Evaluation of the potential performance of hyphenated pyrolysis-anaerobic digestion (Py-AD) process for carbon negative fuels from woody biomass

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1   # Evaluation of the potential performance of hyphenated Pyrolysis-Anaerobic

2   # Digestion (Py-AD) process for carbon negative fuels from woody biomass.

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13

14   **Abstract**

15   A novel hyphenated Pyrolysis-Anaerobic Digestion prototype (Py-AD) was tested in order to

16   evaluate the potential of hybrid thermochemical biological process to produce methane from woody

17   biomass. An auger intermediate pyrolyzer was directly coupled to two biological reactors optimized

18   for the digestion of residual condensable compounds and gas produced by pyrolysis of softwood.

19   The Py-AD was monitored for 16 months and a detailed chemical analysis of the main fractions,

20   gas (pyrobiogas), biochar aqueous phase and pyrolytic lignin was performed under regime

21   conditions. The results from Py-AD and those from experiments with bench-scale pyrolysis and

22   fermentation reactors analysis provided information on the overall performance of the Py-AD and

23   mass and energy balance based on chemical oxygen demand.

24   Py-AD allowed to obtain, with acceptable volumetric productivity, a pyrobiogas with a composition

25   approaching that of biogas (47 %v/v CH_4 and 45 %v/v CO_2). Pyrobiogas yield was about half of the

26   theoretical value calculated from gas and liquid fractions. A preliminary technical evaluation of the

27   process confirmed the feasibility of Py-AD and its value to produce carbon negative fuels with

28   simple equipment and low waste generation. Important key constraints of the process were also

29   evidenced in the study.

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

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33   **1. Introduction**

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

Intermediate or slow pyrolysis (temperature of 400-500°C and reaction time longer than 1 min) yields char (20-30%), gas (10-20%) and 50-60% w/w of a pyrolysis liquid with relatively high water content (about 50% w/w).[1,2] These systems require quite a low heating rate that can be easily obtained with technically simple equipment, like auger reactors. Although a large portion of chemical energy is retained by biochar, its use for carbon storage in soil amendment enables the production of energy/fuels with negative CO_2 emissions. [3] Gas contribution increases by catalysis and higher vapor residence time, when secondary cracking reactions become relevant.[4,5] Condensable substances can be subsequently categorized into water soluble low molecular weight organics (semi-volatiles), high molecular weight organics (oligomers), and water insoluble organics, the latter consisting by definition of pyrolytic lignin.[6] It is worth to notice that pyrolysis gas and water soluble substances can be used as substrates in anaerobic digestion (AD), [7-12] producing a biogas that can be easily used in internal combustion engines,[13] as well as upgraded to methane (CH_4) usable as a drop in fuel.[14] This finding has recently suggested the concept of "hybrid thermochemical-biological process", in which thermochemical treatments enhance the bioavailability of organic substrates towards anaerobic digestion for their conversion into biogas (a mixture of CH_4 and CO_2).[15-17] This approach is of particular interest to the aim of converting the fraction of biomass that is highly refractory to fermentation into biogas. In fact, this fraction represents the hurdle to the utilization of woody biomass for the production of biogas. Therefore, this hybrid approach can be envisaged as a suitable way for producing a biofuel with negative emission of CO_2 assisted by the co-production of biochar as carbon sequestering agent. In general, the two treatments (pyrolysis and anaerobic digestion) are coupled in an "off-line" configuration in which products are separately collected in the first treatment (pyrolysis, Py) and thereafter send to the second one (anaerobic digestion, AD).[18] To the best of our knowledge, the potential of an "on-line" configuration in which pyrolysis and anaerobic digestion are directly interfaced (as 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.

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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±2% C, 5.5±1% H,

79   46.6±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 °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

measured temperature of about 500°C at the bottom of the reactor. The motion was applied by means of an electrical engine that moved the shaft with 1 rpm angular speed acting intermittently to have the set biomass flow rate (1 kg h^{-1}). A flow of N_2 at 0.1 L min^{-1} was provided for safety reasons nearby the airlock shaft coupling. The reactor was coaxially attached to a U-tube heat exchanger (stainless steel, AISI 304) and biomass/biochar flowed by means of two opposite radial openings for entrance of biomass from airlock feed, and biochar discharge opposed to shaft coupling. The heat exchanger receiving the volatile pyrolysis product stream was connected to two anaerobic digesters in series (reactor R1 and R2) by means of 23 mm ID silicone flexible hose pipe. Pyrolysis liquid condensate flowed spontaneously into the bottom part of the U-tube heat exchanger and was recovered, on daily basis, from a manual valve. The system was optionally used as standalone pyrolyzer (Py) for comparison with Py-AD by means of a bypass valve, which swept the pyrolysis gas directly to the flare. In this configuration, a peristaltic pump was used to withdraw the pyrolysis liquid from the bottom of heat exchanger and injected it, through a 5 mm ID dish nozzle, in the top of the same heat exchanger.

The residence time in the heated zone was set to 30 min and the biomass feed rate to 1 kg h^{-1}. The U-Tube heat exchanger cooled down the pyrolysis products to 60°C, causing the condensation of the liquid product, that was collected from the basis of the exchanger. The incondensable products and residual aerosols were bubbled in the first biological reactor (R1, CSTR reactor) by means of a 25 mm OD inch silicone flexible pipe, 600 mm below the liquid level. R1 consisted in an insulated vertical tank with a total volume of 450 L (600 mm diameter), filled with 300 L of liquid (inoculum and water) and with a 150 L empty gas dome. The inoculum was a mesophilic anaerobically digested excess sludge from a wastewater treatment plant (Hera s.p.a) located in Forlì (Emilia-Romagna region, Italy), with 35 g L^{-1} of volatile suspended solids (VSS). R1 was kept at 45°C by means of auxiliary resistances. A recirculating gas-blower drew the gas from the dome and injected it in the bottom of the R1 through a polypropylene sponge with 5-10 mm porosity. This created bubbles with 10-20 mm diameters and concurrently provided mixing of R1. To avoid excessive formation of foam, 10 mL of sunflower oil per week were added as anti-foam agent. Produced/converted gas from R1 was injected into the top of the second biological reactor (R2) proceeding downward into R2. Gas from the R2 exits 300 mm from the bottom of the same, which is connected, by means of flexible hose, to a gas holder and, a gas meter. R2 was designed according to Burkhardt *et al.* (2015), with slight modifications. [21] Briefly it consisted in a 350 L trickled bed reactor, namely a tank filled with 300 L of random fill high surface media (140 m^2/m^3) and 50 L of liquid. The trickling bed is kept wet by means of a progressing cavity pump that pumped liquid digestate from the bottom of R2 to the top of the same through a deflector plate

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

2.3 Anaerobic digestion of aqueous condensed phase

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

2.4 Analysis of gas, aqueous phases and water insoluble phase

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

with the following thermal program: 9 min at 50 °C, then 8 °C min^{-1} to 80 °C. Quantitation was performed using the calibration mixture Scotty Analyzed Gases Supelco, Sigma-Aldrich.

The determination of volatile fatty acids (VFAs) in WI, APL and liquid digestate was performed by solvent extraction and GC-MS analysis following the analytical method developed by Ghidotti *et al.*[22] The analytical characterization of WI and APL was performed following the solvent fractionation procedure and analysis described in Busetto *et al.* (2011).[23] Elemental analysis (C, H, and N) was performed using a Thermo Fisher Elemental Analyzer (Flash 2000), configured for solid samples with a copper/copper oxide column and calibrated with 2,5-bis(5-*tert*-butyl-2-benzo-oxazol-2-yl) thiophene (BBOT).

The quantitation of GC-MS detectable organics in APL, WI and liquid digestate was performed after water evaporation, trimethylsylilation and GC-MS analysis following the procedure described in detail elsewhere. [24]

The theoretical oxygen demand (ThOD, gCOD g[-1]), accordingly to OECD guideline 301F, [25] was calculated from elemental analysis using the following formula:

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

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

$$COD\ yield = ThOD\ yield = Y_i \cdot ThOD_i / ThOD_{feedstock}$$

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

3. Results and discussion

3.1 Bench scale pyrolysis tests

To better understand the intrinsic constraints of a Py-AD approach based on intermediate pyrolysis, some preliminary bench scale tests were targeted to the evaluation of maximum amounts of chemical energy released as bioavailable products, namely water-soluble pyrolysis products and pyrolysis gas. The Chemical Oxygen Demand (COD, gO$_2$/g$_{substrate}$) is a way to measure the energy stored in chemical substances, and can be directly translated into a theoretical biomethanation potential. On the basis of stoichiometry and high heating value (HHV), empirical calculations show that 1 kg of COD stores about 15 MJ energy, and the anaerobic digestion of 4 kg of COD as organic matter is required to obtain 1 kg of methane. Figure 3 shows the COD balance of intermediate pyrolysis performed with reactor temperature between 400 and 650°C and time ranging between 2 and 16 minutes. With the exception of torrefaction-like conditions (short pyrolysis time and low

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

3.2 Py-AD prototype
3.2.1 Set up and preliminary experiments

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

7

products were observed, in accordance with previous literature data.[7,10] The ratio between gaseous constituents of biogas (CH_4 and CO_2) and "pyrogenic" gases (H_2 and CO) increased over time reaching a plateaux after 120 days. After 120 days, although a residual amount of H_2 and CO was present, the composition gas produced was close to that of biogas.

The increase of gas conversion rate took more than 4 months and was slower than what observed in previous studies that occurred in few weeks; [7] this can be attributed to the need of active biofilm growth in R2. The conversion rate observed after 120 days was equal to 2.7 $Nm^3 m^{-3} d^{-1}$ for biogas and 1.4 $Nm^3 m^{-3} d^{-1}$ for biomethane. This value falls in the middle of the volumetric productivity in literature, which shows a large productivities range between 0.1 $Nm^3 m^{-3} d^{-1}$ and 7 $m^3 m^{-3} d^{-1}$.[28] Although the system used here includes a bubbled reactor (R1) and trickle bed reactor (R2), observed value is close to what observed with trickle bed reactor with similar specific surface area, namely 1.5 $Nm^3 m^{-3} d^{-1}$ obtained by Burkhardt *et al.*,[21] with mixed inocula, on H_2/CO_2 mixtures and 1.6 $Nm^3 m^{-3} d^{-1}$ obtained by Klasson *et al.* using a triculture onto syngas.[29]

3.3.2 Continuous test

After having reached the system stability, the input rate of the system was increased to 1 kg h^{-1}, using this regime conditions for one month. During this time, conversion performances and overall yields was measured. Figure 5 shows the composition of gas during regime operations. After increase of input rate of feedstock, a significant increase of CO and H_2 concentrations were observed suggesting an incomplete conversion of incoming pyrolysis gas until day 4. This decrease in conversion rate was accompanied by an increase in VFA concentration in the R1 from 0.4 baseline to 0.95 g L^{-1} in the first 6 days (Figure 6). This increase in VFA concentration was not observed in R2, in which VFA concentration fell below 0.3 g L^{-1} for all the duration of the study. After that, the concentration of pyrogenic gas, showed a variable trend until the day 14. After day 14 the gas composition was dominated by CH_4 and CO_2 with minimal amount of CO and H_2. This trend suggests an adaptation of the microbial consortia to the organic load applied. The initial unbalance mainly involved R1, and therefore could be related to increased load of residual condensables of raw pyrolysis gas, which mainly involved R1. Nonetheless, the overall trend observed suggested that the co-digestion of all raw pyrolysis gas constituents (including semi-volatile constituents) can be feasible with an adapted microbial consortia.

3.3.3 Mass and energy balance. Comparison with Py

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

was slightly modified by using the pyrolysis liquid as scrubbing agent. The purpose of this implementation was that to obtain a pyrolysis gas with a low content of residual aerosols comparable with that observed for Py-AD. The Py test was performed for 8 h test in which the various fractions were collected and analysed. Overall yields, on mass basis and COD basis, obtained by Py and Py-AD tests are shown in Table 1. The biochar yields resulted identical in both systems, confirming the replicability of Py. The standalone Py yielded 28% kg/kg_{wood} of a biochar with the following elemental composition 77±3% carbon, 2.5±0.5% hydrogen, 19±3.5% oxygen and 1.4 ±0.5% ash (mean ± standard deviation, n=5). Under these conditions, the liquid product yields of Py was 63% kg/kg_{wood} (17% organic fraction and 83% water phase) and gas yield was 9% kg/kg_{wood}. Data are in accordance with the literature concerning slow/intermediate pyrolysis of wood in comparable reactors.[5,2] The coupling with of AD changed deeply the volatile/gas product distribution of Py of wood. Py-AD yielded less liquid, namely 28% kg/kg_{wood} , with concurrent increased production of pyrobiogas 19% kg/kg_{wood} and a relevant production of digestate reach in water. Stoichiometry of CO conversion, which involve increase in biogas mass through water-gas shift, partially explain this increase of gas yield. In addition, significant portion of pyrolysis water and volatile organics (e.g. acetic acid) that were condensed in Py alone configuration were probably transferred in the AD. These organics were converted to gas or transferred to digestate when Py-AD configuration is used. Gas produced by means of intermediate Py were mainly formed by CO (62% v/v) and CO_2 (24% v/v) with minimal amount of CH_4 and H_2 (11 and 2% v/v respectively), with composition comparable to that reported in literature for intermediate/slow pyrolysis with low reaction temperature.[30] Gas produced by Py-AD system showed an average composition that is similar to that of biogas with increased content of CH_4 and CO_2 (47.4% v/v and 44.6% v/v respectively), decreased content of CO (6.7% v/v) and comparable concentration of H_2. This change in composition was similar to that observed in studies focused on syngas biomethanation,[7] and confirms the biological conversion of both gaseous and semi-volatile products that reach the AD system.

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

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

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

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

	% 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
H$_2$	0.01	0.03	0.1	0.2
CH$_4$	0.4	6.2	1.7	20
CO$_2$	2.4	16	0	0
CO	4.0	1.5	2.3	0.7
C$_n$H$_m$	0.1	-	0.4	-

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

3.3 Anaerobic digestion of Aqueous Pyrolysis liquid (APL)

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

aqueous phase (APL, 87% w /w, average of all the tests) and an organic (<10% water content)

bottom phase (WI, 13% w/w) with minimal amount of extractives (<1% w/w). The relative

composition of the phases was relatively constant with average relative standard deviations of the

above reported values less than 5%. APL from Py-AD was mainly formed by 80% w/w water and

8% w/w pyrolytic "sugars". APL contained about 2%w/w VFA (mostly acetic acid) and minimal

amount of phenols, which probably were partitioned to WI. Organics content and VFA

concentration in APL from Py-AD were lower than the literature related to intermediate pyrolysis

for wood.[23,33,34] This is probably due to low temperature pyrolysis (400°C) and specific

reaction configuration, that imply a relatively low recovery of more volatile pyrolysis products

(VFA or alcohols), which on the opposite were deliberately transferred to the AD system. This

phenomena could be one of the source of biogas produced by Py-AD (see above in section 3.2).

As far as the organic bottom phase is concerned, this portion of pyrolysis liquid was subjected to

solubilization test in order to establish residual solubility in water, analyzed by elemental analysis,

GC-MS, derivatization/GC-MS and Gel Permeation Chromatography. Even if diluted to less than 1

g L^{-1} concentration, WI showed a negligible (<10%) solubilization in water. Moreover, the

chemical analysis indicated that WI was mainly formed by phenols and lignin oligomers, with a

significant amount of polycyclic aromatic hydrocarbons (PAHs, 120 mg kg^{-1}) and quite low (<2%)

content of water soluble pyrolysis products. The composition of both APL and WI suggested a large

partitioning of organic compounds on the basis of water solubility. Analysis showed an almost

complete partition of hydrophobic constituent, namely lignin oligomers and PAHs, in the WI and

partition of VFA and sugar like, which are potentially biodegradable compounds, in the APL.

According to composition and expected chemical behavior of the two liquid fractions obtained by

pyrolysis, namely APL and WI, it can be concluded that APL can be, in principle, considered a

good feedstock for biological valorization. In fact, it was previously demonstrated that using a

portion of biochar produced in the AD it is possible to overcome the toxicity of APL.[10]

On the opposite, the relative low yield of WI, that concentrates several compounds with potential

concern for biological valorization, suggests higher suitability of different applications.

Although APL could be potentially digested directly in on-line Py-AD the further optimization of

Py-AD system needs to know exactly the maximum organic loading rate and yield for each fraction

(e.g. gas, volatile compounds and APL) and to perform a longer test for establishing potential long

term inhibition due to heavy constituents of APL. Therefore, a small scale AD system for APL was

set up on and monitored. The system was made by an 80 mL Upflow Anaerobic Sludge Blanket

(UASB) and was described in detail in section 2.3 and in Figure 2. Besides APL and inoculum, the

system was added with biochar in order to minimize the toxic effect of APL, as shown in previous

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

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

Table 2: degree of biodegradation of main APL constituents detected by GC-MS after silylation of 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

3.4 Overall performance of Py-AD

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

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

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

4. Conclusions

This study put into practice the idea of a direct coupling between pyrolysis (Py) and anaerobic digestion (AD) to the end of converting woody biomass into a "pyrobiogas" fuel rich in biomethane and biochar. Experiments with bench-scale reactors suggested that low pyrolysis temperatures are preferable in order to increase the yield of potentially fermentable materials, which includes NCG (e.g. CO, H_2) and water-soluble organic compounds of pyrolysis liquid. These two fractions exhibited a summed limit value that approaches to the 50% of chemical energy of input softwood biomass feedstock. In particular, chemical analyses showed an almost complete biodegradation under anaerobic conditions of semi-volatile components detectable by GC-MS. On the basis of the results from laboratory and available literature data, a Py-AD prototype, where the hyphens indicate that the pyrolyzer was physically interfaced with two biological reactors, was operated and monitored for more than 16 months. This long-term experiment enabled the identification of pros and cons of the concept in a real case. The Py-AD produced pyrobiogas, namely an aerosol-free biogas (CH_4 47.1%v/v and 44.6 %v/v CO_2) containing residual carbon monoxide (6.7% w/w) and hydrogen (1.6%) with a yield of 0.21 Nm^3 $kg_{feedstock}^{-1}$. Experimental results were used for a preliminary technical evaluation of the whole process, which resulted reliable in term of energy balance and volumetric productivity.

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

List of Abbreviations

AD: Anaerobic Digestion

APL: Aqueous phase of pyrolysis liquid

COD: Chemical Oxygen Demand

CSTR: Continuously Stirred Tank Reactor

NCG: Non Condensable Gas

OLR: Organic Loading Rate

PAHs: Polyciclic Aromatic Hydrocarbons

Py: Pyrolysis

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

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502   **References**

503

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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

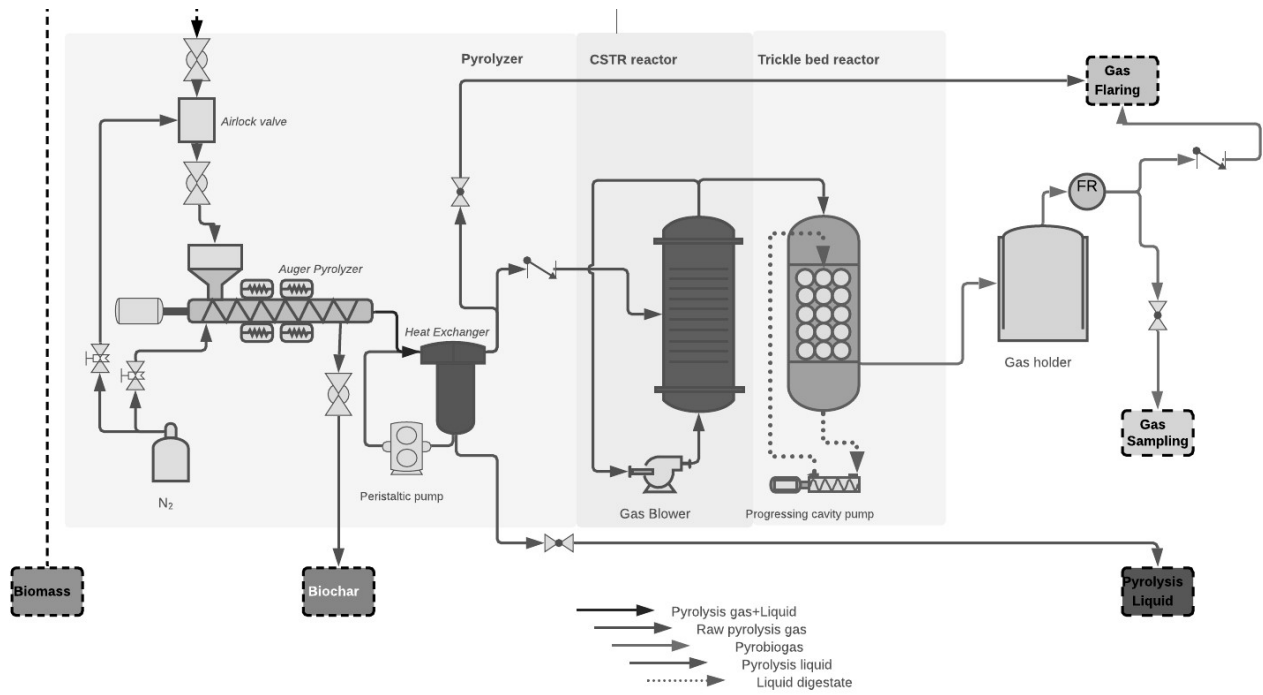622 residual APL obtained from Py-AD experiment.

623

Figure 8: Graphical description of the input/outputs of chemical energy of the Py-AD system proposed here. All data are expressed as % of initial chemical energy stored in pine wood biomass.
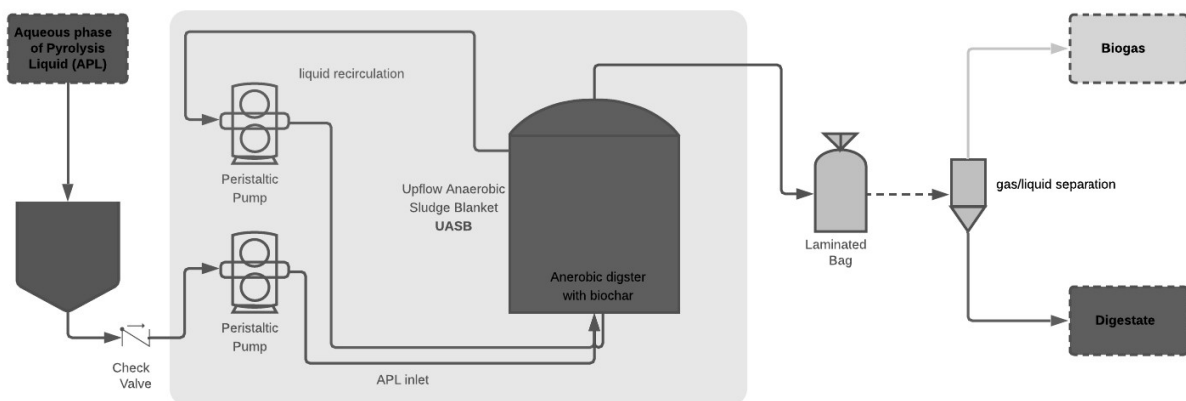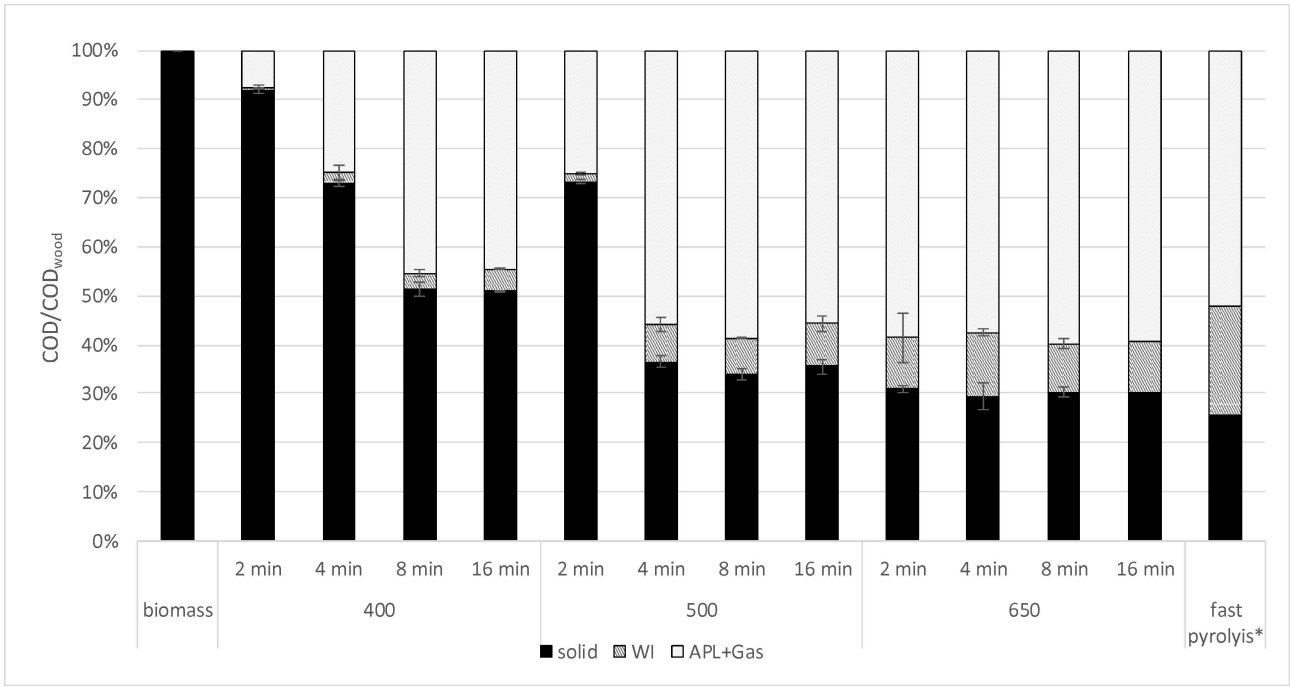
626

Figures

Figure 1

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Figure 2

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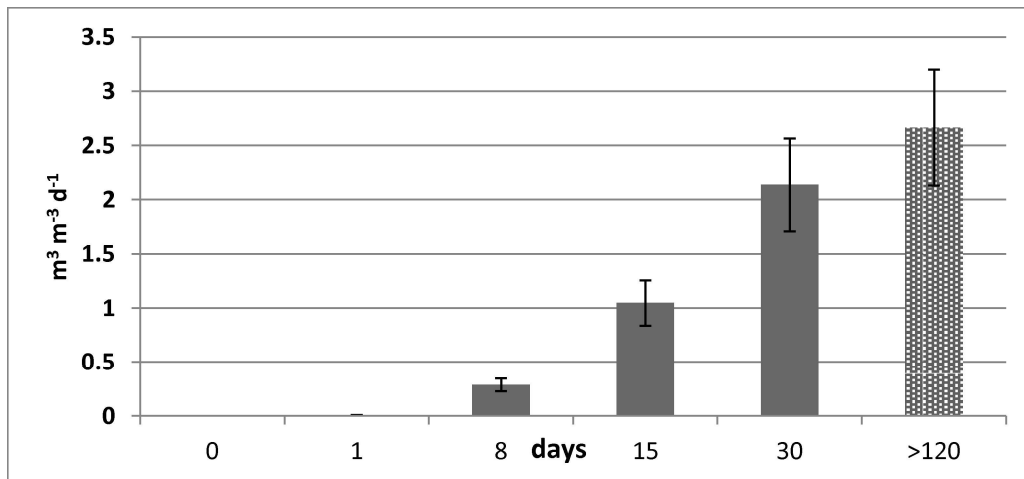*Figure 3*

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Figure 4

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Figure 5

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Figure 6

Figure 7

Figure 8