

Research Article

Waste Polyethylene Terephthalate (PETE-1) Conversion into Liquid Fuel

Moinuddin Sarker, Aminul Kabir, Mohammad Mamunor Rashid, Mohammed Molla, and A. S. M. Din Mohammad

*Department of Research and Development, Natural State Research, 37 Brown House Road, Stamford CT-06902, USA
Address correspondence to Moinuddin Sarker, msarker@naturalstateresearch.com*

Received 21 December 2010; Accepted 11 February 2011

Abstract Polyethylene terephthalate (PETE) consists of polymerized repeating units of ethylene terephthalate ($C_{10}H_8O_4$) monomer. PETE is a recyclable plastic with identification code “1”. World-wide PETE-1 is used as a synthetic fiber, polyester, packaging materials, containers of soft drinks and etc. The molecular weight of PETE-1 is 192 gm/mole and out this 62.5% is Carbon (C), 33.3% Oxygen (O) and 4.2% Hydrogen (H). The main objective of this research is to convert the waste PETE-1 into liquid hydrocarbon fuel. The world-wide use of PETE-1 has gradually increased and most of the waste PETE-1 is being dumped into the environment instead of recycling; this creates environmental problem. In thermal degradation process, PETE-1 is being decomposed. It produces very hard solid complex substances of terephthalic acid and benzoic acid, which are not bio-degradable. NSR's experiment utilized Calcium Hydroxide ($Ca(OH)_2$) as catalyst at 400–530 °C to obtain the liquid hydrocarbon fuel from PETE-1.

Keywords hydrocarbon; thermal decomposition; PETE plastic; condensation; sublimate substances catalyst (calcium hydroxide); fuel; DSC; FTIR; GC/MS

1 Introduction

According to the National Association of PETE-1 Container Resources (NAPCOR) in 2005, in the USA approximately 31% bottles are made from PETE or PET. The United States manufacturers produced 5.075 billion lb (~ 2.38 million ton) PETE products and 23.1% of that amount was collected for recycling [9]. In PETE-1 production process, a certain amount of waste is produced. Similarly after the use of PETE product, approximately 63% to 77% of PETE production waste ends up in the landfill (earth911.com). If the current rate of waste PETE disposal continues, approximately 40 billion lb (~ 20.046 million ton) will be added in landfill within a decade [9]. In the global estimate, approximately 3 million tons of PETE was produced to make PETE bottles in 2007 [6].

Every day PETE plastics are being used all over the world and after use it is discarded in the landfill. The presence of the waste PETE in the landfill causes a variety of environmental and economical problems because PETE does not biodegrade in landfills. Waste PETE goes through photo-degradation and turns into minuscule particles, which enter the food chain and cause harmful health hazard to habitants. In the incineration process, PETE forms a very hard solid complex sublimate substance which causes severe environmental problems. Furthermore, incineration encourages the emission of harmful green house gases [8]. In a statement, pacific institute showed that 1 ton of PETE produces approximately 3 tons of CO_2 and only water bottled created more than 2.5 million tons of CO_2 in 2006 [10].

Many scientists are performing the research on PETE-1 recycling. At present, waste PETE-1 is converted into fuel by Pyrolysis [1,2]. Some reports of thermal degradation have been also reported [3,4,7,12,13]. PETE has been also treated using plasma treatments [18] and gasification [11], recycled using molded injection [16] and glycolytic recycling [5], and degraded using kinetic poly condensation [14,15]. In these methods, PETE-1 is converted to dimethyl terephthalate (DMT) and ethylene glycol (EG) or a monomer such as dihydroxyethyl terephthalate (DHET) but it creates a lot of environmental hazards [17]. Some scientists also experimented the thermal degradation of waste PETE into liquid fuel.

NSR has developed a simple thermal catalytic conversion process of PETE into liquid fuel. The catalyst can accelerate the degradation process of the long chain hydrocarbon and create a short-chain hydrocarbon fuel. NSR process has been carried out utilizing $Ca(OH)_2$ as a catalyst at 400–530 °C and converting waste PETE into liquid fuel without producing any sublimate substances. The influences of catalyst particles, time factor and temperature on the overall catalytic activity during the fuel production process are still under investigation.

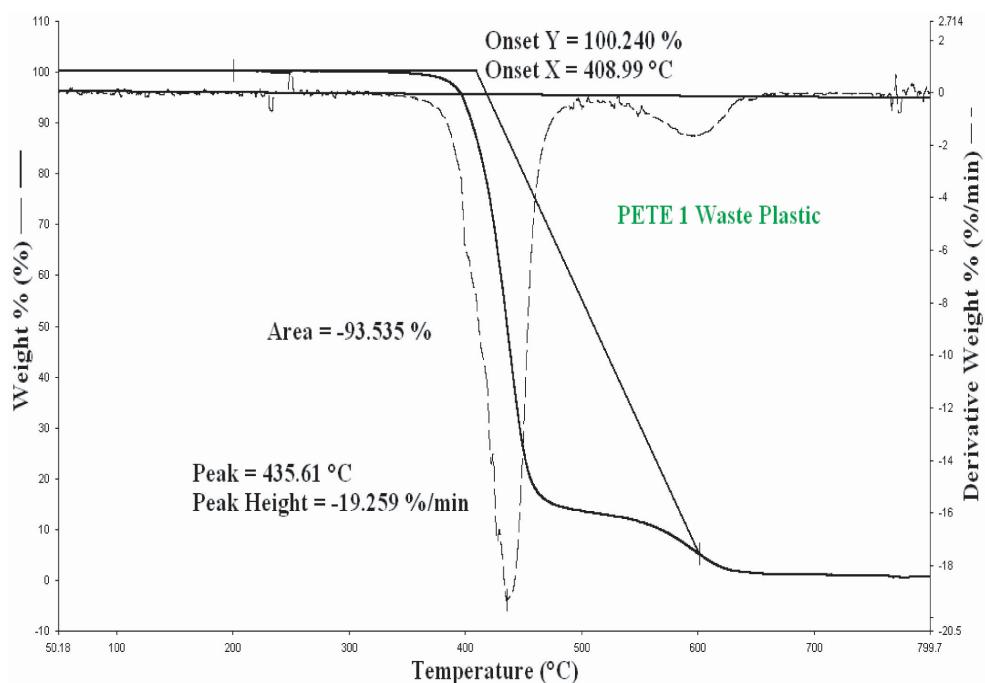


Figure 1: TGA graph of PETE-1 solid waste plastic.

Plastic name	Density (g/cm ³)	Melting point (°C)
PETE-1	1.4	250–260

Table 1: Physical properties of waste PETE plastic.

2 Experimental process description

2.1 Material

Waste polyethylene terephthalate (PETE-1) pellets or chips used in this experiment are waste PETE-1 water bottles. The shapes of PETE pellets are not specific; most of the shapes are 5.205–15.225 mm and see Table 1 for the density and melting point of PETE-1.

Before performing an experiment of the solid waste PETE-1 conversion into fuel, primarily NSR is required to know the melting temperature (onset temperature) of PETE-1. A thermo gravimetric analyzer (TGA) graph of PETE (Figure 1) signified the onset temperature of solid waste PETE-1 at 408.33 °C.

2.2 Catalyst

Many researchers used FeOOH, Fe₂O₃, Ni(OH)₂ and Ca(OH)₂ as a catalyst with waste PETE plastic to produce fuel. NSR has used only the calcium hydroxide (Ca(OH)₂) (catalyst powder GRACS, EMD Chemicals Inc., Catalog number CX 0220-1, CAS number 1305-62-0, Lot number 44203533) for PETE experiment. NSR succeeded in degrading PETE to produce liquid fuel by using Ca(OH)₂.

In order to break down the terephthalic acid, a catalyst is needed for cracking the carbonyl groups of terephthalic acid.

2.3 Equipments and accessories

- (i) 250 mL round bottom boiling flask;
- (ii) 500 mL collection flask;
- (iii) heat mantle (Glas-Col, Cat. no. TM102);
- (iv) condenser;
- (v) variac (Glas-Col, Cat. no. 104 APL120, temperature controller);
- (vi) holding cork.

2.4 Sample preparation and placement

Waste PETE sample wt.: 40 gm
Ca(OH)₂ catalyst wt.: 80 gm

First, 40 gm of Ca(OH)₂ catalyst were placed in the boiling flask with 40 gm of waste PETE samples. Finally, 40 gm of Ca(OH)₂ were placed on the top of samples within the same boiling flask (as sandwich system). The catalyst to sample ratio was 2:1.

2.5 Experimental procedure

A boiling flask with sample was placed into a heat mantle (Figure 2) with a variac (temperature controller 1% = 4.5 °C). Initially, the boiling flask was heated at 405 °C with 90% variac efficiency for quick melting of PETE plastic.

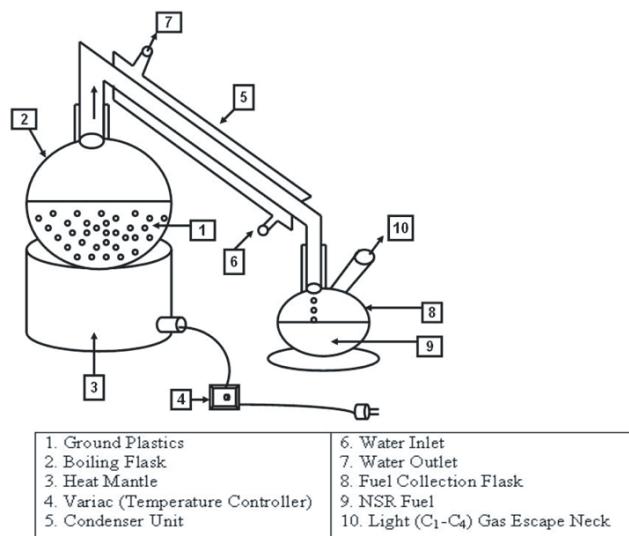


Figure 2: Waste PETE-1 to fuel production process.

Within 10 min vapor started to form in the condenser pipe, but the initial vapor did not condense. The vapor traveled to the collection flask through the condenser pipe. After 13 min vapor began to condense and accumulate in the collection flask through the condenser pipe drop by drop. At 20 min the heat mantle temperature was reduced to 315 °C with 70% variac efficiency to avoid any consequences and continued to heat for another 15 min, after that no vapors were produced and the experiment was concluded.

3 Result and discussion

3.1 Result

- 6.3 mL liquid NSR PETE fuel was obtained from the experiment which represent 14.25% of the total weight of PETE plastic sample.
- 12.5% volatile gas produced.
- 20.6 gm residue was found as a left over, which equal to 51.5% of the total weight of PETE plastic sample because of the 33.3% oxygen present in the PETE sample.
- 8.7 gm water of which 21.75% from PETE sample was also produced with PETE fuel during production period.
- Density of PETE fuel was 0.90 g/mL.
- Color of the PETE fuel was yellowish.
- Condenser unit or any other pipelines did not clog up in the whole experiment.
- Physical appearances of PETE residues were hard crystalline powder.
- Colors of the residue were a mixture of ash and yellowish black.

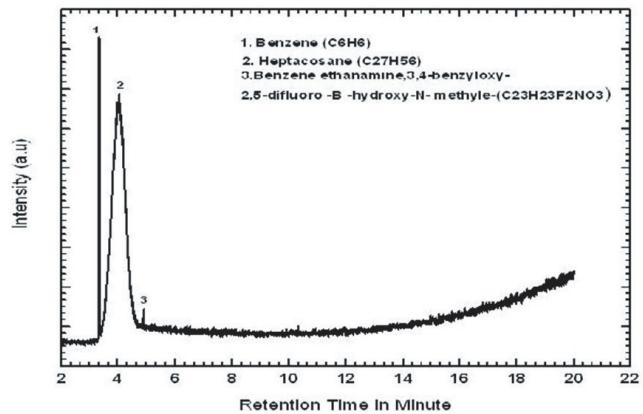


Figure 3: GC/MS chromatogram of PETE-1 to fuel.

3.2 Characterization of PETE-1 to produce fuel

3.2.1 Physical analysis

Physical: viscous liquid with yellowish color with an obnoxious odor.

Flammability: highly flammable and burned completely without any left over residue.

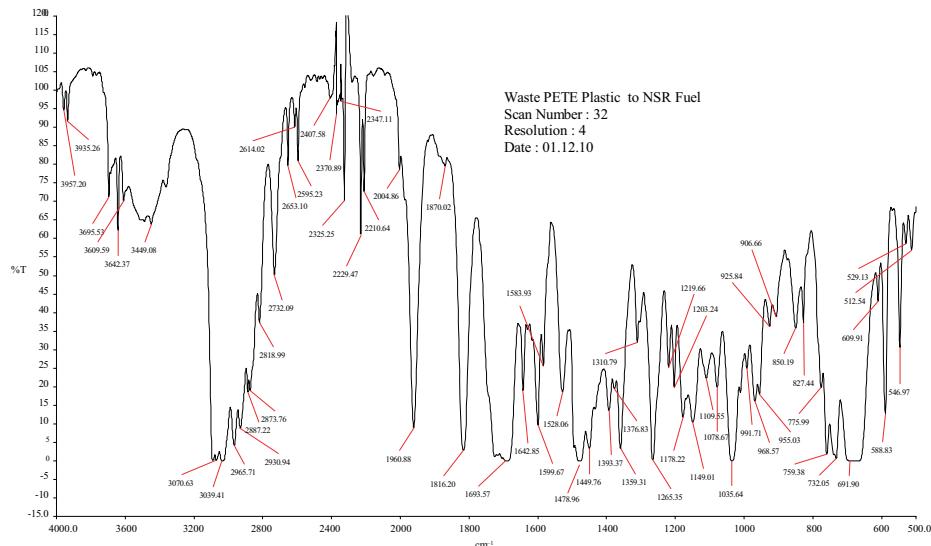
3.2.2 Instrumental analysis

The product of the PETE liquid fuel was characterized utilizing the sophisticated laboratory equipments (GC/MS Clarus 500, FTIR Spectrum 100 and Jade DSC).

In the gas chromatograph/mass spectrophotometer (GC/MS) Clarus 500, the PETE fuel sample was analyzed. The GC/MS identified the PETE fuel's compounds. Chromatogram of the GC/MS showed only three (3) conformed peaks. The chromatogram of the PETE fuel (Figure 3) is shown in a long carbon chain and the compounds were verified by peak intensity. The hydrocarbon chain lengths of (C_6-C_{27}) are present in the PETE fuel. Library search conforms that the name of the compounds are benzene (C_6H_6) at retention time (RT) 3 min 36 s, heptacosane ($C_{27}H_{56}$) at retention time (RT) 4 min 07 s and benzene ethanamine 3,4 benzyloxy-2,5-difluoro- β -hydroxyl-N-methyl-($C_{23}H_{23}F_2NO_3$) at retention time (RT) 4 min 91 s. The GC/MS data indicated that NSR PETE fuel has a wide range of hydrocarbon groups resulting in a higher thermal substance.

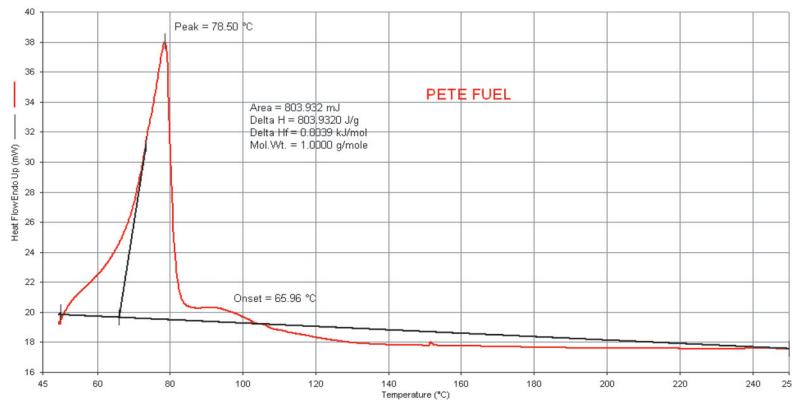
FTIR spectrum-100 test was performed to identify the characteristics of the NSR PETE fuel. PETE fuel showed (Figure 4) the following functional groups; free OH, =C–H, C–CH₃, CH₂, CH, CH₃, –C=CH₂, –CH=CH- (trans).

Differential scanning calorimeter (DSC) curve of PETE fuel (Figure 5) represents the boiling point as an onset temperature. By performing the test, NSR PETE fuel has showed an onset temperature of 65.96 °C.



Waste PETE Plastics to NSR PETE FUEL .sp/mi rlib.dlb Euclidean Search Hit List

0.569 F80072 BIS (3, 5, 5-TRIMETHYL HEXYL) PHTHALATE
 0.532 F11960 BENZALACETONE
 0.503 F00780 ACETONYLACETONE
 0.496 F35038 1, 1-DICHLOROACETONE
 0.495 F80102 DIBUTYL PHTHALATE
 0.490 F99999 ACETOPHENONE
 0.488 F48805 GERANYLACETONE
 0.486 F39895 N,N-DIMETHYL-2-CHLOROACETOACETAMIDE
 0.469 F00570 ACETONE ABS. AND RESISTANT AGAINST OXIDATION
 0.454 F65470 3-METHYLACETOPHENONE

Figure 4: FTIR spectra and FTIR library compounds list of PETE-1 to fuel.**Figure 5:** DSC graph of PETE-1 to produce fuel.

4 Conclusion

The thermal degradation process involves a catalytic conversion to convert the waste PETE plastic into hydrocarbon fuel. Both GC/MS and DSC indicated that the NSR PETE fuel contains high volatile hydrocarbon compounds. FTIR also indicated that the functional groups of PETE fuel contain hydrocarbon and hydroxyl group. NSR will continue to conduct experiments, analysis and characterization with PETE and pursue to obtain the best results.

Acknowledgments The author acknowledges the support of Dr. Karin Kaufman, the founder and sole owner of Natural State Research, Inc. (NSR). The author acknowledges the valuable contributions of NSR laboratory team members during the preparation of this manuscript.

References

- [1] T. Bhaskar, J. Kaneko, A. Muto, Y. Sakata, E. Jakab, T. Matsui, et al., *Effect of poly(ethylene terephthalate) on the pyrolysis of brominated flame retardant containing high impact polystyrene and catalytic debromination of the liquid products*, *J Anal Appl Pyrolysis*, 71 (2004), 765–777.

- [2] ———, *Pyrolysis studies of PP/PE/PS/PVC/HIPS-Br plastics mixed with PET and dehalogenation (Br; Cl) of the liquid products*, J Anal Appl Pyrolysis, 72 (2004), 27–33.
- [3] M. Brebu, T. Bhaskar, K. Murai, A. Muto, Y. Sakata, and M. Azhar Uddin, *The effect of PVC and/or PET on thermal degradation of polymer mixtures containing brominated ABS*, Fuel, 83 (2004), 2021–2028.
- [4] L. T. Duarte, E. M. Paula e Silva, J. R. T. Branco, and V. F. C. Lins, *Production and characterization of thermally sprayed polyethylene terephthalate coatings*, Surface and Coatings Technology, 182 (2004), 261–267.
- [5] D. Gintis, *Glycolytic recycle of poly(ethylene terephthalate) (PET)*, Makromolekulare Chemie. Macromolecular Symposia, 57 (1992), 185–190.
- [6] P. H. Gleick and H. S. Cooley, *Energy implications of bottled water*, Environ Res Lett, 4 (2009), 014009.
- [7] H. A. Lecomte and J. J. Liggat, *Commercial fire-retarded PET formulations: relationship between thermal degradation behaviour and fire-retardant action*, Polym Degrad Stab, 93 (2008), 498–506.
- [8] N. Miskolezi, L. Bartha, G. Déak, and B. Jóver, *Thermal degradation of municipal plastic waste for production of fuel-like hydrocarbons*, Polym Degrad Stab, 86 (2004), 357–366.
- [9] Napcor (National Association for PETE Container Resources), P.O. Box 1327, 2008 Report on Postconsumer PETE Container Recycling Activity, available online at <http://www.napcor.com/pet/products.html>.
- [10] Pacific Institute, Bottle water and energy, available online at http://www.pacinst.org/topics/water_and_sustainability/bottled_water/bottled_water_and_energy.html.
- [11] M. Pohořelý, M. Vosecký, P. Hejdová, M. Punčochár, S. Skoblja, M. Staf, et al., *Gasification of coal and PET in fluidized bed reactor*, Fuel, 85 (2006), 2458–2468.
- [12] B. Saha and A. K. Ghoshal, *Thermal degradation kinetics of poly(ethylene terephthalate) from waste soft drinks bottles*, Chemical Engineering Journal, 111 (2005), 39–43.
- [13] Y. Sakata, M. Azhar Uddin, K. Koizumi, and K. Murata, *Thermal degradation of polyethylene mixed with poly(vinyl chloride) and poly(ethyleneterephthalate)*, Polym Degrad Stab, 53 (1996), 111–117.
- [14] U. R. Vaidya and V. M. Nadkarni, *Unsaturated polyesters from PET waste: kinetics of polycondensation*, Journal of Applied Polymer Science, 34 (1987), 235–245.
- [15] ———, *Polyester polyols for polyurethanes from PET waste: kinetics of polycondensation*, Journal of Applied Polymer Science, 35 (1988), 775–785.
- [16] M. Wu and L. L. Shaw, *On the improved properties of injection-molded, carbon nanotube-filled PET/PVDF blends*, Journal of Power Sources, 136 (2004), 37–44.
- [17] T. Yoshioka, M. Ota, and A. Okuwaki, *Conversion of a used poly(ethylene terephthalate) bottle into oxalic acid and terephthalic acid by oxygen oxidation in alkaline solutions at elevated temperatures*, Industrial and Engineering Chemistry Research, 42 (2003), 675–679.
- [18] S. Zanini, P. Massini, M. Mietta, E. Grimoldi, and C. Riccardi, *Plasma treatments of PET meshes for fuel-water separation applications*, J Colloid Interface Sci, 322 (2008), 566–571.