

9-1-2016

# Pyrolysis of Dried Wastewater Biosolids Can Be Energy Positive

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# Pyrolysis of Dried Wastewater Biosolids Can Be Energy Positive

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**ABSTRACT:** Pyrolysis is a thermal process that converts biosolids into biochar (a soil amendment), py-oil and py-gas, which can be energy sources. The objectives of this research were to determine the product yield of dried biosolids during pyrolysis and the energy requirements of pyrolysis. Bench-scale experiments revealed that temperature increases up to 500 °C substantially decreased the fraction of biochar and increased the fraction of py-oil. Py-gas yield increased above 500 °C. The energy required for pyrolysis was approximately 5-fold less than the energy required to dry biosolids (depending on biosolids moisture content), indicating that, if a utility already uses energy to dry biosolids, then pyrolysis does not require a substantial amount of energy. However, if a utility produces wet biosolids, then implementing pyrolysis may be costly because of the energy required to dry the biosolids. The energy content of py-gas and py-oil was always greater than the energy required for pyrolysis. *Water Environ. Res.*, **88**, 804 (2016).

**KEYWORDS:** biochar, bio-oil, py-gas, enthalpy, sustainability, water resource reclamation facilities, wastewater treatment, drying, biosolids handling.

doi:10.2175/106143016X14609975747441

## Introduction

Biosolids are a potential resource produced throughout the world at water resource recovery facilities (WRRFs). In the U.S., over 7 million tons of biosolids are produced (Zerzghi et al., 2010), and over half of all biosolids are land applied (USEPA, 2012). Biosolids can be a beneficial soil amendment product that contain nutrients needed for plant growth (Hossain et al. 2011). The organic matter in biosolids also enriches soil health by replacing organic matter that is degraded over time in soil (USEPA, 2012). Of the 45% of biosolids that are not reused in the US, 63% are sent to landfills and 33% are incinerated (NEBRA, 2007). In cases where methane is not recovered at landfills from the digested solids that are further degraded to methane over longer periods of time or heat is not recovered in incinerators, discarding biosolids is a wasted energy recovery opportunity. Novel biosolids processing that yields other valuable products with low energy inputs would be beneficial (Blöcher et al. 2012; Chen et al. 2008; Shen et al. 2003).

Besides the aforementioned disposal pathways, there are many other biosolids treatment and disposal technologies in use or under development, such as thermal hydrolysis, anaerobic digestion, thermophilic digestion, hydrothermal processing, gasification, and pyrolysis (Bridle and Skrypski-Mantele, 2004; Chen et al., 2008; Lumley et al., 2014; McNamara et al., 2012). Thermal hydrolysis, hydrothermal processing, and digestion of biosolids are an intermediate processing step which cannot recover all the energy and resources or produce value added products. The remaining biosolids still require final disposal. Gasification is similar to pyrolysis in that it takes place under anoxic conditions, but gasification occurs at higher temperatures and does not yield a high quality soil-amendment product such as biochar because the biomass is converted to ash and gas (Ahmed and Gupta, 2010; Wang et al., 2008; Lee et al., 1998; Xu et al. 1998). Incineration is also a thermal processing technology that can be used for energy production, but similar to gasification, it does not yield a high quality soil-amendment product (Liu et al., 2010; Marani et al., 2003). Moreover, incineration has many emission problems such as concentration of heavy metals and toxic hydrocarbons in ash (Liu et al. 2010; Marani et al. 2003; Deng et al. 2009). Compared to incineration and gasification, biosolids pyrolysis was found to be favorable for energy savings, material recovery and materials production, providing a zero waste solution in Europe (Samolada and Zabaniotou, 2014). Even though it is difficult to judge which thermochemical disposal process is the best ultimate solution, pyrolysis could be a biosolids handling process that offers simultaneous energy recovery and production of a value-added soil amendment (Bridle and Pritchard., 2004). Pyrolysis is the decomposition of organic matter upon heating under anaerobic conditions and is typically conducted at temperatures greater than 400 °C (Laird et al., 2009; Brisolara and Qi, 2011; Yuan et al., 2013).

Pyrolysis of carbonaceous materials like biosolids produces a residual solid phase called biochar, a liquid phase that condenses upon cooling called py-oil, and a permanent gas-phase referred to as py-gas (Laird et al., 2009). Unused biosolids from WRRFs are a potential feedstock for pyrolysis which could help recover energy. All three products from pyrolysis are potentially useable. As a soil amendment, biochar can sequester carbon and be used as a beneficial soil amendment product (Laird et al., 2009; Lehmann et al., 2006). Specifically, biochar enriched with digester filtrate can improve turf-grass growth, in part because of the added ammonia and potassium that the biochar adsorbs from the filtrate (Carey et al., 2015). Biochar has been used to improve moisture holding capacity in golf greens (Major, 2010), improve crop yields for agricultural purposes (Major et al. 2010),

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and sorb metals (Wu et al., 2012). Additionally, microconstituents such as triclosan and triclocarban, which are linked to increased antibiotic resistance genes in biosolids, are removed from the biochar during pyrolysis (Ross et al., 2016; Carey et al., 2016; McNamara et al., 2014b).

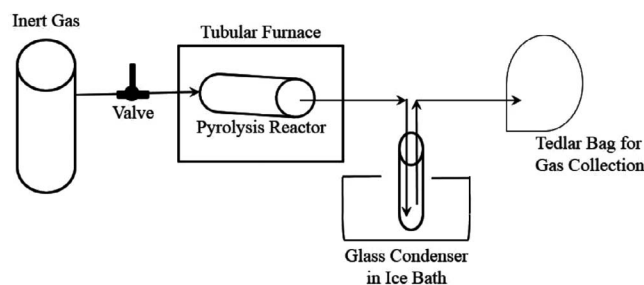
Py-oil can be burned for energy recovered in industrial boilers (Laird et al. 2009; Brammer et al., 2006; Stamatov et al., 2006). Additionally, py-oil could be added to anaerobic digesters to increase gas production if the py-oil is readily degradable and not toxic to the digester. Py-gas, which contains hydrogen ( $H_2$ ), carbon monoxide ( $CO$ ), methane ( $CH_4$ ), carbon dioxide ( $CO_2$ ) and other hydrocarbon gases, can be burned to provide energy needed to heat the pyrolysis process (Laird et al., 2009). At a pilot-scale pyrolysis plant that processes biosolids, the py-gas is also used to produce diesel fuel (Gildea, 2015). Knowing the energy recovery and requirements for pyrolysis is important to assess the feasibility of implementing pyrolysis at WRRFs.

The energy required for the pyrolysis reaction of biosolids, a.k.a. the enthalpy of pyrolysis, is not yet well known, but the enthalpy of pyrolysis for other types of biomass, which should be similar in order of magnitude, has been investigated. For example, the enthalpies of pyrolysis for oat hulls and pine wood, on a dry basis, are  $0.78 \pm 0.20$  MJ/kg and  $1.64 \pm 0.33$  MJ/kg, respectively (Daugaard and Brown, 2003). For pyrolysis of wastewater sludges, between 0.708 and 1.18 MJ/kg were required to heat the sludge from room temperature to  $550^\circ C$  (Hossain et al., 2009). For one of the three sludge samples investigated by Hossain et al. (2009), the energy content in the py-gas was greater than the energy required to heat the sample. Depending on the sludge characteristics and pyrolysis conditions, the py-gas may provide sufficient energy for the pyrolysis reaction, but more work needs to be performed to confirm this belief. To the best of our knowledge, the enthalpy of pyrolysis for municipal wastewater biosolids has not been defined, and therefore, the energy requirements for pyrolysis have not been sufficiently determined. In addition to pyrolysis energy requirements, WRRF's will have to consider the energy required to dry their biosolids in preparation for pyrolysis, a hurdle which may be prohibitory from an energy cost standpoint.

The objectives of this research were to determine the product yields following pyrolysis of heat-dried biosolids and the energy requirements of pyrolysis (enthalpy of pyrolysis) relative to drying energy requirements. It was expected that energy demand for drying wet biosolids would be substantial relative to the pyrolysis energy demand. The decision to implement pyrolysis would be greatly influenced by the type of biosolids being produced (wet vs. dry). The drying energy requirements were calculated to help determine what the total energy demand would be to implement pyrolysis for a utility that produces wet biosolids since drying before or during pyrolysis is necessary. Lab-scale pyrolysis experiments were performed on heat-dried biosolids, and solid, liquid, and gas product yields and associated energy contents were quantified.

## Materials and Methods

**Lab-scale Experiments.** Pyrolysis experiments were performed in a batch pyrolysis reactor, and products were collected for quantification (see Figure 1 for schematic of experimental setup). The stainless steel cylindrical pyrolysis reactor had a diameter of 8.89 cm (3.5 inches) and height of 25.4 cm (10 inches) with an internal volume of 1.57 L (96 cubic inches). The

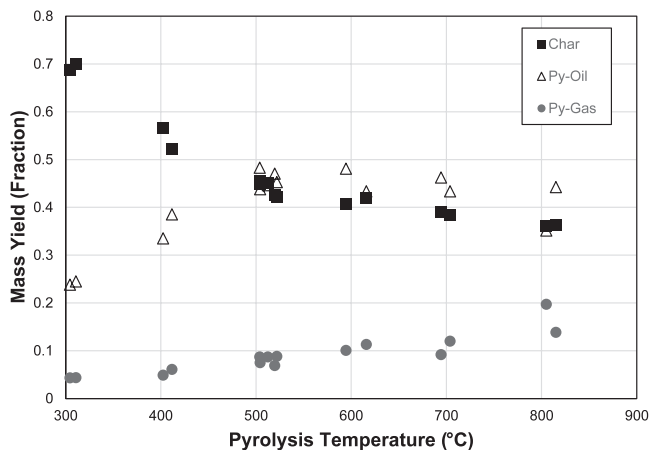


**Figure 1—Schematic of experimental setup. Inert gas was used to flush the system and remove the oxygen prior to running the furnace and pyrolyzing the 100 g of biosolids. Produced vapors exited the reactor and were separated into condensable (at  $0^\circ C$ ) and non-condensable fractions.**

reactor was housed in a temperature-controlled tubular furnace (model 55642, Thermo Fisher Scientific, Waltham MA), and rested at an angle of  $14^\circ$  from the furnace floor. Compressed, inert gas cylinders were connected to the pyrolysis reactor by copper and stainless steel tubing. After initial reactor gas flushing, a valve was closed between the reactor and the gas cylinder and produced vapors flowed towards a glass condenser comprised of a gas washing bottle housed in an ice bath. Stainless steel tubing (extending from inside the furnace to outside the furnace), copper tubing (connected to a hose barb), and santoprene tubing (connecting hose barb to glass gas washing bottle) were used to carry product vapors from the pyrolysis reactor to the condenser. Non-condensable, permanent gas (py-gas) flowed through the santoprene tubing from the condenser to Tedlar® bags (Zefon International, Ocala, FL) for gas collection, whereas condensable vapors (py-oil) remained in the glass gas washing bottle and to a lesser extent, in the tubing.

Heat dried biosolids (Milorganite®) produced from a blend of anaerobically digested primary sludge and raw waste activated sludge from the Milwaukee Metropolitan Sewerage District (MMSD) water reclamation facilities were pyrolyzed. Approximately 100 g of biosolids (~95% solids by weight) were added to the pyrolyzer. No pyrolysis experiments on wet biosolids were conducted. The system was flushed with inert gas, either nitrogen or argon, for at least 10 minutes prior to each experimental run. Target temperatures ranged from  $300^\circ C$  to  $800^\circ C$ , and experiments lasted for at least 40 min including ramping and holding time. The complete list of ramp-rates, duration of experiment and temperatures for each experiment are shown in the supporting information, Table S1.

Biochar and py-oil yields were quantified gravimetrically following pyrolysis experiments. Gas volumes were determined using a wet test meter (Scientific Petroleum Instruments, San Antonio, TX). Gas composition was determined using gas chromatograph (GC) with a thermal conductivity detector (7890A, Agilent Technologies, Santa Clara, CA) (TCD). Argon flow was 30 mL/min, and GC inlet temperature was  $200^\circ C$ . Four GC columns in series were employed for separation (G3591-80000, G3591-80001, G3591-80002 and G3591-80003, Agilent, Santa Clara, CA). The oven temperature was initially set to  $90^\circ C$  and was held for 16.7 min. A ramp-rate of  $120^\circ C$  per min was then employed to reach  $225^\circ C$  and held for 4.7 min for a total run time of 22.5 min (McNamara et al., 2014a). Major gas products (>1% by mole fraction) included  $H_2$ ,  $CH_4$ , ethane,



**Figure 2—The effect of reactor temperature on mass yields of solid, liquid, and gas phases during slow pyrolysis.**

pentane, ethylene, CO<sub>2</sub>, and CO. N-butane and iso-butane were quantified, but were never greater than 1% of the total mole fraction. Nitrogenous gaseous compounds are typically less than 1% of total mass yield during pyrolysis of sewage sludge and therefore were not measured (Tian et al., 2013).

**Energy Balance.** Bomb calorimetry (Parr 1341, Plain Jacket Calorimeter, Parr Instrument Company, Moline, IL) was used to quantify the energy content (kJ/kg or BTU/lb) of the biosolids fed to the pyrolysis reactor, the biochar, and the py-oil. Standard bomb calorimetry protocol was followed as described elsewhere (ASTM D5865, Parr). At a pyrolysis temperature of 300 °C, the condensate had too much water content to combust in the bomb calorimeter, so chemical oxygen demand (COD) measurements were performed on these samples. A correlation between the COD and the heating value from Heidrich and Dolfig (2010) was used in place of the bomb calorimetry. The higher heating value (HHV in kJ/kg-gas mixture) of py-gas was calculated from the measured mole fractions and published heating values of constituents (Cengel and Boles, 2014). The heating value of each product was multiplied by its mass fraction within the product mixture ( $mf_i$ ) to determine the energy yield per kg of biosolids pyrolyzed (KJ/kg-biosolids).

The goal was to predict the pyrolysis conditions under which the py-gas and py-oil could be burned to theoretically provide the energy required for the pyrolysis reaction. It was thus necessary to compare the py-gas and py-oil chemical energy to the enthalpy of pyrolysis. The enthalpy of pyrolysis was calculated using an energy balance that incorporates the chemical energy (heating values) of the products and estimates of the thermodynamic properties of the char and condensate. A sketch of the relevant energy flows are shown in Figure S1. Descriptions of the measurements and assumptions used to determine the enthalpy of pyrolysis,  $h_p$  (MJ/kg of biosolids), are represented mathematically by eq 1. The heating values (HHV) were determined as described above. The necessary sensible and latent enthalpy changes were estimated between the reference temperature,  $T_{ref} = 25$  °C, which was assumed to be the biosolid reactant temperature, and the product temperature,  $T$  (the temperature of the reactor). For the char, an average heat capacity of  $c_{p, char} = 1.0$  kJ/(kg K) (based on softwood charcoal) was used (Gupta et al., 2003) to determine the sensible enthalpy

change. For the gases, the sensible enthalpy change was calculated from temperature-dependent heat capacities (Cengel and Boles, 2014). The enthalpy change of the py-oil ( $h - h_{ref}$ )<sub>oil</sub> between the reference and product temperature was calculated from the properties of petroleum with a specific gravity of 0.95 (United States Bureau of Standards, 1929); it includes both sensible and latent enthalpy changes.

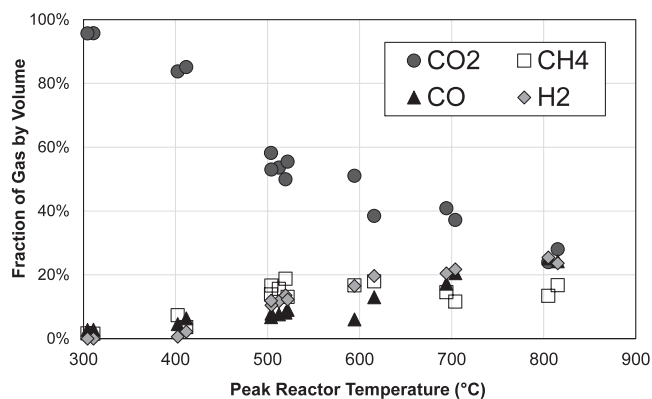
$$h_p = mf_{char} [HHV_{char} + c_{p, char} (T - T_{ref})] + mf_{oil} [HHV_{oil} + (h - h_{ref})_{oil}] + \sum_{pygases} mf_i \left[ HHV_i + \int_{T_{ref}}^T c_{p,i} dT \right] - HHV_{biosolid} \quad (1)$$

## Results and Discussion

**Product Yields from Pyrolysis of Biosolids.** Temperature impacted yields of all three products. Increasing the temperature from 300 °C to 500 °C greatly reduced biochar yield, but increasing the temperature beyond 500 °C resulted in only minor losses of biochar (Figure 2). Inguanzo et al. (2002) also observed slight decreases in biochar, from 45% down to 40% yield, as temperature increased from 450 °C to 850 °C. Conversely, py-oil yield increased substantially from 300 °C to 500 °C, and then plateaued as temperature increased from 500 °C to 800 °C. The constant py-oil yield, but decreasing biochar yield at higher temperatures was balanced by a constant increase in py-gas yield as pyrolysis temperature increased. The product yields observed in this study were in line with yields observed in previous sewage sludge pyrolysis studies. In a pilot-scale, continuous feed system operated at 450 °C, the py-gas yield was 14%, the char yield was 43%, and the py-oil yield was 43% by mass (Bridle & Skryski-Mantele, 2004). In our study the py-oil and char yields were nearly the same fraction at 500 °C. Hossain et al. (2009) found that, at 550 °C, the char yield was 64%, the py-oil yield was 30.4%, and the py-gas yield was only 5.6%. In their experiments the reactions were stopped once pyrolysis temperature was reached, whereas in our experiments the temperature was typically held for at least 30 minutes allowing for greater reduction of biochar yield. Ostensibly, reaction time, along with reaction temperature, plays an important role in determining product yields.

Temperature also had a large impact on the composition of py-gas. As temperature increased, the molar fraction of CO<sub>2</sub> continually decreased and the molar fraction of CO continually increased (Figure 3). The molar fraction of CH<sub>4</sub> peaked at 500 °C and then remained relatively constant as temperature was increased. H<sub>2</sub> was not a significant fraction of the gas below 500 °C, but at temperatures of 500 °C and higher, the H<sub>2</sub> concentrations increased. Similarly, Inguanzo et al. (2002) observed that H<sub>2</sub> concentration substantially increased at temperatures above 450 °C, and CO<sub>2</sub> decreased as temperature increased from 350 °C to 800 °C.

Pyrolysis temperature greatly impacted the quantity of py-gas produced, but did not impact the energy content on a per-volume of gas basis above 500 °C. The energy content of the py-gas approximately tripled as temperature increased from 400 °C to 500 °C (Figure 4a). The py-gas energy content was essentially unchanged as temperature increased to 800 °C, and had a heating value that was approximately 70% of the heating value of municipal anaerobic digester biogas comprised of 60% CH<sub>4</sub> and 40% CO<sub>2</sub>. Even though the energy content on a volumetric basis

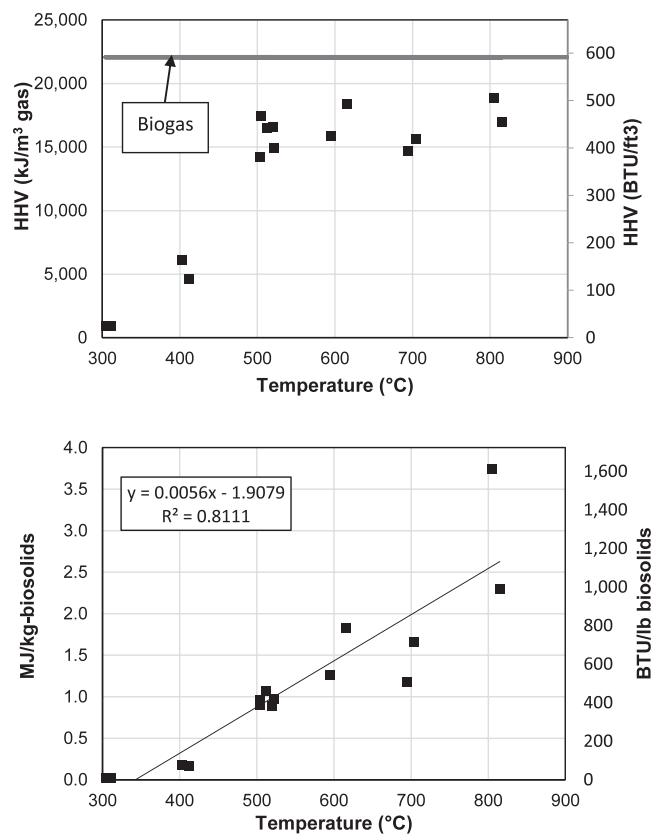


**Figure 3—The impact of reactor temperature on gas composition of CO<sub>2</sub>, CO, CH<sub>4</sub>, and H<sub>2</sub>. Values represent volumetric fraction of gas. The complete data set for gas composition including gases that are less than 5% of volumetric composition are shown in Supporting Information, Table S2.**

plateaued as temperatures increased above 500 °C, the net energy available in the form of py-gas increased linearly as temperature increased because more py-gas was being produced (Figure 4b).

**Energy Costs of Pyrolysis.** The theoretical energy cost of pyrolysis is the thermal energy input required to execute the process. Thermodynamically, the cost can be divided into three types of internal energy: sensible, latent, and chemical. Starting with ambient biosolids, thermal energy input initially raises the temperature and drives water out of the solids; the water evaporation constitutes the bulk of the drying energy cost. The enthalpy of vaporization of water is 2.26 MJ/kg at 100 °C whereas the change in sensible enthalpy of water is only around 0.33 MJ/kg between 20 °C and 100 °C. In typical dryers with non-unity efficiency, the drying process costs about 3.4 MJ per kilogram of removed water. Drying is considered largely complete as the solids begin to exceed the boiling point of water, nominally around 110 °C in an atmospheric pressure reactor. With continued energy addition, the temperature continues to rise, leading to chemical decomposition of the organic matter and the creation and evaporation of additional compounds that become the products of the pyrolysis process. It is this extra energy in addition to the drying cost that must be quantified to better understand the prospects of pyrolysis. Using dried biosolids as a reactant, the sensible, latent, and chemical energy requirements to heat and transform the solids into py-gas, py-oil, and biochar at a high product temperature is how we define the enthalpy of pyrolysis, *i.e.*, the energy required for the pyrolysis reaction to take place *after* drying.

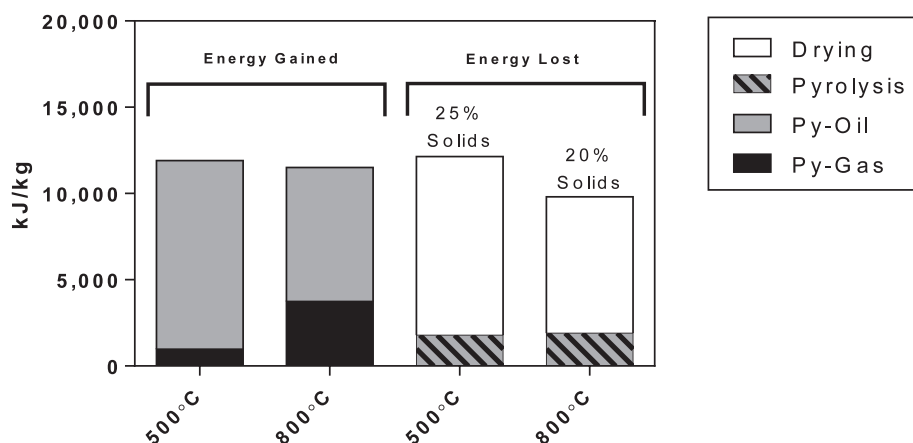
The enthalpy of pyrolysis for biosolids was calculated as the difference between the energy outputs (heating values of char, py-oil, py-gas plus sensible and latent heat losses) and the energy input (heating value of the biosolids feed); a graph of these values is shown in Figure S2. The enthalpy of pyrolysis ranged from  $-2.1$  MJ/kg-feed biosolids to  $3.0$  MJ/kg-feed biosolids; this variability is due to experimental variation. The average enthalpy of pyrolysis value ( $n = 11$ ) was  $0.083$  MJ/kg and the standard deviation was  $1.9$  MJ/kg (see Supporting Information, Table S3 for a list of all enthalpy values). The enthalpy of pyrolysis is not clearly endothermic (positive) or exothermic (negative). Indeed,



**Figure 4—(top) The impact of temperature on the energy content of py-gas based on volume of gas at 20 °C and 1 atm. Black squares are experimental values and the red “biogas” line depicts the energy content of biogas containing 60% CH<sub>4</sub> and 40% CO<sub>2</sub>. (bottom) The impact of temperature on the total energy yield in the form of py-gas.**

Hossain et al. (2009) reported that biosolids pyrolysis was endothermic under 300 °C, and either endothermic or exothermic as temperatures increased depending on the type of biosolids. The average enthalpy of pyrolysis values of oat hulls and pine ranged from  $0.78$  to  $1.64$  MJ/kg which is the same order of magnitude as the results observed in this biosolids work (Daugaard and Brown, 2003).

The enthalpy of pyrolysis is not a substantial energy cost compared to the energy requirements of biosolids drying. The energy content of the py-gas was greater than the enthalpy of pyrolysis in eight of the eleven experiments (Supporting Information, Table S3). A much larger fraction of energy was available in the py-oil compared to the py-gas (Figure 5). If only energy requirements for drying and pyrolysis are considered, and assuming the biosolids are either 20 or 25% solids after dewatering processes, then drying energy constitutes more than 70% of the combined drying and pyrolysis energy requirements. As seen in Figure 5, if a utility dewateres their biosolids to  $>25\%$  solids, then pyrolysis could recover some additional energy because the most energy intensive step, drying, is already occurring. The additional energy required for the pyrolysis of dried biosolids is very low compared to the energy content of the py-gas and py-oil.



**Figure 5—The energy available in py-gas and py-oil can offset the energy required for pyrolysis, but the energy required for drying is much greater than energy required for pyrolysis. The moisture content has a substantial impact on the energy required for biosolids drying. If a WRRF already dries their biosolids then pyrolysis could off-set energy drying costs by recovering energy from py-gas and py-oil. Additional energy could be recovered by using a heat exchanger to capture sensible and latent heat losses.**

## Conclusions

Biosolids pyrolysis has potential to contribute to future sustainability plans of WRRFs because it produces 1) energy sources in py-gas and py-oil, and 2) biochar which can be land-applied as a soil amendment and simultaneously contribute towards carbon sequestration. In fact, carbon from biochar can have a residence time greater than 1000 years when applied to soils (Singh et al., 2012). For WRRFs that produce dried biosolids, pyrolysis may be a viable polishing treatment process because the energy contained in py-gas alone could off-set the energy required for pyrolysis. The energy produced from py-gas could be recovered and used to provide heat for pyrolysis and pyrolysis could be sustained by feeding dried biosolids and recycling py-gas. Additionally, py-oil contains energy that could be sold or recovered for internal use. For WRRFs that do not dry their biosolids, implementing pyrolysis could be costly from an energy standpoint because the energy contained in py-gas and py-oil would have to be completely recovered to off-set the added energy requirements for drying. In other words, the energy required for pyrolysis is minimal compared to the energy required for drying biosolids. In addition to energy considerations, the value of biochar as a marketable product will vary widely and should be assessed for each WRRF. More research should be conducted to specifically determine how biochar derived from wastewater biosolids, as opposed to other sources of biomass, can impact crop yields, soil moisture holding capacity, and retention of nutrients.

## Acknowledgements

This work was funded by the Milwaukee Metropolitan Sewerage District. We appreciate the laboratory assistance provided by Kevin Berg and Jack Lawinger.

*Submitted for publication August 14, 2015; revised manuscript submitted January 14, 2016; accepted for publication January 31, 2016.*

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## Supporting Information

**Table S1—Experimental Parameters.**

Nominal temp (°C)	Avg temp (°C)	Ramp rate (°C/min)	Duration (min)
500	504	7	97
800	815	10	106
500	512	11	82
500	520	12	76
700	694	13	85
700	704	17	75
300	304	18	96
600	616	20	67
500	522	21	40
300	311	24	88
600	594	32	42
600	594	32	42
400	402	37	40
400	412	40	44
800	805	40	51
500	504	NA	NA

**Table S2—Volumetric Composition of Py-Gas.**

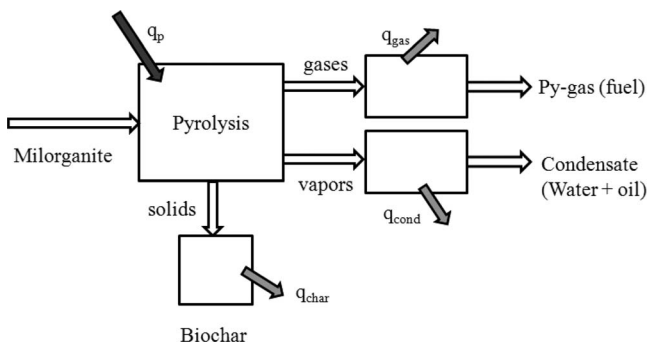
Avg temp (°C)	Ramp rate (°C/min)	Duration (min)	Hydrogen	Propane	iso-butane	n-Butane	Carbon dioxide	Ethane	Ethylene	Methane	Carbon monoxide
311	24	88	0.000	0.000	0.000	0.000	0.957	0.000	0.000	0.015	0.027
304	18	96	0.000	0.000	0.000	0.000	0.957	0.000	0.000	0.016	0.027
402	37	40	0.006	0.012	0.000	0.000	0.837	0.026	0.000	0.073	0.045
412	40	44	0.022	0.020	0.000	0.000	0.851	0.006	0.002	0.036	0.063
504	NA	NA	0.118	0.032	0.003	0.000	0.582	0.044	0.015	0.138	0.067
522	21	40	0.122	0.033	0.002	0.003	0.555	0.042	0.022	0.131	0.090
594	32	42	0.165	0.038	0.000	0.000	0.510	0.027	0.033	0.166	0.060
694	13	85	0.000	0.000	0.000	0.000	0.400	0.000	0.000	0.600	0.000
704	17	75	0.217	0.026	0.000	0.000	0.372	0.040	0.024	0.116	0.205
815	10	106	0.236	0.020	0.000	0.000	0.280	0.035	0.019	0.167	0.242
805	40	51	0.254	0.024	0.000	0.000	0.239	0.033	0.064	0.134	0.251

**Table S3—Product Yields and Enthalpy of Pyrolysis from Batch Pyrolysis Experiments.**

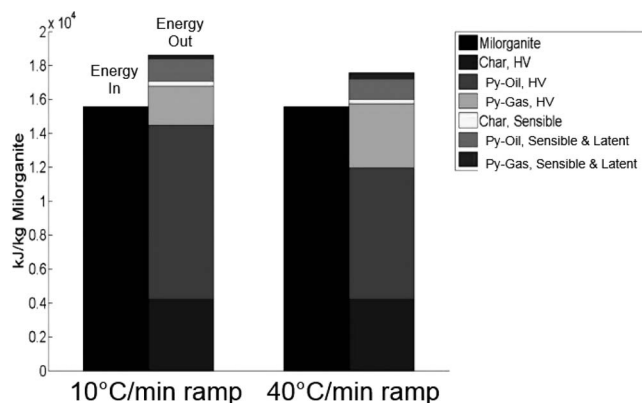
Avg temp (°C)	Ramp rate (°C/min)	Duration (min)	Gas energy yield (kJ/kg-fuel)	Oil energy yield (kJ/kg-fuel)	Char energy yield (kJ/kg-fuel)	Enthalpy of pyrolysis (kJ/kg-fuel)
311	24	88	22	1042	12 711	-990
304	18	96	22	1589	13 057	-168
402	37	40	177	3935	9099	-1266
412	40	44	166	4522	8385	-1366
504	NA	NA	902	10 733	5636	3048
522	21	40	969	10 939	5078	1790
594	32	42	1267	5779	4910	-2125
694	13	85	1802	6178	4850	-1126
704	17	75	1652	5790	4775	-1776
815	10	106	2297	9764	4237	2998
805	40	51	3745	7762	4209	1901

**Table S4—Chemical Oxygen Demand (COD) in mg/L of Py-Oil Produced at 300 °C.**

Sample number	COD
1	320 000
2	470 000



**Figure S1—Relevant heat flows during pyrolysis of biosolids. Red arrow indicates heat required and blue arrows indicate heat released.**



**Figure S2—Example energy contents before and after pyrolysis of biosolids. The set of bars on the left hand side are for one pyrolysis experiment at 800 °C at 10 °C/min ramp-rate. The set of bars on the right hand side of the plot are for one pyrolysis experiment at 800 °C at 40 °C/min ramp-rate. The left bar for each set represents energy content of the feed, i.e. biosolids. The right bar for each set represents the energy content of the products (biochar, py-oil, py-gas) and sensible and latent heat losses. The difference between the left bar and right bar is the energy cost of pyrolysis, i.e. enthalpy of pyrolysis.**