polyolefins can be minimized through the pyrolysis process. Functional groups of liquid petrochemicals were recorded through FT-IR; their groups were related to hydrocarbon. Petrochemicals have promising potential for a sustainable economy, but they can minimize pollution problems and global warming due to waste plastics. Physiochemical properties were suitable for petrol and diesel. Fossil fuel-based energy assets to renewable energy sources could help lessen climate alternate and its effect.

Conflict of Interest

The authors declare no conflict of interest.

Supporting information

Applicable.

Reference
