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Effect of Sawdust Addition and Composting of Feedstock on Renewable Energy and Biochar Production from Pyrolysis of Anaerobically Digested Pig Manure

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A B S T R A C T

Pyrolysis experiments were conducted on the separated solid fraction of anaerobically digested pig manure (SADPM). The aim of these experiments was to investigate the influence of (1) sawdust addition and (2) composting the feedstock, on the products of pyrolysis and on the net energy yield from the pyrolysis process. Mixtures of SADPM and sawdust were made to give the following treatments; manure only, 4:1(w/w) and 3:2(w/w). These mixtures were pyrolized at 600°C both before and after aerobic composting. The yields of the biochar, bio-liquid and gas were influenced by the addition of sawdust to the SADPM and by composting of the feedstock. With the addition of sawdust, biochar and gas higher heating values (HHV) increased, while bio-liquid HHV decreased. More than 70% of the original energy in the feedstock remained in the biochar, bio-liquid and gas after pyrolysis, increasing as the proportion of sawdust increased. The HHV of the biochar decreased, while the HHV of the bio-liquid increased, after the feedstocks were composted. The energy balance showed that increasing the rate of sawdust addition to SADPM resulted in an increased net energy yield. The addition of a composting stage increased the net energy yield for the manure only feedstock only. However, with increasing sawdust addition, composting of the feedstock reduced the net energy yield.

Keywords: pyrolysis; pig manure; energy; sawdust; biochar.

Abbreviations

SADPM:	separated anaerobically digested pig manure
NACP:	nutra ammonium citrate soluble P
WSP:	water soluble P
ABC:	acid binding capacity
BUF:	buffering capacity
TGA:	thermo gravimetric analysis

1 Introduction

In the European Union (EU), thirty percent of sows are located in a major pig production basin which stretches from Denmark, through north western Germany and the Netherlands to Vlaams Gewest in northern Belgium [1]. Pig manure in these concentrated pig farming areas has to be transported to less pig-dense areas for landspreading, thereby increasing the cost of manure handling. Landspreading legislation (Nitrates Directive, 91/676/EEC) [2] has reduced the amount of organic fertilizers which can be spread on land, increasing the cost of manure disposal. There is much interest in anaerobic digestion (AD) as a method of generating renewable energy from manures. However, AD does not reduce the nutrient content of pig manure which still needs to be recycled. One alternative to the problem of landspreading of these digested manures may be to use pyrolysis to produce renewable energy and biochar.

Pyrolysis is a process whereby a biomass feedstock, such as woodchips, crop residues or manure, is heated to high temperatures in an oxygen-free atmosphere to produce a solid (biochar), a liquid (bio-liquid) and a gaseous fraction. The proportion of biochar, bio-liquid and gas produced is dependant on the heating rate, the reactor temperature and the residence time of the reactor [3,4]. Gases and bio-liquids produced may be used to provide the energy needs for the pyrolysis process, or converted to electricity and heat. The biochar can be used as a fuel or, alternatively, applied to land as a low-grade fertilizer, soil addendum [5-8] or for carbon sequestration [9-12]. Biochar addition to soil may mitigate the negative effects of removing crop residues from soil [13]. Studies in tropical soils of low organic matter (OM) have shown increased biomass yield and plant growth using biochar additions in conjunction with another nutrient source [5,14]. Biochar has been shown to reduce nutrient leaching in soils [15,16], increase nutrient availability for plants and enhance the efficiency of fertilizers [14]. Biochar has also been shown to influence the soil physico-chemical properties, such as pH, porosity, bulk density and water holding capacity [8,14,17].

The use of manure biochars may have additional benefits to farmers, as it can be used to alleviate the problems of nitrogen (N) leaching from soils which is a characteristic of the use of manure as a fertilizer [9]. Research has shown an increase in N availability in soil with the addition of biochar from chicken manure [18]. The phosphorus (P) and potassium (K) contents of manure are almost completely recovered in the biochar, leading to higher concentrations in the biochar than in the original manure [19]. Due to its higher N, P and K concentrations, biochar from manure may offer additional benefits as a low-grade fertilizer, even when used without other forms of fertilisation.

Pyrolysis could be used as a tool to combat global warming which, according to the International Panel on Climate Change, is very likely due to the combined influences of greenhouse gas (GHG) increases and stratospheric ozone depletion [20]. The generation of renewable energy through pyrolysis has been shown to result in net reductions in GHG emissions compared to fossil fuel combustion [21]. However, the net energy generation from the drying and pyrolysis of manure has been shown to be negative due to the high water content (WC) of manures [19]. The addition of sawdust to separated manure reduces the WC and may result in a positive net energy yield. Composting also reduces the WC of the feedstock [22] and may also be incorporated into the treatment process to alter the net energy yield. Some research has been performed on biochar production from manures [19,23,24]; however, no study has yet characterized the biochar and renewable energy production from pig manure after AD.

The effect of composting the feedstocks before pyrolysis has also never been previously studied. The objectives of this study were to: (1) investigate the effect of sawdust addition on the products of pyrolysis of separated anaerobically digested pig manure (2) analyze the effect of composting the feedstocks before pyrolysis, and (3) investigate the effect of composting and sawdust addition to the energy balance.

2 Materials and Methods

2.1 Feedstock

The pig manure was taken from an 800-sow pig farm in Roughty Valley Pig Unit, Kilgarven, County Kerry, Ireland. This farm contained pigs from all stages of production, fed with a dry feeding system and housed in slatted sheds above underground manure storage tanks. The liquid manure was transferred from the underground storage tanks to a 45m^3 overground storage tank prior to anaerobic digestion. The anaerobic digested manure was generated in a mesophilic anaerobic digester with a residence time of 20 to 30 days. The anaerobically digested pig manure was separated by decanter centrifuge (GEA Westfallia Separator UCD 205, Bönen, Germany). The separated solids of AD pig manure (SADPM) had an average dry matter content of 310 g kg^{-1}. This SADPM was mixed with Sitka Spruce sawdust, produced without bark (WC = 144 g kg^{-1} ±27 g kg^{-1}, bulk density = 40 kg m^{-3} ±2 kg m^{-3}), at different rates (4:1 and 3:2) based on their wet weights. These feedstocks were then pyrolised both before and after composting. The feedstocks were: SADPM only (MO); SADPM and sawdust mixed at a 4:1 ratio (4:1); SADPM and sawdust mixed at a 3:2 ratio (3:2); composted SADPM (MO(CP)); SADPM and sawdust mixed at a 4:1 ratio and composted (4:1(CP)), and SADPM and sawdust mixed at a 3:2 ratio, and composted (3:2(CP)). The composting process consisted of 56 day aerobic composting in small-scale (40 - 50 kg of compost was produced for each mixture of SADPM and sawdust) composting tumblers similar to the methods described by Nolan et al. [25]. All materials were dried at 60^{o}C for 48 hours and milled before storage in a refrigerator (~4^{o}C) prior to pyrolysis and analysis.

2.2 Pyrolysis

A laboratory-scale pyrolysis reactor (5cm i.d.) was used to produce the biochar, bio-liquid and gases. A temperature of 600±10 ^{o}C and a residence time of 15 minutes were used for all feedstocks. Approximately 50g of feedstock was used for each pyrolysis run. The vapor exhaust end of the pyrolysis reactor was connected to a condensing zone which was maintained at a temperature of -7±1^{o}C. A flow of 50 $cm^3 \cdot min^{-1}$ N_2 for 15 minutes before pyrolysis commenced, ensured that the atmosphere inside the reactor was oxygen free. The vapours produced by the pyrolysis process were carried through to the condensing zone, where the condensable fractions were converted to bio-liquid. The bio-liquid was collected in a round bottomed flask at the end of the condensing zone and the gases were collected in Tedlar gas sampling bags.

After pyrolysis, the biochar was moved to the cooling zone of the pyrolysis reactor and allowed to cool in the N atmosphere before being removed from the reactor. The mass of the biochar and bio-liquid was determined after pyrolysis to allow calculation of the percentage yield of biochar and bio-liquid. Gas yield was calculated from the difference after biochar and bio-liquid yield calculation.

2.3 Chemical and Physical Properties of Biochar

Feedstock and biochars were subjected to proximate analysis for WC (B/EN 14774:3:2009), ash content (BS/EN 14775:2009) and volatile matter content (VM) (BS/EN 15148:2009).

Ultimate analyses of duplicate samples of feedstock and the biochars were performed. Samples were analyzed for total carbon (C), nitrogen (N), sulphur (S) and hydrogen (H) contents in accordance with CEN/TS 15104:2005. Elemental analysis was undertaken using a "CHNOS Elemental Analyser Vario EL Cube" (Elemental Analysensysteme GmbH, Hanau, Germany) operated at a combustion temperature of 1100 – 1200^{o}C. All analysis was preformed on a dry basis (db). H/C ratio was calculated from the ultimate analyses as the mol ratio on a dry basis. Higher heating value (HHV) (MJ kg^{-1}) was calculated from the ultimate analyses using the equation (1) [26]:

$$HHV = 0.3491\, C + 1.1783\, H + 0.1005\, S - 0.1034\, O - 0.0151\, N - 0.0211\, Ash \qquad (1)$$

Biochar pH measurements were performed in water solution using a bench top meter (SevenEasy, Mettler-Toledo, Switzerland) at a biochar/distilled water ratio of 1:10 (w/v). Acid binding capacity (ABC) and buffering capacity (BUF) were measured after Lawlor et al. [27] to final pH values of 6.5 and 7. In this method, 0.5g of biochar was suspended in 50cm^{3} de-ionized water and continuously stirred. Titrations of 100 mol m^{-3} hydrochloric acid were performed using increments from 0.01cm^{3} to 0.1cm^{3} until a pH of 6.5 and a pH of 7 were attained. Acid binding capacity was calculated as the amount of acid in milli-equivalents required to reach the target pH. Buffering capacity was calculated by dividing the ABC by the change in pH units. This test was repeated using lime to compare the potential of the biochar as a replacement for lime.

The fertilizer value of the biochar was investigated by determining the concentrations of P and K. The amount of P available to plants is given by the nutra ammonium citrate soluble P (NACP) concentration [28]. This test is used to denote the P content of common fertilizers. Formic acid soluble P relates to less available P [29], and is often found in high concentrations in slow release fertilizers, often utilised in forest plantations. Total P was analyzed by acid digestion according to Standard Method 4500-P B&E [30]. Water soluble P, nutra ammonium citrate soluble P, and formic acid soluble P were determined after Byrne [31]. Total K was also determined after Byrne [31]. Brunauer-Emmet-Teller (BET) surface area of the biochars was measured by nitrogen gas sorption analysis at 77K using a surface area analyser (Micromeritics Gemini 2375 V5.01). Samples were pre-treated by degassing at 300^{o}C for 4 hours in nitrogen gas.

2.4 Thermo Gravimetric Analysis

The six feedstocks were subject to thermo gravimetric analysis runs (TGA) using a TGA analyser (Q600 TGA/DTA Thermal Analyser System, TA Instruments). Samples were placed in open top alumina crucibles and were pyrolised with N as a carrier gas at a flow rate of 100cm^{3} min^{-1}. A temperature ramp of 10K min^{-1} from ambient temperature up to 600^{o}C was used to create a temperature-based mass profile.

2.5 Gas and Bio-liquid Analyses

Elemental analyses of duplicate samples of the bio-liquids were preformed in accordance with CEN/TS 15104:2005 as above. Samples were analyzed on the same day as production to ensure there was no reduction in the quality of the bio-liquids associated with storage. Higher heating values (MJ kg^{-1}) were calculated from the ultimate analyses using equation (2) [32]:

$$HHV = 3.55\ C^2 - 232\ C - 2230\ H + (51.2\ C \cdot H) + 131\ N + 20600 \qquad (2)$$

Analysis of the major non-condensable gases produced by pyrolysis was undertaken using a gas chromatograph (Agilent Micro GC, Agilent Technologies). The yields were quantified by calibration with a standard gas mixture consisting of N_2, H_2, CO, CO_2, CH_4, C_2H_4, C_2H_6 and C_2H_2 in helium. Higher heating values ($MJ \cdot m^{-3}$) under standard conditions were calculated from the gas composition results using the equation (3) [33]. Standard conditions were taken as a temperature of $20^{o}C$ and a pressure of 100 kPa.

$$HHV = 39.82\ CH_4 + 12.63\ CO + 12.74\ H_2 + 7.29\ C_2H_6 + 63.42\ C_2H_4 + 58.06\ C_2H_2. \quad (3)$$

2.6 Energy Balance

The energy required to treat digested manures, through pyrolysis, can be split into four processes: separation, composting, drying, and pyrolysis (Figure 1). The separation energy requirements of anaerobically digested pig manure using a decanter centrifuge was taken as 7.92 MJ t^{-1} manure input [34] and the quantity of manure solids produced per tonne of anaerobically digested pig manure input was taken as 0.07 t [35]. The energy use during composting was estimated to be 18.4 MJ t^{-1} input material [36]. The overall mass reduction of the composting pile from the beginning to end of the composting process was taken to be 50% [37], including a reduction of 15% in the water content. The drying energy requirement was estimated by adding the heat required to increase the temperature of the wet feedstock from ambient (10^{o}C) to 100 ^{o}C, plus the latent heat required to evaporate the water from the feedstock [19]. The heat capacity of the wet manure was estimated to be 3.292 kJ kg^{-1} K^{-1} [38], while the heat capacity of sawdust with a WC of 120 g kg^{-1} was estimated to be 1.5 kJ kg^{-1} K^{-1} [39]. The efficiency of the drying process was estimated at 80% [19].The energy requirement for pyrolysis was the energy required to increase the temperature of the dried feedstock from 100 ^{o}C to 600 ^{o}C. The heat capacity of the dried manure was estimated to be 0.92 kJ kg^{-1} K^{-1} [38], while the heat capacity of dry sawdust was estimated to be 2.51 kJ kg^{-1} K^{-1} [39]. The energy loss during pyrolysis is estimated to be 5% [19].

There are two output options investigated (Figure 1) with regards to the end use of the products (bio-liquid, biochar and gases). For option one, all three pyrolysis products are used as a fuel. Option two uses the bio-liquid and gases as a fuel, while the biochar is used as a soil addendum. When calculating the energy production from combustion of the biochar, bio-liquid and gases, a combined heat and power (CHP) efficiency of 80% was assumed.

“(Figure 1 here)”

2.7 Statistical Analysis

Data was analyzed using the Statistical Analyses System (SAS, V9.1.3, 2002-2003). Comparison of yield, elemental analyses, proximate analyses and HHV were performed using the Proc Mixed SAS procedure. Treatment was included as a fixed effect. For all analyses, significance was at $p < 0.05$.

3 Results and Discussion

3.1 Feedstock Characteristics

Proximate and ultimate analyses of the biomass feedstock are given in Table 1. The addition of sawdust to the SADPM resulted in higher VM and FC contents ($p < 0.001$ and $p < 0.01$, respectively), while the ash and N contents decreased with sawdust addition ($p < 0.01$ for both). Feedstock MO(CP) was an exception to this, where the N content was unusually low. The low N content was most likely caused by leaching which occurred from this feedstock during the composting process. There was an increase in C contents when sawdust was added to the SADPM, although this increase was not significant ($p = 0.26$). There was no significant difference in feedstock HHV with increasing sawdust addition ($p > 0.05$). Composting of the feedstocks resulted in lower VM contents ($p < 0.001$). Ash contents were also higher, although the increase was not significant ($p > 0.05$). Organic matter is decomposed by microorganisms during composting, resulting in higher ash contents, while VM is lost as gases during the composting process [22]. There was a reduction in C contents after composting, although the decrease was only significant in the 4:1 treatment ($p < 0.05$). Carbon is lost during the composting process, primarily as carbon dioxide [22]. The decrease in C contents and the increase in ash contents, following composting, resulted in a decrease in HHV in the composted feedstock ($p < 0.001$).

"(Table 1 here)"

3.2 Biochar Characteristics

The biochar yields obtained from the pyrolysis process are shown in Figure 2. Biochar yield was influenced by feedstock composition. However, composting of the feedstock had no significant effect of biochar yield ($p > 0.05$). The addition of sawdust to SADPM reduced biochar yield significantly ($p < 0.05$). In a study using poultry manure [24], the increasing addition of wood also resulted in decreasing biochar yield. The higher biochar yield for the manure only feedstock was due to changes in the high ash content of the manure, which decreased with sawdust addition (Table 1).

"(Figure 2 here)"

The results of proximate and ultimate analyses of the biochars are shown in Table 2. The C content of the biochar increased as the proportion of sawdust in the feedstock was increased ($p < 0.01$ for non-composted feedstock and $p < 0.05$ for composted feedstock). This resulted in an increase in HHV and a reduction in the H/C ratio ($p < 0.05$ for both). This was a result of the higher C content and lower ash contents of the feedstocks with added sawdust. The FC was also increased ($p < 0.05$), while ash and N contents decreased with sawdust addition ($p < 0.05$ and $p < 0.001$, respectively). Composting of the feedstock increased VM and N contents in the sawdust amended treatments only ($p < 0.05$ and $p < 0.001$, respectively). In the MO feedstock, there was no significant increase in VM and N contents when the feedstocks were composted ($p = 0.83$ and 0.13, respectively). Carbon and FC contents in the biochars were not significantly changed when the feedstocks were composted ($p > 0.05$ for both). With composting, biochar HHV was not significantly changed ($p > 0.05$). Biochar surface area increased with sawdust addition to the SADPM, but decreased when the feedstocks were composted.

"(Table 2 here)"

The MO biochars without sawdust addition had a HHV lower than a low-rank coal (lignite, 16 $MJ.kg^{-1}$). The 3:2 biochars with the higher rate of sawdust addition had a HHV in the range of bituminous coal (17-23 MJ kg^{-1}), and above that of peat (14-21 MJ kg^{-1}). On the basis of yield and HHVs of the feedstock and biochar, 26-38% of the non-composted feedstocks energy was retained in the biochar. However, when the feedstock was composted, this proportion increased to 35-44%.

The H/C ratios decreased from 1.28 and greater for the feedstocks to less than 0.50 in the biochars. This reduction indicates an increase in aromaticity in the biochars when compared to the feedstocks. Charring of lignin and cellulose has been reported to cause loss of aliphatic components along with the conversion of ring structures into aromatic compounds [40]. This increase in aromaticity can also be seen in the increased FC contents of the biochars when compared to their feedstock. Increases of 181-243% were shown in the FC contents of biochars from non-composted feedstock, while increases of 117-222% were found in the FC contents of biochars from composted feedstock.

The concentration of total P, the soluble fractions of P and total K in the biochar are given in Table 2. Composting of the feedstock resulted in no major change in biochar total K concentrations and small increases in total P concentrations. Biochar total P and total K decreased with increasing sawdust addition. The amount of P leached from soil is dependant on the amount of water soluble P (WSP) available [41]. Concentrations of WSP are generally very high (150-500 g kg^{-1}) in super phosphate fertilizers. The WSP concentrations in the biochars studied are very low (< 0.16 g kg^{-1}), indicating unsuitability as a fast release fertilizer. However, it also indicates that P leaching from the biochar would probably be very small and that biochars might be suitable as a slow release P fertilizer.

The concentration of NACP decreased when feedstocks were composted and when sawdust was added, reducing the fertilizer value of the biochar. The percentage of total P which is available to plants also decreases when feedstocks are composted and amended with sawdust. Plant-available P decreased from 97% of total P for the MO biochar to 32% of the total P for the 3:2(CP) biochar. Formic acid P accounted for between 14% and 34% of the total P concentration. There was a decrease in formic acid P concentrations with sawdust addition and after composting of the feedstock.

Acid binding capacities and BUF to achieve pH values of 6.5 and 7.0 are given in Table 3. The optimum pH for grass, wheat, barley and maize is reported to be 6.5, while a soil pH of 7 is recommended for white clover, beet, beans, peas and oilseed rape [42]. The biochar from SADPM alone had the highest BUF for both pH 6.5 and 7.0. The addition of sawdust to the SADPM resulted in a lower ABC and BUF in the biochar for both pH values. Composting of the feedstock also reduced ABC and BUF. In comparison, when this test was repeated using lime in place of biochar, values of 161 and 307 were recorded for BUF-6.5 and BUF-7, respectively. This demonstrates that lime has a significantly greater buffering capacity, indicating that while biochars offer some ability to increase soil pH when added to acid soils, they are not an adequate replacement for lime.

“(Table 3 here)”

3.3 Thermo Gravimetric Analyses

Figure 3 (a) and (b) show the mass (Thermo gravimetric (TG)) and derivative of TG curves (DTG) of the feedstocks, respectively. The TG analyses show the loss of mass of the feedstock as the temperature increases from ambient temperature to 600^{o}C.

The primary devolatilisation stage is indicated by the highest peaks on the DTG curve (Figure 3b). The temperatures of primary devolatilisation are shown in Table 4. The onset temperature (T_{on}) was determined as the point of 5% loss of weight (db). The temperature at maximum devolatilisation (T_{max}) was determined from the peaks on the DTG curves. The final temperature of primary devolatilisation (T_f) was determined from the DTG curve as the temperature corresponding to the intersection of the tangent lines in the primary and secondary devolatilisation stages. The final temperature of primary devolatilisation was similar for all feedstock at 370 ^{o}C ± 6^{o}C. The temperature range (T_r) of devolatilisation is the difference between T_f and T_{on}. The primary devolatilisation stage is followed by the secondary devolatilisation stage (Figure 3b) when heavier chemical structures are degraded [43].

Similarly to the results seen in Section 3.2, sawdust addition and composting of the feedstocks reduced biochar yield. The MO feedstocks had a greater secondary devolatilisation stage, indicating the presence of heavier chemical structures in the manure [43]. This stage was reduced with sawdust addition.

The addition of sawdust to SADPM increased T_{on} due to the presence of more complex compounds in the sawdust. Composting of the feedstock caused a reduction in T_{on}. This is due to the degradation of complex compounds into simpler molecules during the composting process [22]. These simpler compounds are more easily volatilised at lower temperatures. The temperature at maximum devolatilisation increased with sawdust addition and with composting of the feedstocks. The temperature range reduced with sawdust addition and increased with composting of the feedstock due to the changes in T_{on}.

“(Table 4 here)”

“(Figure 3 here)”

3.4 Characteristics of Bio-liquid and Gas

Bio-liquid yield ranged from 110 to 300 g kg^{-1} (Figure 2). Sawdust addition to SADPM increased bio-liquid yield ($p < 0.01$), however, composting of the feedstock did not significantly alter the yield ($p > 0.05$). Between 21 and 46% of the volatiles were found to be condensable. Similar to the overall bio-liquid yield, sawdust addition and composting increased the proportion of volatiles which were condensable. Elemental analyses of the bio-liquids are shown in Table 5. Carbon contents of the bio-liquids decreased as the proportion of sawdust in the feedstock increased ($p < 0.01$). This results in a decrease in HHV ($p < 0.01$). Mante and Agblevor [24] also found increased bio-liquid yields, decreased C and N contents and HHV values by adding wood to poultry manure. Composting of the feedstock resulted in increased C and N contents ($p < 0.01$ and $p < 0.05$, respectively) and HHV of the bio-liquids ($p < 0.01$).

“(Table 5 here)”

Gas yield ranged from 340 to 510 g kg^{-1} (Figure 2). Yields decreased significantly when the feedstocks were composted ($p < 0.05$). This is because gases, primarily carbon dioxide (CO_2) and ammonia (NH_3), but also nitrous oxide (N_2O) and methane (CH_4), are lost during the composting process [22]. The compositions of the non-condensable gases are given in Table 6. As N_2 was used as a carrier gas during pyrolysis, the proportion found in the produced gas was artificially high. Therefore, the proportion of N_2 in the manure only feedstock was estimated to be 10%, as found in Ro et al. [19] and this was revised downwards for all other feedstocks based on the proportion of manure to sawdust in the feedstock. The largest component gas in the mixtures was CO_2 (35-48%) followed by CO (15-37%). CO_2 decreases the overall quality of the gas produced, therefore, pyrolysis conditions which reduce the production of CO_2 are desirable [13,23]. Increasing the rate of sawdust addition to SADPM decreased the CO_2 concentration and increased the CO concentrations in the gas produced, similar to the finding of a similar study by Mante and Agblevor [24] using poultry manure. The addition of sawdust to the SADPM also increased the concentrations of CH_4 and H_2, while there was a reduction in C_2H_4 concentration. There was little difference in the overall gas composition or HHV when the feedstock was composted.

"(Table 6 here)"

More than 54% of the original energy in the feedstock remained in the biochar, bio-liquid and gas after pyrolysis. This figure ranged from 54-81% for the non-composted feedstock, increasing as the proportion of sawdust increased. For the composted feedstock, the figure was higher (70-94%) and rose with increasing sawdust addition.

3.5 Energy Balance

The inputs required and the outputs obtained from each feedstock are given in Table 7. All values are calculated on the basis of one tonne of liquid pig manure after anaerobic digestion.

3.5.1 Inputs

There are no differences between feedstocks for the separation energy requirement. However, following separation, different quantities of sawdust were mixed with the separated manure solids to form the various feedstocks (Table 7). The addition of sawdust to SADPM increased the energy requirements for composting, drying and pyrolysis, due to the increased mass of the feedstock. The quantity of bio-liquid, gases and biochar produced were increased, resulting in greater energy generation.

The input energy required for the composting process was relatively small in comparison to the other processes. However, the inclusion of a composting step had a large influence on the energy requirements of the drying and pyrolysis processes. The energy required for drying showed a decrease of approximately 58% when a composting stage was included. The energy required for pyrolysis also showed a reduction of between 31 and 43% with the addition of a composting stage. These reductions were due to a mass reduction of 50%, including a 15% decrease in water content, which occurs during the composting process [37].

3.5.2 Outputs

The amount of biochar, bio-liquids and gases is dependant on whether a composting stage is applied. The quantity of biochar produced decreased by between 20 and 38% when a composting stage was incorporated. Similarly, bio-liquid and gas production decreased by between 36 and 47% with the addition of a composting stage. The severity of these reductions increased with sawdust addition. This resulted in reduced energy generation when a composting step was applied. Therefore, although the inclusion of a composting stage reduced the energy requirements for drying and pyrolysis, there was a decrease in energy production.

3.5.2.1 Output 1: Using Biochar as a Fuel

The results of using the biochar produced through pyrolysis as a fuel are shown in Table 7. There was a positive net energy yield for all feedstocks, except for the MO treatment. However, the addition of sawdust to SADPM substantially increased the net energy yield. The addition of a composting stage resulted in a reduced net energy yield with the exception of the MO treatment, where the addition of a composting stage changed a negative net energy yield to a positive net energy yield.

3.5.2 Output 2: Using Biochar as a Soil Addendum

The results of using the biochar produced through pyrolysis as a soil addendum are shown in Table 7. There was a positive net energy yield only when sawdust was added to SADPM. For the MO treatment, the energy generated from the combustion of the bio-liquid and gas was not sufficient to sustain the treatment processes. The addition of sawdust substantially increased the net energy yield. The addition of a composting stage had a positive effect in treatments MO and 4:1, while for 3:2, the addition of a composting stage reduced the net energy yield. Some feedstocks did show a small increase in the biochar nutrient concentrations (Table 2) when a composting step was incorporated. However, the nutrient concentration of the biochar produced decreased with sawdust addition to the manure (Table 2), decreasing the value of the biochar as a soil addendum.

"(Table 7 here)"

4 Conclusions

The influence of (1) the addition Sitka Spruce sawdust and (2) composting of the feedstock on the products of pyrolysis of anaerobically digested pig manure was significant. The proportion of biochar, bio-liquid and gas produced, and the physical and chemical characteristics of these products were influenced by both sawdust addition and feedstock composting. Increasing the sawdust content in the wood/manure mixture decreased the biochar yield and increased the bio-liquid yield. The biochar showed increased heating values, but reduced nutrient concentrations with increasing sawdust addition. The heating value of the gases produced also increased, while that of the bio-liquid was decreased with sawdust addition. Composting of the feedstock before pyrolysis increased the biochar and bio-liquid yield, but decreased the gas yield. The biochar showed reduced heating values, while the bio-liquid heating values were increased with composting.

The net energy yield from biochar and renewable energy production increased with sawdust addition to the manure digestate. The energy yield also increased when the manure only (without sawdust addition) feedstock was composted before pyrolysis. However, with increasing sawdust addition, composting of the feedstock reduces the net energy yield. If the biochar is used as a fuel, all feedstocks except for the non-composted manure only feedstock, produced a positive net energy yield. Should the biochar be used as a soil addendum, then sawdust addition to the manure may be required to produce a positive energy yield.

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Figure Captions

Figure 1: Schematic outlining the process, inputs and outputs for the energy balance.

Figure 2: Pyrolysis product yield: effect of sawdust addition and composting of feedstock.

Figure 3: (a) Mass (TG) curves and (b) derivative mass (DTG) curves during N pyrolysis: ambient – 600^{o}C, 10K min^{-1}; mass (%) is the percentage of actual weight.

Table 1. Proximate and Ultimate Analysis of Feedstock before Pyrolysis

Parameters	MO	4:1	3:2	MO (CP)	4:1 (CP)	3:2 (CP)
Water content (g kg^{-1})	85	70	74	90	62	58
Volatile matter (g $kg^{-1}{}_{db}$)	697	718	755	628	663	740
Fixed C (g $kg^{-1}{}_{db}$)	81	150	163	108	171	170
Ash (g $kg^{-1}{}_{db}$)	222	132	82	264	166	90
N (g $kg^{-1}{}_{db}$)	45	30	17	19	42	30
C (g $kg^{-1}{}_{db}$)	452	476	490	406	414	442
H (g $kg^{-1}{}_{db}$)	51	53	52	47	47	51
O (g $kg^{-1}{}_{db}$)	219	301	354	258	319	378
H/C (mol ratio $_{db}$)	1.37	1.34	1.28	1.39	1.35	1.37
HHV (MJ kg^{-1})	19.1	19.5	19.5	16.5	16.4	17.3

db=dry basis; (CP)=composted feedstock; HHV=higher heating value

Table 2. Yield, Chemical Analysis, Higher Heating Value and Surface Area of Biochar

Parameters	MO	4:1	3:2	MO(CP)	4:1(CP)	3:2(CP)
Yield (g kg^{-1})	434	321	306	493	391	345
Water content (g kg^{-1})	53	55	77	30	48	58
Volatile matter (g $kg^{-1}{}_{db}$)	226	166	171	230	204	192
Fixed C (g $kg^{-1}{}_{db}$)	262	423	561	233	372	547
Ash (g $kg^{-1}{}_{db}$)	512	412	268	536	424	261
N (g $kg^{-1}{}_{db}$)	38	27	22	40	33	27
C (g $kg^{-1}{}_{db}$)	338	516	669	330	501	624
H (g $kg^{-1}{}_{db}$)	10	11	11	13	11	13
H/C (mol ratio $_{db}$)	0.34	0.26	0.20	0.48	0.26	0.25
HHV (MJ kg^{-1})	11.3	18.2	24.0	11.6	17.9	22.1
Total P (g $kg^{-1}{}_{db}$)	31.8	23.4	23.7	32.1	30.2	25.9
Water Sol. P (g $kg^{-1}{}_{db}$)	0.13	0.15	0.15	0.11	0.09	0.09
NACP (g $kg^{-1}{}_{db}$)	30.7	19.6	14.8	27.3	15.1	8.4
Formic Acid P (g $kg^{-1}{}_{db}$)	10.8	7.5	5.5	8.8	5.9	3.6
Total K (g $kg^{-1}{}_{db}$)	16.1	12.3	9.0	16.6	12.3	8.6
S_{BET} (m^2 g^{-1})	17.0	19.4	24.4	14.2	17.4	23.2

db=dry basis; (CP)=composted feedstock; HHV=higher heating value; S_{BET}=BET surface area, NACP=Nutra Ammonium Citrate Soluble P.

Table 3. pH, Acid Binding Capacity (ABC) and Buffering Capacity (BUF) of Biochar

Parameters	MO	4:1	3:2	MO (CP)	4:1 (CP)	3:2 (CP)
pH	9.3	9.0	8.9	9.4	9.5	8.7
ABC-6.5	158	90	42	140	72	27
ABC-7.0	95	55	25	94	51	14
BUF-6.5	41	27	13	39	21	8
BUF-7.0	56	36	18	48	24	12

(CP)=composted feedstock

Table 4. Temperatures of Primary Devolatilisation (^{o}C)

Parameters	MO	4:1	3:2	MO (CP)	4:1 (CP)	3:2 (CP)
T_{on}	191	202	223	124	172	191
T_{max}	323	342	347	331	349	354
T_{r}	184	167	149	240	202	184

(CP)=composted feedstock; T_{on}=onset temperature; T_{max}=maximum temperature; T_{r} =temperature range

Table 5. Yield, Elemental Analysis and Higher Heating Value of Bio-liquid

Parameters	MO	4:1	3:2	MO(CP)	4:1(CP)	3:2(CP)
Yield (g kg^{-1})	119	163	255	169	208	303
N (g kg^{-1})	45	36	26	56	48	34
C (g kg^{-1})	388	358	354	438	421	394
H (g kg^{-1})	92	94	94	90	88	95
HHV (MJ kg^{-1})	15.3	13.6	13.2	18.1	17.1	15.4

(CP)=composted feedstock; HHV=higher heating value

Table 6. Yield, Composition (volume fraction) and Higher Heating Value of Non-condensable Gases

Parameters	MO	4:1	3:2	MO (CP)	4:1 (CP)	3:2 (CP)
Yield (g kg^{-1})	447	516	439	338	401	352
N_2	10.0	5.6	3.2	10.0	5.6	3.2
CH_4	6.1	11.3	13.5	6.2	11.5	11.7
CO_2	43.2	34.8	35.2	47.5	38.7	34.5
CO	19.3	31.0	36.2	14.8	25.6	37.2
H_2	2.4	3.4	3.5	2.5	3.2	3.3
C_2H_6	0.9	1.5	1.4	1.1	1.3	1.3
C_2H_4	8.9	6.7	5.7	10.0	8.0	6.9
C_2H_2	0.3	0.3	0.3	0.3	0.3	0.2
Other C_xH_y*	8.8	5.4	1.1	7.5	5.9	1.6
HHV (MJ m^{-3})	11.7	14.4	15.1	12.0	14.4	15.2

(CP)=composted feedstock; HHV=higher heating value; *=by difference

Table 7: Inputs and Outputs from each Feedstock and Process (Values per tonne liquid manure)

	MO	4:1	3:2	MO(CP)	4:1(CP)	3:2(CP)
Inputs						
Separation (MJ)	-7.9*	-7.9	-7.9	-7.9	-7.9	-7.9
Composting (MJ)	0.0	0.0	0.0	-1.3	-1.6	-2.1
Drying Heat (MJ)	-168.9	-177.8	-192.7	-72.3	-76.2	-81.3
Pyrolysis (MJ)	-9.5	-29.8	-63.7	-6.6	-18.3	-36.3
Sawdust (t)	0.0	0.0175	0.0467	0.0	0.0175	0.0467
Outputs						
Bio-liquid & gases (t)	0.0112	0.0238	0.0425	0.0069	0.0131	0.0224
CHP Generated (MJ)	86.0	217.6	413.2	63.6	133.8	239.3
Biochar (t)	0.0084	0.0112	0.0188	0.0067	0.0084	0.0117
CHP Generated (MJ)	76.2	163.1	361.1	61.8	119.7	207.6
Output 1:Biochar as a Fuel						
Energy Balance (MJ)	-24.1	165.1	509.9	37.3	149.5	319.2
Output 2: Biochar to Soil						
Energy Balance (MJ)	-100.4	1.9	148.9	-24.5	29.8	111.7

* Positive values indicate an energy generation, while negative values indicate an energy requirement.

Figure 1

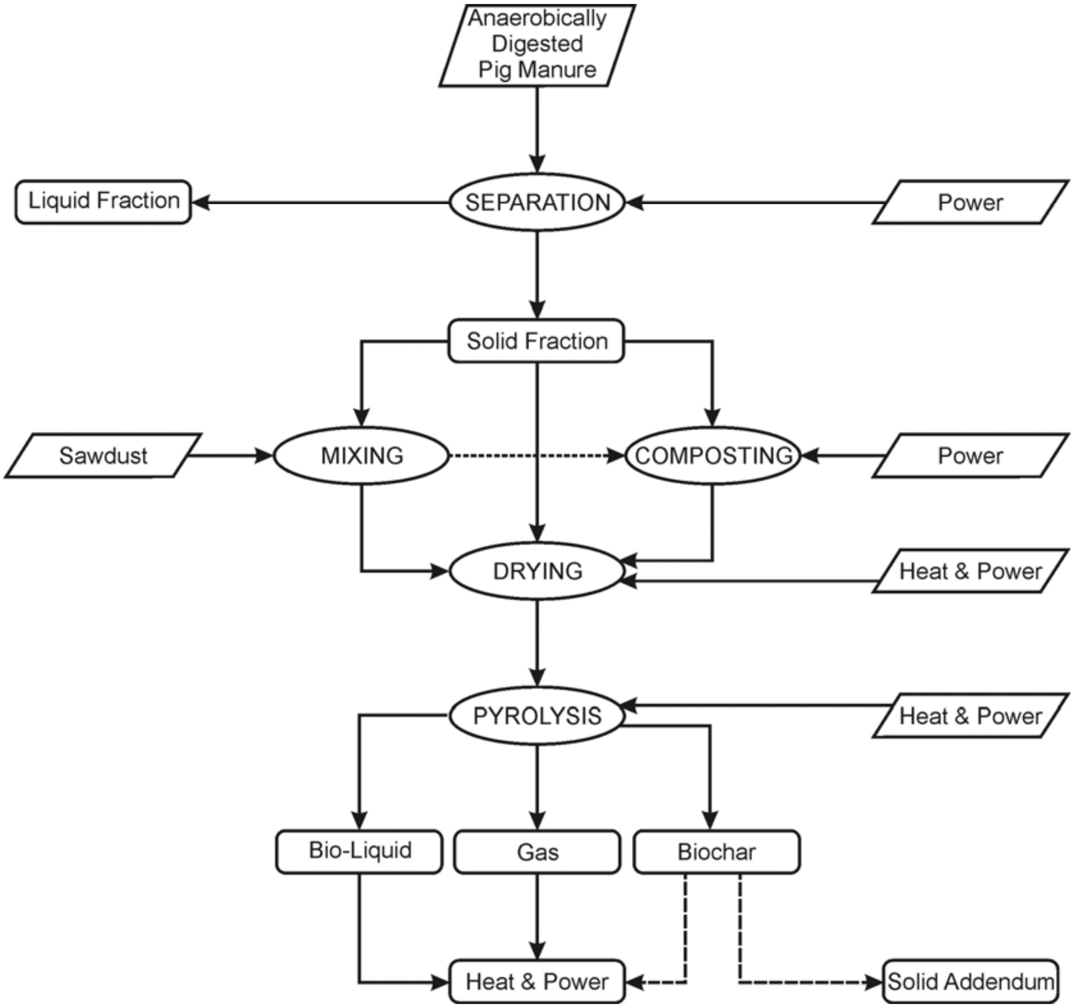

Anaerobically Digested Pig Manure
Liquid Fraction
SEPARATION
Power
Solid Fraction
Sawdust
MIXING
COMPOSTING
Power
DRYING
Heat & Power
PYROLYSIS
Heat & Power
Bio-Liquid
Gas
Biochar
Heat & Power
Solid Addendum

Figure 2

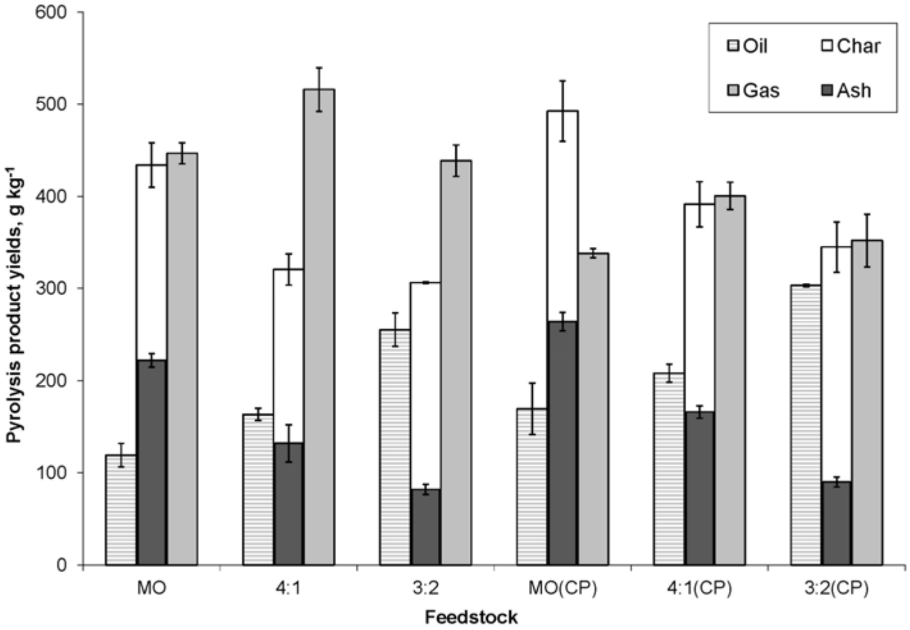
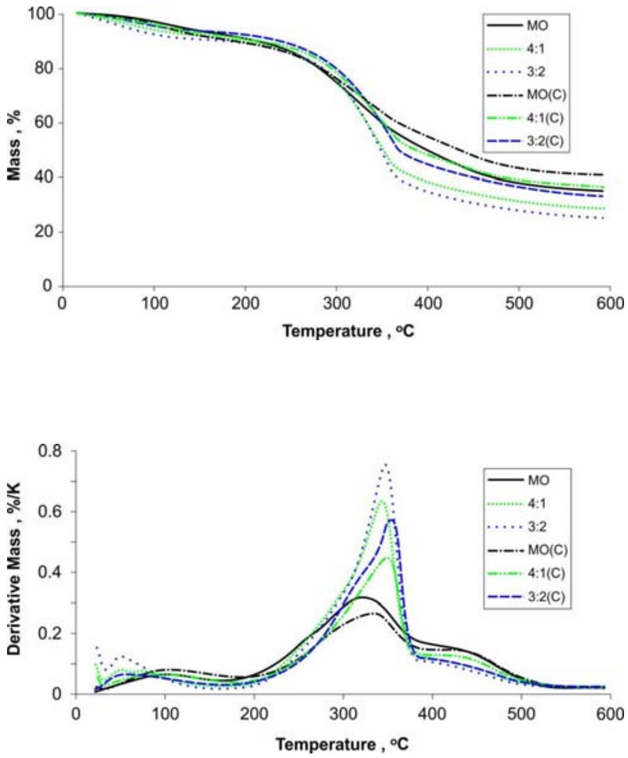

600
500
400
300
200
100
0
Pyrolysis product yields, g kg⁻¹
▨ Oil
☐ Char
▨ Gas
■ Ash
MO
4:1
3:2
MO(CP)
4:1(CP)
3:2(CP)
Feedstock

Figure 3


Mass , %
100
80
60
40
20
0
0
100
200
300
400
500
600
Temperature , °C
MO
4:1
3:2
MO(C)
4:1(C)
3:2(C)
Derivative Mass , %/K
0.8
0.6
0.4
0.2
0
0
100
200
300
400
500
600
Temperature , °C
MO
4:1
3:2
MO(C)
4:1(C)
3:2(C)