Research article

Thermal Degradation of Poly (ethylene terephthalate) Waste Soft Drinks Bottles and Low Density Polyethylene Grocery Bags

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Abstract

Thermal degradation process for fuel production from 10 gm polyethylene terephthalate (PET) and 50 gm of low density polyethylene waste plastics was heated up in an atmospheric Pyrex glass reactor of laboratory-scale. PET waste plastic is combination of hydrocarbon, benzene, and oxygen group. PET plastic has high percentage of oxygen content. For experimental temperature range was 250 - 400 °C and product fuel density was 0.76 gm/ml. Fuel production liquid conversion rate was 53.5%, gas generated 11.83%, and wax and residue was 34.67%. Fuel was analysis by GC/MS, and GC/MS chromatogram compounds chain showed C₃ to C₂₂. Residue percentage is higher because PET has oxygen content. Light gases are combination of methane, ethane, propane and butane. Fuel can use for refinery process further modification and power plant for electricity generation. **Copyright © IJSEE, all rights reserved.**

Keywords: thermal degradation, waste plastic, soft drink bottle, polyethylene, polyethylene terephthalate, GC/MS

Introduction

Polyethylene terephthalate (PET) is the most important polyester resin currently produced because of its excellent mechanical and chemical properties [1]. Since PET also presents low permeability to gases and solvents, it is a potential corrosion barrier. This polymer is derived commercially from reaction between terephthalic acid and ethyleneglycol [2] and its properties depend on its molecular weight, molecular structure, crystallinity and the presence of impurities. The chemical structure of PET repetition unity is shown in Fig. 1. Thermal degradation of PET may proceed at elevated temperatures by a random scission of ester linkages, resulting in the formation of a vinyl-ester end-group and a carboxyl end-group. Because end- groups in PET are predominantly hydroxyl-esters,

trans-esterification of the vinyl-esters formed on degradation can take place to give vinyl alcohol, which may be transformed to acetaldehyde. Eventually the hydroxyl-ester end-groups can react between themselves or with carboxyl end-groups. This process would regenerate PET chains and maintain an average molecular weight [3–5]. PET is a thermoplastic material largely used in the form of fiber, sheet and film. The PET consumption for packing applications has increased significantly in the last three decades. However, PET recycling has not been carried out in the same amount as its production [6].

Municipal waste plastic represents about 8 wt% of the municipal solid waste and it generally consists of mixture of different kind of plastics: 40.5 wt% HDPE and L/LDPE, 19.6 wt% PP, 11.9 wt% PS/EPS, 10.7 wt% PVC, 8.1 wt% PET, and about 5 wt% ABS and 4.2 wt% other polymers [7]. This waste is difficult to be treated or recycled due to its complex nature and composition, structural deterioration of the polymeric components and the contamination with various organic, inorganic or biological residues. Pyrolysis is one of the best methods to recover the material and energy from polymer waste, as only about 10% of the energy content of the waste plastic is used to convert the scrap into valuable hydrocarbon products [8-9]. Gasification, as one of the thermochemical conversion methods, has been known and studied for decades. However, it is still the focus of research due to the promising features, such as high fuel conversion efficiency which saves energy sources, effective processing of low-grade fuels or waste, and production of gaseous fuel from solid fuel, which is more convenient feedstock for further treatment. The gaseous product, called producer gas, can be effectively utilized in a variety of ways ranging from electricity production to chemical industry (as feedstock). Fossil fuels still play an important role as a source of energy in the production of electricity. Nowadays, however, it is combustion process with lower efficiency that is being mainly used and therefore implementation of more efficient technologies, involving gasification, combined cycles and fuel cells, would be a key issue in the plans for more efficient power generation. In addition, fossil fuels can be saved by their being partially replaced by renewable or alternative fuels. Plastic waste seems to be a reasonable possibility, considering the increase in waste production. Waste plastics are especially rich in calorific content and thus they can be thermally processed with high benefit [10]. Pyrolysis was reported as a viable option for waste plastics treatment with the aim to gain gaseous and liquid products [11–13]. The higher the temperature and residence time, the higher the yield of gaseous products were observed. In polypropylene pyrolysis high yields of up to 82 wt. % of gaseous hydrocarbons were produced in so-called moving-bed reactor, where pyrolysis took place in a heated screw conveyor [11]. The yields from a batch-operated tube reactor filled with a blend of waste plastics were significantly lower, about 30 wt.% [12] or about 25 wt.% at 520 °C [13]. An approach combining the two reaction zones (pyrolyzer and combustor) in the continuously operated fluidized bed reactor was examined by Wang et al. [14].

Materials and Method



Figure 1: Chemical structure of PETE

Waste material polyethylene terephthalate (PETE) soft drink bottle and low density polyethylene grocery bag was collected from local super market. Collected waste materials were washing with soap and water and cut into small pieces and placed into reactor chamber. Soft drink bottle color was transparent and grocery bag color was white. Low density waste plastic has carbon and hydrogen combination and polyethylene terephthalate has carbon, hydrogen, oxygen, and benzene combination. LDPE and PETE to fuel production process temperature range was 250 - 400 °C and experimental process was batch process. 50 gm low density polyethylene was taken by weight and 10 gm polyethylene terephthalate was taken by weight. Total sample was use for experimental purpose only 60 gm. Experimental process diagram shown into figure 2 for visual understanding and experimental setup was properly under laboratory fume hood prevent gas escape into environment. Experimental setup purposed accessories and equipment was required such as glass pyrex chamber for reactor, heat mental for liquefaction, variac for temperature control, condensation unit for vapor condensation, fuel collection container, light gas cleaning purpose NaOH, NaHCO3, and water, small pump for light gas transfer into Teflon bag. Above all of required accessories and equipment was setup properly in to batch process one by one.



Figure 2: Polyethylene terephthalate and low density polyethylene waste plastic mixture to fuel production process



Figure 3: PETE and LDPE waste plastic to fuel production period was collected from condensation unit

PETE and LDPE waste plastics mixture to fuel production period observed that PET and LDPE produce vapor travel into condensation unit and produce waxy part (Figure 3) tendency to block the condensation unit. Only hydrocarbon part was condenses and rest of waxy part was settle into condensation unit and it was collected after finished the whole experiment. LDPE percentage was higher than PETE waste plastic in this experiment and whole experiment done only thermal process and experimental finish time was 4.40 hours. Some portion of waxy materials also comes with liquid fuel and fuel was filtered by micron filter with RCI technology provided purification system. Waxy materials was stuck into filter paper only hydrocarbon part was come out by fuel filter system and liquid hydrocarbon fuel was analysis by GC/MS and analysis result describe into result and discussion section. PETE and LDPE waste plastic to fuel production period some lighter gas also generated because light fraction compounds has negative boiling point which was not condense it room temperature. Light gas can collected as a liquid in to negative temperature but room temperature it can be only light gas. Gas was clean with alkali wash and water wash to remove contamination and transfer into Teflon bag for future use. In mass balance calculation showed 60 gm mixture of PETE and LDPE waste plastic to liquid fuel was 32.1 gm, residue weight 20.8 gm with waxy materials (residue 10.1 gm + wax 10.7 gm) and light gas as sample 7.1 gm. Input electricity was required for fuel production purposed 0.525KWh.

Results and Discussion



Figure 4: GC/MS chromatogram of PETE and LDPE waste plastic mixture to fuel

Table 1: GC/MS chromatogram compounds list of PETE and LDPE waste plastic mixture to	fuel
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Number of Peak	Retention Time	Trace Mass	Compound Name	Compound Formula	Molecular Weight	Probability %	NIST Library
	(min.)	(m/z)					Number
1	1.49	41	Propane	C3H8	44	53.9	18863
2	1.61	43	Butane	C4H10	58	62.1	18940
3	1.66	41	2-Butene, (E)-	C4H8	56	25.7	105
4	1.87	42	Cyclopropane, ethyl-	C5H10	70	25.9	114410
5	1.91	43	Pentane	C5H12	72	84.8	114462
							81

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6	1.95	55	2-Pentene, (E)-	C5H10	70	19.3	291780
7	2.06	67	1,3-Pentadiene, (Z)-	C5H8	68	18.3	160480
8	2.13	67	1,3-Pentadiene	C5H8	68	16.8	291890
9	2.25	67	Bicyclo[2.1.0]pentane	C5H8	68	19.2	192491
10	2.32	42	Cyclopropane, ethyl-	C5H10	70	8.96	114410
11	2.50	41	1-Hexene	C ₆ H ₁₂	84	25.2	227613
12	2.58	57	Hexane	C ₆ H ₁₄	86	83.5	291337
13	2.63	55	3-Hexene, (E)-	C ₆ H ₁₂	84	29.1	19325
14	2.68	41	2-Pentene, 3-methyl-, (Z)-	C ₆ H ₁₂	84	18.1	114483
15	2.84	67	1,3-Hexadiene,c&t	C ₆ H ₁₀	82	8.58	118864
16	2.90	56	Cyclopentane, methyl-	C ₆ H ₁₂	84	62.1	114428
17	2.96	67	3-Hexyne	C ₆ H ₁₀	82	18.3	19282
18	3.00	79	2,4-Hexadiene, (Z,Z)-	C ₆ H ₁₀	82	16.1	113646
19	3.06	79	1,3-Cyclopentadiene, 5- methyl-	C ₆ H ₈	80	23.4	419
20	3.14	67	Cyclopentene, 3-methyl-	C ₆ H ₁₀	82	15.3	114408
21	3.27	78	Benzene	C ₆ H ₆	78	74.5	114388
22	3.30	41	Cyclohexane	C ₆ H ₁₂	84	13.6	228008
23	3.38	79	1,3-Cyclopentadiene, 1- methyl-	C ₆ H ₈	80	16.8	164279
24	3.42	43	Hexane, 3-methyl-	C7H16	100	61.5	113081
25	3.62	41	1-Heptene	C7H14	98	36.3	107734
26	3.74	43	Heptane	C7H16	100	78.3	61276
27	4.07	81	Cyclopentane, 1-methyl-2- methylene-	C7H12	96	11.0	62523
28	4.17	83	Cyclohexane, methyl-	C7H14	98	67.8	118503
29	4.30	69	Cyclopentane, ethyl-	C7H14	98	33.2	940
30	4.38	79	3-Oxabicyclo[4.3.0]non-8- en-2-one, cis-	C ₈ H ₁₀ O ₂	138	4.88	153194
31	4.44	81	3,4-Heptadiene	C7H12	96	17.0	54096
32	4.49	79	1,3,5-Hexatriene, 2-methyl-	C7H10	94	12.6	60713
33	4.55	81	3,5-Dimethylcyclopentene	C7H12	96	13.7	113640
34	4.61	67	1-Ethylcyclopentene	C7H12	96	48.9	114407
35	4.73	41	1-Octyn-3-ol	C ₈ H ₁₄ O	126	28.2	113255
36	4.80	91	1,3,5-Cycloheptatriene	C_7H_8	92	37.0	230230
37	8.86	81	Cyclohexene, 3-methyl-	C7H12	96	9.83	139433
38	4.91	79	1,3-Cyclopentadiene, 5,5- dimethyl-	C7H10	94	9.21	161866
39	5.04	79	Cyclopentene, 3-ethenyl-	C7H10	94	11.3	154143
40	5.15	41	1-Octene	C8H16	112	26.0	1604
41	5.23	55	Cyclopentane, 1-ethyl-2- methyl-	C ₈ H ₁₆	112	19.9	150594
42	5.30	43	Octane	C8H18	114	46.8	229407
43	5.39	55	Cyclohexane, 1,2-dimethyl-, cis-	C ₈ H ₁₆	112	15.2	113985
44	5.73	81	1,4-Octadiene	C_8H_{14}	110	10.9	113431
45	5.80	67	1-Methyl-2-	C_8H_{14}	110	38.2	113437

			methylenecyclohexane				
46	5.85	68	1,4-Heptadiene, 3-methyl-	C ₈ H ₁₄	110	17.9	1484
47	5.91	41	2-Octyn-1-ol	C ₈ H ₁₄ O	126	5.86	53364
48	5.97	83	Cyclohexane, ethyl-	C ₈ H ₁₆	112	63.1	113476
49	6.02	55	3-Octyn-1-ol	C ₈ H ₁₄ O	126	20.5	113251
50	6.12	67	Cyclopentene, 1-propyl-	C ₈ H ₁₄	110	15.6	142659
51	6.24	81	1,4-Hexadiene, 3-ethyl-	C ₈ H ₁₄	110	9.10	1483
52	6.31	93	Cyclohexanemethanol, 4-	C ₈ H ₁₄ O	126	12.7	114791
53	6 5/	81	Spiro[2 5]octane	$C_{0}H_{14}$	110	9.70	113446
54	6.58	67	1-Methyl-2-	C ₈ H ₁₄	110	11.9	113437
	6 7 0		methylenecyclohexane	C II	104	12.6	107522
55 57	6.70	55 57	1,8-Nonadiene	С9Н16	124	13.6	10/523
56	6.86	56	1-Nonene	С9Н18	126	18.3	107756
57	7.02	43	Nonane	C9H ₂₀	128	31.5	249212
58	7.10	55	4-Nonene	С9Н18	126	16.0	113904
59	7.26	55	2,4-Pentadien-1-ol, 3- propyl-, (2Z)-	C ₈ H ₁₄ O	126	32.1	142179
60	7.65	55	Cyclopentane, butyl-	C9H18	126	7.96	114172
61	8.47	70	2-Octene, 3,7-dimethyl-, (Z)-	C ₁₀ H ₂₀	140	8.22	150584
62	8.58	56	1-Decene	C ₁₀ H ₂₀	140	17.2	107686
63	8.73	57	Decane	C10H22	142	40.6	291484
64	8.79	55	2-Decene, (Z)-	C ₁₀ H ₂₀	140	14.8	114151
65	10.11	70	3-Undecene, (Z)-	C ₁₁ H ₂₂	154	5.97	142598
66	10.23	55	1-Undecene	C ₁₁ H ₂₂	154	7.46	34717
67	10.29	55	1,12-Tridecadiene	C13H24	180	4.00	158325
68	10.36	57	Undecane	C11H24	156	33.7	107774
69	10.42	55	3-Undecene, (Z)-	C11H22	154	12.4	142598
70	10.57	55	3-Undecene, (Z)-	C11H22	154	7.32	142598
71	11.58	105	Benzenecarboxylic acid	C7H6O2	122	25.9	290514
72	11.66	70	5-Undecene, 9-methyl-,	C ₁₂ H ₂₄	168	4.84	61879
73	11.73	41	1-Dodecene	C12H24	168	15.1	107688
74	11.91	57	Dodecane	C12H26	170	34.6	291499
75	11.96	55	3-Dodecene, (E)-	C12H24	168	12.6	113960
76	12.48	41	Oxirane, dodecyl-	C14H28O	212	5.45	290804
77	12.61	55	Cyclohexane, hexyl-	C12H24	168	7.75	113994
78	12.81	41	7-Tetradecene	C14H28	196	5.75	70643
79	13.13	55	Z-10-Pentadecen-1-ol	C15H30O	226	6.41	245485
80	13.15	55	1-Tridecene	C13H26	182	15.8	107768
81	13.20	57	Tridecane	C12H28	184	38.1	114282
82	13.57	55	5-Tridecene (E)-	C12H26	182	9 72	142619
83	14.63	55	1-Tetradecene	C14H20	196	7 34	69725
84	14 74	57	Tetradecane	C_{14}	198	43.9	113925
85	14.78	55	2-Tetradecene. (E)-	C1/H20	196	7.05	142622
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86	15.83	55	E-2-Octadecadecen-1-ol	C ₁₈ H ₃₆ O	268	7.57	131102
87	15.93	55	1-Pentadecene	C ₁₅ H ₃₀	210	12.3	69726
88	16.03	57	Pentadecane	C ₁₅ H ₃₂	212	31.2	107761
89	16.07	55	E-2-Hexadecacen-1-ol	C ₁₆ H ₃₂ O	240	8.20	131101
90	17.17	55	1-Hexadecene	C ₁₆ H ₃₂	224	9.67	69727
91	17.25	57	Hexadecane	C ₁₆ H ₃₄	226	37.6	114191
92	17.29	55	1-Hexadecanol	C ₁₆ H ₃₄ O	242	7.35	114116
93	17.43	55	Cyclohexadecane	C ₁₆ H ₃₂	224	3.61	258206
94	18.33	56	E-14-Hexadecenal	C ₁₆ H ₃₀ O	238	9.82	130980
95	18.41	57	Heptadecane	C ₁₇ H ₃₆	240	25.1	107308
96	18.59	55	8-Heptadecene	C17H34	238	8.64	113620
97	19.36	55	E-2-Octadecadecen-1-ol	C ₁₈ H ₃₆ O	268	6.80	131102
98	19.44	55	E-15-Heptadecenal	C ₁₇ H ₃₂ O	252	15.7	130979
99	19.51	57	Nonadecane	C19H40	268	15.9	114098
100	19.69	57	1-Decanol, 2-hexyl-	C ₁₆ H ₃₄ O	242	6.88	113815
101	20.49	55	9-Nonadecene	C19H38	266	10.7	113627
102	20.55	57	Nonadecane	C19H40	268	32.0	114098
103	20.74	55	1-Eicosanol	C ₂₀ H ₄₂ O	298	6.07	113075
104	21.49	55	5-Eicosene, (E)-	C ₂₀ H ₄₀	280	8.15	62816
105	21.55	57	Eicosane	C ₂₀ H ₄₂	282	17.9	290513
106	22.46	55	10-Heneicosene (c,t)	C ₂₁ H ₄₂	294	10.9	113073
107	22.51	57	Heneicosane	C ₂₁ H ₄₄	296	19.2	107569
108	23.38	55	1-Docosene	C22H44	308	9.71	113878
109	23.43	57	Nonadecane	C19H40	268	14.6	114098
110	24.27	55	1-Nonadecene	C19H38	266	6.83	113626
111	24.32	57	Nonadecane	C19H40	268	18.5	114098
112	25.13	55	1-Docosene	C ₂₂ H ₄₄	308	8.00	113878
113	25.17	57	Nonadecane	C19H40	268	21.2	114098
114	26.01	57	Nonadecane	C19H40	268	19.6	114098
115	26.82	57	Eicosane	C ₂₀ H ₄₂	282	6.74	53470

LDPE and PETE waste plastics mixture into fuel was analysis by GC/MS and check the compound structure shown figure 4 and table 1. For GC/MS analysis purpose carbon disulfide (C2S) was use as a solvent and capillary column was use for GC column. Perkin Elmer (Clarus 500 model) GC/MS chromatogram analysis result showed product fuel has hydrocarbon compounds with oxygen content and alcoholic group compounds. All compounds are traced based on trace mass (m/z), retention time (m) molecular weight, probability percentage and NIST library number followed. In analysis result showed product fuel hydrocarbon compounds range C_3 to C_{22} . Compounds are traced lower boiling point to higher boiling point wise. Starting compounds Propane (C3H8) (t=1.49, m/z=41), then rest of all compounds are appeared low number carbon chain to higher number carbon chain such as Pentane (C5H12) (t=1.91, m/z=43), Hexane (C6H14) (t=2.58, m/z=57), methyl-Cyclopentane (C6H12) (t=2.90, m/z=56), Benzene (C6H6) (t=3.27, m/z=78), Heptane (C7H16) (t=3.74, m/z=43), ethyl-Cyclopentane (C7H14) (t=4.30, m/z=69), 1-Ethylcyclopentene (C7H12) (t=4.61, m/z=67), 5,5-dimethyl-1,3-Cyclopentadiene (C7H10) (t=4.91, m/z=79), Octane (C8H18) (t=5.30, m/z=43), 1-Methyl-2-methylenecyclohexane (C8H14) (t=5.80, m/z=67), ethyl-Cyclohexane (C8H16) (t=5.97, m/z=83), 3-ethyl-1,4-Hexadiene (C8H14) (t=6.24, m/z=81), 1-Methyl-2-methylenecyclohexane (C8H14) (t=6.58, m/z=67), Nonane (C9H20) (t=7.02, m/z=43), butyl-Cyclopentane (C9H18) (t=7.67, m/z=55),

Decane (C₁₀H₂₂) (t=8.73, m/z=57), 1-Undecene (C₁₁H₂₂) (t=10.23, m/z=55), Undecane (C₁₁H₂₄) (t=10.36, m/z=57), (Z)-9-methyl-5-Undecene (C₁₂H₂₄) (t=11.66, m/z=70), Dodecane (C₁₂H₂₆) (t=11.91, m/z=57), hexyl-Cyclohexane (C₁₂H₂₄) (t=12.61, m/z=55), Tridecane (C₁₃H₂₈) (t=13.37, m/z=57), Tetradecane (C₁₄H₃₀) (t=14.74, m/z=57), Pentadecane (C₁₅H₃₂) (t=16.03, m/z=57), Hexadecane (C₁₆H₃₄) (t=17.25, m/z=57), Heptadecane (C₁₇H₃₆) (t=18.41, m/z=57), Nonadecane (C₁₉H₄₀) (t=19.51, m/z=57), Eicosane (C₂₀H₄₂) (t=21.55, m/z=57), Heneicosane (C₂₁H₄₄) (t=22.51, m/z=57), 1-Docosene (C₂₂H₄₄) (t=25.13, m/z=55) and so on. Alcoholic group and oxygen content compounds are cis-3-Oxabicyclo[4.3.0] non-8-en-2-one (C₈H₁₀O₂), 1-Octyn-3-ol (C₈H₁₄O), 2-Octyn-1-ol (C₈H₁₄O), dodecyl-Oxirane (C₁₄H₂₈O), Z-10-Pentadecen-1-ol (C₁₅H₃₀O), E-2-Octadecadecen-1-ol (C₁₆H₃₂O), 1-Hexadecanol (C₁₆H₃₄O), E-14-Hexadecenal (C₁₆H₃₀O), E-2-Octadecadecen-1-ol (C₁₈H₃₆O), E-15-Heptadecenal (C₁₇H₃₂O), 2-hexyl-1-Decanol (C₁₆H₃₄O), 1-Eicosanol (C₂₀H₄₂O). This experiment was in presence of oxygen and PETE waste plastic has 35% oxygen content for that reason oxygen and alcoholic compounds appeared.

Conclusion

PETE waste plastic and LDPE waste mixture to fuel production process was successfully in presence of oxygen. PETE waste plastics and LDPE waste plastic to fuel production process showed that residue percentage higher then light gas percentage. Because PETE waste plastics have oxygen content this is not conversable. Plastic has additives and additives can remain as residue after finished the experiment. PETE mixture with LDPE waste plastic to fuel production period creating wax problem which shown into figure 3. Product fuel color is light yellow and product fuel density is 0.76 g/ml. GC/MS analysis result showed product fuel has hydrocarbon compounds with alcoholic and oxygen content. Product fuel has short chain hydrocarbon compounds to long chain hydrocarbon compounds and compounds chin are C₃-C₂₂. Using this technology can convert PETE waste plastic and LDPE waste plastic to fuel without using any kind of catalyst. Only thermal degradation process was using for liquefaction process. PETE drinking bottle and LDPE grocery bag problem can solve using this technology. GC/MS analysis compounds table showed product fuel has short chain hydrocarbon to long chain hydrocarbon compounds, and fuel can use internal combustion engine and internal combustion engine can produce energy.

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