Resources, Conservation & Recycling 128 (2018) 69–77

Contents lists available at ScienceDirect

Resources, Conservation & Recycling

journal homepage: www.elsevier.com/locate/resconrec

Full Length Article

Valorization of packaging plastic waste by slow pyrolysis

Pallab Das, Pankaj Tiwari*

Department of Chemical Engineering, Indian Institute of Technology Guwahati, Guwahati, Assam 781039, India

ARTICLE INFO

Keywords:
Low temperature pyrolysis
Plastic waste
Fuel
Hydrocarbon
NMR

ABSTRACT

Low and high-density polyethylene (LDPE and HDPE) and polypropylene (PP) are three most common polyolefins profusely used as packaging materials and abundantly found in the plastic waste stream. These plastic waste samples were collected from household waste and converted into plastic derived oil (PDO) by low temperature (300 °C to 400 °C) slow pyrolysis (long isothermal holding time) in a semi-batch reactor. The PDO samples obtained had shown variation in their compositions and fuel properties based on the pyrolysis temperature. PDO from the pyrolysis of PP has high octane number (~92) and low viscosity. Noticeably, the PDO samples obtained at low temperature pyrolysis are lighter with low viscosity, high octane number and having high calorific values. ^{1}H NMR analysis revealed that the oil samples mostly consist of paraffinic and olefinic hydrocarbons. Simulated distillation (SimDist) of PDO indicated that the liquid products resemble the characteristic closer to middle distillate of petroleum fraction having very low pour point and flash point. The temperature with long pyrolysis time also influenced the evolved gas composition and yield. Trace amount of hydrogen, carbon monoxide and carbon dioxide were present in the gaseous product along with various hydrocarbon gases ranging from C_1–C_5. The degradation mechanism follows end chain scission which produces monomer units whereas random scission results most of the hydrocarbon products. Subsequent reactions like radical recombination and inter or intra molecular hydrogen transfer results in the formation of most of the olefinic components.

1. Introduction

Plastics are a standard group of synthetic or natural materials, produced from high molecular chains consist of carbon as sole or major element. Plastics are highly durable, strong, elastic and less expensive to produce, which make them ideal choice for packaging and storage applications. The global production of plastics keeps on increasing, and so does the waste generation. The lifetime span of plastics products varies from weeks for packaging to several years for building appliances (Buekens, 2006; Lazarevic et al., 2010). Packaging plastics are major contributor to the vastly generated plastic waste. India produces more than 15000 tons of plastics waste per day, majority of which are packaging waste (Kamyotra and Sinha, 2016). The high calorific value of most of the plastics (manufactured from fossil fuel) urges one to reuse them productively. Packaging plastics, used containers, used toothbrush and broken plastic utensils are very common in the dry solid waste generated in any household. These plastics are also abundantly present in municipal solid waste (MSW). Low and high density polyethylene (LDPE & HDPE) and polypropylene (PP) are three major components of any plastic waste stream. Due to the lack of management from the governing organizations, the plastic waste goes to dumping sites along with other waste materials. In India, 60% of total plastic waste is recycled and rest goes for landfilling and incineration with other solid waste (Kamyotra and Sinha, 2016).

Pyrolysis is one of the ubiquitous process converting organic materials into various useful forms via thermochemical decomposition at elevated temperature under oxygen starving environment. The major advantage of the pyrolysis process is the conversion of low energy density material into high energy density products. Over the years, pyrolysis has been adopted as an alternative approach to upgrade plastic waste into useful products. Although, large scale application of pyrolysis in plastic waste disposal is still lacking compared to landfilling and incineration due to the process economy (high energy consumption) and the complexity involved. Pyrolysis of plastics is generally carried out at fast heating rate to a final temperature up to 700 °C or at moderate temperature (~500 °C) in presence of catalyst (Chattopadhyay et al., 2016; Kaminsky et al., 1995; Kumar et al., 2011; Siddiqui and Redhwi, 2009; Williams and Williams, 1997a, 1999b). Fast pyrolysis increases the gaseous yield and the quality of liquid fuel produced requires post pyrolysis up-gradation for using in petroleum blends (Joo and Guin, 1998). Pyrolysis of individual and mix (Williams and Slaney, 2007) plastic have been studied and carried out in batch

* Corresponding author.
E-mail address: pankaj.tiwari@iitg.ernet.in (P. Tiwari).

http://dx.doi.org/10.1016/j.resconrec.2017.09.025
Received 20 June 2017; Received in revised form 22 September 2017; Accepted 25 September 2017

Table 1
Comparison of %yield and liquid product quality obtained from the pyrolysis of various polyolefins (LDPE, HDPE and PP) and various mix plastic studied in various literature.

Material	Process	Yield (% wt)			Liquid product quality	Reference
		Liquid	Gas	Residue		
LDPE	Fluidized bed reactor (T = 500 °C, 3 g/batch, t = 15 s)	89.2	10.8	0	Wax 49%; Oil 51%	Williams and Williams (1999a)
LDPE	Fixed bed reactor (T = 700 °C, β = 25 °C/min)	84.3	15.1	0	Wax	Williams and Williams (1999b)
LDPE	Spouted bed reactor (T = 450 °C)	80	20	0	Wax	Aguado et al. (2002b)
HDPE	Microwave induced pyrolysis (T = 500 °C)	81	19.0	0	Oil/wax	Ludlow-Palafox and Chase (2001a)
HDPE	Steam Fluidized bed reactor (T = 600 °C, 3.4 kg, t = 3 h)	41	31	28	87% aliphatic	Kaminsky et al. (1995)
HDPE	Batch autoclave reactor (T = 500 °C, P = 19.2 MPa, t = 1 h)	93	7	0	Unknown	Williams and Slaney (2007)
HDPE (Waste)	Batch reactor (T = 440 °C, t = 2 h)	74	9	17	Crude	Sharma et al. (2014)
HDPE	Two stage free fall reactor (T = 500 °C, 0.14 g/min, t = 20 min)	97.4	1.8	0.8	Oil/wax; 97.36% C_5-C_{60}, < 0.05% Aromatic	Mastral et al. (2006)
HDPE	Fixed bed reactor (T = 700 °C, β = 25 °C/min)	79.7	18.0	0	Wax	Williams and Williams (1999b)
HDPE	Spouted bed reactor (T = 450 °C)	80	20	0	Wax	Aguado et al. (2002c)
PP	Batch autoclave reactor (T = 500 °C, P = 19.2 MPa, t = 1 h)	95	5	0	Unknown	Williams and Slaney (2007)
PP	Fixed bed reactor (T = 700 °C, β = 25 °C/min)	84.4	15.3	0.2	Wax	Williams and Williams (1999b)
PP	Spouted bed reactor (T = 450 °C)	92	8	0	Wax	Aguado et al. (2002c)
PP	Batch reactor (T = 740 °C β = 10 °C/min)	48.8	49.6	1.6	> 40% olefins	Demirbas (2004)
Real waste (PE, PP, PS, PET, PVC)	Batch reactor (T = 500 °C, β = 20 °C/min, t = 30 min)	40.9	25.6	33.5	93.4% Aromatics	Adrados et al. (2012)
Simulated waste (PE, PP, PS, PET, PVC)	Batch reactor (T = 500 °C, β = 20 °C/min, t = 30 min)	65.2	34.0	0.8	73.9% Aromatics	Adrados et al. (2012)
Mixture (American plastic council)	Tubing bomb micro reactor (T = 445 °C, P = 800 psig, t = 60 min)	~85	~10	~5	Crude	Shah et al. (1999)

T = pyrolysis temperature; P = reactor pressure; t = residence time or reaction time and β = heating rate, PS = polystyrene, PET = polyethylene terephthalate, PVC = polyvinyl chloride and FBP = final boiling point.

(Onwudili et al., 2009), semi-batch (Lopez-Urionabarrenechea et al., 2012) and fluidized bed reactors (Costa et al., 2010; Kaminsky et al., 2004; Liu et al., 2006; Williams and Williams, 1997b, 1999b). Various other reactor configurations like conical spouted bed reactor (Aguado et al., 2002c; Elordi et al., 2009), rotary kiln reactor (Aguado et al., 2002a; Serrano et al., 2003), microwave pyrolysis (Ludlow-Palafox and Chase, 2001b; Undri et al., 2013) etc. have also been utilized. The recent review articles (Chaukura et al., 2016; Lopez et al., 2017; Miandad et al., 2016) summarize the overall waste plastics treatment schemes in detail. Table 1 summarizes the key results obtained from the pyrolysis of plastics (LDPE, HDPE, PP and their mixture) using various reactor configurations. However, the detail analysis of fuel properties of the pyrolysis products and the effect of pyrolysis conditions on fuel properties have not been reported.

Onwudili et al. (2009) investigated the effect of temperature (350–500 °C) and time duration (1 h and 2 h) on the compositions of the products obtained when pure LDPE and polystyrene (PS) and their mixture were pyrolysed in a pressurized batch reactor under inert N_2 atmosphere. They suggested that LDPE thermally degrades into oil at 425 °C, and the extent of oil production decreases beyond this temperature. Wong and Broadbelt (2001) studied the effect of long-duration by maintaining two moderate temperatures, 350 and 420 °C for 180 min and 18 h while performed the pyrolysis of polypropylene and polystyrene. They observed that the conversion of polypropylene increased with reaction time at 350 °C while no significant change happened at 420 °C beyond 90 min. Long reaction time can improve the product quality as heavier components decompose into lighter and low molecular weight products, which would be useful as fuels and chemicals. A detailed study considering the effect of reaction time at varying temperature on the quality of plastic pyrolysis products and their physical properties can be a useful insight to the applicability of such process in a more economical way. Properties of liquid products and gas composition were investigated in detail and it has been highly anticipated that the results obtained will ascend the understanding of the applicability and limitation of these waste materials as a feedstock for the production of alternative liquid fuel.

2. Materials and methods

2.1. Materials

The pyrolysis experiments were performed with both virgin and waste plastics. For the pyrolysis of individual plastics, virgin samples were used while the mixed sample was prepared using waste plastics. Virgin LDPE, HDPE, and PP were procured from Haldia Petrochemicals Limited, India. Physical properties of these plastics are reported in Table 2. The materials received were in pellet form of size around 3–5 mm. The collected materials were manually cut to make 1–2 mm average particle size before subjecting to thermal gravimetric analysis (TGA). Granulated samples were directly used for the lab scale pyrolysis experiments.

For a comprehensive understanding, waste samples of above three plastics were collected from household waste like packaging plastics, empty plastic containers, and bottles. Materials collected were cleaned and segregated according to their resin identification code. Dry samples were cut manually into small pieces of size 1–2 cm for the pyrolysis

Table 2
Physical properties of the materials.

Plastics	Density (kg/m^3)	Glass transition temperature (°C)	Melting point (°C)
LDPE	934	−125	111 ± 2
HDPE	950	−80	132 ± 1
PP	900	−10	168 ± 1