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Title	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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Publication Date	2013
Publication Information	Shane M. Troy, Tereza Nolan, James J. Leahy, Peadar G. Lawlor, Mark G. Healy, Witold Kwapinski (2013) 'Effect of sawdust addition and composting of feedstock on renewable energy and biochar production from pyrolysis of anaerobically digested pig manure'. <i>Biomass &amp; Bioenergy</i> , 49 :1-9.
Item record	<a href="http://hdl.handle.net/10379/3251">http://hdl.handle.net/10379/3251</a>

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1      *Published as: Troy, S.M., Nolan, T., Leahy, J.J., Lawlor, P.G., Healy, M.G., Kwapinski, W.*  
2      *2013. Effect of sawdust addition and composting of feedstock on renewable energy and*  
3      *biochar production from pyrolysis of anaerobically digested pig manure. Biomass and*  
4      *Bioenergy 49: 1 – 9.*

5

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

8

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17

18     **A B S T R A C T**

19     Pyrolysis experiments were conducted on the separated solid fraction of anaerobically  
20     digested pig manure (SADPM). The aim of these experiments was to investigate the  
21     influence of (1) sawdust addition and (2) composting the feedstock, on the products of  
22     pyrolysis and on the net energy yield from the pyrolysis process. Mixtures of SADPM  
23     and sawdust were made to give the following treatments; manure only, 4:1(w/w) and  
24     3:2(w/w). These mixtures were pyrolyzed at 600°C both before and after aerobic  
25     composting. The yields of the biochar, bio-liquid and gas were influenced by the

26 addition of sawdust to the SADPM and by composting of the feedstock. With the  
27 addition of sawdust, biochar and gas higher heating values (HHV) increased, while bio-  
28 liquid HHV decreased. More than 70% of the original energy in the feedstock remained  
29 in the biochar, bio-liquid and gas after pyrolysis, increasing as the proportion of sawdust  
30 increased. The HHV of the biochar decreased, while the HHV of the bio-liquid  
31 increased, after the feedstocks were composted. The energy balance showed that  
32 increasing the rate of sawdust addition to SADPM resulted in an increased net energy  
33 yield. The addition of a composting stage increased the net energy yield for the manure  
34 only feedstock only. However, with increasing sawdust addition, composting of the  
35 feedstock reduced the net energy yield.

36

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

38

39 **Abbreviations**

40 SADPM: separated anaerobically digested pig manure

41 NACP: nutra ammonium citrate soluble P

42 WSP: water soluble P

43 ABC: acid binding capacity

44 BUF: buffering capacity

45 TGA: thermo gravimetric analysis

46

47

48

49

50      **1 Introduction**

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

62            Pyrolysis is a process whereby a biomass feedstock, such as woodchips, crop  
63          residues or manure, is heated to high temperatures in an oxygen-free atmosphere to  
64          produce a solid (biochar), a liquid (bio-liquid) and a gaseous fraction. The proportion of  
65          biochar, bio-liquid and gas produced is dependant on the heating rate, the reactor  
66          temperature and the residence time of the reactor [3,4]. Gases and bio-liquids produced  
67          may be used to provide the energy needs for the pyrolysis process, or converted to  
68          electricity and heat. The biochar can be used as a fuel or, alternatively, applied to land  
69          as a low-grade fertilizer, soil addendum [5-8] or for carbon sequestration [9-12].

70          Biochar addition to soil may mitigate the negative effects of removing crop residues  
71          from soil [13]. Studies in tropical soils of low organic matter (OM) have shown  
72          increased biomass yield and plant growth using biochar additions in conjunction with  
73          another nutrient source [5,14]. Biochar has been shown to reduce nutrient leaching in

74 soils [15,16], increase nutrient availability for plants and enhance the efficiency of  
75 fertilizers [14]. Biochar has also been shown to influence the soil physico-chemical  
76 properties, such as pH, porosity, bulk density and water holding capacity [8,14,17].

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

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

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

103

104 **2 Materials and Methods**

105 **2.1 Feedstock**

106 The pig manure was taken from an 800-sow pig farm in Roughty Valley Pig  
107 Unit, Kilgarven, County Kerry, Ireland. This farm contained pigs from all stages of  
108 production, fed with a dry feeding system and housed in slatted sheds above  
109 underground manure storage tanks. The liquid manure was transferred from the  
110 underground storage tanks to a 45m<sup>3</sup> overground storage tank prior to anaerobic  
111 digestion. The anaerobic digested manure was generated in a mesophilic anaerobic  
112 digester with a residence time of 20 to 30 days. The anaerobically digested pig manure  
113 was separated by decanter centrifuge (GEA Westfallia Separator UCD 205, Bönen,  
114 Germany). The separated solids of AD pig manure (SADPM) had an average dry matter  
115 content of 310 g kg<sup>-1</sup>. This SADPM was mixed with Sitka Spruce sawdust, produced  
116 without bark (WC = 144 g kg<sup>-1</sup> ±27 g kg<sup>-1</sup>, bulk density = 40 kg m<sup>-3</sup> ±2 kg m<sup>-3</sup>), at  
117 different rates (4:1 and 3:2) based on their wet weights. These feedstocks were then  
118 pyrolysed both before and after composting. The feedstocks were: SADPM only (MO);  
119 SADPM and sawdust mixed at a 4:1 ratio (4:1); SADPM and sawdust mixed at a 3:2  
120 ratio (3:2); composted SADPM (MO(CP)); SADPM and sawdust mixed at a 4:1 ratio  
121 and composted (4:1(CP)), and SADPM and sawdust mixed at a 3:2 ratio, and

122 composted (3:2(CP)). The composting process consisted of 56 day aerobic composting  
123 in small-scale (40 - 50 kg of compost was produced for each mixture of SADPM and  
124 sawdust) composting tumblers similar to the methods described by Nolan et al. [25]. All  
125 materials were dried at 60°C for 48 hours and milled before storage in a refrigerator  
126 (~4°C) prior to pyrolysis and analysis.

127

## 128 **2.2 Pyrolysis**

129 A laboratory-scale pyrolysis reactor (5cm i.d.) was used to produce the biochar,  
130 bio-liquid and gases. A temperature of 600±10 °C and a residence time of 15 minutes  
131 were used for all feedstocks. Approximately 50g of feedstock was used for each  
132 pyrolysis run. The vapor exhaust end of the pyrolysis reactor was connected to a  
133 condensing zone which was maintained at a temperature of -7±1°C. A flow of 50  
134 cm<sup>3</sup>·min<sup>-1</sup> N<sub>2</sub> for 15 minutes before pyrolysis commenced, ensured that the atmosphere  
135 inside the reactor was oxygen free. The vapours produced by the pyrolysis process were  
136 carried through to the condensing zone, where the condensable fractions were converted  
137 to bio-liquid. The bio-liquid was collected in a round bottomed flask at the end of the  
138 condensing zone and the gases were collected in Tedlar gas sampling bags.

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

144

## 145 **2.3 Chemical and Physical Properties of Biochar**

146 Feedstock and biochars were subjected to proximate analysis for WC (B/EN  
147 14774:3:2009), ash content (BS/EN 14775:2009) and volatile matter content (VM)  
148 (BS/EN 15148:2009).  
149 Ultimate analyses of duplicate samples of feedstock and the biochars were performed.  
150 Samples were analyzed for total carbon (C), nitrogen (N), sulphur (S) and hydrogen (H)  
151 contents in accordance with CEN/TS 15104:2005. Elemental analysis was undertaken  
152 using a “CHNOS Elemental Analyser Vario EL Cube” (Elemental Analysensysteme  
153 GmbH, Hanau, Germany) operated at a combustion temperature of 1100 – 1200°C. All  
154 analysis was preformed on a dry basis (db). H/C ratio was calculated from the ultimate  
155 analyses as the mol ratio on a dry basis. Higher heating value (HHV) ( $\text{MJ kg}^{-1}$ ) was  
156 calculated from the ultimate analyses using the equation (1) [26]:

157

158  $\text{HHV} = 0.3491 \text{ C} + 1.1783 \text{ H} + 0.1005 \text{ S} - 0.1034 \text{ O} - 0.0151 \text{ N} - 0.0211 \text{ Ash}$  (1)

159

160 Biochar pH measurements were performed in water solution using a bench top  
161 meter (SevenEasy, Mettler-Toledo, Switzerland) at a biochar/distilled water ratio of  
162 1:10 (w/v). Acid binding capacity (ABC) and buffering capacity (BUF) were measured  
163 after Lawlor et al. [27] to final pH values of 6.5 and 7. In this method, 0.5g of biochar  
164 was suspended in 50cm<sup>3</sup> de-ionized water and continuously stirred. Titrations of 100  
165 mol m<sup>-3</sup> hydrochloric acid were performed using increments from 0.01cm<sup>3</sup> to 0.1cm<sup>3</sup>  
166 until a pH of 6.5 and a pH of 7 were attained. Acid binding capacity was calculated as  
167 the amount of acid in milli-equivalents required to reach the target pH. Buffering  
168 capacity was calculated by dividing the ABC by the change in pH units. This test was  
169 repeated using lime to compare the potential of the biochar as a replacement for lime.

170       The fertilizer value of the biochar was investigated by determining the  
171   concentrations of P and K. The amount of P available to plants is given by the nutra  
172   ammonium citrate soluble P (NACP) concentration [28]. This test is used to denote the  
173   P content of common fertilizers. Formic acid soluble P relates to less available P [29],  
174   and is often found in high concentrations in slow release fertilizers, often utilised in  
175   forest plantations. Total P was analyzed by acid digestion according to Standard Method  
176   4500-P B&E [30]. Water soluble P, nutra ammonium citrate soluble P, and formic acid  
177   soluble P were determined after Byrne [31]. Total K was also determined after Byrne  
178   [31]. Brunauer-Emmet-Teller (BET) surface area of the biochars was measured by  
179   nitrogen gas sorption analysis at 77K using a surface area analyser (Micromeritics  
180   Gemini 2375 V5.01). Samples were pre-treated by degassing at 300°C for 4 hours in  
181   nitrogen gas.

182

#### 183   ***2.4 Thermo Gravimetric Analysis***

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

189

#### 190   ***2.5 Gas and Bio-liquid Analyses***

191       Elemental analyses of duplicate samples of the bio-liquids were preformed in  
192   accordance with CEN/TS 15104:2005 as above. Samples were analyzed on the same  
193   day as production to ensure there was no reduction in the quality of the bio-liquids

194 associated with storage. Higher heating values ( $\text{MJ kg}^{-1}$ ) were calculated from the  
195 ultimate analyses using equation (2) [32]:

196

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

198

199 Analysis of the major non-condensable gases produced by pyrolysis was  
200 undertaken using a gas chromatograph (Agilent Micro GC, Agilent Technologies). The  
201 yields were quantified by calibration with a standard gas mixture consisting of  $\text{N}_2$ ,  $\text{H}_2$ ,  
202  $\text{CO}$ ,  $\text{CO}_2$ ,  $\text{CH}_4$ ,  $\text{C}_2\text{H}_4$ ,  $\text{C}_2\text{H}_6$  and  $\text{C}_2\text{H}_2$  in helium. Higher heating values ( $\text{MJ} \cdot \text{m}^{-3}$ ) under  
203 standard conditions were calculated from the gas composition results using the equation  
204 (3) [33]. Standard conditions were taken as a temperature of  $20^\circ\text{C}$  and a pressure of 100  
205 kPa.

206

207  $\text{HHV} = 39.82 \text{ CH}_4 + 12.63 \text{ CO} + 12.74 \text{ H}_2 + 7.29 \text{ C}_2\text{H}_6 + 63.42 \text{ C}_2\text{H}_4 + 58.06 \text{ C}_2\text{H}_2$ . (3)

208

209 **2.6 Energy Balance**

210 The energy required to treat digested manures, through pyrolysis, can be split  
211 into four processes: separation, composting, drying, and pyrolysis (Figure 1). The  
212 separation energy requirements of anaerobically digested pig manure using a decanter  
213 centrifuge was taken as  $7.92 \text{ MJ t}^{-1}$  manure input [34] and the quantity of manure solids  
214 produced per tonne of anaerobically digested pig manure input was taken as  $0.07 \text{ t}$  [35].  
215 The energy use during composting was estimated to be  $18.4 \text{ MJ t}^{-1}$  input material [36].  
216 The overall mass reduction of the composting pile from the beginning to end of the  
217 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 ( $10^{\circ}\text{C}$ ) to  $100^{\circ}\text{C}$ , plus the latent heat required to evaporate the water from the feedstock [19]. The heat capacity of the wet manure was estimated to be  $3.292 \text{ kJ kg}^{-1} \text{ K}^{-1}$  [38], while the heat capacity of sawdust with a WC of  $120 \text{ g kg}^{-1}$  was estimated to be  $1.5 \text{ kJ kg}^{-1} \text{ K}^{-1}$  [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  $100^{\circ}\text{C}$  to  $600^{\circ}\text{C}$ . The heat capacity of the dried manure was estimated to be  $0.92 \text{ kJ kg}^{-1} \text{ K}^{-1}$  [38], while the heat capacity of dry sawdust was estimated to be  $2.51 \text{ kJ kg}^{-1} \text{ K}^{-1}$  [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)”*

235

## 236 **2.7 Statistical Analysis**

237 Data was analyzed using the Statistical Analyses System (SAS, V9.1.3, 2002-  
238 2003). Comparison of yield, elemental analyses, proximate analyses and HHV were  
239 performed using the Proc Mixed SAS procedure. Treatment was included as a fixed  
240 effect. For all analyses, significance was at  $p < 0.05$ .

241

242     **3 Results and Discussion**

243     ***3.1 Feedstock Characteristics***

244                 Proximate and ultimate analyses of the biomass feedstock are given in Table 1.

245     The addition of sawdust to the SADPM resulted in higher VM and FC contents ( $p <$

246      $0.001$  and  $p < 0.01$ , respectively), while the ash and N contents decreased with sawdust

247     addition ( $p < 0.01$  for both). Feedstock MO(CP) was an exception to this, where the N

248     content was unusually low. The low N content was most likely caused by leaching

249     which occurred from this feedstock during the composting process. There was an

250     increase in C contents when sawdust was added to the SADPM, although this increase

251     was not significant ( $p = 0.26$ ). There was no significant difference in feedstock HHV

252     with increasing sawdust addition ( $p > 0.05$ ). Composting of the feedstocks resulted in

253     lower VM contents ( $p < 0.001$ ). Ash contents were also higher, although the increase

254     was not significant ( $p > 0.05$ ). Organic matter is decomposed by microorganisms during

255     composting, resulting in higher ash contents, while VM is lost as gases during the

256     composting process [22]. There was a reduction in C contents after composting,

257     although the decrease was only significant in the 4:1 treatment ( $p < 0.05$ ). Carbon is lost

258     during the composting process, primarily as carbon dioxide [22]. The decrease in C

259     contents and the increase in ash contents, following composting, resulted in a decrease

260     in HHV in the composted feedstock ( $p < 0.001$ ).

261     “(*Table 1 here*)”

262

263     ***3.2 Biochar Characteristics***

264                 The biochar yields obtained from the pyrolysis process are shown in Figure 2.

265     Biochar yield was influenced by feedstock composition. However, composting of the

266 feedstock had no significant effect of biochar yield ( $p > 0.05$ ). The addition of sawdust  
267 to SADPM reduced biochar yield significantly ( $p < 0.05$ ). In a study using poultry  
268 manure [24], the increasing addition of wood also resulted in decreasing biochar yield.  
269 The higher biochar yield for the manure only feedstock was due to changes in the high  
270 ash content of the manure, which decreased with sawdust addition (Table 1).

271 “*(Figure 2 here)*”

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

287 “*(Table 2 here)*”

288 The MO biochars without sawdust addition had a HHV lower than a low-rank  
289 coal (lignite,  $16 \text{ MJ} \cdot \text{kg}^{-1}$ ). The 3:2 biochars with the higher rate of sawdust addition had

290 a HHV in the range of bituminous coal (17-23 MJ kg<sup>-1</sup>), and above that of peat (14-21  
291 MJ kg<sup>-1</sup>). On the basis of yield and HHVs of the feedstock and biochar, 26-38% of the  
292 non-composted feedstocks energy was retained in the biochar. However, when the  
293 feedstock was composted, this proportion increased to 35-44%.

294       The H/C ratios decreased from 1.28 and greater for the feedstocks to less than  
295 0.50 in the biochars. This reduction indicates an increase in aromaticity in the biochars  
296 when compared to the feedstocks. Charring of lignin and cellulose has been reported to  
297 cause loss of aliphatic components along with the conversion of ring structures into  
298 aromatic compounds [40]. This increase in aromaticity can also be seen in the increased  
299 FC contents of the biochars when compared to their feedstock. Increases of 181-243%  
300 were shown in the FC contents of biochars from non-composted feedstock, while  
301 increases of 117-222% were found in the FC contents of biochars from composted  
302 feedstock.

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

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

320       Acid binding capacities and BUF to achieve pH values of 6.5 and 7.0 are given  
321   in Table 3. The optimum pH for grass, wheat, barley and maize is reported to be 6.5,  
322   while a soil pH of 7 is recommended for white clover, beet, beans, peas and oilseed rape  
323   [42]. The biochar from SADPM alone had the highest BUF for both pH 6.5 and 7.0.  
324   The addition of sawdust to the SADPM resulted in a lower ABC and BUF in the  
325   biochar for both pH values. Composting of the feedstock also reduced ABC and BUF.  
326   In comparison, when this test was repeated using lime in place of biochar, values of 161  
327   and 307 were recorded for BUF-6.5 and BUF-7, respectively. This demonstrates that  
328   lime has a significantly greater buffering capacity, indicating that while biochars offer  
329   some ability to increase soil pH when added to acid soils, they are not an adequate  
330   replacement for lime.

331   “*(Table 3 here)*”

332

### 333   **3.3 Thermo Gravimetric Analyses**

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

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

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

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

360 "(Table 4 here)"

361 “(Figure 3 here)”

362

363 **3.4 Characteristics of Bio-liquid and Gas**

364 Bio-liquid yield ranged from 110 to 300 g kg<sup>-1</sup> (Figure 2). Sawdust addition to  
365 SADPM increased bio-liquid yield ( $p < 0.01$ ), however, composting of the feedstock did  
366 not significantly alter the yield ( $p > 0.05$ ). Between 21 and 46% of the volatiles were  
367 found to be condensable. Similar to the overall bio-liquid yield, sawdust addition and  
368 composting increased the proportion of volatiles which were condensable. Elemental  
369 analyses of the bio-liquids are shown in Table 5. Carbon contents of the bio-liquids  
370 decreased as the proportion of sawdust in the feedstock increased ( $p < 0.01$ ). This  
371 results in a decrease in HHV ( $p < 0.01$ ). Mante and Agblevor [24] also found increased  
372 bio-liquid yields, decreased C and N contents and HHV values by adding wood to  
373 poultry manure. Composting of the feedstock resulted in increased C and N contents ( $p$   
374  $< 0.01$  and  $p < 0.05$ , respectively) and HHV of the bio-liquids ( $p < 0.01$ ).

375 “(Table 5 here)”

376 Gas yield ranged from 340 to 510 g kg<sup>-1</sup> (Figure 2). Yields decreased  
377 significantly when the feedstocks were composted ( $p < 0.05$ ). This is because gases,  
378 primarily carbon dioxide (CO<sub>2</sub>) and ammonia (NH<sub>3</sub>), but also nitrous oxide (N<sub>2</sub>O) and  
379 methane (CH<sub>4</sub>), are lost during the composting process [22]. The compositions of the  
380 non-condensable gases are given in Table 6. As N<sub>2</sub> was used as a carrier gas during  
381 pyrolysis, the proportion found in the produced gas was artificially high. Therefore, the  
382 proportion of N<sub>2</sub> in the manure only feedstock was estimated to be 10%, as found in Ro  
383 et al. [19] and this was revised downwards for all other feedstocks based on the  
384 proportion of manure to sawdust in the feedstock. The largest component gas in the

mixtures was CO<sub>2</sub> (35-48%) followed by CO (15-37%). CO<sub>2</sub> decreases the overall quality of the gas produced, therefore, pyrolysis conditions which reduce the production of CO<sub>2</sub> are desirable [13,23]. Increasing the rate of sawdust addition to SADPM decreased the CO<sub>2</sub> 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<sub>4</sub> and H<sub>2</sub>, while there was a reduction in C<sub>2</sub>H<sub>4</sub> 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.

400

### 401 **3.5 Energy Balance**

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

405

#### 406 **3.5.1 Inputs**

407 There are no differences between feedstocks for the separation energy  
408 requirement. However, following separation, different quantities of sawdust were mixed

409 with the separated manure solids to form the various feedstocks (Table 7). The addition  
410 of sawdust to SADPM increased the energy requirements for composting, drying and  
411 pyrolysis, due to the increased mass of the feedstock. The quantity of bio-liquid, gases  
412 and biochar produced were increased, resulting in greater energy generation.

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

421

### 422         **3.5.2 Outputs**

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

431

#### 432         *3.5.2.1 Output 1: Using Biochar as a Fuel*

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

439

440   *3.5.2 Output 2: Using Biochar as a Soil Addendum*

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

452   “*(Table 7 here)*”

453

454   **4 Conclusions**

455       The influence of (1) the addition Sitka Spruce sawdust and (2) composting of the  
456   feedstock on the products of pyrolysis of anaerobically digested pig manure was

457 significant. The proportion of biochar, bio-liquid and gas produced, and the physical  
458 and chemical characteristics of these products were influenced by both sawdust addition  
459 and feedstock composting. Increasing the sawdust content in the wood/manure mixture  
460 decreased the biochar yield and increased the bio-liquid yield. The biochar showed  
461 increased heating values, but reduced nutrient concentrations with increasing sawdust  
462 addition. The heating value of the gases produced also increased, while that of the bio-  
463 liquid was decreased with sawdust addition. Composting of the feedstock before  
464 pyrolysis increased the biochar and bio-liquid yield, but decreased the gas yield. The  
465 biochar showed reduced heating values, while the bio-liquid heating values were  
466 increased with composting.

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

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596    **Figure Captions**

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

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

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602    Figure 3: (a) Mass (TG) curves and (b) derivative mass (DTG) curves during N  
603    pyrolysis: ambient – 600°C, 10K min<sup>-1</sup>; mass (%) is the percentage of actual weight.

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620 **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 <sup>-1</sup> )	85	70	74	90	62	58
Volatile matter (g kg <sup>-1</sup> db)	697	718	755	628	663	740
Fixed C (g kg <sup>-1</sup> db)	81	150	163	108	171	170
Ash (g kg <sup>-1</sup> db)	222	132	82	264	166	90
N (g kg <sup>-1</sup> db)	45	30	17	19	42	30
C (g kg <sup>-1</sup> db)	452	476	490	406	414	442
H (g kg <sup>-1</sup> db)	51	53	52	47	47	51
O (g kg <sup>-1</sup> 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 <sup>-1</sup> )	19.1	19.5	19.5	16.5	16.4	17.3

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

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**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 <sup>-1</sup> )	434	321	306	493	391	345
Water content (g kg <sup>-1</sup> )	53	55	77	30	48	58
Volatile matter (g kg <sup>-1</sup> db)	226	166	171	230	204	192
Fixed C (g kg <sup>-1</sup> db)	262	423	561	233	372	547
Ash (g kg <sup>-1</sup> db)	512	412	268	536	424	261
N (g kg <sup>-1</sup> db)	38	27	22	40	33	27
C (g kg <sup>-1</sup> db)	338	516	669	330	501	624
H (g kg <sup>-1</sup> 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 <sup>-1</sup> )	11.3	18.2	24.0	11.6	17.9	22.1
Total P (g kg <sup>-1</sup> db)	31.8	23.4	23.7	32.1	30.2	25.9
Water Sol. P (g kg <sup>-1</sup> db)	0.13	0.15	0.15	0.11	0.09	0.09
NACP (g kg <sup>-1</sup> db)	30.7	19.6	14.8	27.3	15.1	8.4
Formic Acid P (g kg <sup>-1</sup> db)	10.8	7.5	5.5	8.8	5.9	3.6
Total K (g kg <sup>-1</sup> db)	16.1	12.3	9.0	16.6	12.3	8.6
S <sub>BET</sub> (m <sup>2</sup> g <sup>-1</sup> )	17.0	19.4	24.4	14.2	17.4	23.2

645 db=dry basis; (CP)=composted feedstock; HHV=higher heating value; S<sub>BET</sub>=BET surface area,

646 NACP=Nutra Ammonium Citrate Soluble P.

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**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

667 (CP)=composted feedstock

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693 **Table 4. Temperatures of Primary Devolatilisation (°C)**

Parameters	MO	4:1	3:2	MO (CP)	4:1 (CP)	3:2 (CP)
T <sub>on</sub>	191	202	223	124	172	191
T <sub>max</sub>	323	342	347	331	349	354
T <sub>r</sub>	184	167	149	240	202	184

694 (CP)=composted feedstock; T<sub>on</sub>=onset temperature; T<sub>max</sub>=maximum temperature; T<sub>r</sub>=temperature range

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728 **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 <sup>-1</sup> )	119	163	255	169	208	303
N (g kg <sup>-1</sup> )	45	36	26	56	48	34
C (g kg <sup>-1</sup> )	388	358	354	438	421	394
H (g kg <sup>-1</sup> )	92	94	94	90	88	95
HHV (MJ kg <sup>-1</sup> )	15.3	13.6	13.2	18.1	17.1	15.4

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

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761 **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 <sup>-1</sup> )	447	516	439	338	401	352
N <sub>2</sub>	10.0	5.6	3.2	10.0	5.6	3.2
CH <sub>4</sub>	6.1	11.3	13.5	6.2	11.5	11.7
CO <sub>2</sub>	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 <sub>2</sub>	2.4	3.4	3.5	2.5	3.2	3.3
C <sub>2</sub> H <sub>6</sub>	0.9	1.5	1.4	1.1	1.3	1.3
C <sub>2</sub> H <sub>4</sub>	8.9	6.7	5.7	10.0	8.0	6.9
C <sub>2</sub> H <sub>2</sub>	0.3	0.3	0.3	0.3	0.3	0.2
Other C <sub>x</sub> H <sub>y</sub> *	8.8	5.4	1.1	7.5	5.9	1.6
HHV (MJ m <sup>-3</sup> )	11.7	14.4	15.1	12.0	14.4	15.2

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

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788 **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)
<b>Inputs</b>						
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
<b>Outputs</b>						
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
<b>Output 1:Biochar as a Fuel</b>						
Energy Balance (MJ)	-24.1	165.1	509.9	37.3	149.5	319.2
<b>Output 2: Biochar to Soil</b>						
Energy Balance (MJ)	-100.4	1.9	148.9	-24.5	29.8	111.7

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

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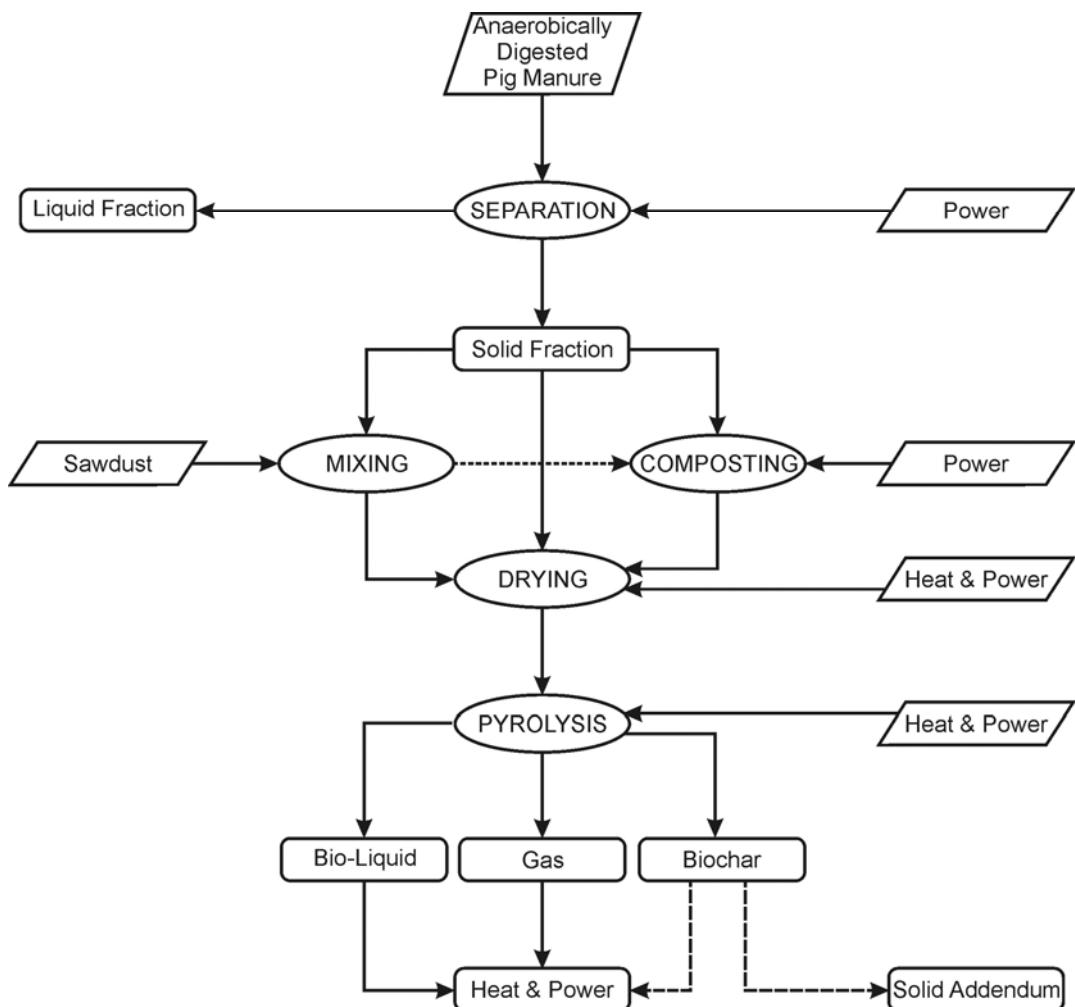
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803     Figure 1



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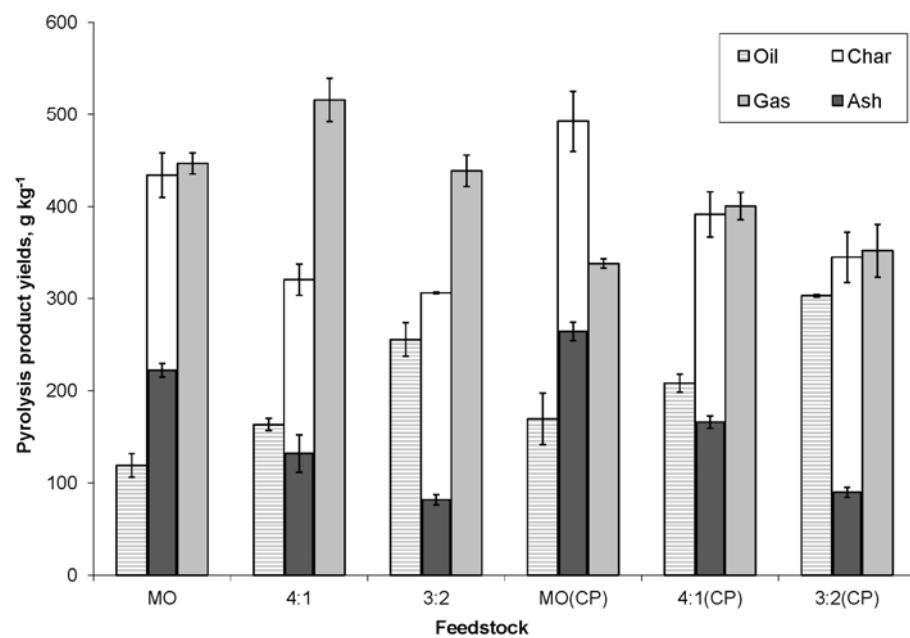
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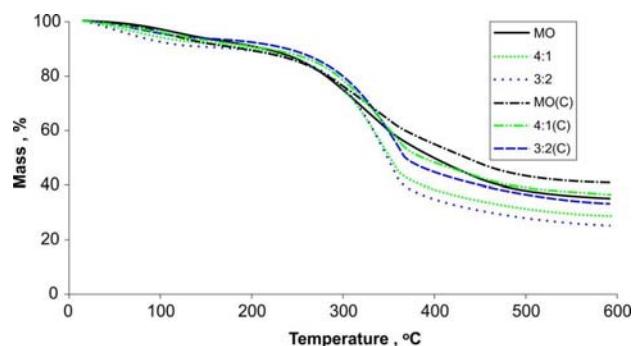
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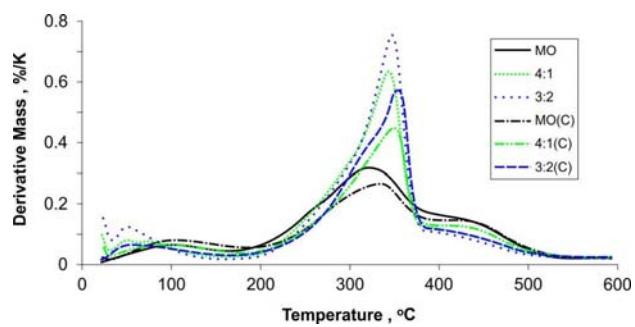
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826    Figure 3



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