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Emission Characteristics during Combustion of Torrefied PET-Biomass Composite Pellets

Ukrit Samaksaman*[*], Rattanaporn Punthurat*, Chanyud Kritsunankul*, Kanit Manatura**
Kittikorn Sasujit* and Sirinuch Chindaraksa******
*Department of Natural Resources and Environment, Faculty of Agriculture,
Natural Resources and Environment, Naresuan University, Phitsanulok 65000, Thailand
**Department of Mechanical Engineering, Faculty of Engineering,
Kasetsart University Kamphaeng Saen Campus, Nakhon Pathom 73140, Thailand
***Renewable Energy College, Maejo University, Chiang Mai 50290, Thailand
****Department of Physics, Faculty of Science, Naresuan University, Phitsanulok 65000, Thailand
[*]E-mail : ukrits@nu.ac.th

Abstract

Most of polyethylene terephthalate (PET) bottles, though, has been taken into a recycling system, it still has some problems after preparation and the mechanical process. Waste of PET from the mechanical process is useless and non-recyclable. Pelletizing of such PET waste with biomass such as teak sawdust (TS), eucalyptus sawdust (ES), and corncob (CC) were investigated. Torrefaction of PET-biomass composite pellets was manipulated after pelletizing. Proximate and ultimate analysis as well as the high heating value were deployed to analysis. Moreover, emission characteristics during the combustion of samples of non-torrefied and torrefied pellets; PET/TS, PET/ES, and PET/CC were studied in a lab-scale fixed bed reactor. Emission of flue gas (O_2, CO_2, CO, SO_2, and NO_x) and gaseous pollutants (polycyclic aromatic hydrocarbons; PAHs and aromatic hydrocarbons such as benzene, toluene, ethylbenzene, and xylene; BTEX) were determined. The results indicated that flue gases such as CO_2, CO and NOx were decreased in the samples of torrefied pellets. SO_2 could not be detected due to no sulfur content of the origin materials. The torrefied PET/TS and PET/ES pellets could reduce PAHs compared to the nontorrefied samples indicated as 0.07 and 0.03 g/Nm^3, respectively. While emissions of BTEX could not be detected in samples of torrefied PET/TS and PET/ES. Combustion of the torrefied PET/CC pellets caused emissions of PAHs and BTEX with the total concentrations of 6.45 and 0.01 g/Nm^3, respectively. Therefore, the torrefaction was a suitable pretreatment method for PET-biomass composite pellets and altered emission characteristics during the combustion.

Keywords : combustion; composite; gaseous emission; PET-biomass; pellets; torrefaction

Introduction

The increasing of polyethylene terephthalate (PET) bottles usage has been represented by the daily amount of PET wastes generated in the municipal solid waste stream. The PET recycling is a process of plastic utilization that turns the undesired PET wastes to the useful PET-plastics. Processes of mechanical recycling include collecting, sorting, separation of contaminants or other plastic, size reduction, milling, washing, sterilizing, and drying [1]. This process can be turned PET bottles to flake-PET for producing goods with up- or down-cycling of PET-plastics. Nevertheless, it occurred the undesired materials such as PET waste. In general, PET waste was found in the forms of sludge, debris, tiny pieces of PET, dust, and microplastic [2]. There was the secondary waste released from the processes and occurred in a general waste of a mechanical recycling plant which was useless and non-recyclable.

Energy recovery of plastic wastes by combustion can be made in several types of incinerators to provide energy in the forms of steam, heat and/or electricity [3, 4]. Alternatively, plastic wastes are gasified to give synthesis gas (syngas) and pyrolysed to give liquid fuel, which used to generate steam via combustion boilers or after removal of impurities, particles, and tar, to produce electricity in the gas engine, and for high efficiency electricity production in a gas turbine or fuel cell [3]. In addition, PET waste from a mechanical recycling plant had high energy potential and good in physical-chemical properties which can be used to improve the high heating value for solid fuels such as refuse derived fuel (RDF), solid recovered fuel (SRF), and processed engineer fuel (PEF). There are alternative solid fuels commonly used in industrial scale [4]. However, PET waste was not suitable to convert as a liquid fuel form via pyrolysis due to terephthalic acid and benzoic acid contaminants in a liquid fuel form occurred [3].

Pelletizing is a process of handling powder-like materials such as PET sludge, debris, tiny pieces of PET, dust, and micro-plastic that lead the preferable material resources from the existing PET recycling facilities. Fuels pellets can be specifically tailored for ease of transportation and for different uses where industrial heat is required. This makes suitable alternatives to fossil fuels. Moreover, PET waste differ from the conventionally alternative solid fuels (RDF, SRF, and PEF) in terms of PET production initiated with the best material possible as the main feedstock, then the selected industrial, commercial usage, and known of recycling and by-products turn-back as fuels. The preference of using PET waste as an the raw material in fuel pellets is to improve the mixture and thus achieve the desired qualified specifications of solid fuels [5]. Moreover, as a replacement for fossil fuels such as oil, coal, gas, and solid waste fuels and alternative solid fuels, PET waste can be burned to generate electricity with a smaller carbon footprint [6].

Torrefaction is considered one of dominant thermal treatment techniques to produce an alternative fuel to solid fuel market share with coal and other alternative fuels. Torrefaction is the process of low-temperature treatment which was carried out in a temperature range of 200-300 °C with a residence time of 10-30 min [7]. Properties and thermogravimetric behavior of PET and biomass composites pellets were relevantly discussed [2]. In addition, the emission characteristics during these solid fuels (PET-biomass composite pellets) combustion have not been yet studied. The present study aimed to investigate the physico-chemical and thermal properties of the non-torrefied and torrefied PET-biomass composite pellets. Emissions analysis under the combustion was performed in a lab-scale fixed bed combustor. Flue gas and gaseous pollutants emitted from an exhaust included carbondioxide (CO_2), carbonmonoxide (CO), sulfurdioxide (SO_2), oxides of nitrogen (NOx), and oxygen (O_2), 13 substances of polycyclic aromatic hydrocarbons; PAHs and aromatic hydrocarbons such as benzene, toluene, ethylbenzene, and xylene; BTEX were undertaken.

Material and Method

PET waste received from the mechanical recycling plant for PET-plastics in Surin province, which contain different sizes of <1.0 to 2.5 mm in diameter. Biomass such as teak sawdust (TS), eucalyptus sawdust (ES), and corncob (CC) received from the sawmills and agricultural areas nearby Naresuan University, Phitsanulok province. In this study, PET waste had been used as a major material for pelletizing amounted for 85% by weight. Biomass had been used as an additive material that was about 15% by weight.

Hydraulic press machine was used to be a tool for pelletizing with a condition of hydraulic pressure of 100 kg/cm^2, at temperature of 100 $^{\circ}$C, and time of 2 min for each pellet production. Properties of raw materials and pellets such as proximate and ultimate analysis and drop shatter index (DSI) were determined as well as the analyses of calorific value of samples used a bomb calorimeter (LECO, AC-500).

The torrefy reactor was made of the stainless steel (304L) tube equipped with screw cover and sealer to prevent torrefy-gas leakage. The gas outlet was connected with an air pump for controlling gas flow rate ranged of 1-10 L/min. Prior to testing, 10 g of PET-biomass composite pellets put inside the torrefy reactor placed at the top of heat source (flame). The condition of torrefaction temperature set at 225 $^{\circ}$C (measuring by an infrared thermometer, Aeropak, AIT-42R), an air pump was operated at 1 L/min of gas flow rate (under the vacuum condition), and residence time of 10 min. After the torrefy reactor was cooled at room temperature, samples were collected and kept in plastic bags for further tests.

Combustion test

Figure 1 illustrates the experimental setup for combustion test and gas sampling. The lab-scale fixed bed combustor made from stainless steel (304L) tube (2.5 inch of a diameter) equipped with ceramic heaters, type-k thermocouples, and PID controller. The combustion temperature set around 850 $\pm$ 20 $^{\circ}$C. The sample of pellets was feeding at the top of combustor with the rate of 0.5 g/min. The gas sampler was connected and equipped with cotton filter, cooling system, XAD-4 absorber (Sigma-aldrich), gas flow meter, air pump, and exhaust to a fume hood. Flue gas and gaseous pollutants were sampled by isokinetic condition at 1 L/min flow rate passed through the flue gas analyzer (Testo-350H) and 2 L/min flow rate of gaseous pollutants passed through and absorbed by XAD-4 resin. In addition, the flue gas analyzer connected in a series from the exhaust pipe was continuously analyzed for O_2, CO_2, CO, NOx, and SO_2.

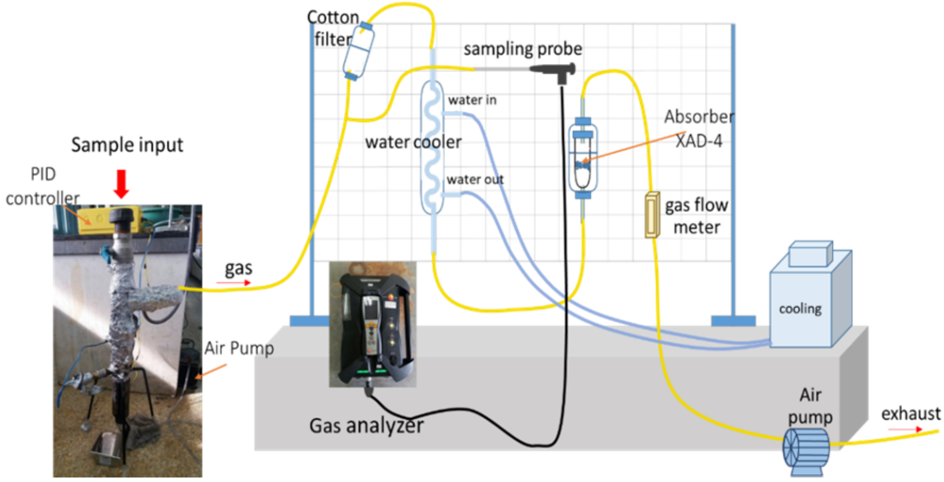

Figure 1 Experimental setup for combustion test and gas sampling

Gaseous pollutants analysis

Gaseous pollutants (PAHs and BTEX) were sampled at 5-10, 15-20, and 25-30 min of the operation time. PAHs and BTEX were extracted from XAD-4 resin using the Soxhlet extraction apparatus with the mixture of solution of hexane: dichloromethane with the ratio of 1:1 (250 ml) and the extraction time for 24 hr with temperature of 65 °C. Then, the volume of solution was reduced to 1 ml by using a vacuum evaporator and purified the solution by filtering through a nylon micro-filter. Analysis of 13 substances of PAHs included Acenaphthylene, Fluorene, Phenanthrene, Anthracene, Pyrene, Benzo (a) anthracene, Chrysene, Benzo (b) fluoranthene, Benzo (k) fluoranthene, Benzo (a) pyrene, Dibenz (a,h) anthracene, Benzo (g,h,i) perylene, Indeno (1,2,3-cd) pyrene, and 5 substance of BTEX using gas-chromatography mass spectrometer (Shimadzu, QP2010Plus). Figure 2 presents non-torrefied and torrefied pellets of (a, b) PET/TS, (c, d) PET/ES, and (e, f) PET/CC.

Results and Discussion

Properties of raw materials are shown in Table 1. PET waste samples contained lower moisture content (MC) than biomass samples. However, the highest ash composition occurred in the PET sample because it was composted of sludge, debris, sand, machinery cake, other plastic contaminants, etc. The volatile matter values were in the range of 89-92% for all of raw materials. Elemental analysis results indicated that PET waste had lower of C and O elements than biomass samples. Terephthalate polymer mostly contained of C and H and less of O element in chemical formula. Sulfur (S) element was not found in all of raw materials of this study, which suitable for combusting without SO_2. A PET sample had the highest ratio of C/H as 12.7 and other biomass raw materials resulted as TS (C/H = 7.52), ES (7.04), and CC (6.72) (Table 1). In addition, values of HHV and LHV of PET were 18.52 and 17.82 MJ/kg, TS were 19.56 and 18.03 MJ/kg, ES were 18.41 and 16.92 MJ/kg, and CC were 17.95 and 16.42 MJ/kg, respectively. Moreover, the experimental results indicated that PET waste could provide an energy-rich portion for composite pellets and suitable for thermo-chemical conversion process.

Pelletizing of PET-biomass composite

PET/TS, PET/ES, and PET/CC pellets produced by hydraulic press machine at the condition of 100 kg/cm^2 of hydraulic pressure,

Table 1 Proximate and ultimate analysis of raw materials

Test	Properties of materials			
	PET	TS	ES	CC
Proximate (%)				
MC	1.09	7.42	8.35	5.51
Ash	7.17	3.46	1.47	2.22
VM	91.77	89.12	90.18	92.27
Ultimate (%)				
C	38.41	47.58	44.22	42.91
H	3.02	6.32	6.28	6.39
N	0.08	0.06	0.16	0.27
O	21.54	51.56	51.56	50.41
S	ND	ND	ND	ND
C/H	12.7	7.52	7.04	6.72
O/C	0.56	1.08	1.12	1.17
HHV (MJ/kg) [a]	18.52	19.56	18.41	17.95
LHV (MJ/kg) [a]	17.82	18.03	16.92	16.42

ND: not detected, MC: moisture content, Ash: ash content, VM: volatile matter, HHV: Higher heating value, LHV: Lower heating value, and [a]The values of HHV and LHV were calculated according to the formula of Nhuchhen and Afzal, 2017 [8].

100 °C of temperature, and 2 min of press time. Pellets dimension had the length of 2.4 cm and 0.8 cm of diameter (an average pellets density of 1.66 g/cm^3) with an average weight of 2 g per piece. Figure 2 shows the non-torrefied and torrefied pellets with different compositions of biomass. TS, ES, and CC portions of pellets were illustrated different colors from dark brown to light brown. After torrefaction process at 225 °C, for 10 min and 1 L/min of airflow rate under vacuum condition. The determination of physical abilities of pellets revealed that torrefaction of pellets increased durability of pellets body resulted by DSI values as seen in Table 2. High heating values (HHV) of PET-biomass composite pellets were determined by bomb calorimetric technique. The results indicated that torrefaction decreased HHV values of all samples. The reduction of HHV might be induced by the releasing of volatile matter and organic components during torrefaction. Whereas, the durability of pellets increased in DSI values because PET melted and formed in terms of adhesive inside the pellets. This also indicated strong adhesion between PET and biomass. However, in the case of torrefied biomass prior pelletizing with plastics resulted in inconsistent with this study. Chiou et al., 2015 [9] reported that the torrefied biomass composition with polypropylene (PP) had negative results in tensile strength and elongation at break values. The addition of weak adhesive material such as the torrefied biomass caused debonding to occur at the interface between filler and polymer matrix.

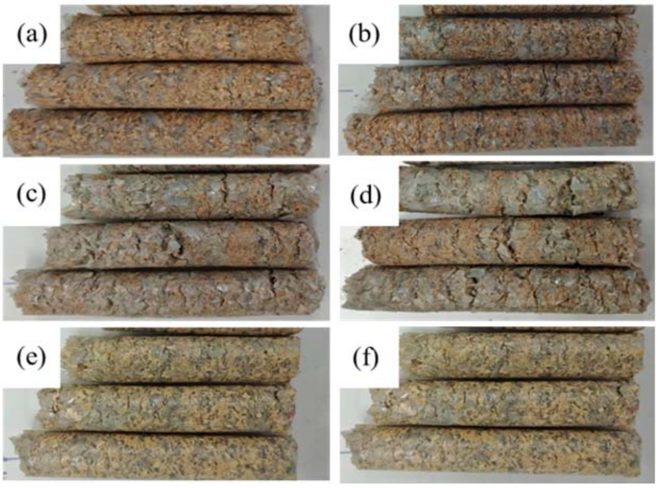

Figure 2 Non-torrefied and torrefied pellets of (a, b) PET/TS, (c, d) PET/ES, and (e, f) PET/CC

Table 2 Characterization of non-torrefied and torrefied PET-biomass composite pellets

Pellets	Test	Non-torrefied pellets	Torrefied pellets
PET/TS	HHV [a] DSI	22.38 0.9988	21.86 0.9999
PET/ES	HHV [a] DSI	22.20 0.9976	21.60 0.9994
PET/CC	HHV [a] DSI	21.84 0.9974	21.68 0.9997

[a] *HHV (MJ/kg) analyzed by a bomb calorimeter., DSI : Drop shatter index ($\geq$ 0.95)*

Flue gas emitted during combustion

Flue gas emitted during combustion of PET-biomass composite pellets tested in the lab-scale fixed bed combustor is shown in Table 3. Flue gas including O_2, CO_2, CO, NOx, and SO_2 was analyzed. Prior fuel pellets were feeding into the combustor, O_2 concentration showed stabilized result about 20 ± 2%. After feeding the fuel pellets, O_2 emitted from the combustion of non-torrefied pellets and torrefied pellets were in the ranges of 4.71-9.90 and 8.14-11.85%, respectively. Emission of SO_2 was none due to the original materials had no sulfur content. Gases including CO_2, CO, and NOx were decreased in the tests of torrefied PET/CC pellets. However, the results of CO_2 and CO were unstable in the overall period of the operation time. CO concentration emitted over the threshold limitation of the standard because of the effect of incomplete combustion during the tests. Concentration of CO emission was in the ranges of 2,941-12,337 ppm. The limitation of

Table 3 Flue gas analysis of pellets combustion

Sample	Time (min)	Non-torrefied pellets			Torrefied pellets		
		CO_2 (%)	CO (ppm)	NOx (ppm)	CO_2 (%)	CO (ppm)	NOx (ppm)
PET/TS	5-10	3.55	2,614	289	2.25	6,661	152
	15-20	2.54	4,772	106	2.34	12,220	144
	25-30	5.50	1,436	220	3.87	10,364	81
	Average	3.86	2,941	205	2.82	9,748	126
PET/ES	5-10	1.92	1,135	69	4.09	11,587	148
	15-20	8.09	14,579	47	2.32	11,312	141
	25-30	4.66	5,410	108	3.46	14,111	65
	Average	4.89	7,041	75	3.29	12,337	118
PET/CC	5-10	9.91	10,603	76	1.19	1,175	56
	15-20	2.76	15,361	47	3.98	12,813	70
	25-30	6.60	1,501	133	0.91	1,502	61
	Average	6.42	9,155	85	2.03	5,163	52

this study was operated in the lab-scale fixed-bed reactor which was not preferred owing to the short residence time of flue gas inside a reactor, bad mixing condition, and low combustion efficiency. Nevertheless, NOx emissions were in the ranges of 52-205 ppm that as the result of fuel-N for NOx formation during the tests. For NOx remaining in flue gas emitted by the production of torrefied pellets (PET/TS, PET/ES, and PET/CC), it might be noticed that torrefaction could not completely eliminate fuel-N in the composite pellets. Otherwise, some portions in the composite pellets such as substances with low-temperature of volatilization could be eliminated under the process of torrefaction [7].

Emissions of PAHs and BTEX

Figure 3(a) illustrates emissions of PAHs concentration from combustion tests of the non-torrefied and torrefied PET/TS, PET/ES, and PET/CC. Total concentration of PAHs in non-torrefied pellets and torrefied pellets of PET/TS, PET/ES, and PET/CC were 8.85 and 0.07, 2.34 and 0.03, and 6.46 and 6.45 g/Nm^3, respectively. Phenanthrene was the highest pollutants found in samples of non-torrefied PET/TS, PET/ES, and PET/CC shown by the results of 3.57, 0.86, and 2.24 g/Nm^3, respectively, and followed by Pyrene > Anthracene > Fluorene > Acenaphthylene > Benzo (a) anthracene, Chrysene, Benzo (b) fluoranthene, Benzo (k) fluoranthene, Benzo (a) pyrene, Dibenz (a,h) anthracene, Benzo (g,h,i) perylene, and Indeno (1,2,3-cd) pyrene. Combustion test of the torrefied pellets of PET/TS and PET/ES presented the reduction of PAHs emissions compared to the tests of non-torrefied with the results of the total concentration of 0.07 and 0.03 g/Nm^3, respectively. Combustion test of the torrefied pellets of PET/CC indicted the emissions of PAHs with the total concentrations of 6.45 g/Nm^3. It was similar to the results of non-torrefied pellets of PET/CC but

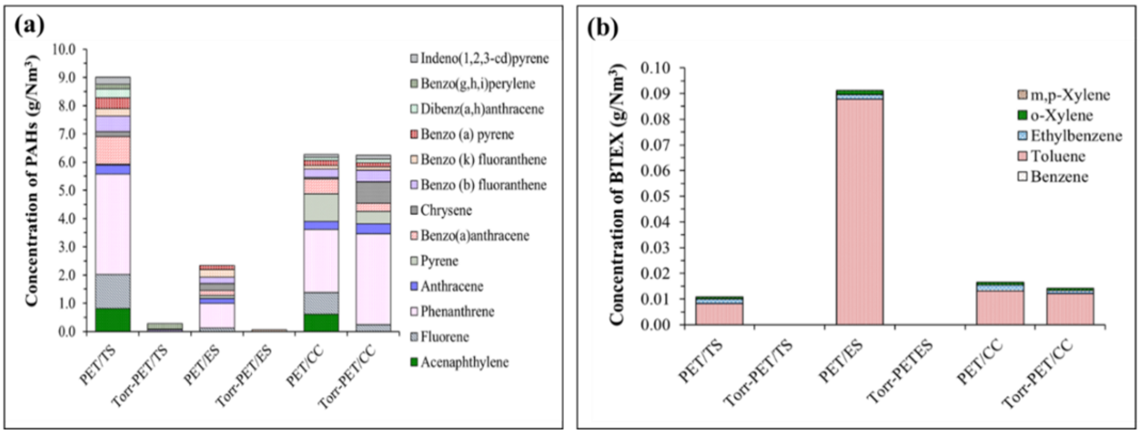

Figure 3 Concentrations of (a) PAHs and (b) BTEX emissions of pellets combustion

emission of Phenanthrene was higher than the torrefied pellets of PET/CC. In regard with the physical and chemical properties of corncob (raw material), it had no significant change at low temperature of torrefaction at about 225 °C and 10 min of residence time. This result was similar to Kanwal et al., 2019 [10] finding that there was no significant improvement in the physical and chemical characteristics of the torrefied corncob at low-torrefy temperatures of 200-225 °C.

The highest value of BTEX emission was found in the tests of non-torrefied pellets of PET/ES with the total concentration of 0.09 g/Nm^3 as seen in Figure 3(b). The tests of non-torrefied pellets of PET/CC and PET/TS were in the range of 0.02 and 0.01 g/Nm^3, respectively. For the tests of torrefied pellets of PET/TS and PET/ES, BTEX emission were not detected, while the test of torrefied pellets of PET/CC BTEX emission was slightly decreased to 0.01 g/Nm^3. The previous study reported that process of torrefaction played a role in decomposition of monocyclic aromatic hydrocarbons such as phenolic compounds from cellulose fiber. Torrefaction has the potential to increase the relative content of BTX compounds. However, the total values of BTX compounds decreased with the increase in torrefaction severity [11].

Conclusion

Pelletizing of PET waste with biomass was a good process for handling powder-like materials such as sludge, debris, tiny pieces of PET, dust, and micro-plastic as well as agricultural wastes i.e. sawdust to be a waste-to-energy challenge. The increasing of HHV occurred after pelletizing process and improved the properties of fuel pellets as well as PET-biomass composite pellets suitable for thermo-chemical conversion process. Torrefaction influenced physical properties of composite pellets by enhancing the durability of pellets and increased a value of DSI. Moreover, torrefy temperature at 225 °C played a role on PET melted and formed in terms of adhesive inside the pellets. The combustion tests of the torrefied PET-biomass composite pellets showed a significant in the alteration of gaseous emissions by reducing pollutants. The torrefied PET-biomass composite pellets could be utilized as a primary or secondary fuel sources in the stationary combustor with lower CO, NOx, and CO_2 emissions. In addition, the experimental results indicated that each test could not be detected emission of SO_2 due to the original materials had no sulfur content. The lower gaseous pollutants such as PAHs and BTEX had been found in all tests of the torrefied PET-biomass composite pellets.

Acknowledgments

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