



A Study on Thermo - Catalytic Degradation of PET (Polyethylene Terephthalate) Waste for Fuel Production and Chemical Products

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Plastic consumption is a significant part of everyday life and has revolutionized the way we live. Polyethylene terephthalate or PET is a notable example. PET has become a material of choice for bottling beverages and other uses such as microwave trays and food films. As a result, there is an exorbitant amount of waste disposal of this particular polymer throughout our environment, particularly in landfills and even in the oceans. A significant factor is the fact that this polymer is difficult to eliminate due to a slow degradation process and its inability to incinerate. Furthermore, incineration is not recommended due to the aromatic ring and its molecular structure that may cause adverse health effects. For this reason, this research studied the effects of residual PET by catalytic thermal degradation as a recycling method to generate fuel or new chemical products. The PET sample was pyrolyzed using different ratio proportions of calcium hydroxide catalyst/sample at temperatures ranging from 370 to 507 °C. Subsequently, the samples were analyzed by GC-MS chromatography technique to characterize their composition. All samples obtained from the experiments had two phases, oil and aqueous, respectively. The Benzene production was obtained in the range of 70% to 80% in the oil phase which can be used to produce of polymeric materials. On the other hand, ethane with composition at approximately 38% was obtained from the aqueous phase. The results are promising and can be maximized by additional techniques such as hydrogenation and hydrodeoxygenation to obtain value-added products.

1. Introduction

In the last century, polymers in general, whether fossil or plant-based, are increasing its production in an accelerated way. In this framework, many domestic and industrial applications can be used, such as automobile parts, pipes, toys, and packages for several products. As a result, there is production of polymeric materials due to this industrial evolution. In 2010, around 265 million tons of polymeric material was produced. There was a significant increase between 2010 and 2011, where the production achieved approximately 280 million tons (Figueiredo, 2015).

It is important to note that this increase was similar in pattern in 1950. The polymers with a higher rate of production and the most widely used in Brazil are: poly(ethylene) - PE, poly(propylene) - PP, poly(vinyl chloride) - PVC, poly(styrene) - PS and poly(ethylene terephthalate) - PET. This research will have PET as the main polymer evaluated because, according Romão et al. (2009), it is one of the largest polymer waste disposed in the environment. For this purpose, it is necessary to explain that the polymer is a high molecular weight molecule with repeating segments along its chain. The origin of the word is explained by itself: *poly* means many and *mer* means parts, within the chemical context, the term polymer is used specifically for large molecules formed from repeats of small structures. The poly(ethylene terephthalate) - PET, by definition, is a thermoplastic material consisting of 62.5% carbon, 33.3% oxygen, and 4.2% hydrogen atoms. However, the consumption of plastic products over the years has been producing large numbers of this material waste which accumulates in landfills causing considerable environmental problems. Furthermore, polymers that are not biodegradable, such as PET, contribute to this problem through its high resistance to degradation, taking many years to decompose.

Therefore, researchers and industry professionals have been seeking alternatives to minimize the environmental impacts caused by improper disposal of this material to the environment, and developed the so-called biopolymers. This classification was given to polymers which have a sustainable benefit, that is, biopolymers produced from renewable raw materials which have a shorter life cycle compared to fossil sources. However, investment in the biopolymer market is few in relation to the perceived potential for strong growth. On the other hand, studies of recycling and reuse of alternative practices and appropriate disposal of these products have been developing. Finally, the main aim of this work is reuse the PET waste to fuel production at high temperatures as a sustainable alternative for the environment.

2. Energy recovery by thermal degradation of PET

2.1 Pyrolysis

Pyrolysis is a process whose main application is the treatment and final destination of residues, being self-sustainable energy without the need for external energy, which arouses great attention and makes it fascinating from a scientific and practical point of view (Mirante, 2000). The waste that feed the pyrolytic reactor can be derived from household and polymeric/industrial processing waste.

According to Mirante (2000), the process consists on cracking these residues that should be pre-selected and after that sent to the pyrolytic reactor where an endothermal reaction generates and separates by products at each stage of the process.

Pyrolysis is a process that cannot replace the sanitary landfills but can considerably reduce the volume of waste in those places. There are several reactors in operation with various types of applied technologies to process products removal, however, it is not possible to affirm that all variables involved are properly under control, a fact that should make this procedure considered as a prospect for the future which can surely show itself as appropriate in specific situations (Sarker et al. 2011). Nevertheless, this kind of process cannot be generically applied, particularly in the case of small and/or medium-sized urban cleaning systems (Mirante, 2000).

2.2 Catalytic Pyrolysis

Catalytic Pyrolysis is considered as an advanced conversion technology which a plastic waste degradation reaction at high temperature is reached with total or partial absence of oxygen to obtain liquids, solids, and gas products. As pyrolytic processes are endothermic unlike the combustion process the supply of heat is essential to the system (Carlson et al. 2009).

The thermal processes and all catalytic processes of polymer recycling are economically and environmentally acceptable where a liquid mixture of hydrocarbons is produced. This product or mixture may or may not be used in the synthesis of new plastics by the petrochemical industry.

Thus, pyrolysis of plastics waste aggregate value to this residue into fuel or feedstock for the petrochemical industry and decrease the large amount of plastic waste discarded in the environment (Sarker et al. 2011).

At the operational point of view, thermal pyrolysis is conducted usually at temperatures between 350 and 900°C which coal fines and volatile fractions are formed. Besides that, it can be separated into liquid hydrocarbons and non-condensable gases with high calorific value. The extensions of each fraction and its compositions depend primarily on the nature of the plastic waste or process conditions. The pyrolysis of polymers with high hydrocarbon content is quite beneficial due to the high rates of conversion into liquid product (pyrolytic oil), which can be used as fuel or as raw material (feedstock) in refineries.

3. Materials and experimental methodology

This experiment was based on the use of catalytic pyrolysis technique. In this case, calcium hydroxide ($\text{Ca}(\text{OH})_2$) was used as a catalyst with experimental temperatures of 370 to 507°C. Table 1 shows the experimental statistical planning with the process variables: temperature, ratio of catalyst/polymer, and reaction time. The statistical software STATISTICA 7 from Statsoft Inc was used to create the design matrix.

Calcium hydroxide as a catalyst accelerates the pyrolysis up to 25 minutes according to the studies of Scheirs and Kaminsky (2006), so that this interaction between the catalyst and the polymer used (PET) becomes appropriate to obtain great results. For this experiment, simple and manual procedures were used by gathering PET bottles of mineral water and soft drink packages. In addition, colorless bottles were chosen and their labels and covers were removed and then employed a simple wash and let dried naturally. The bottles were manually cut with scissors to remove the bottom and the neck. After that, a longitudinal cut to open a cylindrical area on a flat surface was done. Then, grinding of PET blades was executed by a CDs shredder to ensure the uniformity of the cut and grain size.

Table 1: Design matrix with independent process variables

Experiment	Temperature (C ⁰)	Ratio polymer/Catalyst	Time (min)
1	480	1:1	20
2	480	1:1	40
3	480	1:3	20
4	480	1:3	40
5	400	1:1	20
6	400	1:1	40
7	400	1:3	20
8	400	1:3	40
9	507	1:2	30
10	373	1:2	30
11	440	1:0,3	30
12	440	1:4	30
13	440	1:2	13
14	440	1:2	47
15	440	1:2	30
16	440	1:2	30
17	440	1:2	30

A similar assembly and experiment was employed such as in the study of Sarker et al. (2011). Figure 1 shows the experiment components.

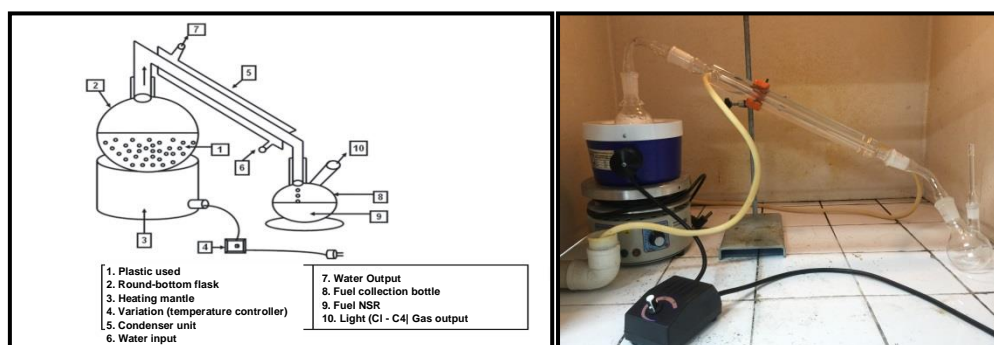


Figure 1: Scheme of the catalytic pyrolysis (Sarker et al. 2011) and assembly for PET degradation experiment

Initially, the polymer and catalyst were placed inside the mixture round-bottom flask in exact amounts proposed in Table 1, wherein the ratio of polymer/catalyst are varied from 1:0.3; 1: 3. After this step, the flask with the mixture was placed in the heating mantle in a way that the round-bottom flask touches all its lower end in the equipment so that heating occurred evenly throughout the flask diameter and initialize the pyrolysis. The round-bottom flask was connected to the condenser so that the steam generated by the reaction, derived from the heat emitted by the isomantle, was condensed as a result of temperature exchange with the water that flows inside the condenser and was collected in a twin-neck flask connected to the right side, as shown in Figure 1. Then, each sample was collected from the twin-neck flask and then forwarded to the chromatographic analysis.

4. Results and discussion

The samples showed a similar characteristic pattern between them, namely: yellowish and two phases, some with suspended volatile and translucent solids. The samples were sent for chromatography where the technique used was the Gas Chromatography applied to mass Spectroscopy GC-MS by PONA method. This second method of Blomberg et al. (2009) consists of identifying compounds through relative retention time and an identification window. Moreover, this method is called PONA because it allows a single-column characterization analysis for Paraffins (P), Olefins (O), Naphthenes (N) and Aromatics (A) (PONA). The GC-MS was developed due to the complexity of the samples and the need for identifying the presence of hydrocarbons.

According to the analyses provided by CENPES - PETROBRAS, most of the samples had two phases, one oily and another aqueous. Furthermore, the oil phases of all samples, except for the samples 1, 2, 3, and 11, because it was impossible to separate the phases, were analyzed. Table 2 shows the results of composition (mass %) of the several samples executed by chromatographic analysis.

Table 2: Oily Effluent Composition (% m/m)

N	Component	t _{RETENTION}	4	5	6	7	8	9	10	12	13	14	15	16	17
1	Acetaldehyde	5.927	0.534	1.614	1.220	0.302	0.378	1.178	1.499	0.606	1.487	1.093	0.351	1.941	0.196
2	Ethanol	6.109	0.425	0.334	0.350	0.306	0.149	0.214	0.274	0.693	0.646	0.172	0.187	0.455	0.305
3	Acetone	6.261	1.600	0.852	1.982	1.259	0.858	1.728	1.259	1.518	1.952	0.152	1.671	1.516	1.854
4	2-Butanone	6.844	0.168	0.098	0.186	0.275	0.214	0.157	0.130	0.282	0.331	0.140	0.179	0.185	0.160
5	2-Butenal	7.259	0.694	0.332	0.306	0.368	0.222	0.314	1.010	0.608	0.611	0.414	0.322	0.957	0.850
6	Benzene	7.544	71.12	78.37	72.51	76.18	75.33	76.46	78.13	81.08	76.66	77.51	33.80	75.73	76.43
7	1,1-Diethoxyethane	8.044	0.231	0.250	0.306	0.216	0.145	0.177	0.258	0.812	0.262	0.154	0.247	0.428	0.250
8	Toluene	8.668	2.685	3.063	3.282	2.556	2.441	2.714	2.433	2.492	2.322	2.829	3.894	2.532	2.407
9	Ethylbenzene	9.831	2.750	2.308	2.789	2.762	2.787	2.337	1.970	2.353	2.300	2.114	4.590	1.975	1.980
10	Styrene	10.175	1.278	0.751	1.219	1.293	1.261	0.863	0.892	1.079	1.101	0.936	1.753	1.020	0.777
11	Isopropylbenzene	10.657	0.392	0.309	0.371	0.329	0.301	0.350	0.330	0.303	0.317	0.278	0.769	0.281	0.319
12	Benzaldehyde	10.996	0.493	0.545	0.626	0.423	0.464	0.477	0.479	0.301	0.410	0.452	1.213	0.518	0.449
13	1-Ethyl-3-methylbenzene	11.171	0.140	0.065	0.064	0.133	0.138	0.078	0.101	0.117	0.091	0.082	0.275	0.090	0.073
14	a-Methylstyrene	11.369	0.598	0.381	0.637	0.590	0.521	0.531	0.476	0.490	0.578	0.534	1.358	0.469	0.465
15	1-Methylstyrene	12.015	0.268	0.163	0.208	0.292	0.321	0.215	0.192	0.230	0.236	0.189	0.600	0.193	0.187
16	Acetophenone	12.577	11.10	4.692	8.533	9.083	10.02	6.746	6.525	4.834	7.970	6.341	18.24	7.195	6.735
17	Benzoic acid	14.065	0.328	2.646	1.809	0.274	0.339	1.057	0.299	0.941	0.264	0.731	3.761	0.305	0.277
18	1-Methylacetophenone	14.354	0.294	0.677	0.321	0.234	0.263	0.265	0.222	0.128	0.200	0.268	1.239	0.224	0.224
19	Naphthalene	14.730	0.266	0.157	0.142	0.154	0.161	0.190	0.160	0.137	0.112	0.200	0.885	0.154	0.157
20	3-Ethylacetophenone	15.737	0.109	0.361	0.527	0.315	0.419	0.318	0.350	0.074	0.057	0.111	0.329	0.168	0.145
21	Biphenyl	16.723	2.397	1.035	1.231	1.509	1.969	1.982	1.285	0.276	0.794	1.734	10.06	1.710	1.855
22	Di-phenylmethane	17.794	0.195	0.186	0.123	0.129	0.178	0.251	0.139	0.002	0.078	0.123	1.273	0.231	0.227
23	Di-phenylethane	18.081	0.117	0.198	0.228	0.097	0.125	0.259	0.090	0.048	0.069	0.208	1.396	0.155	0.205
24	Fluorene	18.998	0.186	0.128	0.204	0.154	0.173	0.218	0.152	0	0.097	0.203	1.304	0.245	0.216
25	1,2-Di-phenylethene	19.911	0.007	0.008	0.060	0.070	0.060	0.085	0.011	0	0.010	0.057	0.611	0.012	0.010
26	Fluorenone	20.593	0.045	0.035	0.028	0.032	0.031	0.174	0.067	0	0.057	0.080	0.535	0.111	0.112
27	Biphenylacetophenone	21.106	0.115	0.131	0.157	0.110	0.115	0.106	0.115	0	0.076	0.181	1.191	0.203	0.207
28	o-Terpenil	21.892	0	0	0	0	0	0	0	0	0	0.072	0.315	0	0
29	2-Phenyl-naphthalene	23.413	0	0	0	0	0	0	0	0	0	0.070	0.271	0	0
30	m-Terpenil	26.523	0.028	0	0	0	0	0	0.024	0	0	0.072	0.451	0	0
31	p-Terpenil	27.058	0.079	0	0	0	0	0	0.075	0	0	0.117	0.818	0.123	0.124
32	Not identified	-	1.345	0.311	0.573	0.553	0.603	0.555	1.051	0.589	0.909	2.382	6.106	0.866	2.802
33	Aromatics (BTES)	-	77.83	84.49	79.88	82.79	81.86	82.37	83.42	87.01	82.38	83.39	44.03	81.26	81.59

According to the table above, the compounds with higher composition are benzene, acetone, toluene, ethylbenzene, styrene, acetophenone, and biphenyl. The best process to obtain these compounds (Toluene, styrene, acetophenone, biphenyl, and ethylbenzene) in the PET pyrolysis experiment, according to the obtained results, must be performed in a temperature, ratio of sample catalyst, and reaction time of 440°C, 1:2, and about 30 minutes, respectively. However, to maximize the benzene production, the best process in

the PET pyrolysis experiment is performed in a temperature, ratio of sample-catalyst, and reaction time of 440°C, 1:4, and about 30 minutes, respectively.

The data regarding these compounds is important because according to Heleno et al. (2000), the industries intertwined with benzene production in Brazil are the petrochemical and steel plants. They produce benzene and are used as feedstock for the production of ethylbenzene, cumene, caprolactam, linear alkylbenzene, and maleic anhydride, and finally the anhydrous alcohol mills which employ azeotropic distillation in benzene.

In terms of the aqueous phase only sample 13 was analyzed. The operating condition of this sample showed the highest amount of the aqueous phase and was easily separated from the oily part. In this case, the amount of ethanol present was 38% by weight of the composition, an excellent proposal as complement to fuels. The experimental statistical design in this sample was operating at a 440°C temperature, ratio sample/catalyst of 1:2, and a time of reaction of 13 minutes.

Table 3 shows the results of composition (mass %) of sample 13 analyzed by GC-MS technique. In this analysis it is clear that the presence of aromatic is minimal; in other words there is only 0.3% of Benzene.

Table 3: Composition of aqueous phase (% m/m) of sample 13 (dry base composition-excluding water)

N	Component	t _{RETENTION}	% Sample 13
1	Acetaldehyde	5.938	31.254
2	Ethanol	6.128	38.144
3	Acetone	6.280	25.055
4	2-Butanone	6.868	0.858
5	2-Butenal	7.272	1.243
6	Benzene	7.432	0.359
7	Dioxane	7.592	0.530
8	1,1-Diethoxy-ethane	7.892	0.682
9	3-Hydroxy-butanal	8.269	0.448
10	Acetophenone	12.557	1.423
11	Not identified	-	0.004

In this case, the aqueous sample showed a significant return to ethanol when applied by the hydrogenation technique. The compounds as acetaldehyde can be converted into ethanol, thereby maximizing the production of this compound in the catalytic pyrolysis process. This compound can be supplied to industry as a component to be added to fuels, since ethanol is added to the fuel at up to 27% according to ANP resolution No. 19 as of 04.15.2015 - republished of the Brazilian official gazette as of 04.20.2015.

5. Conclusions

Pyrolysis is a strong ally for revaluation of PET waste, adding value and inserting it again in the industrial production processes generating a new purpose for this type of waste.

Calcium hydroxide catalyst showed a remarkable efficiency in catalytic pyrolysis process by reducing the temperature and reaction time, respectively, optimizing the entire process.

All samples generated by the experiment had the same standard product. This standard was two phased (oil and water) and flammable. With this fact, is possible to map the best experimental design for the production of a particular product.

The technique was proven very effective in the production of aromatics and oxygenates. The aromatics are used in industry for the manufacturing of polymers. In this case, it is necessary to add hydrodeoxygenation to maximize the production of aromatics removing oxygenates in the oil phase. Thus, we can see that the oil phase of the samples represent a recycling of products needed for the production of these polymeric materials. Therefore, the most interesting use of this product of pyrolysis would be for the production of aromatic compounds such as BTX and BTE. By virtue of the detail of the compositions made by GC-MS in the oil phase of the samples, it was observed that the aromatic content was very high, being the sum more than 80% m/m in the production of BTES (benzene, toluene, ethylbenzene and styrene) and in most cases, benzene was the majority compound, accounting for more than 70% m/m of the sample.

Fraga (2009) states that the pyrolysis derived gasoline from natural gas cracking as quantities of aromatics compounds reached around 50% m since Castaño et al. (2007) discusses that the quantity of aromatics from naphtha cracking can reach 70% m/m and Medeiros et al. (2007) mentions values around 61% m/m.

Therefore, we see that the aromatic content of the oil phases in the samples are higher than those found in naphtha gasoline, making PET pyrolysis gasoline very attractive for the extraction of BTX.

On the aqueous phase only sample 13 was analyzed, in which case the quantity of ethanol present represents almost 38% of the weight composition, an excellent proposal as complement to fuels.

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