

Effect of Co-Pyrolysing Biomasswaste with Plastics Waste

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Abstract: *With the on-going depletion of fossil fuel reserve, biomass originated fuel has been studied widely. Bio-oil from pure biomass is known to contain high level of oxygenated species resulting to poor quality and yield; hence normally required upgrading before it can be applied to engines. However when co-pyrolysed with plastics at some particular composition, free radicals coming off from decomposed plastics during pyrolysis contains high amount of hydrogen radicals which are capable of bonding with oxygen free radicals from the biomass thereby improving the quality and yield of the bio-oil, a mechanism referred to as synergetic reaction. Mixtures of elephant grass (Biomass) and plastic wastes were co-pyrolyzed with the aim of improving the quality and quantity of bio-oil. The effect of plastic waste addition to biomass wastes on bio-oil yield and quality was investigated. Temperature effect on bio-oil yield was also studied. Experimental conditions (temperature and plastics addition) influenced product quality and yields: An increase in reaction temperature between 450 and 500°C led to an increase in bio-oil yield. Plastics addition to biomass was found to have synergetically upsurge the bio-oil yield. Bio-oil quality significantly improved by the addition of plastics as all the quality parameters investigated shows improved quality for the bio-oil obtained from blended feed (biomass and plastics) when compared to the non-blended feed.*

Keywords: Synergetic reaction, co-pyrolysing, free radicals, non-blended feed, blended feed

1. Introduction

The emergence of alternative sources of energy (biofuel) has been explored in the past decades. However the discoveries of huge petroleum deposits kept fossil fuel cheap for decades, and biofuels were largely overlooked. But, with the recent rise in oil prices, along with growing concern about global warming caused by carbon dioxide emissions, biofuels have been regaining attractiveness and has been studied widely leading to the development/invention of newer technologies (1-6). The goal of those technologies/research is to recover energy from unused materials, including biodegradable materials, such as municipal solid wastes, agricultural wastes, biomass, and high energy density materials such as plastics and rubbers (1-6).

Plastics are non-biodegradable polymers containing carbon, hydrogen and others elements (chlorine, nitrogen, etc.). Due to their non- degradability, they significantly contributes to the problem of waste management. In 2017, world plastics production totalled around 430 million metric tons, a dramatic increase compared to the 335 million tonnes produces in 2016 (21). Nevertheless, plastics/rubber contains a significant amount of energy owing to the feedstock used for it production (crude oil). Therefore, sending non-degradable plastics to landfill not only contribute to environmental pollution, but also result to a significant wastage of high amount of energy that could be used in the generation of electricity and heat. Biomass on the other hand is an organic material that comes from plants and animals and it is a renewable source of energy. Biomass contains stored energy from the sun. Plants absorb the sun's energy in a process called photosynthesis. When biomass is burned, the chemical energy in biomass is released as heat. Biomass can be burned directly or converted to liquid biofuels or biogas that can be used as fuels (4).

Diverse environmentally friendly methods are available for plastics and biomass wastes recycling as opposed to incineration and landfills disposal (7). According to ASTM these wastes can be reprocessed via four methods depending on the desired end product needed (8), one of them being recycling of the waste chemically. In this technique, liquid fuels and chemicals with high added value can be obtained via chemical degradation (pyrolysis) from the waste fragments (8, 22, 23). Pyrolysis is the thermal decomposition of long chained hydrocarbon compounds into smaller ones in absence of oxygen at temperatures above 500°C generating gaseous and liquid products (8, 22, 23). The bio oil obtained may be directly used as a fuel and the gases which is normally composed of C1–C4 hydrocarbons and hydrogen is used as fuel to provide the heat for the pyrolysis process in most plants around the world. Also, the inorganic portion of the plastic remains virtually unchanged from their solid state allowing their separation and retrieval for successive reuse, as carbon black or upgraded for the production of an activated carbon (8, 22, 23).

Since pyrolysis of waste plastics and biomass can create an alternative fuel source which can be used in engines without any modification, it is worthy to be considered as a major research area in order to expand and improve on product quality and yield. Moreover, biomass-based organic wastes constitute a larger fraction of municipal solid waste (MSW) with plastics wastes assorted with it. Segregation of plastic waste and biomass wastes in municipal solid waste (MSW) involves intense labour which is more or less impossible to accomplish. Furthermore, biomass wastes obtainability is subject to seasonal variations, therefore the inclusion of another feedstock would aid to keep a steady source of the feedstock throughout off-season of a particular biomass. Hence, understanding co-pyrolysis of plastics and biomass waste could be useful in exploiting MSW as a source of energy.

The properties of bio-oil obtained via pyrolysis of biomass have been studied by many biographers, showing its suitability to be used in vehicle engines (9-12). However its performance and emission properties were much poorer when compared to diesel fuel but has been demonstrated to be lead, sulphur and nitrogen free and meet quality standard of the regular diesel. Also, most of the research findings highlighted the need for further upgrading of pyrolysis oil from biomass so as to combat all the hurdles in its usage as a suitable alternative for diesel fuel (10, 12).

Co-pyrolysis of plastics and biomass wastes is an interesting way of upgrading bio-oil from pure biomass, in that plastics contribute to increasing the content of hydrogen in the feed (13-20). High concentration of oxygenated compounds are usually present in bio-oil produced from pure biomass which normally affect the quality of the product (high concentration of oxygen can result in bad thermal stability, high viscosity, significant corrosion and poor heating value) and thus need upgrading. However this situation can be minimised/controlled by the addition of plastics to biomass during pyrolysis (co-pyrolysis), whereby hydrogen radicals originating from plastics decomposition can bond with oxygen radicals from biomass thereby resulting in a reduction in oxygenated species in the product (bio-oil), subsequently improving the quality of the bio-oil. The process is normally referred to as synergetic effect. Also the presence of hydrogen radicals is beneficial in the reduction of char formation during pyrolysis, thereby increasing the bio-oil yield (13, 16, 17). Studies on co-conversion (13-20) have also reported synergetic interactions between intermediate species derived from both plastic and biomass during co-pyrolysis, thus improving the properties and quality of the final products (23).

Bearing all of the above reasons in mind, the research aims to technically evaluate the potential of converting waste biomass (elephant grass) to high-quality bio-oil by co-pyrolysis with plastics waste. With the objective of studying the effect of plastic waste addition to biomass wastes on bio-oil yield and quality, the study will also look at the effect of temperature on bio-oil yield.

2. Materials and Methods

Feedstock

A mixture of waste water plastics made from Polyethylene terephthalate (PET or PETE) which are the major plastic of Municipal Solid Wastes in Freetown and mostly posed a serious threat to the Freetown waste management team and elephant grass was the biomass species selected for this work, because of its easy accessibility as it is normally regarded as waste.

Pre-treatment of Feedstock

The waste plastics were collected at Grandville Brook dumpsite located along the western area of Freetown. The plastics were then washed to remove stains, and dirt to

avoid contamination. They were then dried under the sun for one week until they become fragile to ensure that no water molecules are attached to the plastics before the pyrolysis process, thereafter the dry plastics were then sliced into flakes of very tiny sizes and crushed into powder and sieved in order to obtain fine particles size of less than 0.2 mm by using a metal sieve.

The elephant grasses were collected at the botanical garden Fourah Bay College and dried under the sun for 2 weeks until the green colour of the grass turns brown (indicating little or no water content). Thereafter a second drying process was employed by placing the feedstock in an oven at the temperature of 100°C for another 12 hours. The dried biomass was then crushed into a powder and sieved in order to obtain fine particles size of less than 0.2 mm by using a metal sieve.

Experimental procedure

The pyrolysis was conducted in a high temperature resistance round bottom flask, connected to a heat source with a thermometer for temperature control. Setup description/schematic diagram of the pyrolysis unit has been described in Figure 1. Figure 2 summarised the pyrolysis process. The run temperature was around 300–600°C; with a reaction time of 50 min and a pressure 0.3–1.0 MPa.

The waste biomass was first subjected to the pyrolysis process at varying temperature ranging from 300°C to 600°C while all other parameters were kept constant. This is done to study the effect of temperature on bio oil yield. This was also done for pure plastics, thereafter plastics were mixed with the biomass in equal proportion which was then pyrolysis in the same manner as the pure biomass and pure plastics so as to also study the effect of temperature on yield. Then subsequent pyrolysis was then carried out by varying the mass of plastics added to the biomass from zero to 90 wt. % in order to evaluate the effect of plastics addition to biomass on the overall yield and quality.

The gases from the reactor were condensed to produce the bio-oil. The bio-oil was collected, weighed and stored in a bottle. Water in bio-oil was removed by refluxing toluene solution using a Dean-stark apparatus. The total yield weight of the bio-oil was then calculated. Physical properties of the water-free bio-oil were measured for basic fuel properties such as flash point, API gravity, pour point, density, viscosity, PH and Heating Value.

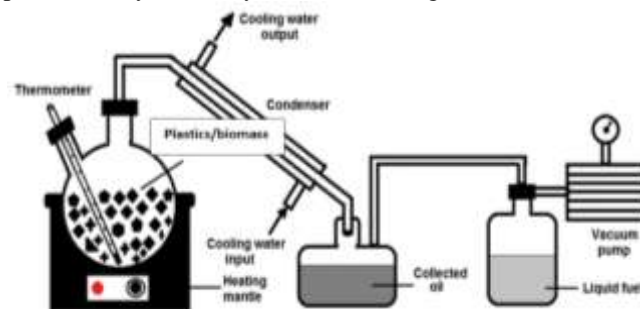


Figure 1: Description/schematic diagram of the pyrolysis setup

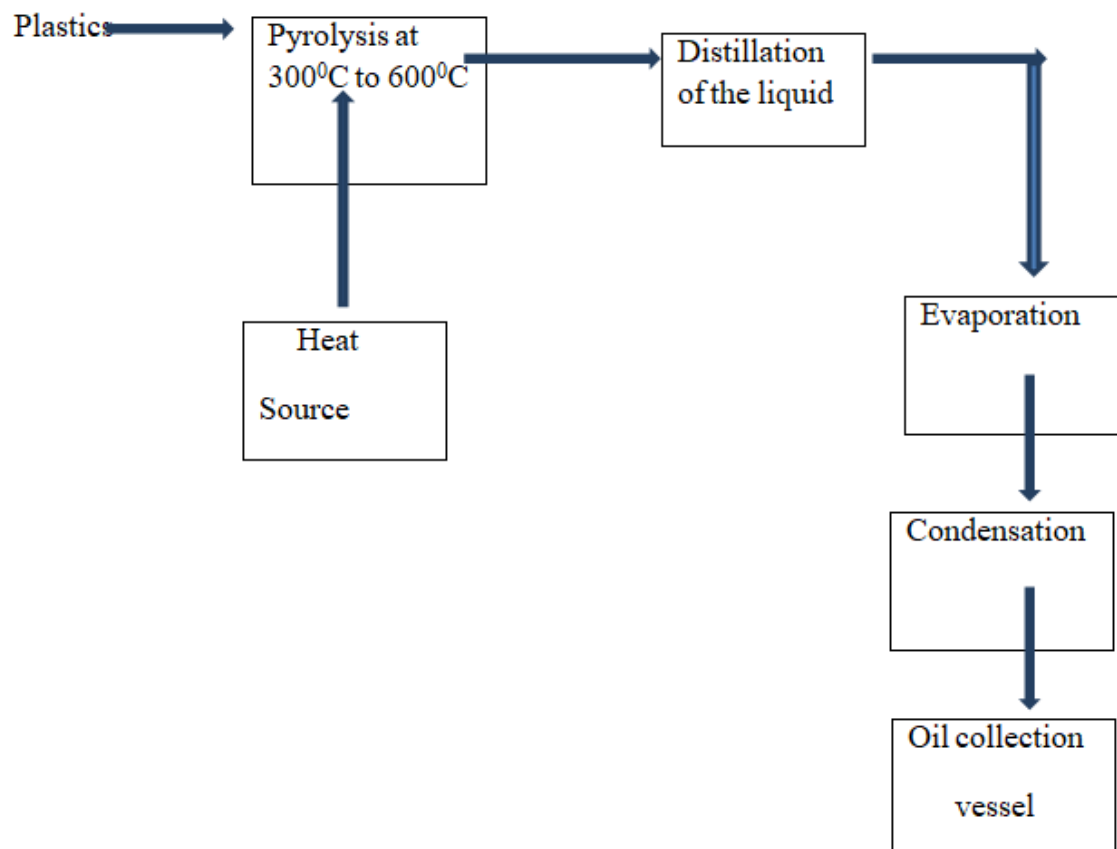


Figure 2: Flow chart for the pyrolysis process of plastic wastes and biomass.

3. Results and Discussion

1. The Influence of plastics on bio-oil Properties

When considering a suitable substitute for fossil crude oils, the substitute (biofuels) must meet certain standard specifications and quality properties, in order for it to be integrated directly to the existing carbon infrastructure. Standards are set by governmental policies and differ from country to country. It is necessary to characterise bio-crude comparably to conventional crude, in so doing direct comparison can be made easier. Therefore fuels from biomass or plastics blended feed have to meet those

specifications, and reliant on the use more extensive or less extensive upgrading has to be applied to the bio-crude.

Bio-oil from pure plastics was found to be yellowish in colour while that from pure biomass and co-feedstock was brownish in colour with a pungent odour. This can be explained in terms of the high concentration of oxygenated compounds in the biomass feedstock/blend feed leading to oxidation and thus producing a brown colour. Table 1 shows results for the quality parameters of the produced bio-oil compared with fossil diesel oil.

Table 1: Bio-oil Properties

| Properties | Plastics Bio-oil (PB) | Biomass Bio-oil (BB) | Plastics & biomass Bio-oil (PBB) | Fossil diesel oil. |
|---|-----------------------|----------------------|----------------------------------|---|
| Density (kg/m^3 at 40°C) | 921 | 968 | 833 | 780-860 |
| API gravity ($^\circ\text{C}$) | 58 | 42 | 62 | 10 -70 |
| Pour point ($^\circ\text{C}$) | -15 | -13 | -13 | -30 |
| Flash point ($^\circ\text{C}$) | 14 | 14 | 14 | 40 minimum |
| Viscosity (m^2/s at 40°C) | $1.9 \cdot 10^{-6}$ | $4.4 \cdot 10^{-6}$ | $3.2 \cdot 10^{-6}$ | $2.0 \cdot 10^{-6}$ - $4.0 \cdot 10^{-6}$ |
| PH | 4 | 2.8 | 4.9 | - |
| Heating Value (MJ/kg) | 34 | 19 | 29 | 47 |

An important contributor to biofuel density is their contents of oxygenate compounds. Density is a vital property of any liquid fuel/fuel oil. High fuel density will result in less fuel consumption while low density fuel will lead to high fuel consumption (24). This can cause deterioration / damage to the engine. Thus, very low or very high density fuel is undesirable.

From Table 1, the densities of PB and BB were found to be 921 kg/m^3 and 968 kg/m^3 respectively, which are higher than that of PBB (833 kg/m^3) which falls within the density of fossil diesel oil ($780\text{-}860 \text{ kg/m}^3$). Thus co-pyrolysing biomass with plastics created a significant impact on the bio-oil density.

Crudes are divided into classes as regards their American Petroleum Institute (API) gravity. The API gravity is related to the quality of crude. The API gravity is a special function of relative density i.e. lower API gravity implies a heavier and a lesser quality crude (24). From Table 1, bio-oil obtained from blended feed shows a significant improvement in API value, i.e. 58 for bio-oil produced from pure plastics, 42 for bio-oil produced from pure biomass to 62 for the blended feed. Thus co-pyrolysing biomass with plastics significantly influences the API gravity. These results also confirm the densities of the different products as lower API gravity infers to higher density crude. However, all the three products are within fossil diesel crude (10 -70 °C) with the PBB showing the best API value amongst the three products.

Determination of the Pour point gives an idea of the crude handling properties. Results obtain from the three products (PB, BB, PBB) shows approximately the same pour point around -13 °C to -15°C. However PB has the lowest pour point of -15°C among the three specimens, this may be related to the high aromatic content in the plastics compared to the other product, as in refinery settings, it is recognized, that the higher the pour point the more paraffinic the crude is and the lower the more aromatic it is. This results indicate that plastics addition those not significantly influence the pour point of the bio-oil.

Flash point is the lowest temperature at which fuel can vaporize to form an ignitable mixture in air. Flash point is used to characterize the fire hazards of fuels. The flash point of the three products was around 14°C indicating the presence of highly volatile compounds in the fuel which is a serious safety concern in handling/transporting. The flash point of fossil diesel is higher than the produced bio-oils which indicating its ease of Handling/transporting. This results shows that the flash point of biofuels may be increased by removing lighter components in the bio-oil, rather than co-pyrolysing biomass with plastics.

Viscosity determination gives information about flow properties of the crude and can be correlated to the aromaticity and paraffinicity of the crude (24). It was observed that bio-oil from 100% (pure biomass) accounted for the highest viscosity of $4.4 \cdot 10^{-6} \text{ m}^2/\text{s}$ compared to that of the pure plastics (100% plastics) and blend feed which shows viscosities of $1.9 \cdot 10^{-6} \text{ m}^2/\text{s}$ and $3.2 \cdot 10^{-6}$ respectively. This may be attributed to the fact that plastics normally contains high amount of low molecular weight olefins and paraffins which might have reduced its viscosity. Biomass on the other hand is mainly made of natural polymers such as cellulose, hemicellulose and lignin. Pyrolysis partially disintegrates these polymers to produce molecules of a wide range of molecular sizes, including large polymeric/oligomeric molecules from the partial breakdown of these natural polymers. These polymers make bio-oil highly viscous. However, these polymeric/oligomeric molecules are not the simple fragments of cellulose, hemicellulose and lignin because other reactions may have also taken place during the thermal breakdown of the natural polymers in biomass. Comparing the viscosity of the produced bio-oil with fossil diesel shows that the viscosity of waste plastic

pyrolysis oil was $1.9 \cdot 10^{-6} \text{ m}^2/\text{s}$ which was lower than diesel, while viscosity of the co-feed ($3.2 \cdot 10^{-6} \text{ m}^2/\text{s}$) falls within diesel range ($2.0 \cdot 10^{-6} - 4.0 \cdot 10^{-6} \text{ m}^2/\text{s}$) and that from pure biomass ($4.4 \cdot 10^{-6}$) surpassed that of fossil diesel and co-feed oil. Implying that plastics addition to biomass during pyrolysis can decrease bio-oil viscosity.

The PH of the bio-oil obtained from pure biomass appears to be very low, about 2.8. This may be explained in relation to the constituents of the bio-oil. Normally bio-oil from biomass contains acetic acid and formic acid which contribute to the formation of carboxylic compound (10). Therefore these acids in the bio-oil are responsible for the low PH value. The bio-oil from pure plastics on the other hand, shows a higher PH of 4, indicating a low concentration of acids as the oil is predominantly composed of alkane, olefins and cycloalkanes (10). The low PH value of the bio-oil obtained from plastics also reflected in the blend with a PH of 2.9; suggest that addition of plastic to biomass can reduced the acidity of the oil.

The heating values for the various bio-oil were found to be very low with 34 for PB, 19 for BB and 29 for PBB respectively. These values are very low when compared to that of fossil diesel having a HIV of 47. However, there is a significant difference between the heating value for pure plastics and blended feed bio-oil to that of pure biomass bio-oil. Addition of plastics significantly upsurge the heating value of the pure biomass (from 19 to 29). This may be explained in terms of the moisture content in Bio-oil which normally affects the heating value. The moisture in the biomass feedstock for pyrolysis is condensed into the bio-oil. Additional water is produced during pyrolysis. Bio-oil also has high contents of oxygen, which has originated from the oxygen containing structures in biomass feedstock for pyrolysis. Therefore, bio-oil has lower heating values than petrol or diesel from the refinery of petroleum. Thus in order to improve the heating value of bio-oil, a large fraction of oxygen in bio-oil needs to be removed through a variety of reactions during bio refinery as plastics addition alone cannot salvage the problem as bio-oil from any source contains a significant amount of moisture resulting from both the feed and the pyrolysis process.

Effect of pyrolysis temperature on Bio-oil yield

The effect of pyrolysis temperature on bio-oil yields is presented in Table 2

Table2: Bio-oil yield at different temperature (graph)

| Temperature (°C) | Mass of Feedstocks (kg) | Plastics Bio-oil Yield (Wt%) | Biomass Bio-oil Yield (Wt%) |
|------------------|-------------------------|------------------------------|-----------------------------|
| 300 | 2.0 | 10 | 16 |
| 350 | 2.0 | 18 | 20 |
| 400 | 2.0 | 28 | 47 |
| 450 | 2.0 | 52 | 50 |
| 500 | 2.0 | 58 | 45 |
| 550 | 2.0 | 47 | 31 |
| 600 | 2.0 | 14 | 10 |

Bio-oil yield increase with increase in temperature. However, the maximum bio-oil yields differ depending on the feedstock. PB shows a maximum yield of 58 at 500°C while that of BB was 47 at 400 °C. The bio-oil yield starts to decline continuously from around 550°C with subsequent increase in temperature. This may have occurred probably as a result secondary reactions of pyrolysis products at high temperature. Moreover, extreme temperature in the pyrolysis reactor may affect more decomposition of char leading to a decrease in the liquid yield (10).

Effect of plastics addition on bio-oil yield

Table 3 shows the results obtained from co-pyrolysing plastics waste with elephant grass.

Table 3: Bio-oil Yield with varying plastics weight/quantity

| Mass of Biomass (%weight) | Mass of Plastics (%weight) | Bio-oil Yield (%) |
|---------------------------|----------------------------|-------------------|
| 100 | 0 | 23 |
| 90 | 10 | 23 |
| 80 | 20 | 23 |
| 70 | 30 | 26 |
| 60 | 40 | 35 |
| 50 | 50 | 38 |
| 40 | 60 | 46 |
| 30 | 70 | 52 |
| 20 | 80 | 56 |
| 10 | 90 | 61 |

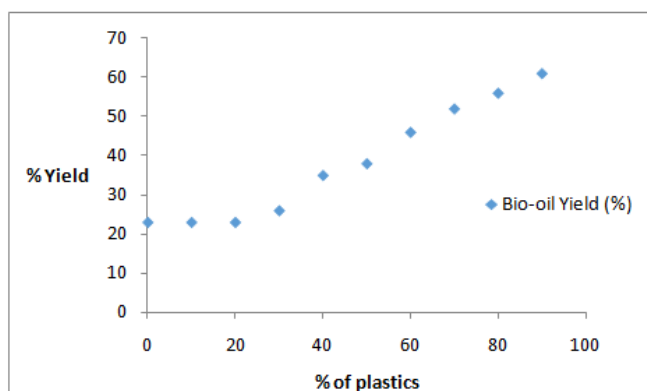


Figure 2: Bio-oil Yield with varying plastics weight/quantity

Table 3 and Figure 2 shows that plastics addition to biomass can synergetically upsurge the bio-oil yield as the percentage yield in the feed blend increases with subsequent increment in the plastics feed (from 30%) and thus depict a linear relationship. It is believed that addition of plastics improves the carbon and hydrogen contents of the feed. This upgrades the qualities/quantity of the bio-oil due the hydrogen transfer from the plastic to biomass. Most biomass constituents decomposed around 400 °C, while plastics decompose above 400 °C, see Table 2. Thus the solid from biomass pyrolysis, which still contains significant oxygenated compounds, could provide radicals to stimulate the hemolytic scission of polymer chains in the plastics (25). Polymer chain degradation entails three significant steps (initiation, propagation and termination steps) (25). In the initiation step, the chain scission is

aided by free radicals derived from biomass decomposition, in addition to self-generated radical. During the termination step, the biomass derived free radicals possibly will be stabilized by obtaining hydrogen from the polymers there by upsurge the liquid yield (bio-oil yield)

4. Conclusion

Mixtures of elephant grass and plastic wastes were co-pyrolyzed with the aim of improving the quality and quantity of bio-oil. Experimental conditions (temperature and plastics addition) influenced product quality and yields: An increase of reaction temperature between 450 and 500°C led to an increase in bio-oil yield. Plastics addition to biomass synergetically upsurge the bio-oil yield as the percentage yield in the feed blend increases with subsequent increment in the plastics feed (from 30%) and thus depict a linear relationship. Bio-oil quality was significantly improved by the addition of plastics as all the quality parameters investigated shows improved quality for the bio-oil obtained from blended feed (biomass and plastics) when compared to the non-blended feed. However, a full characterization of bio-oil produced is still required to ascertain eventual benefits co- pyrolysis of biomass waste with plastic in liquids properties, specifically about its behaviour in diesel engines.

In summary, it is possible to obtain high yield and quality bio-oil from plastic waste and elephant grass (biomass) co-pyrolysis which could be used as an alternative fuel source in Sierra Leone, having two advantages: energy recovery from waste and lessen the environmental harm caused by untreated wastes.

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