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Evaluation of the potential performance of hyphenated Pyrolysis-Anaerobic Digestion (Py-AD) process for carbon negative fuels from woody biomass.

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Abstract

A novel hyphenated Pyrolysis-Anaerobic Digestion prototype (Py-AD) was tested in order to evaluate the potential of hybrid thermochemical biological process to produce methane from woody biomass. An auger intermediate pyrolyzer was directly coupled to two biological reactors optimized for the digestion of residual condensable compounds and gas produced by pyrolysis of softwood. The Py-AD was monitored for 16 months and a detailed chemical analysis of the main fractions, gas (pyrobiogas), biochar aqueous phase and pyrolytic lignin was performed under regime conditions. The results from Py-AD and those from experiments with bench-scale pyrolysis and fermentation reactors analysis provided information on the overall performance of the Py-AD and mass and energy balance based on chemical oxygen demand.

Py-AD allowed to obtain, with acceptable volumetric productivity, a pyrobiogas with a composition approaching that of biogas (47 %v/v CH₄ and 45 %v/v CO₂). Pyrobiogas yield was about half of the theoretical value calculated from gas and liquid fractions. A preliminary technical evaluation of the process confirmed the feasibility of Py-AD and its value to produce carbon negative fuels with simple equipment and low waste generation. Important key constraints of the process were also evidenced in the study.

Keywords: Pyrolysis, Anaerobic digestion, Hybrid thermochemical biological, Biomethane, Biogas

1. Introduction

34 Slow pyrolysis is one of the virtually simplest transformation of biomass among the various
35 thermochemical processes (e.g. fast pyrolysis, hydrothermal liquefaction and gasification).
36 Pyrolysis uses heat in an inert atmosphere without chemical reagents to break down polymeric
37 feedstock into smaller fragments, forming a vapor stream that is cooled down into two fractions: a
38 non-condensable gas and a liquid (named pyro-oil or bio-oil, formed by water and organic
39 substances). A solid residue (named char or biochar) is also formed by pyrosynthesis and
40 carbonization. Therefore, pyrolysis gives a fast and technically simple chemical deconstruction of
41 biomass and transfers the largest part of feedstock energy into gas and liquid, with contemporary
42 production of carbon rich residue that can be directly applied to soil as biochar.

43 Intermediate or slow pyrolysis (temperature of 400-500°C and reaction time longer than 1 min)
44 yields char (20-30%), gas (10-20%) and 50-60% w/w of a pyrolysis liquid with relatively high
45 water content (about 50% w/w).[1,2] These systems require quite a low heating rate that can be
46 easily obtained with technically simple equipment, like auger reactors. Although a large portion of
47 chemical energy is retained by biochar, its use for carbon storage in soil amendment enables the
48 production of energy/fuels with negative CO₂ emissions. [3] Gas contribution increases by catalysis
49 and higher vapor residence time, when secondary cracking reactions become relevant.[4,5]

50 Condensable substances can be subsequently categorized into water soluble low molecular weight
51 organics (semi-volatiles), high molecular weight organics (oligomers), and water insoluble
52 organics, the latter consisting by definition of pyrolytic lignin.[6] It is worth to notice that pyrolysis
53 gas and water soluble substances can be used as substrates in anaerobic digestion (AD), [7-12]
54 producing a biogas that can be easily used in internal combustion engines,[13] as well as upgraded
55 to methane (CH₄) usable as a drop in fuel.[14] This finding has recently suggested the concept of
56 “hybrid thermochemical-biological process”, in which thermochemical treatments enhance the
57 bioavailability of organic substrates towards anaerobic digestion for their conversion into biogas (a
58 mixture of CH₄ and CO₂).[15-17] This approach is of particular interest to the aim of converting the
59 fraction of biomass that is highly refractory to fermentation into biogas. In fact, this fraction
60 represents the hurdle to the utilization of woody biomass for the production of biogas. Therefore,
61 this hybrid approach can be envisaged as a suitable way for producing a biofuel with negative
62 emission of CO₂ assisted by the co-production of biochar as carbon sequestering agent. In general,
63 the two treatments (pyrolysis and anaerobic digestion) are coupled in an “off-line” configuration in
64 which products are separately collected in the first treatment (pyrolysis, Py) and thereafter send to
65 the second one (anaerobic digestion, AD).[18] To the best of our knowledge, the potential of an
66 “on-line” configuration in which pyrolysis and anaerobic digestion are directly interfaced (as
67 symbolized by the hyphen) has never been investigated on a relatively high scale (kg h⁻¹). To the

68 purpose of shading light on the technical feasibility of the process, advantages and constraints of
69 Py-AD, in this paper data from laboratory scale experiments were collected and used to set up the
70 first working Py-AD prototype. The Py-AD prototype was applied to the pyrolysis of a softwood
71 biomass; non-condensable gas and water-soluble fractions were the feed of two in series AD
72 reactors monitored for the production of biogas. Biochar and pyrolytic lignin were also collected
73 and analyzed. The obtained data enabled a preliminary energy balance of the Py-AD.

74

75 **2. Material and Methods**

76 ***2.1 Bench scale pyrolysis of biomass for conditions selection***

77 Commercial pine wood pellets with 2% humidity were used as feedstock for the experiments. This
78 feedstock had the following ultimate analysis (on dry weight basis): $47.5 \pm 2\%$ C, $5.5 \pm 1\%$ H,
79 $46.6 \pm 5\%$ O, and 0.4% ash. In bench scale pyrolysis experiments, about 5 g of biomass sample were
80 pyrolyzed at 400, 500 and 650°C for a set time (2, 4, 8 and 16 min) in a fixed bed quartz reactor at a
81 heating rate of about $100 \text{ }^\circ\text{C min}^{-1}$ by an electrically heated furnace described in detail elsewhere.
82 [19] The sample was inserted in the heated zones and here maintained for the set time. During
83 pyrolysis, pyrolysis vapors were swept by 1 L min^{-1} N_2 flow to a room temperature empty trap
84 (25°C), followed by trapping into 10 mL acetone (0°C). The amount of char produced was
85 measured as the weight of the solid material still present at the end of the pyrolysis run. At the end
86 of pyrolysis, the acetone solution of the second trap was evaporated under N_2 overnight. The
87 residue was added with distilled water (1:10), sonicated and settled overnight. Thereafter, the
88 aqueous solution that includes the non-volatile portion of aqueous pyrolysis liquid (APL) was
89 removed and the water insoluble fraction was dried to remove residual water. The dried water
90 insoluble residue was named as “water insoluble” portion of pyrolysis oil (WI), weighted and
91 subjected to elemental analysis to obtain the theoretical oxygen demand (ThOD, see section 2.4).
92 ThOD of pyrolysis products that can be subjected to fermentation was calculated by difference from
93 the initial chemical oxygen demand (COD) of the feedstock, ThCOD of biochar and ThCOD of WI.

94

95 ***2.2 Py-AD system***

96 The Py-AD plant description is shown in Figure 1. Pyrolyzer (Py) consisted in a single screw auger
97 reactor (stainless steel, AISI 321).[20] The pyrolysis reactor had an external diameter of 114 mm, 6
98 mm thickness and a length of 1350 mm. The central part of the system was equipped with 4 electric
99 jackets (total power 4 kW) that maintained the external temperature of the heated zone measured at
100 the top of the pyrolysis chamber at the set value of 400°C for a length equal to 600 mm. By
101 considering that the electric jackets heated up from the bottom, this corresponded to a maximum

102 measured temperature of about 500°C at the bottom of the reactor. The motion was applied by
103 means of an electrical engine that moved the shaft with 1 rpm angular speed acting intermittently to
104 have the set biomass flow rate (1 kg h⁻¹). A flow of N₂ at 0.1 L min⁻¹ was provided for safety
105 reasons nearby the airlock shaft coupling. The reactor was coaxially attached to a U-tube heat
106 exchanger (stainless steel, AISI 304) and biomass/biochar flowed by means of two opposite radial
107 openings for entrance of biomass from airlock feed, and biochar discharge opposed to shaft
108 coupling. The heat exchanger receiving the volatile pyrolysis product stream was connected to two
109 anaerobic digesters in series (reactor R1 and R2) by means of 23 mm ID silicone flexible hose pipe.
110 Pyrolysis liquid condensate flowed spontaneously into the bottom part of the U-tube heat exchanger
111 and was recovered, on daily basis, from a manual valve. The system was optionally used as
112 standalone pyrolyzer (Py) for comparison with Py-AD by means of a bypass valve, which swept the
113 pyrolysis gas directly to the flare. In this configuration, a peristaltic pump was used to withdraw the
114 pyrolysis liquid from the bottom of heat exchanger and injected it, through a 5 mm ID dish nozzle,
115 in the top of the same heat exchanger.

116 The residence time in the heated zone was set to 30 min and the biomass feed rate to 1 kg h⁻¹. The
117 U-Tube heat exchanger cooled down the pyrolysis products to 60°C, causing the condensation of
118 the liquid product, that was collected from the basis of the exchanger. The incondensable products
119 and residual aerosols were bubbled in the first biological reactor (R1, CSTR reactor) by means of a
120 25 mm OD inch silicone flexible pipe, 600 mm below the liquid level. R1 consisted in an insulated
121 vertical tank with a total volume of 450 L (600 mm diameter), filled with 300 L of liquid (inoculum
122 and water) and with a 150 L empty gas dome. The inoculum was a mesophilic anaerobically
123 digested excess sludge from a wastewater treatment plant (Hera s.p.a) located in Forlì (Emilia-
124 Romagna region, Italy), with 35 g L⁻¹ of volatile suspended solids (VSS). R1 was kept at 45°C by
125 means of auxiliary resistances. A recirculating gas-blower drew the gas from the dome and injected
126 it in the bottom of the R1 through a polypropylene sponge with 5-10 mm porosity. This created
127 bubbles with 10-20 mm diameters and concurrently provided mixing of R1. To avoid excessive
128 formation of foam, 10 mL of sunflower oil per week were added as anti-foam agent.

129 Produced/converted gas from R1 was injected into the top of the second biological reactor (R2)
130 proceeding downward into R2. Gas from the R2 exits 300 mm from the bottom of the same, which
131 is connected, by means of flexible hose, to a gas holder and, a gas meter. R2 was designed
132 according to Burkhardt *et al.* (2015), with slight modifications. [21] Briefly it consisted in a 350 L
133 trickled bed reactor, namely a tank filled with 300 L of random fill high surface media (140 m²/m³)
134 and 50 L of liquid. The trickling bed is kept wet by means of a progressing cavity pump that
135 pumped liquid digestate from the bottom of R2 to the top of the same through a deflector plate

136 nozzle. The Py-AD system was controlled by an Arduino MEGA board, which activated the plant
137 items as a time based sequence. Due to different size of Py and AD system, the Py throughput
138 capacity was higher than that needed for feeding AD system, therefore Py worked in pulsed mode
139 and AD in continuous regime. Therefore, during regime operations, the pyrolyzer worked 1 h every
140 day at noon, providing a feed rate equal to 1 kg day^{-1} , whereas the AD blowers and recirculation
141 pumps operated every hour for 5 min. This provided an adequate mixing of R1 and an adequate
142 trickle bed wetting in R2.

143

144 ***2.3 Anaerobic digestion of aqueous condensed phase***

145 Samples of the liquid product from Py-AD were recovered at the bottom of the condenser with a
146 manual valve. The samples consisted of a biphasic liquid, namely an organic rich bottom phase and
147 an aqueous upper phase, with few droplets on the top (extractives). This mixture was settled into a
148 separator funnel for 4 h to obtain a clear phase separation. The bottom phase, mainly consisting in
149 pyrolytic lignin and other water insoluble products, was recovered and analyzed. The upper aqueous
150 phase of pyrolysis liquid (APL) was analyzed and subjected to anaerobic digestion in an upflow
151 anaerobic sludge blanket reactor (UASB) shown in Figure 2. The UASB consisted in an 80 mL
152 reactor, kept at 40°C and equipped with an inlet at the bottom and an outlet on the top of the
153 reactor. The reactor was initially filled with inoculum (see section 2.2) and 8 g of grinded biochar
154 sampled from that obtained from Py-AD pilot plant experiments described above. A peristaltic
155 pump was used to inject APL in anaerobic reactor at set rate. For technical reasons, APL was
156 provided as several pulses of 0.2 min providing 0.2 mL of liquid per pulse with daily rate in the
157 range of $0\text{-}1 \text{ mL day}^{-1}$. Due to extremely high C/N ratio of APL, additional 1 mL per week of
158 inoculum was added to provide a nitrogen supplementation to the microbial consortia. Mixing of
159 the system was obtained by another peristaltic pump taking the liquid from the top of the reactor (10
160 mm below the reactor roof) and pumping it in the reactor inlet with a pumping rate equal to 10 mL
161 h^{-1} . The outlet of reactor was connected to a Supelco Inert Foil Gas sampling bag used for collecting
162 both biogas and liquid digestate by means of tygon® tubing. Every 2 d, the bag was emptied,
163 measuring the gas and liquid content. The liquid digestate and biogas were analyzed as described in
164 the following section.

165

166 ***2.4 Analysis of gas, aqueous phases and water insoluble phase***

167 Concentration of H_2 , CH_4 , CO_2 in biogas and CO in pyrolysis gas determined by GC-TCD 7820A
168 (GC system, Agilent Technologies) using three packed columns placed in series (HAYASEP 80–
169 100 mesh HAYASEP 0 80–100 mesh, and MOL SIEVE 5A 60–100 mesh (Agilent Technologies))

170 with the following thermal program: 9 min at 50 °C, then 8 °C min⁻¹ to 80 °C. Quantitation was
171 performed using the calibration mixture Scotty Analyzed Gases Supelco, Sigma-Aldrich.
172 The determination of volatile fatty acids (VFAs) in WI, APL and liquid digestate was performed by
173 solvent extraction and GC-MS analysis following the analytical method developed by Ghidotti *et*
174 *al.*[22] The analytical characterization of WI and APL was performed following the solvent
175 fractionation procedure and analysis described in Busetto *et al.* (2011).[23] Elemental analysis (C,
176 H, and N) was performed using a Thermo Fisher Elemental Analyzer (Flash 2000), configured for
177 solid samples with a copper/copper oxide column and calibrated with 2,5-bis(5-*tert*-butyl-2-benzo-
178 oxazol-2-yl) thiophene (BBOT).
179 The quantitation of GC-MS detectable organics in APL, WI and liquid digestate was performed
180 after water evaporation, trimethylsilylation and GC-MS analysis following the procedure described
181 in detail elsewhere. [24]
182 The theoretical oxygen demand (ThOD, gCOD g⁻¹), accordingly to OECD guideline 301F, [25] was
183 calculated from elemental analysis using the following formula:

$$\text{ThOD} = 16 \cdot ((2 \cdot \text{C} / 12 + \text{H} / 2 + 2 \cdot \text{S} / 32 - \text{O} / 16 - 3 \cdot \text{N} / 2)$$

185 COD yield, namely the percent amount of ThOD of the feedstock transferred to certain Py-AD
186 product was calculated with the following formula:

$$\text{COD yield} = \text{ThOD yield} = Y_i \cdot \text{ThOD}_i / \text{ThOD}_{\text{feedstock}}$$

188 Where Y_i is the mass yield (kg/kg_{feedstock}) of a product and ThOD_i is the chemical oxygen demand
189 of the product (gCOD g⁻¹). COD yield of digestate in Py-AD was obtained by difference between
190 100% and the sum of COD yield of pyrobiogas, char and liquid product.

191

192 **3. Results and discussion**

193 **3.1 Bench scale pyrolysis tests**

194 To better understand the intrinsic constraints of a Py-AD approach based on intermediate pyrolysis,
195 some preliminary bench scale tests were targeted to the evaluation of maximum amounts of
196 chemical energy released as bioavailable products, namely water-soluble pyrolysis products and
197 pyrolysis gas. The Chemical Oxygen Demand (COD, gO₂/g_{substrate}) is a way to measure the energy
198 stored in chemical substances, and can be directly translated into a theoretical biomethanation
199 potential. On the basis of stoichiometry and high heating value (HHV), empirical calculations show
200 that 1 kg of COD stores about 15 MJ energy, and the anaerobic digestion of 4 kg of COD as organic
201 matter is required to obtain 1 kg of methane. Figure 3 shows the COD balance of intermediate
202 pyrolysis performed with reactor temperature between 400 and 650°C and time ranging between 2
203 and 16 minutes. With the exception of torrefaction-like conditions (short pyrolysis time and low

204 temperature), which released a negligible amount of COD into non-solid fraction, the amount of
205 COD that was transferred to fermentable products, namely the aqueous phase and pyrolysis gas,
206 represented about an half of the chemical energy of the feedstock and remained almost constant.
207 Comparing the data of intermediate pyrolysis with data from the large literature concerning fast
208 pyrolysis (Figure 3), it appears that a “complete” pyrolysis produces a roughly similar yield of
209 bioavailable compounds, corresponding to 40-60% of chemical energy of the feedstock.
210 Considering the trade-off between operational advantages (e.g. lower temperature) and almost
211 comparable yield of substances amenable to anaerobic fermentation, the Py-AD system was
212 designed to operate at a set temperature of 400-500°C.

213

214 ***3.2 Py-AD prototype***

215 ***3.2.1 Set up and preliminary experiments***

216 Construction of prototype was performed with standard industrial equipments in order to obtain a
217 scalable system suitable to be replicated. The system was improved over time in order to increase
218 its performance. The basic elements of the systems were the pyrolyzer (Py) an heat exchanger at
219 60°C, used to remove a portion of heaviest part of pyrolysis liquid (e.g. water insoluble fraction)
220 and one or two anaerobic reactors (R1 and R2). The initial Py-AD included a pyrolysis reactor, a
221 heat exchanger and one biological reactor. In this configuration the pyrolyzer just bubbled the raw
222 pyrolysis vapours (upon cooling) at the bottom of an anaerobic digester (R1). Such a system
223 typically produced a gas almost unconverted and still rich in aerosols. Therefore, in a second
224 configuration a trickled bed reactor (R2) was added in order to remove aerosols. R2 was filled with
225 high surface spherical elements ($140 \text{ m}^2/\text{m}^3$) for biofilm formation. This configuration allowed the
226 removal of all aerosols from raw pyrolysis gas and provided a significant digestion of non-
227 condensable pyrolysis gases (NCG). Py-AD was finally improved by inserting a system for the
228 recirculation of raw pyrolysis gas into R1 in order to provide adequate mixing of the anaerobic
229 digester. This last configuration, which consisted of a Py with heat exchanger connected to a 300 L
230 CSTR with gas recirculation in turn connected to a 300 L trickled bed reactor (Figure 1) was used
231 for acclimatization and to observe the performance for pyrolysis gas conversion. The first part of
232 the study was performed on the raw pyrolysis gas, discarding the pyrolysis liquid produced. Several
233 preliminary test were performed by pyrolyzing, in discontinuous mode, about 1 kg in 1 test per
234 week. During these preliminary tests the the Py system was run for 1 hour and switched off,
235 keeping the AD part on (blowers and recirculation pump). After this, the concentration of gas
236 constituents was measured over time, providing a conversion rate of gas (Figure 4) at different time
237 after system startup. During the initial phase of the study, a low conversion of pyrolysis gas/volatile

238 products were observed, in accordance with previous literature data.[7,10] The ratio between
239 gaseous constituents of biogas (CH₄ and CO₂) and “pyrogenic” gases (H₂ and CO) increased over
240 time reaching a plateau after 120 days. After 120 days, although a residual amount of H₂ and CO
241 was present, the composition gas produced was close to that of biogas.
242 The increase of gas conversion rate took more than 4 months and was slower than what observed in
243 previous studies that occurred in few weeks; [7] this can be attributed to the need of active biofilm
244 growth in R2. The conversion rate observed after 120 days was equal to 2.7 Nm³ m⁻³ d⁻¹ for biogas
245 and 1.4 Nm³ m⁻³ d⁻¹ for biomethane. This value falls in the middle of the volumetric productivity in
246 literature, which shows a large productivities range between 0.1 Nm³ m⁻³ d⁻¹ and 7 m³ m⁻³ d⁻¹ .[28]
247 Although the system used here includes a bubbled reactor (R1) and trickle bed reactor (R2),
248 observed value is close to what observed with trickle bed reactor with similar specific surface area,
249 namely 1.5 Nm³ m⁻³ d⁻¹ obtained by Burkhardt *et al.*,[21] with mixed inocula, on H₂/CO₂ mixtures
250 and 1.6 Nm³ m⁻³ d⁻¹ obtained by Klasson *et al.* using a triculture onto syngas.[29]

251

252 3.3.2 Continuous test

253 After having reached the system stability, the input rate of the system was increased to 1 kg h⁻¹,
254 using this regime conditions for one month. During this time, conversion performances and overall
255 yields was measured. Figure 5 shows the composition of gas during regime operations. After
256 increase of input rate of feedstock, a significant increase of CO and H₂ concentrations were
257 observed suggesting an incomplete conversion of incoming pyrolysis gas until day 4. This decrease
258 in conversion rate was accompanied by an increase in VFA concentration in the R1 from 0.4
259 baseline to 0.95 g L⁻¹ in the first 6 days (Figure 6). This increase in VFA concentration was not
260 observed in R2, in which VFA concentration fell below 0.3 g L⁻¹ for all the duration of the study.
261 After that, the concentration of pyrogenic gas, showed a variable trend until the day 14. After day
262 14 the gas composition was dominated by CH₄ and CO₂ with minimal amount of CO and H₂. This
263 trend suggests an adaptation of the microbial consortia to the organic load applied. The initial
264 unbalance mainly involved R1, and therefore could be related to increased load of residual
265 condensables of raw pyrolysis gas, which mainly involved R1. Nonetheless, the overall trend
266 observed suggested that the co-digestion of all raw pyrolysis gas constituents (including semi-
267 volatile constituents) can be feasible with an adapted microbial consortia.

268

269 3.3.3 Mass and energy balance. Comparison with Py

270 In order to obtain the net effect of AD on pyrolysis products, a comparison between Py and Py-AD
271 was performed. In order to improve the collection of the liquid in the heat exchanger, the Py system

272 was slightly modified by using the pyrolysis liquid as scrubbing agent. The purpose of this
273 implementation was that to obtain a pyrolysis gas with a low content of residual aerosols
274 comparable with that observed for Py-AD. The Py test was performed for 8 h test in which the
275 various fractions were collected and analysed. Overall yields, on mass basis and COD basis,
276 obtained by Py and Py-AD tests are shown in Table 1. The biochar yields resulted identical in both
277 systems, confirming the replicability of Py. The standalone Py yielded 28% $\text{kg/kg}_{\text{wood}}$ of a biochar
278 with the following elemental composition $77\pm 3\%$ carbon, $2.5\pm 0.5\%$ hydrogen, $19\pm 3.5\%$ oxygen
279 and $1.4\pm 0.5\%$ ash (mean \pm standard deviation, $n=5$). Under these conditions, the liquid product
280 yields of Py was 63% $\text{kg/kg}_{\text{wood}}$ (17% organic fraction and 83% water phase) and gas yield was 9%
281 $\text{kg/kg}_{\text{wood}}$. Data are in accordance with the literature concerning slow/intermediate pyrolysis of
282 wood in comparable reactors.[5,2] The coupling with of AD changed deeply the volatile/gas
283 product distribution of Py of wood. Py-AD yielded less liquid, namely 28% $\text{kg/kg}_{\text{wood}}$, with
284 concurrent increased production of pyrobiogas 19% $\text{kg/kg}_{\text{wood}}$ and a relevant production of digestate
285 reach in water. Stoichiometry of CO conversion, which involve increase in biogas mass through
286 water-gas shift, partially explain this increase of gas yield. In addition, significant portion of
287 pyrolysis water and volatile organics (e.g. acetic acid) that were condensed in Py alone
288 configuration were probably transferred in the AD. These organics were converted to gas or
289 transferred to digestate when Py-AD configuration is used. Gas produced by means of intermediate
290 Py were mainly formed by CO (62% v/v) and CO₂ (24% v/v) with minimal amount of CH₄ and H₂
291 (11 and 2% v/v respectively), with composition comparable to that reported in literature for
292 intermediate/slow pyrolysis with low reaction temperature.[30] Gas produced by Py-AD system
293 showed an average composition that is similar to that of biogas with increased content of CH₄ and
294 CO₂ (47.4% v/v and 44.6% v/v respectively), decreased content of CO (6.7% v/v) and comparable
295 concentration of H₂. This change in composition was similar to that observed in studies focused on
296 syngas biomethanation,[7] and confirms the biological conversion of both gaseous and semi-volatile
297 products that reach the AD system.

298 From the point of view of chemical energy, it is useful to look at the COD balance of Py and Py-AD
299 (right part of Table 1). At 400°C Py and Py-AD, 52 % of the feedstock chemical energy and $46\pm 2\%$
300 of the feedstock carbon are driven to biochar. This is in line with bench scale experiments and
301 match with literature concerning slow/intermediate pyrolysis of wood. For 400°C Py most of the
302 remaining chemical energy ended up in liquid fraction (39% of the feedstock COD) and gas (mainly
303 formed from carbon dioxide and carbon monoxide) retained a minimal amount of initial energy.
304 Such energy distribution observed is in line with that of literature for slow pyrolysis at low
305 temperature (450°C).[5,31]

306 When the raw pyrolysis products were just cooled down to 60°C and directly injected into AD, Py-
 307 AD drastically increased the COD yield of gas by a factor three, with a pyrobiogas yield that
 308 retained 21% of the initial COD of the feedstock. The difference between input and output of COD
 309 was different between both Py (4.4% losses) and Py-AD (13%).

310 In the Py case, the amount of losses can be attributed to the small amount of oxygen present in the
 311 technical grade purge nitrogen (99%), used for safety purpose, and incomplete collection of non-
 312 gaseous constituents, namely aerosols. In the case of Py-AD the gas was clear and without
 313 significant amount of aerosol, and therefore the COD balance observed is probably due to an
 314 incomplete conversion of the pyrolysis products as well as bacterial growth. For Py-AD, the
 315 increase in losses (from 4.4 to 13% of feedstock COD) is opposite to the change of the COD yield
 316 observed for organic fraction of liquid, which decreases from 14 to 4.5 %. In this case the expected
 317 amount of COD converted to bacterial biomass should be well below 2%, [32] this could suggest
 318 that the organic fraction of pyrolysis liquid, although transferred to R1, is not converted effectively
 319 by the AD.

320

321 **Table 1:** comparison of mass and chemical energy yield in Py and Py-AD.

322

	% w/w _{feedstock}		% COD/COD _{feedstock}	
	Py	Py-AD	Py	Py-AD
biochar	28	28	52	52
aqueous phase	53	28	26	10
organic fraction	11	4.0	14	4.5
digestate and losses*	1.0	16	4.4	13
gas	7.0	24	3.6	21
<i>H₂</i>	0.01	0.03	0.1	0.2
<i>CH₄</i>	0.4	6.2	1.7	20
<i>CO₂</i>	2.4	16	0	0
<i>CO</i>	4.0	1.5	2.3	0.7
<i>C_nH_m</i>	0.1	-	0.4	-

323 *includes the net balance between pyrolytic water transferred to AD and evaporation from
 324 digesters.

325

326 3.3 Anaerobic digestion of Aqueous Pyrolysis liquid (APL)

327 As previously mentioned, Py-AD involves the conversion of NCG and the part of semi-volatile
 328 compounds that are transferred to R1. The part of pyrolysis liquid that were collected in the heat
 329 exchanger, was recovered and subject to characterization. This pyrolysis liquid was made by an

330 aqueous phase (APL, 87% w/w, average of all the tests) and an organic (<10% water content)
331 bottom phase (WI, 13% w/w) with minimal amount of extractives (<1% w/w). The relative
332 composition of the phases was relatively constant with average relative standard deviations of the
333 above reported values less than 5%. APL from Py-AD was mainly formed by 80% w/w water and
334 8% w/w pyrolytic “sugars”. APL contained about 2%w/w VFA (mostly acetic acid) and minimal
335 amount of phenols, which probably were partitioned to WI. Organics content and VFA
336 concentration in APL from Py-AD were lower than the literature related to intermediate pyrolysis
337 for wood.[23,33,34] This is probably due to low temperature pyrolysis (400°C) and specific
338 reaction configuration, that imply a relatively low recovery of more volatile pyrolysis products
339 (VFA or alcohols), which on the opposite were deliberately transferred to the AD system. This
340 phenomena could be one of the source of biogas produced by Py-AD (see above in section 3.2).
341 As far as the organic bottom phase is concerned, this portion of pyrolysis liquid was subjected to
342 solubilization test in order to establish residual solubility in water, analyzed by elemental analysis,
343 GC-MS, derivatization/GC-MS and Gel Permeation Chromatography. Even if diluted to less than 1
344 g L⁻¹ concentration, WI showed a negligible (<10%) solubilization in water. Moreover, the
345 chemical analysis indicated that WI was mainly formed by phenols and lignin oligomers, with a
346 significant amount of polycyclic aromatic hydrocarbons (PAHs, 120 mg kg⁻¹) and quite low (<2%)
347 content of water soluble pyrolysis products. The composition of both APL and WI suggested a large
348 partitioning of organic compounds on the basis of water solubility. Analysis showed an almost
349 complete partition of hydrophobic constituent, namely lignin oligomers and PAHs, in the WI and
350 partition of VFA and sugar like, which are potentially biodegradable compounds, in the APL.
351 According to composition and expected chemical behavior of the two liquid fractions obtained by
352 pyrolysis, namely APL and WI, it can be concluded that APL can be, in principle, considered a
353 good feedstock for biological valorization. In fact, it was previously demonstrated that using a
354 portion of biochar produced in the AD it is possible to overcome the toxicity of APL.[10]
355 On the opposite, the relative low yield of WI, that concentrates several compounds with potential
356 concern for biological valorization, suggests higher suitability of different applications.
357 Although APL could be potentially digested directly in on-line Py-AD the further optimization of
358 Py-AD system needs to know exactly the maximum organic loading rate and yield for each fraction
359 (e.g. gas, volatile compounds and APL) and to perform a longer test for establishing potential long
360 term inhibition due to heavy constituents of APL. Therefore, a small scale AD system for APL was
361 set up on and monitored. The system was made by an 80 mL Upflow Anaerobic Sludge Blanket
362 (UASB) and was described in detail in section 2.3 and in Figure 2. Besides APL and inoculum, the
363 system was added with biochar in order to minimize the toxic effect of APL, as shown in previous

364 study.[10] The trend of input and outputs expressed in mg of COD observed in experiments are
365 presented in Figure 7. At the beginning of the experiment a spike in the biogas production was
366 observed ($> 100\%$ of input COD) probably due to the residual activity of the inoculum and
367 degradable organics adsorbed of biochar. After 20 days, the Organic Loading Rate (OLR) of the
368 reactor was increased from $0.25 \text{ gCOD L d}^{-1}$ to $1.25 \text{ gCOD L d}^{-1}$. This change resulted in an
369 acceptable conversion of APL into biogas, with negligible VFA production. After a further increase
370 in OLR from 1.25 g L d^{-1} to 2.5 g L d^{-1} the absolute production of biogas remained rather stable,
371 whereas the concentration of VFA in the effluent increased significantly. To the purpose of
372 avoiding the collapse of the AD, the OLR was switched back to $1.25 \text{ gCOD L d}^{-1}$. This
373 demonstrated that the maximum OLR that can be reached without long term intoxication. This
374 value was actually less than half than that previously obtained for APL from bench scale pyrolysis
375 corn stalk.[10] This could be due to difference in feedstock (woody vs herbaceous biomass) or to
376 the fact that Py-AD, as demonstrated above, produced an APL that was depleted in some of the
377 easily biodegradable compounds (e.g. VFAs) produced by pyrolysis. Nonetheless, the maximum
378 OLR achieved suggested that, in order to simplify the process scheme, APL can be coprocessed in
379 the proposed Py-AD, just by adding biochar in R1 and without large increase of the volume of R1.
380 In order to establish, for the first time, the actual anaerobic biodegradability of pyrolysis products,
381 chemical analysis of input and output of the AD was performed. The results of GC-MS analysis of
382 some relevant compounds showed that for all the duration of the study at any ORL tested, the
383 degradation of was almost complete (Table 2). At the end of the experiment, an average degradation
384 rate of key compounds in the APL was estimated (Table 2). Most of the APL pyrolysis products
385 are degraded effectively under the conditions of this study, but the rate of degradation was larger for
386 carbohydrate derivatives and for compounds with natural analogs (carboxylic acids). On the
387 opposite, substituted phenols (e.g. catechol and methyl-catechols) resulted refractory, with half life
388 more than 20 days and significant accumulation in the system in the late part of the study.
389 The overall biogas yield of the test starting from 20th day to the end of the experiment, was 34% of
390 the fed COD, with a co-production of 18% yield as VFAs. This means that, under the conditions
391 studied here, 52 % of APL was potentially biodegradable under anaerobic conditions. This figure is
392 in line with previous studies on AD of APL from slow pyrolysis.[7,15]
393 It is interesting to notice that when the ORL exceeded the $1.25 \text{ gCOD L d}^{-1}$ value the system still
394 biodegraded more than half of the COD of APL, but was producing more VFA instead of biogas. In
395 conclusion, the residual APL produced by Py-AD presented two main critical issues for AD. One is
396 the the toxicity of the mixture, which was experimentally observed in the middle timespan of the
397 AD experiment. This toxicity could be attributed to trace compounds that are highly toxic to

398 methanogenic archaea or to matter that is non-detectable by GC-MS (e.g. formic acid, oligomers or
 399 trace metals from the alloys used for Py-AD). This problem could be circumvented by means of
 400 process intensification adopting a multi-stage AD system are used or if product different from
 401 biogas could be produced from VFA (e.g. concentrated VFA, polyhydroxyalkanoates or bio-
 402 electricity with microbial fuel cell).[35] The other relevant critical issue of APL is that about 45%
 403 of the APL carbon was not degradable under the conditions used here. This value corresponded to
 404 3.6% of the COD of the initial biomass, therefore it is not highly relevant for the efficiency of the
 405 overall Py-AD system. Nonetheless, these non-negligible constituents will end up in the wastewater
 406 streams generated by Py-AD and, consequentially they should be treated in some way (e.g.
 407 concentrated and fed back to the Py, or oxidized by chemical means).

408
 409 **Table 2:** degree of biodegradation of main APL constituents detected by GC-MS after silylation of
 410 AD effluent.

	% degraded	K_{deg} (d^{-1})	$t_{1/2}$ of Py product in AD (d)
1,6-anhydro-β-glucopyranose	100%	0.19	3.7
1,4-anhydro-β-arabinopyranose	100%	0.19	3.7
hydroxyacetic acid	91%	0.17	4.1
3-methoxy-4-hydroxy-benzene	87%	0.16	4.3
1-methyl-catechol	71%	0.13	5.2
benzoic acid	32%	0.06	12
3,4-hydroxyhydrocinnamic acid	27%	0.05	14
catechol	11%	0.02	34

411

412 **3.4 Overall performance of Py-AD**

413 Data obtained from experiments were used to calculate the expected overall performance of a Py-
 414 AD process finalized to produce biochar and methane enriched fuels. Figure 8 shows the energy
 415 balance of Py-AD expressed as $J/J_{feedstock}$. As a whole, Py-AD is schematized as a functional
 416 element that converts feedstock chemical energy, set equal to 100%, uses high temperature heat
 417 ($>400^{\circ}C$) which is degraded to low temperature ($<60^{\circ}C$) heat, and produces an array of products
 418 whose sum is roughly equal to the chemical energy of the feedstock used. The system tested here
 419 converts half of energy into a biochar, one third into pyrobiogas and about 5% into a water
 420 insoluble organic liquid (WI). Due to conversion of the raw pyrolysis gas and of the most volatile
 421 part of condensable pyrolysis products, the gas produced by the Py-AD system is significantly
 422 higher than that produced by low temperature pyrolysis and close to the yields obtainable by
 423 carbonization at temperature $>450^{\circ}C$. [5]

424 Py-AD processing of 1 kg h^{-1} of wood (1.2 kgCOD h^{-1} corresponding to 5.1 kW energy input),
425 produces 0.3 kgCOD h^{-1} as pyrobiogas (1.3 kW). If burnt into an engine this would provide 0.35 -
426 0.4 kW_{el} and 0.5 - 0.6 kW_{th} power. In order to establish the technical feasibility of a small-scale Py-
427 AD system, a preliminary evaluation of energy requirement of the process can be performed on the
428 basis of the $1 \text{ kg}_{wood} \text{ d}^{-1}$ operation. Excluding the time needed for heating up the reactor, the power
429 consumption of 1 kg h^{-1} Py was around 300 - 400 W . This means that the heat needed for pyrolysis
430 is equal to 1.1 - $1.4 \text{ MJ/kg}_{biomass}$. This energy corresponds to 6 - 8% of the calorific value of the
431 biomass pyrolyzed (17.9 MJ/kg) and 20 - 30% of the energy of pyrobiogas. Despite the low yield of
432 the process, this value is significantly lower than that reported for fast pyrolysis, probably due to
433 low temperature, low heating rate and a certain degree of exothermicity of slow pyrolysis of
434 pelletized biomass.[33] By measuring the difference in temperature of the cooling water used in
435 heat exchanger, it was possible to estimate that a large portion ($>85\%$) of the energy used in
436 pyrolysis can be recovered as sensible and latent heat at 60°C in the heat exchanger. This would
437 suggests again that the slow pyrolysis reaction itself was not endothermic and most of the heat
438 requirement was sensible heat and latent heat of evaporation. From a practical point of view, this
439 heat could be recovered, with high efficiency, to provide the low temperature heat needed to keep
440 reactor warm in cold climates. Main implications of this observation is that, given that the pyrolysis
441 vapours are provided to the biological reactors at temperature slightly higher than 60°C , it is
442 possible to be confident that all the low temperature needs (biological reactors heating) of Py-AD
443 can be fulfilled with waste heat from Py without additional energy input.

444 Given that biological process has lower volumetric productivity than chemical reactors, another
445 important point for hybrid thermochemical-biological system reliability is the space requirement for
446 anaerobic digester. Extrapolating the results presented here, the size of anaerobic digester needed
447 for stable Py-AD of $1 \text{ kgCOD}_{feedstock} \text{ d}^{-1}$ should be around 0.25 m^3 for digestion of raw pyrolysis gas
448 and $0.1 \text{ m}^3 \text{ d}$ for stable digestion of APL produced. This means that, on a conservative basis, a
449 pyrolyzer fed with 1 kg h^{-1} of wood require an AD systems with a total volume equal to 10.4 m^3 . In
450 order to compare such volume with commercial anaerobic digestion systems, this value can be
451 converted in a volume per unit of electrical power produced. For Py-AD, using $\eta=35\%$ for the
452 engine, this means a productivity equal to $43 \text{ W}_{el}/\text{m}^3$, which is comparable with the data of
453 commercial digesters that typically shows volumetric productivities in the 10 - $100 \text{ W}_{el}/\text{m}^3$
454 range.[36,37]

455

456 **4. Conclusions**

457 This study put into practice the idea of a direct coupling between pyrolysis (Py) and anaerobic
458 digestion (AD) to the end of converting woody biomass into a “pyrobiogas” fuel rich in biomethane
459 and biochar. Experiments with bench-scale reactors suggested that low pyrolysis temperatures are
460 preferable in order to increase the yield of potentially fermentable materials, which includes NCG
461 (e.g. CO, H₂) and water-soluble organic compounds of pyrolysis liquid. These two fractions
462 exhibited a summed limit value that approaches to the 50% of chemical energy of input softwood
463 biomass feedstock. In particular, chemical analyses showed an almost complete biodegradation
464 under anaerobic conditions of semi-volatile components detectable by GC-MS. On the basis of the
465 results from laboratory and available literature data, a Py-AD prototype, where the hyphens indicate
466 that the pyrolyzer was physically interfaced with two biological reactors, was operated and
467 monitored for more than 16 months. This long-term experiment enabled the identification of pros
468 and cons of the concept in a real case. The Py-AD produced pyrobiogas, namely an aerosol-free
469 biogas (CH₄ 47.1%v/v and 44.6 %v/v CO₂) containing residual carbon monoxide (6.7% w/w) and
470 hydrogen (1.6%) with a yield of 0.21 Nm³ kg_{feedstock}⁻¹. Experimental results were used for a
471 preliminary technical evaluation of the whole process, which resulted reliable in term of energy
472 balance and volumetric productivity.

473 While this study confirmed the feasibility of Py-AD to convert wood into biogas within a self-
474 sustained process, it also evidenced a relatively low absolute yield that calls for important
475 improvements in the process. The low yield was attributed to the presence of high molecular weight
476 constituents which are refractory to biodegradation, in particular the lignin-derived fraction
477 transferred to biological reactors. According to this, the process could be improved by investigating
478 new microbial communities, diversion of the water insoluble fraction to different purposes, or by
479 targeting the pyrolytic conversion to biodegradable intermediates.

480

481 **List of Abbreviations**

482 AD: Anaerobic Digestion

483 APL: Aqueous phase of pyrolysis liquid

484 COD: Chemical Oxygen Demand

485 CSTR: Continuously Stirred Tank Reactor

486 NCG: Non Condensable Gas

487 OLR: Organic Loading Rate

488 PAHs: Polycyclic Aromatic Hydrocarbons

489 Py: Pyrolysis

490 Py-AD: Hyphenated Pyrolysis-Anaerobic Digestion process

491 R1: first CSTR reactor used for anaerobic digestion of pyrolysis products
492 R2: second plug flow trickling bed reactor for anaerobic digestion of NCG
493 ThOD: Theoretical Oxygen Demand
494 UASB: Upflow Anaerobic Sludge Blanket
495 VFA: Volatile Fatty Acids.
496 WI: Water Insoluble

497

498 **Acknowledgement**

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500 provided.

501

502 **References**

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- 600
- 601

602 **Figure Captions**

603 **Figure 1:** pyrolysis-anaerobic digestion prototype used for Py-AD and Py experiments.

604

605 **Figure 2:** experimental apparatus used for continuous anaerobic digestion of aqueous phase
606 pyrolysis liquid (APL)

607

608 **Figure 3:** partition of chemical oxygen demand upon intermediate pyrolysis of pine wood pellets
609 performed with bench scale pyrolyzer. *data back calculated from yield and composition from ref.
610 [27]

611

612 **Figure 4:** volumetric syngas conversion rate observed during different stages of long term
613 adaptation of microbial consortia to volatile pyrolysis products.

614

615 **Figure 5:** volumetric composition of biogas during 30 days of Py-AD test with constant biomass
616 feed rate.

617

618 **Figure 6:** VFA concentration observed in R1 during 30 days of Py-AD test with constant biomass
619 feed rate.

620

621 **Figure 7:** trend of OLR and yields of VFA and biogas during continuous anaerobic digestion of
622 residual APL obtained from Py-AD experiment.

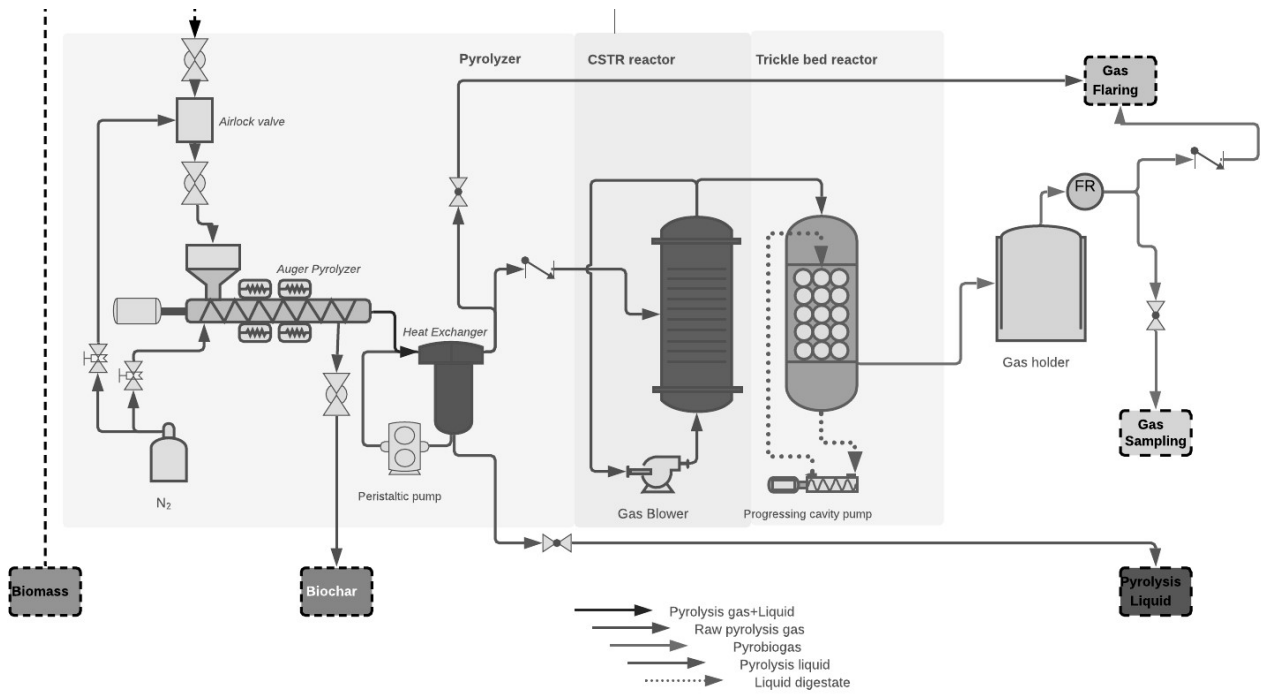
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624 **Figure 8:** Graphical description of the input/outputs of chemical energy of the Py-AD system
625 proposed here. All data are expressed as % of initial chemical energy stored in pine wood biomass.

626

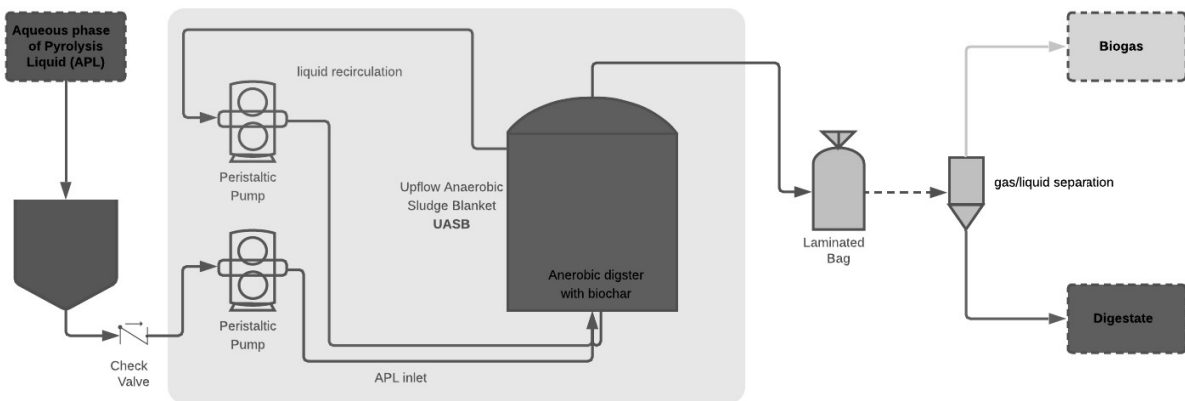
627 **Figures**

628 **Figure 1**



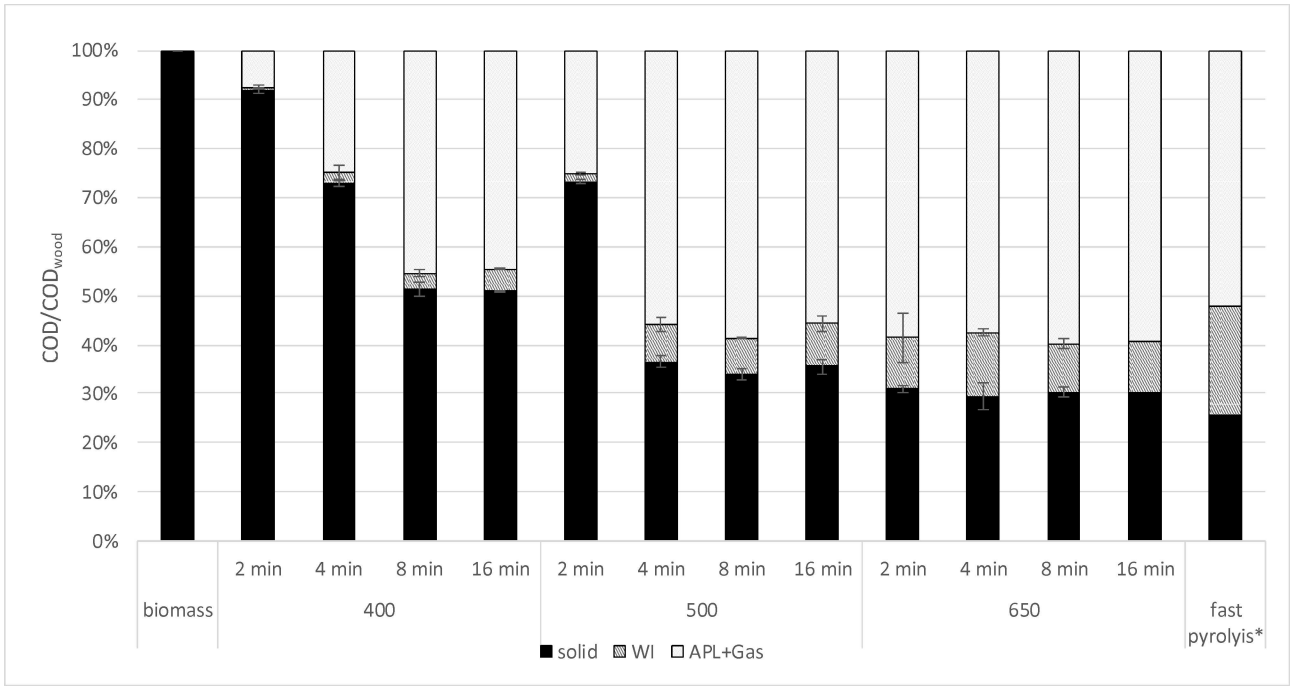
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630 **Figure 2**



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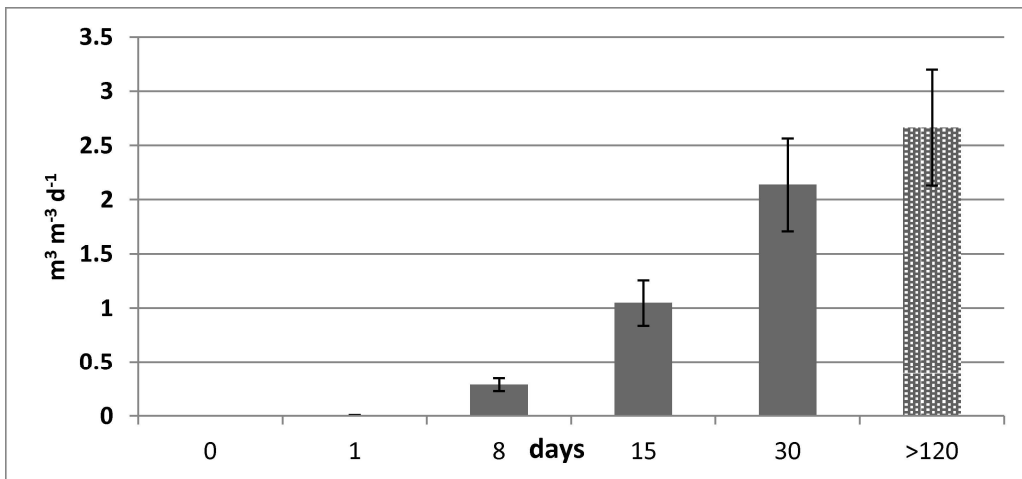
632 **Figure 3**



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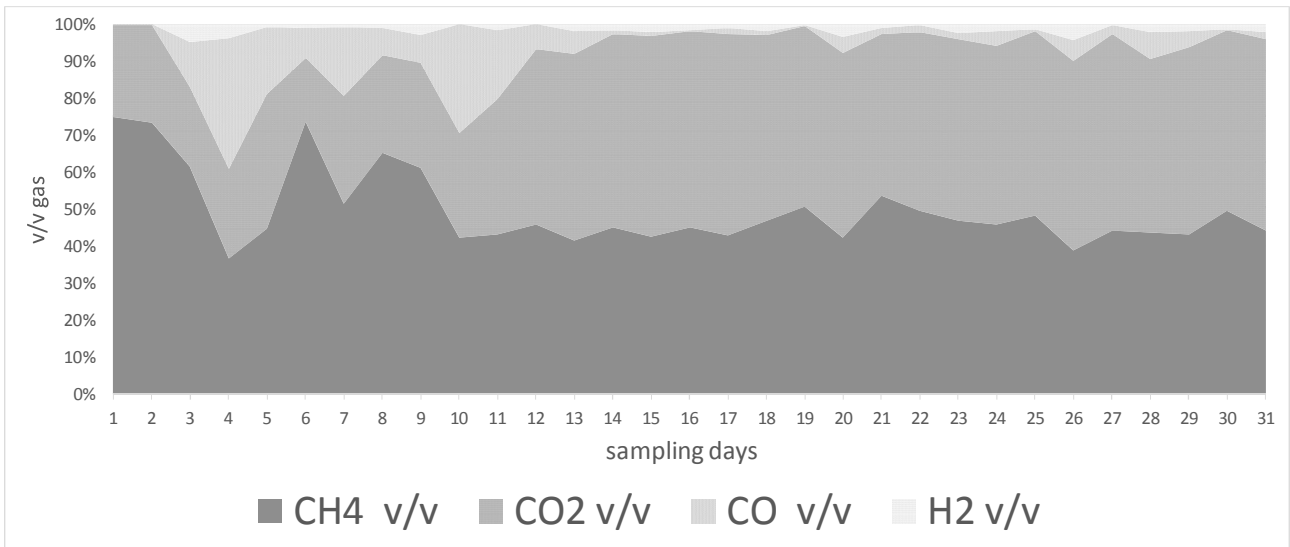
635 **Figure 4**



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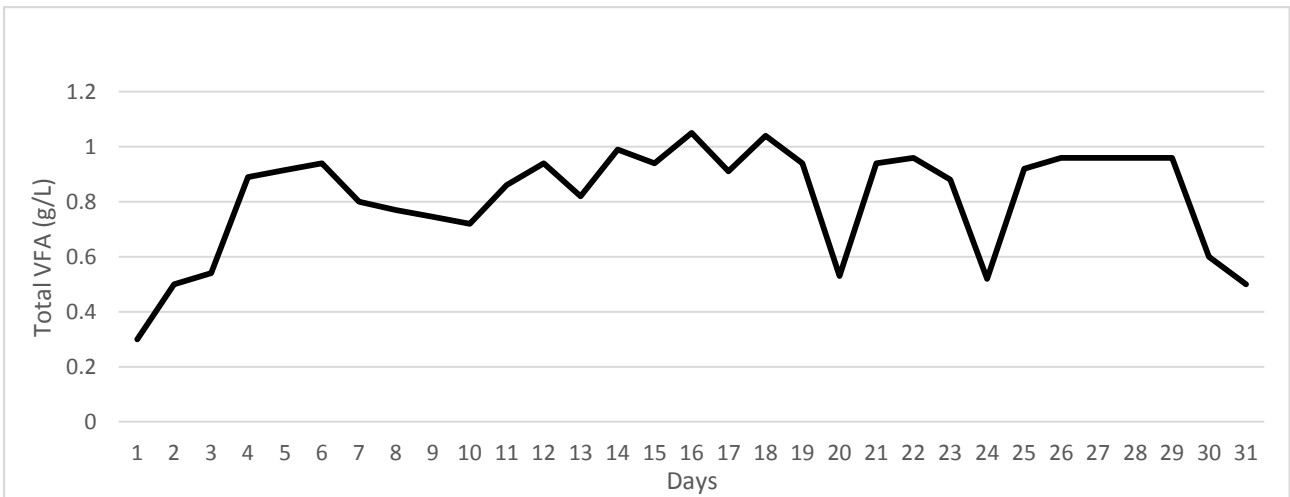
638 **Figure 5**



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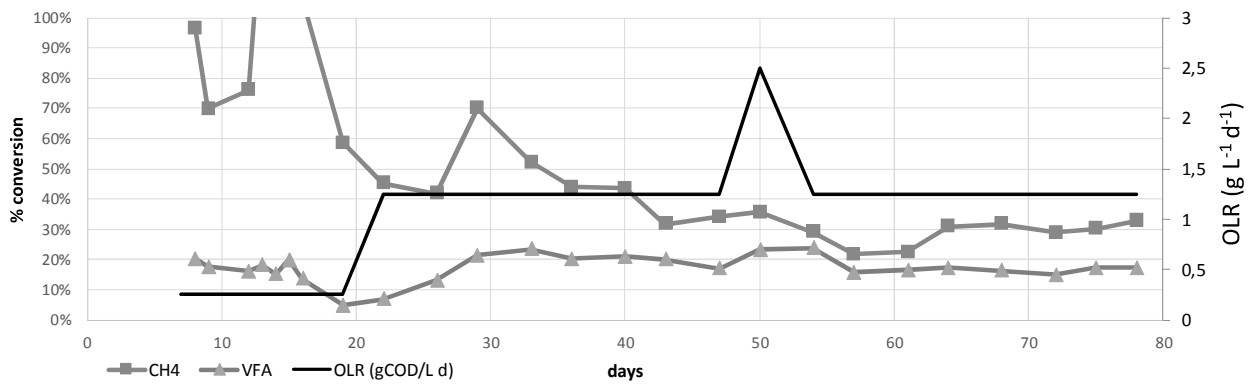
641 **Figure 6**



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644 **Figure 7**



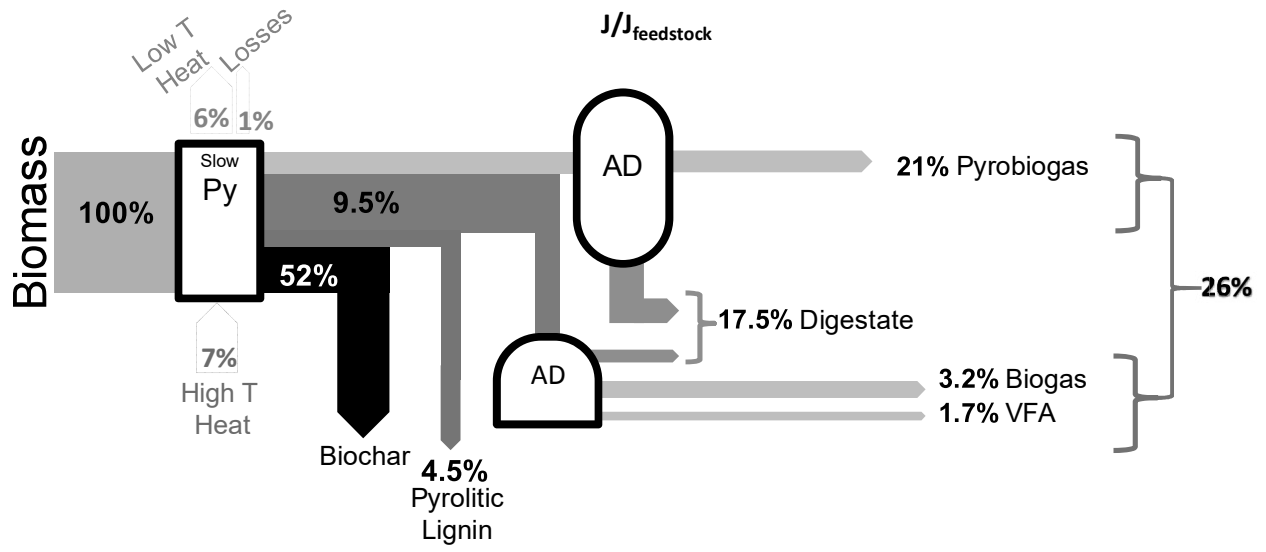
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649 **Figure 8**



650

651

652