



Slow pyrolysis of organic fraction of municipal solid waste (OFMSW): Characterisation of products and screening of the aqueous liquid product for anaerobic digestion



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HIGHLIGHTS

- Slow pyrolysis and anaerobic digestion were integrated for energy recovery from waste.
- Aqueous pyrolysis liquids produced from OFMSW were screened in AD trials.
- Pyrolysis temperature was key factor for liquid yield, energy content, toxicity and COD.
- Organic pyrolysis liquids contain 18.9–63.0% of the product energy.
- Aqueous product contains 1.2–13.1% of product energy and about 50% convertible to CH₄.

ARTICLE INFO

Keywords:

Municipal solid waste
Slow pyrolysis
Anaerobic digestion
Aqueous fraction of pyrolysis liquid
Toxicity assay
Statistical analysis

ABSTRACT

A comprehensive study of the energy yield from slow pyrolysis of the organic fraction of municipal solid waste (OFMSW) and energy recovery from the aqueous liquid product by anaerobic digestion has been carried out. In this paper, the results of the liquid pyrolysis product characterisation are presented, with toxicity and methane potential assessments of the aqueous liquid product. The OFMSW feedstock was obtained from a UK waste treatment plant. Shredded samples dried to different moisture contents (12.7–45.8%) were processed in a 300 g per hour auger screw pyrolysis reactor at temperatures from 450 to 850 °C. Sixteen pyrolysis runs were performed, with process mass balance closures above 90% obtained (wet feed basis). Pyrolysis liquids showed clear phase separation under gravity. With increasing processing temperature, the liquid yield (both organic and aqueous fraction) reduced but the gas yield increased. An investigation into the product energy distribution indicated that processing temperature had a strong effect on the product energy distribution, while the effect of feedstock moisture was relatively small. Batch anaerobic testing of the aqueous fraction showed that toxicity increased with pyrolysis processing temperature and decreased with feedstock moisture content. Statistical analysis confirmed that the pyrolysis processing temperature was the dominant factor affecting the toxicity of the aqueous product. Careful acclimatisation of the microbial consortium to the applied substrate and loading is likely to be necessary for improved digestion of the aqueous fraction.

1. Introduction

Over the past 20 years, the focus of waste management in EU countries has increasingly moved from disposal to prevention, reuse or recycling, or recovery. This has led to a fall in the proportion of municipal solid waste (MSW) sent to landfill from 64% in 1995 to 25% in

2015, with a corresponding increase for alternative approaches [1]. Energy recovery through waste-to-energy processes has contributed to this change and, although it has low priority in the waste management hierarchy, it can provide an effective means of organic waste treatment, sustainable energy generation and resource recovery. Across the EU, an average of 26.6% municipal waste generated in 2015 was incinerated

Abbreviations: AD, anaerobic digestion; ANOVA, analysis of variance; ASTM, American Society for Testing and Materials; cnSMP, cumulative net specific methane production; COD, chemical oxygen demand; DCL, dichlorophenol; EC50, half maximal effective concentration; FID, flame ionisation detector; GC-MS, gas chromatograph–mass spectrometer; HTC, hydrothermal carbonisation; ICP, inductively coupled plasma; KF, Karl Fischer; OFMSW, organic fraction of municipal solid waste; TGA, thermogravimetric analysis; TS, total solids; VOC, volatile organic compound; VS, volatile solids; WW, wet weight

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<https://doi.org/10.1016/j.apenergy.2018.01.018>

Received 15 November 2017; Received in revised form 3 January 2018; Accepted 5 January 2018

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and 16.6% was biologically treated: both processing methods increased by over 10% compared to 1995 levels [1]. In many cases, however, this total processing capacity is in the form of conventional incineration or aerobic biological treatment: while highly effective at stabilising organic matter, these systems may not maximise the energy and resource recovery potential [2,3]. Considerable research and industrial development is therefore currently focused on seeking more efficient and sustainable processing methods with higher value products to meet the anticipated growth in the EU's waste processing market and maximise the benefits of waste conversion [4].

Pyrolysis is a thermochemical conversion process that has been widely used for centuries in the manufacture of charcoal. More recently, it has been the subject of extensive research as a means of processing organic waste for energy recovery, and in particular for converting solid biomass into valuable liquid and gaseous biofuels as well as charcoal [5–7]. Pyrolysis is thermal decomposition occurring in the absence of oxygen. Organic materials are converted to form liquid, gaseous and solid products that can be used as chemicals, biochar and biofuels which may require upgrading to minimise emissions of hazardous gases (e.g. nitrogen and sulphur oxides) and particulates [5,8]. Pyrolysis processes include fast pyrolysis that employs a high heating rate, short hot vapour residence time and rapid vapour cooling to maximise liquid yield; and slow pyrolysis that employs a relatively slow heating rate and long residence time to maximise the solid product. In contrast, anaerobic digestion (AD) is a biological process that is particularly suitable for wet wastes and produces biogas (a mixture of CO₂ and methane) with a semi-solid residue digestate. It has seen increasingly widespread adoption in recent years for the treatment of source segregated organic wastes due to the recovery of a valuable fuel gas and the environmental benefits associated with the process [9], including use of the digestate which may have value as a source of plant nutrients [10].

Linking pyrolysis and AD in an integrated waste treatment process is interesting, as this may offer a means of valorising unusable by-products from the upstream process in the downstream process, potentially increasing the overall energy yield [11–14] and the opportunities for energy recovery from waste. An example is recovery of energy from the aqueous fraction of the pyrolysis liquid which might otherwise be lost or even incur a disposal cost. Recently, some pioneering work has addressed this topic. Hubner and Mumme [15] studied the AD of aqueous products from slow pyrolysis of digestate in a bench-scale rotary kiln reactor. The AD experiments were carried out in mesophilic conditions (40.5 °C) in batch tests with durations of 49–69 days using an unadapted inoculum and initial values of substrate chemical oxygen demand (COD) from 3 to 30 g L⁻¹. This work claimed that most of the volatile organic compounds (VOCs) in the liquid samples, such as levoglucosan, furfural and phenol, could be converted into biogas without the addition of biochar. Initial COD concentrations up to 12 g L⁻¹ were tolerated and COD removal rates of up to 63% were achieved. Liquid samples from lower pyrolysis temperatures (330–430 °C) performed better than those from higher temperatures in terms of COD degradation. Torri and Fabbri [16] investigated the AD of aqueous product from the slow pyrolysis of cornstalk at 400 °C in a fixed bed reactor. AD tests were carried out in 100 mL syringe reactors for micro-batch and semi-continuous tests. Biomethane production was observed, but the methane yield was low at 34% of the theoretical value based on COD. With addition of cornstalk char in the pyrolysis liquid, the yield of methane increased to about 60% of the theoretical value, and the biogas methane content remained stable for the 220-day test period. The authors suggested that this effect was due to the ability of porous char to reduce the toxicity of pyrolysis liquid through selective adsorption favouring the removal of more hydrophobic and toxic furans above that of the more hydrophilic and digestible sugars, which remained in the aqueous phase [17]. Apart from pyrolysis, similar work has also been conducted on linking AD and hydrothermal carbonisation (HTC), which employs water in processing with different temperature and pressure compared

to pyrolysis. Erdogan et al. [18] investigated the HTC of orange pomace and performed anaerobic batch tests on the aqueous phase of the HTC product to determine the resulting biogas and methane potential. Measurement of the COD and total organic carbon (TOC) showed that the liquid samples from higher HTC processing temperature gave lower TOC and COD concentrations. Biogas yield testing (batch fermentation) was carried out in 100 mL syringes at 42 °C for 15 days. It was found that the daily biogas production increased rapidly in the first 7 days but then decreased. The cumulative methane yields marginally decreased with increasing HTC processing temperature. In a different integration mode, Monlau et al. demonstrated the feasibility of coupling pyrolysis to AD as a downstream process. The authors claimed that integrated process could improve the overall energy recovery efficiency by 42% compared to a standalone process [19,20].

Prior to the present work, no research has been found on linking pyrolysis with downstream AD of MSW or related waste materials. This work presents the results of processing the organic fraction of municipal solid waste (OFMSW) in a slow pyrolysis system under an extensive matrix of processing conditions. All liquid, gaseous and solid products were collected and their product energy distributions were analysed. The aqueous fractions of the liquid products were tested for their anaerobic toxicity and biodegradability in batch screening tests. The overall process mass balances under various processing conditions were determined and evaluated. Statistical analysis was employed to assess the effect of processing condition on the process mass balance, product energy distribution and the results of AD screening.

2. Materials and methods

2.1. Feedstock

The feedstock was obtained from Biffa Group Ltd's waste treatment plant in Leicester, UK. The original MSW was collected from households. After mechanical removal of the majority of metals, paper/cardboard, glass and plastics, the raw material mainly consists of the organic fraction of MSW (OFMSW), which comprises small pieces of biomass (wood and grass), plastics, decomposed materials (such as from food waste and paper) and inorganics including metal, ceramics, sand etc. This material was further screened and shredded to reduce its particle size to less than 10 mm for ease of use in the pyrolysis experiments. An illustration of the feedstock samples is shown in Fig. S1.

The characterisation of the as-received feedstock is shown in Table 1. It has a high moisture content (45.8 wt% as received on a wet basis) and high ash content (23.1 wt% wet basis), and the proportions of carbon and oxygen are similar at around 45% (on a dry and ash free

Table 1
Proximate and ultimate analysis of MSW feedstock.

	Unit	Value
<i>Ultimate analysis^a</i>		
C	TS%	35.1
H	TS%	4.7
N	TS%	1.4
S	TS%	0.2
O ^b	TS%	16.1
<i>Proximate analysis</i>		
Moisture ^c	wt.%	45.8
Volatiles ^d	TS%	51.1
Fixed carbon ^a	TS%	6.3
Ash content ^a	TS%	42.6
Measured HHV ^a	MJ kg ⁻¹ dry mass	15.4
Theoretical HHV ^{a,d}	MJ kg ⁻¹ dry mass	15.3

^a Presented on an oven-dried mass basis.

^b Oxygen content was calculated by difference.

^c Moisture content is presented on a wet mass basis.

^d Theoretical HHV calculated according to [24].

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