Abstract: The exponential growth of waste plastic accumulation has had an irreversible and lasting impact on the world. An imminent threat to marine and terrestrial ecosystems of massive proportions, plastic waste accumulation is a global problem that will not only have to be tackled by current generations but for many generations to follow. The scale of current recycling technologies and efforts to reduce consumption by for-profit and non-profit institutions, governments, and consumers will need to be rapidly increased to combat the negative impacts plastic waste has had on the planet since its conception. This is especially the case in areas with limited infrastructure to properly collect, manage, and dispose of plastic waste. Solutions to plastic waste accumulation crisis that are appropriate for the developing world are urgently needed. Conversion of plastic waste to liquid fuel by slow pyrolysis is a technology that is particularly suitable for developing countries due to its ability to convert polyolefin waste plastic into a useful product, thus preventing its eventual accumulation in the ecosystem. However, in developing countries, conversion techniques that do not rely on sophisticated technologies are needed. Since processing time and operating temperature are the simplest variables to control, an analytical study has been conducted to assess how the molecular composition of plastic derived fuel oil (PDFO) is impacted by these parameters. The results of gas chromatography-mass spectrometry (GC-MS) and thermogravimetric analysis (TGA) studies of PDFO from high- and low-density polyethylene plastic waste produced using appropriate technology techniques are presented alongside a comparison with traditional diesel fuel and kerosene. This approach is novel in that it differs from previously conducted research, which has studied the use of catalysts, additives, or single operating temperatures to assess the composition of PDFO. Therefore, this research contribution presents a simplistic and inexpensive approach for tuning PDFO composition in appropriate technology settings.

Keywords: effect of temperature on plastic decomposition; slow-pyrolysis of plastic; gas chromatography-mass spectrometry (GC-MS); thermogravimetric analysis (TGA)

1. Introduction

Recycling post-consumer use plastic is a significant challenge due to the heterogeneity of waste streams. This challenge is compounded in developing or infrastructure limited regions [1–7]. As a result, much of the post-consumer waste generated in the developing world ends up in the environment, where breakdown into microplastics and its migration up the food chain pose a potential threat to human health [8–20]. One solution for reducing the accumulation of mixed polyolefin plastic waste is to convert it into fuel oil via slow pyrolysis [21–33]. This process can be used to generate fuel oil with properties similar to either traditional diesel fuel or traditional kerosene, depending upon the pyrolysis temperature [23,24,32,33]. A low-tech process for reducing waste plastic accumulation in developing regions has been proposed and detailed by Joshi and Seay [34–36] and
Joshi et al. [37,38]. Term as Trash to Tank (3T), this process converts post-consumer waste plastic into plastic-derived fuel oil (PDFO) via slow pyrolysis using the principles of appropriate technology [39]. In order to conform to the principles of appropriate technology, Joshi and Seay [34–36] and Joshi et al. [37,38] have designed a simple, low cost and robust 3T Processor that safely carries out the pyrolysis reaction chemistry at desired temperatures. A photo of the 3T Processor is shown in Figure 1. The 3T processor has been conceived using an open-source design that can be easily built by individuals in developing regions. The processor is low-cost, easy to build and operate, and prioritizes simplicity over sophisticated controls. A schematic of the 3T processor is illustrated in Figure 2. The process consists of a 30-L insulated retort housed in a standard 20-gallon steel drum. The retort is heated using a 240-volt electric band heater and the vapor fuel oil product is condensed using ambient temperature water in a double-pipe heat exchanger. The feedstock used for the 3T processor is a chemical mixture of polyolefin plastics; namely, high-density polyethylene (HDPE) and low-density polyethylene (LDPE). The thermal decomposition of these polymers by slow pyrolysis yields a chemical mixture of hydrocarbon chains similar in carbon number to those found in traditional diesel and kerosene [34,40]. PDFO has beneficial applications in developing regions as an alternative to traditional diesel or kerosene. Particularly, it can be used in diesel generators, vehicles, kerosene cookstoves, and lamps, serving as a reliable source of energy for transportation, cooking and lighting [34].

Figure 1. 3T processor designed using the principles of appropriate technology.

Due to the similarity of PDFO to diesel and kerosene, the objective and novelty of this research contribution is to analyze the molecular composition of PDFO produced from HDPE and LDPE as a function of temperature and processing time. Since pyrolysis temperature and processing time are the two variables that can be easily controlled, they are useful for adjusting the slow pyrolysis reaction chemistry in appropriate technology settings. By using gas chromatography-mass spectrometry (GC-MS) and thermogravimetric analysis (TGA), the composition and stability of liquid PDFO can be assessed and compared with traditional diesel and kerosene. This approach differs from previous GC-MS and TGA-based literature analysis of PDFO where researchers have primarily focused on: the pyrolysis of plastic with catalysts [40–46]; coprocessing of plastic with oil producing biomass [47–49], lubrication oils [50,51], coal [52], and semicoke [53]; analyzed a single op-
ering temperature \cite{54}; or analyzed the composition of the plastic instead of PDFO \cite{55,56}. Since the co-pyrolysis of plastic with additives, such as catalysts, lubrication oils, coal, and semicoke can increase costs and complexity, this research contribution focuses on the utilization of an inexpensive, simplistic, and yet novel approach for adjusting readily available tuning parameters—temperature and time—to study PDFO composition in appropriate technology settings.

![Schematic of 3T processor](image)

**Figure 2.** Schematic of 3T processor. R1: Fabricated carbon steel retort; R2: 3/4” CS Pipe-24” long; R3: 3/4” CS Pipe-6” Long; R4: 3” Screw on Flange; R5: 3” Blind Flange; R6: Flange Gasket; R7: 3/4” CS Pipe Elbow; R8: 3/4” CS Pipe Union; R9: Analog Bi Metal Thermometer; R10: 20 Gallon CS Open Head Drum; R11: Heating Element, 240 V, 1900W; R12: Electronic heater controller; R13: High temperature thermal insulation; R14: NEMA Plug w/Wire Leads; R15: High Temperature Wire; R16: 3/4” Pipe Insulation (3 Feet); R17: 3/4” Elbow Insulation; C1: 3/4” Copper Tubing-24” Long; C2: 1/2” Copper Tubing-30” Long; C3: 1/2” Copper Elbow; C4: 1/2” Solder to 3/4” Male NPT Adapter; C5: Copper Right Angle Tee Reducer; C6: 5/8” Clear Tubing (10 feet).

### 2. Materials and Methods

#### 2.1. Collecting PDFO Samples

To understand the effect of temperature on the composition and stability of PDFO, the 3T processor was modeled using a bench-scale autoclave Parr pressure vessel reactor with a Parr 4843 controller, as shown in Figure 3. This setup was used to generate PDFO from HDPE and LDPE. These plastics were sourced from household waste, including milk jugs (HDPE) and zipper storage bags (LDPE). The plastics were cleaned and cut to small pieces for insertion in the reactor. The temperature of the slow-pyrolysis experiments was varied between 370–400 °C in increments of 10 °C for each plastic type. This range was chosen to reflect optimum PDFO production as a function of temperature, i.e., in general, temperatures below 370 °C produced minimal amount of PDFO, whereas above 400 °C produced wax for plastics such as HDPE. The process was operated at ambient pressure. The PDFO generated through slow pyrolysis was condensed in a double pipe heat exchanger cooled with ambient temperature water. A yield of 1 L of oil is collected for every 1 kg of plastic processed, which is consistent with previous results.
2. Materials and Methods

2.1. Collecting PDFO Samples

To understand the effect of sample retention time on the composition and stability of PDFO, the Parr bench-scale reactor and controller setup was used to generate PDFO from waste HDPE and LDPE at temperatures of only 370 °C and 400 °C. These temperatures were chosen to bookend the impact of temperature on the time-focused experimental runs. Hence, for observing the impact of time, fuel samples were collected at 30-min increments for 2 h after observing the first drop of fuel, or after approximately 4.5 h of starting the experiment for HDPE and 3.5 h for LDPE. The mass balance yields of the experimental runs for both HDPE and LDPE were determined to be on average 81.83% at 370 °C and 73.89% at 400 °C. The loss in mass can be attributed to non-condensable gases produced during thermal decomposition of the polymer chains as well as lower molecular weight hydrocarbon chains that could not be effectively condensed using cooling water. Ambient temperature cooling water in a double pipe heat exchanger was used for condensing during the experimental runs in order to approximate the conditions expected in a developing world setting.

2.2. Analyzing PDFO Samples

GC-MS studies were completed using an Agilent Technologies 7890 A gas chromatograph interfaced with an Agilent Technologies 5975 C mass spectrometer and triple-axis detector. Sample preparation involved taking 500 μL of each sample and diluting to 2.5 mL using pentanes. Injection volume for each sample was 5 μL. Analytes were separated using a capillary column (Agilent Technologies HP-5MS, 30 m 0.25 mm; i.d. 0.25 mm, Santa Clara, CA, USA) and ultra-high purity (>99.999%) helium gas as a mobile phase. The initial oven temperature was set at 60 °C, ramped to 200 °C at a rate of 10 °C/min, then ramped at 5 °C/min to 280 °C. The mass source, quadrupole, and injector were held at a constant temperature of 230 °C, 150 °C, and 300 °C, respectively. The most abundant 20–25 signals in each chromatogram were identified by comparing the fragmentation patterns from the mass spectrum to the National Institute of Standards and Technology (NIST) library. The area under the curve or each chromatogram signal was used to compare the relative abundances of each hydrocarbon present based upon the total number of carbons in each molecule (C₈ through C₃₀). To analyze the thermal stability of PDFO, TGA studies were completed in triplicate on each sample (5–8 mg) using a TA Instruments Q500 TGA with

Figure 3. Parr reactor and Parr 4843 controller setup for slow-pyrolysis experiments.
platinum pans. A heating rate of 10 °C/min from 30 to 600 °C under a constant dry nitrogen flow (40 mL/min) was utilized.

3. Results and Discussion

3.1. Effect of Temperature

3.1.1. GC-MS Results

The effect of temperature variation on hydrocarbon distribution was investigated first by GC-MS. The results indicated that the hydrocarbons present in PDFO composition of all plastics analyzed were primarily aliphatic (alkanes and alkenes) hydrocarbons due to the depolymerization chemistry of the polyethylene, which undergo a random chain scission mechanism during pyrolysis [22,40,41,45,46,57–59]. For PE based plastics, hydrocarbons in the range of C₈–C₃₀ were observed. The identity of the most abundant signals were identified according to their fragmentation pattern from the mass spectrum and the relative abundances from each gas chromatograph were compared and averaged over a set of runs. The results of these analyses are shown in Figure 4. In comparison with petroleum-derived distillates, diesel fuel (No. 2 Fuel Oil) contains approximately 75–90% aliphatic alkanes and cycloalkanes, and 10–25% aromatics and olefins/alkenes [60,61]. Kerosene (No.1 Fuel Oil) is a light distillate primarily consisting of branched chain alkanes, cycloalkanes, and mixed aromatic cycloalkanes [62].

Figure 4. Relative abundances of C₈–C₃₀ hydrocarbons for PDFO as a function of temperature for HDPE waste (top) and LDPE waste (bottom) as determined from GC-MS analysis.
In Figure 4, the percent relative abundance of predominantly present hydrocarbons for HDPE and LDPE shifts from left to right as temperature increases. For instance, the peak of the curves shifts from C\textsubscript{12} at 370 °C to C\textsubscript{15} at 400 °C for both plastics. For the two inner temperatures of 380 °C and 390 °C, percent relative abundance shifts incrementally towards 400 °C. Table 1 summarizes the predominant hydrocarbons present in PDFO derived from each plastic at the two outer temperatures. As the temperature increases, the fraction of heavier hydrocarbons in the PDFO composition increases. This phenomenon may be attributed to the boiling point of heavier hydrocarbons, which vaporize at higher temperatures. For reference, the literature reported diesel and kerosene hydrocarbon ranges which are also reported in Table 1 [60]; however, these ranges vary widely in the literature; diesel hydrocarbon ranges have been reported from C\textsubscript{7}–C\textsubscript{24} and C\textsubscript{8}–C\textsubscript{17} for kerosene [62–65].

<table>
<thead>
<tr>
<th>PDFO Type and Temperature</th>
<th>PDFO Temperature (°C)</th>
<th>Relative Abundance (%)</th>
<th>Standard Deviation</th>
<th>Hydrocarbon Range</th>
</tr>
</thead>
<tbody>
<tr>
<td>HDPE</td>
<td>370</td>
<td>81.17</td>
<td>2.67</td>
<td>C\textsubscript{8}–C\textsubscript{18}</td>
</tr>
<tr>
<td></td>
<td>400</td>
<td>80.82</td>
<td>1.18</td>
<td>C\textsubscript{9}–C\textsubscript{23}</td>
</tr>
<tr>
<td>LDPE</td>
<td>370</td>
<td>80.45</td>
<td>2.30</td>
<td>C\textsubscript{9}–C\textsubscript{18}</td>
</tr>
<tr>
<td></td>
<td>400</td>
<td>80.90</td>
<td>1.53</td>
<td>C\textsubscript{9}–C\textsubscript{22}</td>
</tr>
</tbody>
</table>

3.1.2. TGA Results

Representative TGA thermograms for each PDFO thermal degradation as a function of temperature and waste plastic source are presented in Figure 5. As temperature increased for all plastics analyzed under this study, an increase in thermal stability, or a decrease in volatility, of the PDFO was observed. These results suggest that as the pyrolysis temperature increases, heavier and longer hydrocarbon chains are produced and distilled during the chain scission mechanism [62].
The higher stability of PDFO also leads to increased fuel quality, or the reduction in the degradation of the fuel at ambient conditions due to polymerization, acidity, oxidation, emulsion, and microorganism infestation [66]. However, as with diesel combustion, the efficiency of PDFO combustion is a function of the engine technology [62]. Additionally, the GC-MS results confirmed that no sulfur-containing compounds were present in the product, meaning that no oxides of sulfur were emitted during combustion.

Figure 6 depicts the comparison of PDFO thermal degradation with that of diesel and kerosene. In general, the trend observed in terms of stability is kerosene < diesel < PDFO. However, at lower temperatures of 370 °C, the rate of weight loss for PDFO is more similar to diesel and kerosene than at higher temperatures of 400 °C. This further alludes to the increased presence of longer chain hydrocarbons present in PDFO at increased temperatures.

The higher stability of PDFO also leads to increased fuel quality, or the reduction in the degradation of the fuel at ambient conditions due to polymerization, acidity, oxidation, emulsion, and microorganism infestation [66]. However, as with diesel combustion, the efficiency of PDFO combustion is a function of the engine technology [62]. Additionally, the CG-MS results confirmed that no sulfur-containing compounds were present in the product, meaning that no oxides of sulfur were emitted during combustion.
3.2. Effect of Time

The GC-MS results for studying the impact of sample retention time on composition are presented in Figure 7. The results portray that sample retention time did not have a significant impact on composition. Except for HDPE at 400 °C, the peak hydrocarbon chain length increases by approximately 1–2 carbon numbers from the initial time increment to the final time increment. This implies that slightly heavier hydrocarbons are exiting the reactor at increased run times. However, a clear visible shift in composition is only noticed as temperature increases, that is the peak hydrocarbon chains for all sample run times shifting from approximately C_{12} to C_{16} and as temperature increases from 370 °C to 400 °C. As for the TGA results for the effect of sample retention time on the stability of PDFO, no significant changes in thermal stability were observed as sample retention time increased.

3.3. Discussion

The results obtained from the GC-MS analyses indicated a significant shift from shorter hydrocarbon chain lengths to longer hydrocarbon chain lengths as the temperature increased. Shorter hydrocarbon chain lengths indicate a fuel oil product more similar to kerosene while longer chain hydrocarbon lengths would indicate a product more similar to diesel fuel. This indicates that operating temperatures nearer to 370 °C can be used to generate PDFO similar in composition to cooking fuel or lamp oil, while temperatures nearer to 400 °C can be used to generate PDFO similar in composition to a diesel fuel alternative. In a developing world setting where appropriate technology-based solutions are preferred, temperature is an effective control variable. Of course, adding reflux capabilities will result in a narrower range of hydrocarbon chain lengths; however, this is difficult to achieve using appropriate technology given the constraints of costs and simplicity.

The results from the TGA studies further confirmed that PDFO produced from this method resulted in a wider boiling point range than traditional fuels. Although the impacts of this wider boiling point range on the operation of diesel engines will require further study, the use of PDFO as an alternative to kerosene in cookstoves or lamps would be unlikely to result in adverse effects.
Figure 7. Relative abundances of C8–C30 hydrocarbons for PDFO as a function of temperature and sample time for HDPE waste (top) and LDPE waste (bottom). Note, sample naming convention, “Temperature-Sample Number”; i.e., “370-1” indicates the first sample collected at 370 °C. Samples were collected every hour.

Additionally, the results from the analysis of PDFO produced at varying processing times indicated that the fuel composition remained relatively constant over the entire operating time. This is a significant finding for appropriate technology applications as it indicates that the operator need not be concerned with reaction time durations and can be assured of a consistent PDFO composition output, in case the slow pyrolysis process needed to be stopped before the end of a run. In a developing world setting, this implies that the early termination of a run will not be problematic on the quality of PDFO production due to electricity shortages or intermittent supply of electricity when operating the 3T Processor (depicted in Figures 1 and 2).

4. Conclusions

This research contribution considered the impact of temperature and sample collection time as two variables affecting the composition and stability of PDFO derived from waste HDPE and LDPE using slow pyrolysis. The results indicated that temperature had a significant contribution on PDFO composition and can be used as an effective control variable in appropriate technology-based applications. The effect of sample retention time on composition was determined to be minimal, which means that early batch stoppage will not affect product consistency.

Slow pyrolysis provides an effective and simple method for eliminating plastic waste accumulation. By temperature tuning of the slow-pyrolysis reaction, conversion of waste plastic into products with properties similar to traditional kerosene or diesel fuel is possible. This discovery is especially beneficial for promoting the use of slow-pyrolysis-type appropriate technologies in the developing world to improve management of plastic waste and to generate valuable fuel products that can be directly used by the local communities.
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