

Alma Mater Studiorum Università di Bologna
Archivio istituzionale della ricerca

Life Cycle Assessment of high ligno-cellulosic biomass pyrolysis coupled with anaerobic digestion

This is the final peer-reviewed author's accepted manuscript (postprint) of the following publication:

Published Version:

Righi, S., Bandini, V., Marazza, D., Baioli, F., Torri, C., Contin, A. (2016). Life Cycle Assessment of high ligno-cellulosic biomass pyrolysis coupled with anaerobic digestion. *BIORESOURCE TECHNOLOGY*, 212, 245-253 [10.1016/j.biortech.2016.04.052].

Availability:

This version is available at: <https://hdl.handle.net/11585/554164> since: 2016-07-16

Published:

DOI: <http://doi.org/10.1016/j.biortech.2016.04.052>

Terms of use:

Some rights reserved. The terms and conditions for the reuse of this version of the manuscript are specified in the publishing policy. For all terms of use and more information see the publisher's website.

This item was downloaded from IRIS Università di Bologna (<https://cris.unibo.it/>).
When citing, please refer to the published version.

(Article begins on next page)

1
2
3
4
5
6
7
8
9
10
11
12
13
14
15
16
17
18
19
20
21
22
23
24
25
26
27
28

This is the final peer-reviewed accepted manuscript of:

Serena Righi, Vittoria Bandini, Diego Marazza, Filippo Baioli, Cristian Torri, Andrea Contin, Life Cycle Assessment of high ligno-cellulosic biomass pyrolysis coupled with anaerobic digestion, Bioresource Technology, Volume 212, 2016, Pages 245-253, ISSN 0960-8524.

The final published version is available online at:
<https://doi.org/10.1016/j.biortech.2016.04.052>

Rights / License:

The terms and conditions for the reuse of this version of the manuscript are specified in the publishing policy. For all terms of use and more information see the publisher's website.

1 **Life Cycle Assessment of high ligno-cellulosic biomass pyrolysis coupled with**
2 **anaerobic digestion**

3

4

5 Serena Righi^{1,2,*}, Vittoria Bandini¹, Diego Marazza¹, Filippo Baioli³, Cristian Torri¹, Andrea
6 Contin^{1,2}

7

8

9 ¹ CIRI Energia e Ambiente, U.O. Biomasse, Alma Mater Studiorum - University of Bologna,
10 via S. Alberto 163, 48123 Ravenna, Italy

11 ² Department of Physics, Alma Mater Studiorum - University of Bologna, viale Pichat 6/2,
12 40127 Bologna, Italy

13 ³ CIRSA Centro Interdipartimentale di Ricerca per le Scienze Ambientali, Alma Mater
14 Studiorum - University of Bologna, via dell'Agricoltura 5, 48123 Ravenna, Italy

15

16

17

18

19

20

21

22

23 * Corresponding author. Tel./fax: +39 0544 937306, e-mail: serena.righi2@unibo.it

24

1 **Abstract**

2 A life cycle assessment is conducted on pyrolysis coupled to anaerobic digestion to treat
3 corn stovers and to obtain bioenergy and biochar. The analysis takes into account the
4 feedstock treatment process, the fate of products and the indirect effects due to crop
5 residue removal. The biochar is considered to be used as solid fuel for coal power plants
6 or as soil conditioner. All results are compared with a corresponding fossil-fuel-based
7 scenario. It is shown that the proposed system always enables relevant primary energy
8 savings of non-renewable sources and a strong reduction of greenhouse gases emissions
9 without worsening the abiotic resources depletion. Conversely, the study points out that
10 the use of corn stovers for mulch is critical when considering acidification and
11 eutrophication impacts. Therefore, removal of corn stovers from the fields must be planned
12 carefully.

13 **Keywords**

14 Biochar; bioenergy; hybrid thermochemical processing; crop residue; trade-off

15 **1. Introduction**

16 Today transition from a fossil-based economy to a bio-economy (European Commission,
17 2012) is justified by the need of an integrated response to several global mega-trends
18 such as: food security, the need of strengthening energy security, increasing demand of
19 biological resources for bio-based products, GHG emission reduction, the need of moving
20 towards a zero-waste society, environmental sustainability of primary production systems,
21 increasing land use competition (Nita et al., 2013). Sustainable bio-refineries can play an
22 important role to address concerns about climate change and security of energy supply,
23 while contributing to economic growth and employment, particularly in rural areas
24 (European Commission, 2014). According to the Impact Assessment to the 2030 Climate
25 and Energy Framework, biomass use in the heat and power sectors is expected to further
26 increase in the medium term, following the EU effort to move to a low-carbon economy by

1 the middle of the century. Residual biomasses – such as manure, pruning, straw or other
2 by-products of farming – are a low cost feedstock source that represents an untapped
3 source for energy production. Moreover, the use of residual non-edible biomass is less
4 controversial than harvested biomass, which raises environmental concerns or issues
5 related to competition with food needs (FAO, 2010; FAO, 2012; HLPE, 2013). These
6 concerns and issues have resulted in growing interests in alternative, non-edible biomass
7 resources.

8 Corn stovers - consisting of cobs, ear husks, stalks and leaves of maize - are abundantly
9 present and very interesting due to their energy content. Corn stovers can be left in the
10 fields after the harvest and used for soil mulching, disposed of, or burnt directly on the
11 field. Corn stovers, typically composed of 35-40% cellulose, 20-25% hemicellulose, and
12 15-20% lignin, are recalcitrant to aerobic and anaerobic bioconversion, because of the
13 high ligno-cellulosic content and this characteristic represents the major obstacle to a cost-
14 effective exploitation. Lignin, the most abundant aromatic biopolymer on Earth, is
15 extremely recalcitrant to degradation and preliminary treatments are necessary in order to
16 facilitate its degradation by bacteria.

17 Intermediate pyrolysis consists in the controlled heating (at temperature between 350 and
18 600°C) of biomass in an inert atmosphere, obtaining gas, liquid (bio-oil) and a
19 carbonaceous residue (char). In turn, these pyrolysis products can be upgraded to
20 fuels/materials or can be burnt to produce thermal energy. Besides chemical and
21 thermochemical processes, which include hydrotreating/cracking or gasification of bio-oil
22 for syngas production, a recent approach is the coupling of pyrolysis with a biological
23 upgrading system, by hybrid techniques (Jarboe et al., 2011). In principle, coupling
24 anaerobic digestion (which produces biogas) with a thermic de-polimerizing system, such
25 as pyrolysis, allows to overcome the recalcitrant feature of certain feedstock. Therefore, it
26 could be a relatively simple and low-cost solution for overtaking the problems which affect

1 both technologies. In particular, the conversion to biogas allows the use of mixed microbial
2 consortia which can operate with low quality bio-oil and gas - especially with high water
3 content or with inorganic contaminants - and produces a biogas which is compatible with
4 existing power generating facilities. This solution has been proven as an alternative to
5 catalytic methanation for converting syngas into methane (Guiot et al., 2011) and allows
6 the treatment of the whole gas/bio-oil mix at low temperature (Lewis, 2012) without the
7 need of tar reforming and syngas purification. Preliminary data showed that, once the
8 microbial consortium has adapted, it is possible to digest anaerobically the bio-oil from
9 intermediate pyrolysis with satisfactory yield (Torri and Fabbri, 2012).

10 Research within the Interdepartmental Centre for Industrial Research (CIRI) Energy and
11 Environment focuses on technologies for the pre-treatment of biomasses before their
12 anaerobic digestion (DA) (Torri and Fabbri, 2014). In this context the goal of the research
13 is to evaluate, firstly at small scale (Bandini et al., 2014) and subsequently at a larger
14 prototype scale, the environmental performances of pyrolysis coupled to anaerobic
15 digestion for the processing of corn stover. Combination of pyrolytic and anaerobic
16 digestion techniques is named PYDA in the following. This study aims to assess the
17 potential environmental impacts and benefits of the large scale prototype (named hereafter
18 PYRO2012) in order to support and inform the development of this process for the
19 exploitation of residual biomasses with high ligno-cellulosic content. The study applies an
20 attributional Life Cycle Assessment (LCA) adopting a 'cradle-to-grave' perspective.

21 **2. Materials and Methods**

22 **2.1 Experimental plant**

23 Experimental data used in this study has been obtained by a pilot scale pyrolyzer
24 (described below) and lab scale anaerobic digestion (AD) system running in batch
25 operation: bio-oil and gas outputs are stored into frozen bottles and tedlar bags and then
26 introduced into the AD device. Anaerobic digestion tests of oil and syngas were performed

1 off-line as shown in Torri and Fabbri (2014) using 1 L pressurised reactor (pyrolysis liquid)
2 and 100 ml syringes (gas). This batch procedure provided the data concerning the
3 pyrolysis-anaerobic digestion coupling.

4 The pyrolysis reactor is essentially constituted by a hopper, a 100 mm cylindrical pyrolysis
5 chamber, a tank for the collection of the biochar and a scrubber/heat exchanger for the
6 collection of oil, a tee for gas sampling, a hydraulic seal system consisting of a steel
7 bubbler with 1 m depth water and a controlled torch at the end of the system. The pyrolysis
8 reactor is equipped with an electric heating system and a motorized auger (which is
9 coaxial with the reaction chamber) and is flushed by 1000 ml min⁻¹ of nitrogen for safety
10 reasons. The biomass is progressively taken by the auger from the hopper, through the
11 loading channel, and then conveyed through the pyrolysis chamber (T=400°C, residence
12 time=10 min). Pyrolysis vapours are collected in the heat exchanger/scrubber, where a
13 peristaltic pump continuously takes the oil from the bottom and rises it to the heat
14 exchanger inlet.

15 In order to obtain samples and pyrolysis data (e.g. energy consumption), an intermediate
16 pyrolysis plant with throughput of 10 kg h⁻¹ was built and operated semi-continuously in 10
17 tests, for a total test time of 60 h. During the middle portion of the test (excluding first and
18 last hour of start-up and shut-down), yield and actual energetic consumption were
19 measured upstream by means of electricity meter.

20 2.2. LCA method

21 Life Cycle Assessment (LCA) is the method chosen for assessing the environmental
22 performances of PYDA. The LCA of a product or process is generally performed in order to
23 identify the 'hot spots' in the life cycle in order to reduce consumption of energy and raw
24 materials, and emission/waste production, as well as to identify possible improvements
25 towards the achievement of a more environmentally sustainable result. When dealing with
26 experimental methods which are in progress, LCA can support, in an iterative way, the

1 undergoing research: by giving a highlight on the most impacting processes in the system,
2 it points to where more progress is needed; by defining thresholds (i.e. minimum
3 performances required for having a net energy gain) it can identify some basic
4 performances which have to be achieved before moving to any scaling-up phase. When
5 evaluating different scenarios for product development, a prospective or comparative life
6 cycle assessment is realized, which analyses possible future changes between alternative
7 product systems or configurations (Azapagic and Clift, 1999).

8 The LCA method is standardized by ISO 14040 and 14044 (ISO, 2006a and 2006b) and
9 comprises four phases: (1) goal and scope definition; (2) inventory analysis; (3) impact
10 assessment; (4) interpretation. Below, data used and approaches applied in each of these
11 phases are described.

12 *2.2.1. Goal and scope definition*

13 Goal and scope focus on environmental performances of the PYDA system for the
14 treatment of corn stovers while exclude the assessment of its economic potential.

15 The EU Renewable Energy Directive (European Union, 2009) assigns agricultural residues
16 and wastes “zero life-cycle greenhouse gas emissions up to the process of collection of
17 those materials”; this principle has been adopted with respect to global warming potential
18 (GWP) and extended to the outstanding impact categories such as eutrophication
19 potential, abiotic resources depletion, etc. (see below Life Cycle Impact Assessment). In
20 order to define the system boundaries, particular attention has been paid to the removal
21 and use of stovers. Elimination of stovers from the field has been considered to require a
22 fertilizer offset since corn stovers are usually left on field for soil mulching thank to their
23 nitrogen, phosphorous and potassium content. As a further, indirect consequence, fertilizer
24 emissions due to the offsetting of fertilizers have been considered inside the system
25 boundaries. These fertilizers emissions are mainly due to the production of nitrous oxide
26 which in turn is due to nitrification and denitrification processes (FAO, 1996).

1 Therefore the system boundaries of the study include the following processes: 1) fertilizer
2 offset; 2) fertilizer offset emissions that includes emissions to air due to fertilizer application
3 but also avoided CO₂ emissions resulting from carbon storage in the biochar; 3) transport
4 of corn stovers; 4) pyrolysis of corn stovers, with the production of bio-oil, gas and biochar;
5 5) anaerobic digestion of bio-oil and gas; 6) production of electricity and heat in a
6 Combined Heat and Power (CHP) unit; 7) transport of biochar (to agricultural field or to
7 power plant).

8 The functional unit is defined as 1 ton of dried corn stovers treated (humidity <10%) - from
9 which 300 kg of biochar are obtained. A higher heating value (HHV) of 17.4 MJ/kg for
10 stovers has been assumed.

11 *2.2.2. Scenario description*

12 Two different utilization ways for biochar have been analyzed: a) burning into a hard coal
13 power plant ('Combustion' scenarios) and b) addition to soil as amendment ('Amendment'
14 scenarios). For each of the two utilization ways, three sub-scenarios have been evaluated,
15 which differ in the technical performance of 5 key parameters: 1) electricity consumption of
16 the pyrolyzer; 2) biogas yield from anaerobic digestion; 3) percentage of methane in the
17 biogas; 4) electrical efficiency of the CHP unit; 5) thermal efficiency of the CHP unit. Note
18 that the parameters are mutually independent. The values of each parameter have been
19 classified according to three levels of performance - the worst, the average, the best (see
20 Table 1) - set based on experimental results for parameters 1, 2 and 3, and on data
21 resulting from literature for parameters 4 and 5.

22 Each of the six resulting scenarios has been compared to two 'Reference scenarios':
23 'Electricity' which supplies the same quantity of electricity from the national grid and
24 'Electricity and thermal energy' which supplies the same quantity of electricity from the
25 national grid and the same quantity of thermal energy by a natural gas burner.

1 The following cut-off rules, assumptions and limitations have been adopted: i) harvesting
2 of the stovers has not been included; ii) transport by lorry (Euro 0-5 mix) with a 17.3-t-
3 payload and for a distance of 50 km has been assumed; iii) according to the EU
4 Renewable Energy Directive (European Union, 2009), only the operational phase has
5 been considered, excluding manufacturing of machinery and equipment, maintenance and
6 dismantling. This is a relatively usual practice in LCAs about technical systems with a long
7 life (Hischier et al., 2005); moreover, studies on pyrolysis systems have shown that the
8 environmental impacts from construction and dismantling are negligible (Roberts et al.,
9 2009; Ibarrola et al., 2012); iv) all electricity comes from the Italian national grid power; v)
10 direct coupling of pyrolysis and anaerobic digestion system without any storage has been
11 hypothesized and the digester size was assumed suitable to that needed for continuous
12 processing of the pyrolysis product; vi) the electricity produced by the system replaces an
13 equivalent amount, composed as the Italian grid mix; vii) the heat produced by the system
14 replaces an equivalent amount produced by a CHP unit burning natural gas; viii) biogenic
15 CO₂ has been excluded from the calculation of the Global Warming Potential. This is in
16 accordance to the EU Renewable Energy Directive (European Union, 2009), which
17 indicates as zero the carbon dioxide emissions from the use of biofuels or bio-liquids; ix)
18 the CHP is assumed to have a 38-40% electric efficiency and a 32-48% thermal efficiency
19 (IEA ETSAP, 2010); x) the fertilizer amount applied to the soil due to fertilizer offset when
20 exporting stovers from the field has been calculated as described by Cherubini and Ulgiati
21 (2010); xi) 75% of the biochar's carbon is in a recalcitrant form and will remain confined in
22 the soil after a 100 years timespan (Benini and Torri, 2010).

23 *2.2.3. Life cycle inventory*

24 Primary data have been used for the processes taking place in the laboratories, databases
25 have been used for background processes and estimates have been used for emissions
26 or processes not taking place in the current plant, such as the CHP process. LCA was

conducted utilizing GaBi 6 software (Thinkstep, 2015a). The databases used for obtaining background data were Gabi Professional Database (Thinkstep, 2015b) and Ecoinvent Database (Ecoinvent Centre, 2012). All main background processes used in this study are shown in Table 2.

2.4. Life Cycle Impact Assessment

The well-established midpoint CML method (Guinee et al., 2002) was applied for impact assessment. Impact categories considered include 'Primary energy demand from non-renewable resources' (PED) in MJ, 'Global Warming Potential' (GWP), excluding biogenic carbon in kg CO₂-eq, 'Acidification Potential' (AP) in kg SO₂-eq, 'Eutrophication Potential' (EP) in kg PO₄³⁻-eq, 'Abiotic Depletion' (AD) in kg Sb-eq.

3. Results and discussion

Figure 3 shows the LCIA of pyrolysis-anaerobic digestion (PYDA) of 1 t corn stover considering the two alternative ways of biochar exploitation presented above (combustion or soil amendment) and taking into account three different levels of technical performances (worst, average, best). Each scenario is compared to corresponding ones, i.e. 'Electricity' and 'Electricity and thermal energy'. Table 3 illustrates the difference between the impact scores of the reference scenarios 'Electricity' and those of the PYDA process: the first three columns display the values obtained by subtracting 'Combustion' scenarios from 'Electricity' scenarios, while the second group of three columns displays the difference between 'Amendment' scenarios and 'Electricity' scenarios. In the same way, Table 4 shows the difference between the impact scores of the reference scenarios 'Electricity and thermal energy' and those of the PYDA process. In both tables, negative values indicate that the PYDA process causes lower environmental impacts than reference scenarios, positive values indicate that impacts caused by the PYDA process are higher than those caused by reference scenarios. Finally, Fig. 4 shows the relative contributions of the stages considered in each scenario: fertilizer offset, fertilizer offset emissions, pyrolysis,

1 anaerobic digestion, cogeneration, biochar combustion (only for 'Combustion' scenarios)
2 and transportation.

3 As regards primary energy demand (PED), modest changes are observed among PYDA
4 scenarios (about 700 MJ per FU); conversely, PED ranges from 2000 to 15000 MJ in the
5 reference scenarios (as shown in Fig. 3). Comparing the two biochar utilization pathways,
6 the greatest advantage is obtained when the biochar is combusted as hard coal.

7 Nevertheless, even when the biochar is used to improve soil quality and save fertilisers,
8 the advantage of the PYDA process over the reference scenarios is very large. Note that
9 the gain of PED is calculable subtracting the energy demand of the PYDA process from
10 the energy demand of reference scenarios. It approximately varies from 1,000 to 9,000 MJ
11 per FU considering the 'Electricity' scenarios (Table 3) and from about 3,000 to 15,000 MJ
12 per FU considering the 'Electricity and thermal energy' scenarios (Table 4).

13 The two main contributions of the primary energy are due to fertiliser offset (about 50%)
14 and pyrolysis of corn stovers (30-40%) (see Fig. 4). The energy demand of the latter is due
15 to the liquid nitrogen consumption; in fact the pyrolysis is self-sufficient from the energy
16 point of view thanks to the cogeneration of electricity and heat during the AD process.

17 Electricity generation through CHP unit is 980, 1900 and 3200 MJ per FU for the worst, the
18 average and the best scenario (the last one is reported in Fig. 1), respectively. Consider that
19 in all three configurations, both the oil and syngas produced is used to produce electricity.

20 These figures are comparable to those predicted by Ibarrola et al. (2012) for pyrolysis of ten
21 types of biodegradable wastes (where both oil and syngas are combusted). The worst and
22 the average scenarios are also well comparable with findings of Hammond et al. (2011).

23 Further electricity energy - about 1640 MJ - is generated in the 'Combustion' scenarios by
24 the combustion of biochar (the value is obtainable comparing electricity of Fig. 1 with the
25 one of Fig. 2).

1 As regards GHGs emissions, measured by the indicator GWP, all six PYDA scenarios entail
2 negative net emissions with respect to the reference scenarios, as shown in Tables 3 and 4.
3 These results agree with findings of Ibarrola et al. (2012) who calculated that pyrolysis
4 technologies are able to generate carbon abatement by the treatment of several different
5 biodegradable wastes either when the biochar produced is used for soil enhancement or for
6 combustion activities. The net GHG abatement ranges from -127 to -933 kg CO₂-eq t⁻¹ of
7 corn stovers according to findings of other authors. A similar large range was observed by
8 Hammond et al. (2011) and Ibarrola et al. (2012); both studies report carbon abatement of
9 about 0.7-1.3 t CO₂-eq per dry ton of a series of feedstock. Roberts et al. (2009) estimate
10 GHG emissions reductions at -864 kg CO₂-eq per ton of dry stovers. Note also that
11 'Amendment' scenarios show better performances than 'Combustion' ones (Tables 3 and 4).
12 This finding is clearly observable also from Fig. 3, where 'Amendment' scenarios show
13 negative net values of GHG emissions. Similarly, Gaunt and Lehmann (2008), Roberts et
14 al. (2009) and Ibarrola et al. (2012) report that more GHG emissions reductions are made
15 when the biochar is applied to soil rather than used as a fuel. The later result can be
16 explained as in Roberts et al. (2009) and Benini and Torri (2010) and depends on the CO₂
17 sequestration by biochar. More precisely, the application of biochar to soil provides a
18 relevant carbon storage effect thanks to the stability of carbon into the structure of biochar.
19 The three amendment scenarios show similar performances. Anyway, it is interesting to note
20 that the GHG saving of 'scenario 4' is slightly higher than the one of 'scenario 5' and even
21 higher than 'scenario 6'. This result is due to the lower CH₄ emissions from the anaerobic
22 digestion phase of scenario 4 - due to the inherent lower biogas production - compared to
23 scenarios 5 and 6. In any case, as it is possible to see from Tables 3 and 4, 'scenario 6'
24 provides the highest difference between PYDA and reference scenarios. Fig. 4 shows that,
25 'fertilizer offset emissions' is the main contributor to GHG emissions (negatively or
26 positively). In fact, in the 'combustion' scenarios the removal of corn stovers from soil brings

1 to a larger use of fertilizers and, subsequently, to larger emissions of GHGs (in particular
2 N₂O). On the contrary, the use of biochar as amendment saves GHG emissions (in particular
3 CO₂). As Meyer et al. (2011) emphasize, biochar sequestration in the soil is one of the main
4 factors positively influencing the GHG balance of biomass pyrolysis conversion process.
5 Other processes contribute very slightly to this impact category (see Fig. 4), according to
6 Ibarrola et al. (2012) who observe that the pyrolysis process and transportation emissions
7 are a minor proportion of the overall abatement. Also Roberts et al. (2009) affirm that
8 biomass transport, biochar transport and avoided fertilizer production contribute little to GHG
9 emissions. It is remarkable that present study and authors above mentioned indicate that
10 transportation is not a significant concern regarding CO₂ emissions. About this, also
11 Hammond et al. (2011) observe that transport distances can be increased vastly and still
12 have little impact on over GHG emissions. Therefore preliminary results suggest that 'in situ'
13 plants do not present great advantages from the GHG emissions point of view.
14 Regarding acidification emissions, Fig. 3 shows that the acidification potential of PYDA
15 scenarios is always higher than the one due to reference scenarios. In particular,
16 acidification emissions of 'Combustion' scenarios (4 kg of SO₂-eq per FU) are 2-4 times
17 higher than the corresponding reference, while in the 'Amendment' scenarios (1.5 kg of SO₂-
18 eq per FU) the scores are 0.5-2 times higher than the corresponding reference. Only in the
19 case of scenario 6, and only when the thermal energy is also exploited, the impact of PYDA
20 is equal to its reference (see also Tables 3 and 4). Common important contributors are
21 fertilizer offset emissions and cogeneration (Fig. 4). Removal of corn stovers from fields
22 requires an additional amount of fertilizers compared to the situation in which stovers are
23 left on the field, and therefore PYDA scenarios have higher emissions of acidifying
24 compounds to air and to soil with respect to reference scenarios. This effect occurs only if
25 the original use of corn stovers is soil mulching; if burning on the field or disposal are the
26 reference practice, the PYDA systems are expected to maintain or improve the scores. Along

1 the production chain, cogeneration produces NO_x and SO_x which contribute heavily to the
2 acidification potential. Finally, the “Combustion” scenarios have a combustion stage of
3 biochar that causes severe further acidification emissions (over 60% of the total).

4 In the case of emissions with eutrophication potential, PYDA scenarios have always much
5 higher impacts (about one order of magnitude) than those due to the reference scenarios.
6 On the contrary, the differences between ‘Combustion’ (0.78 kg of PO₄³⁻-eq per FU) and
7 ‘Amendment’ (0.63 kg of PO₄³⁻-eq per FU) scenarios are smaller than 15%. As Fig. 4
8 shows, the most impacting stages are fertilizers offset, fertilizer offset emissions and
9 cogeneration. In the case of ‘Combustion’ scenarios, the biochar combustion also plays an
10 important role. The contribution of combustion stages are largely due to the air emission of
11 nitrogen compounds which have a significant eutrophication potential. It has to be noticed
12 that literature has been highlighting the capacity of biochar used as amendment to adsorb
13 ammonia (Clough and Condon, 2010; Taghizadeh-Toosi et al., 2012) and to sorb excess
14 nitrogen in the environment (Raave et al., 2014). In the light of this, eutrophication
15 potential of biochar should be reviewed according to the capacity to sequester nitrogen
16 from the environment. As a consequence, eutrophication is expected to be assigned lower
17 scores in the near future.

18 Acidification and eutrophication values from this study are hardly comparable with the results
19 from other studies due to a lack of literature regarding such impacts related to pyrolysis of
20 biodegradable waste. Khoo (2009) reports acidification emissions of about 0.85 kg of SO₂-
21 eq per ton of pyrolysed municipal solid waste but he does not account cogeneration through
22 the CHP unit. The risk of increasing environmental impacts as acidification and
23 eutrophication has been recognized also by Ibarrola et al. (2012), but it has been not
24 quantified.

25 The last impact category analysed is ‘Abiotic depletion’. As it can be seen from Fig. 3,
26 PYDA ‘Combustion’ scenarios show approximately lower or equal consumptions of abiotic

resources (around 1.3×10^{-4} kg of Sb-eq per FU) than their corresponding reference scenarios. On the contrary, in the case of 'Amendment' scenarios (around 1.1×10^{-4} kg of Sb-eq per FU) only the best performance causes lower impacts than the reference. For this impact category, the main contributors are fertilizer offset and biochar combustion. The major amount of abiotic resources saved of 'Combustion' scenarios compared to 'Amendment' ones (Tables 3 and 4) is due to the higher consumption of abiotic resources of the first group of reference scenarios (combustion of fossil fuels) compared to the second one (fertilizers).

In general the multi-criteria analysis does not point to a best choice between 'Combustion' and 'Amendment' scenarios. The best performance of biochar combustion provides a saving of over 14,000 MJ from non-renewable sources when electric and thermal energies are exploited; when biochar is valorised as soil amendment the non-renewable energy saving is 11,000 MJ. On the other hand, the GHGs saving is higher in 'Amendment' scenarios (max value: 885 kg of CO₂-eq) than in 'Combustion' scenarios (max value: 740 kg of CO₂-eq). When compared to reference scenarios, the use of biochar as soil amendment does not reduce the acidification emissions since the emissions saved by electric and thermal energy production are overtaken by the acidification emissions due to cogeneration and major fertilizer application on soil when corn stover is removed. The best case the use of biochar as amendment reaches a balance between emission and saving of acidifying compounds, while biochar combustion always causes high level of acidifying emissions (2-3 kg of SO₂-eq per FU). From the eutrophication point of view, no evident difference can be pointed out between 'Combustion' and 'Amendment' scenarios. Lastly, the abiotic resources saved by 'Combustion' scenarios are larger than in best case 'Amendment' scenario.

The analysis shows that in the combination of the processes the critical point may be represented by the biological process, which is still affected by high sensitivity to key

parameters, associated with high variability biogas yield and methane biogas content (see Table 1). More control on this part of the technology would be very important.

From the thermochemical processes point of view, an important factor is the size of the pyrolysis reactor, since the larger is the size, the lower is the energy consumption due to heat dispersions and, therefore, the higher is the efficiency of pyrolysis process. On the other hand, large-scale plants are likely to have higher transportation costs per unit biomass transported as a result of longer transportation distances (Bridgwater, 2006); in addition, this could affect negatively the environmental performances of the process (additional vehicular traffic, pollution, etc.).

The proposed conversion system allows the transformation of a solid fuel (stover) in a gaseous one (biogas); this can be considered an overall improvement, as gaseous fuels offer much more flexibility of use and cleanliness than solid ones. It is also clear that the possibility to store energy in the form of concentrated bio-oil may play a relevant role and represent a key feature in the next years.

4. Conclusions

This study shows how the PYDA system enables relevant primary energy savings of non-renewable sources without worsening abiotic resources depletion; moreover a strong reduction of GHGs emissions is shown in all tested scenarios. By contrast, the impacts on eutrophication and acidification are higher than in reference scenarios. The former is due to the indirect effects of fertiliser offsetting and related emissions, whereas the latter occurs when using biochar as solid fuel. The PYDA system can always be recommended as a better option when corn stovers are not used for mulch.

Acknowledgments

This study was conducted within the framework of the APQ Ricerca Intervento a “Sostegno dello sviluppo dei Laboratori di ricerca nei campi della nautica e dell’energia per il Tecnopolo di Ravenna” “Energia, parte Biomasse” between Università di Bologna and

1 Regione Emilia Romagna (Italy). The collaboration with RES Reliable Environmental
2 Solutions in fed-batch test is acknowledged.

3 **References**

4 Azapagic, A., Clift, R., 1999. Life cycle assessment and multiobjective optimization. J.
5 Cleaner Prod. 7, 135-143.

6 Bandini, V., Righi, S., Buscaroli, A., Marazza, D., Torri, C., 2014. Biorefining of high ligno-
7 cellulosic waste biomass via pyrolysis coupled with anaerobic digestion. An LCA study, in:
8 Fava, F., (Ed.), Green economy e sua implementazione nel Mediterraneo. Ecomondo
9 2014, 5-8 November 2014, Maggioli Editore, Rimini, Italy, pp. 635-640.

10 Benini, L., Torri, C., 2010. Soil organic carbon enrichment and carbon sequestration from
11 residual biomass through pyrolysis and bio-char application to soils: preliminary
12 assessment in the Ravenna province countryside, in: Proceedings of the 18th EU BC&E, 3-
13 7 May, Lyon, France.

14 Bridgwater, T., 2006. Review: Biomass for energy. J. Sci. Food Agric. 86, 1755-1768.

15 Cherubini, F., Ulgiati, S., 2010. Crop residues as raw materials for biorefinery systems - A
16 LCA case study. Appl. Energy. 87, 47-57.

17 Clough, T.J., Condon, L.M., 2010. Biochar and the nitrogen cycle: Introduction. J. Environ.
18 Qual. 39, 1218-1223.

19 Ecoinvent Centre, 2012. Ecoinvent database. Available at:

20 <http://www.ecoinvent.org/database/database.html> (visited on January 2016)

21 European Commission, 2012. Innovating for Sustainable Growth: a Bioeconomy for
22 Europe. Brussels, 13.2.2012. COM(2012) 60 final.

23 European Commission, 2014. Towards a circular economy: a zero waste programme for
24 Europe. Brussels, 2.7.2014. COM(2014) 398 final.

25 European Union, 2009. Directive 2009/28/EC of the European Parliament and of the
26 Council of 23 April 2009, on the promotion of the use of energy from renewable sources

1 and amending and subsequently repealing directives 2001/77/EC and 2003/30/EC. Official
2 Journal of the European Union L140, vol. 52, 16-62.

3 FAO 1996. Control of water pollution from agriculture. Ongley, E.D. (Ed.), Rome, Italy.

4 FAO, 2010. Bioenergy and food security. The BEFS analytical framework. Rome, Italy.

5 FAO, 2012. Biofuel co-products as livestock feed - Opportunities and challenges. Harinder,
6 P.S.M. (Ed.), Rome, Italy.

7 Gaunt, J.L., Lehmann, J., 2008. Energy balance and emissions associated with biochar
8 sequestration and pyrolysis bioenergy production. Environ. Sci. Technol. 42, 4152-4158.

9 Guinée, J.B., Gorée, M., Heijungs, R., Huppes, G., Kleijn, R., de Koning, A., Van Oers, L.,
10 Wegener Sleeswijk, A., Suh, S., Udo de Haes, H.A, De Bruijn, J.A., Van Duin R.,
11 Huijbregts, M.A.J. 2002. Handbook on Life Cycle Assessment: Operational Guide to the
12 ISO Standards. Series: Eco-efficiency in industry and science. Kluwer Academic
13 Publishers. Dordrecht (Hardbound, ISBN 1-4020-0228-9; Paperback, ISBN 1-4020-0557-
14 1).

15 Guiot, S.R., Cimpola, R., Carayon, G., 2011. Potential of Wastewater-Treating Anaerobic
16 Granules for Biomethanation of Synthesis Gas. Environ. Sci. Technol. 45, 2006-2012.

17 Hammond, J., Shackley, S., Sohi, S., Brownsort, P., 2011. Prospective life cycle carbon
18 abatement for pyrolysis biochar systems in the UK. Energ. Policy. 39, 2646-2655.

19 Hischier, R., Hellweg, S., Capello, C., Primas, A., 2005. Establishing Life Cycle Inventories
20 of chemicals based on differing data availability. Int. J. LCA10, 59-67.

21 HLPE, 2013. Biofuels and food security. A report by the High Level Panel of Experts on
22 Food Security and Nutrition of the Committee on World Food Security, Rome 2013.

23 Ibarrola, R., Shackley, S., Hammond, J., 2012. Pyrolysis biochar systems for recovering
24 biodegradable materials: a life cycle carbon assessment. Waste Manage. 32, 859-868.

25 IEA ETSAP, 2010. Technology brief E05. Biomass for Heat and Power, May 2010.

1 ISO, 2006a. Environmental Management-Life Cycle Assessment-Principles and
2 Framework, second ed., ISO 14040; 2006-07-01; ISO: Geneva, Switzerland.

3 ISO, 2006b. Environmental Management-Life Cycle Assessment-Requirements and
4 Guidelines, first ed., ISO 14040; 2006-07-01; ISO: Geneva, Switzerland.

5 Jarboe, L.R., Wen, Z., Choi, D.W., Brown, R.C., 2011. Hybrid thermochemical processing:
6 fermentation of pyrolysis-derived bio-oil. *Appl. Microbiol. Biotechnol.* 91, 1519-1523.

7 Khoo, H., 2009. Life cycle impact assessment of various waste conversion technologies.
8 *Waste Manage.* 29, 1892-1900.

9 Lewis, F.M., 2012. Pyrobiomethane process, US Patent US 2012/0073199 A1.

10 Meyer, S., Glaser, B., Quicker, P., 2011. Technical, economical, and climate-related
11 aspects of biochar production technologies: a literature review. *Environ. Sci. Technol.* 45,
12 9473-9483.

13 Nita, V., Benini, L., Ciupagea, C., Kavalov, B., Pelletier, N., 2013. Bio-economy and
14 sustainability: a potential contribution to the Bio-economy Observatory. European
15 Commission, Joint Research Centre, Institute for Environment and Sustainability.

16 Raave, H., Keres, I., Kauer, K., Nöges, M., Rebane, J., Tampere, M., Loit, E., 2014. The
17 impact of activated carbon on NO₃-N, NH₄⁺-N, P and K leaching in relation to fertilizer
18 use. *Eur. J. Soil Sci.* 65, 120-127.

19 Roberts, K.G., Gloy, B.A., Joseph, S., Scott, N.R., Lehmann, J., 2009. Life cycle
20 assessment of biochar systems: estimating the energetic, economic, and climate change
21 potential. *Environ. Sci. Technol.* 44, 827-833.

22 Taghizadeh-Toosi, A., Clough, T.J., Sherlock, R.R., Condon, L.M., 2012. Biochar adsorbed
23 ammonia is bioavailable. *Plant soil.* 350, 57-69.

24 Thinkstep, 2015a. Available at: [http://www.gabi-software.com/software/gabi-software/gabi-](http://www.gabi-software.com/software/gabi-software/gabi-5/)
25 [5/](http://www.gabi-software.com/software/gabi-software/gabi-5/) (visited on January 2016)

- 1 Thinkstep, 2015b. Available at: <http://www.gabi-software.com/databases/gabi->
2 [databases/professional/](http://www.gabi-software.com/databases/gabi-databases/professional/) (visited on January 2016)
3 Torri, C., Fabbri, D., 2012. Biological upgrading of pyrolysis oil and gas to methane and
4 hydrogen by means of adapted anaerobic bacteria consortium, in: Proceedings of the 20th
5 EU BC&E, Milan, 18-22 June.
6 Torri, C., Fabbri, D., 2014. Biochar enables anaerobic digestion of aqueous phase from
7 intermediate pyrolysis of biomass. *Bioresour. Technol.* 172, 335-341.

8

1 **Figure captions**

2 Fig. 1 System boundaries of the three 'Combustion' scenarios. Mass and energy balance
3 of scenario 3 'Combustion-Best' is reported.

4 Fig. 2 System boundaries of the three 'Amendment' scenarios. Mass and energy balance
5 of scenario 6 'Amendment-Best' is reported.

6 Fig. 3 Environmental impacts due to the coupled treatment pyrolysis-anaerobic digestion
7 of 1 t corn stovers. Two alternative ways of biochar exploitation are considered
8 (combustion and amendment) and three different levels of technical performances (worst,
9 average, best) are taken into account. Each scenario is compared to the reference
10 scenarios 'Electricity' and 'Electricity and thermal energy'.

11 Fig. 4 Process contributions to the environmental impact of 1 t corn stover treatment of
12 each considered stage: fertilizer offset, fertilizer offset emissions, pyrolysis, anaerobic
13 digestion, cogeneration, biochar combustion and transport.

14

15

1

2 **Table 1. Technical performances of the six analysed scenarios**

3

Scenarios	Biochar utilization	Pyrolysis electricity consumption (MJ/kg)	Biogas yield (L/kg)	Methane in biogas	Electric efficiency cogenerator	Thermal efficiency cogenerator
1 Combustion-Worst	Combustion	2.05	290	55%	38%	32%
2 Combustion-Average	Combustion	1.64	415	60%	39%	40%
3 Combustion-Best	Combustion	0.25	540	65%	40%	48%
4 Amendment-Worst	Amendment	2.05	290	55%	38%	32%
5 Amendment-Average	Amendment	1.64	415	60%	39%	40%
6 Amendment-Best	Amendment	0.25	540	65%	40%	48%

4

5

6

7

1 **Table 2. Main processes used in this study**

Country	Process name	Data Source
RER	urea, as N, at regional storehouse	Ecoinvent
RER	triple superphosphate, as P ₂ O ₅ , at regional storehouse	Ecoinvent
RER	potassium chloride, as K ₂ O, at regional storehouse	Ecoinvent
NL	nitrogen	Thinkstep
DE	municipal waste water treatment (agricultural sludge application)	Thinkstep
RER	lubricating oil, at plant	Ecoinvent
RER	hard coal power plant	Ecoinvent
RER	chlorine, liquid, production mix, at plant	Ecoinvent
RER	SO _x retained, in hard coal flue gas desulphurization	Ecoinvent
GLO	NO _x retained, in SCR	Ecoinvent
RER	light fuel oil, at regional storage	Ecoinvent
RER	transport, freight, rail	Ecoinvent
IT	disposal, hard coal ash, 0% water, to residual material landfill	Ecoinvent
CH	disposal, residue from cooling tower, 30% water, to sanitary landfill	Ecoinvent
RER	water, completely softened, at plant	Ecoinvent
RER	water, decarbonised, at plant	Ecoinvent
GLO	lorry transport; Euro 0, 1, 2, 3, 4 mix; production mix; 22 t total weight, 17.3 t max payload	Thinkstep
EU-27	diesel mix at refinery	Thinkstep
IT	electricity grid mix	Thinkstep
CH	heat, at cogeneration 50kWe lean burn, allocation energy	Ecoinvent
CH	used mineral oil, 10% water, to hazardous waste incineration	Ecoinvent

2

3

4

Table 3. Difference between LCIA scores related to PYDA scenarios and ‘Electricity’ scenarios. FU is 1 ton of treated corn stovers. Negative values indicate that PYDA scenarios bring advantages compared to reference scenarios.

IMPACT CATEGORIES	1-Comb worst	2-Comb average	3-Comb best	4-Amend worst	5-Amend average	6-Amend best
PED (MJ)	-4.65×10^3	-6.53×10^3	-9.13×10^3	-1.35×10^3	-3.23×10^3	-5.83×10^3
GWP (kg CO₂-eq)	-1.27×10^2	-2.47×10^2	-4.15×10^2	-2.73×10^2	-3.93×10^2	-5.61×10^2
AP (kg SO₂-eq)	3.19×10^0	2.86×10^0	2.41×10^0	1.18×10^0	8.49×10^{-1}	3.96×10^{-1}
EP (kg PO₄³⁻-eq)	6.99×10^{-1}	6.72×10^{-1}	6.34×10^{-1}	6.06×10^{-1}	5.79×10^{-1}	5.41×10^{-1}
AD (kg Sb-eq)	3.21×10^{-5}	-1.72×10^{-6}	-4.84×10^{-5}	7.83×10^{-5}	4.45×10^{-5}	1.40×10^{-4}

Table 4. Difference between LCIA scores related to PYDA scenarios and ‘Electricity and thermal energy’ scenarios. FU is 1 ton of treated corn stovers. Negative values indicate that PYDA scenarios bring advantages compared to reference scenarios.

IMPACT CATEGORIES	1-Comb worst	2-Comb average	3-Comb best	4-Amend worst	5-Amend average	6-Amend best
PED (MJ)	-6.29×10 ³	-9.73×10 ³	-1.45×10 ⁴	-2.98×10 ³	-6.43×10 ³	-1.12×10 ⁴
GWP (kg CO₂-eq)	-2.40×10 ²	-4.67×10 ²	-7.87×10 ²	-3.86×10 ²	-6.13×10 ²	-9.33×10 ²
AP (kg SO₂-eq)	3.06×10 ⁰	2.61×10 ⁰	1.98×10 ⁰	1.05×10 ⁰	5.98×10 ⁻¹	-2.83×10 ⁻²
EP (kg PO₄³⁻-eq)	6.74×10 ⁻¹	6.22×10 ⁻¹	5.50×10 ⁻¹	5.81×10 ⁻¹	5.29×10 ⁻¹	4.57×10 ⁻¹
AD (kg Sb-eq)	2.50×10 ⁻⁵	-1.57×10 ⁻⁵	-7.21×10 ⁻⁵	7.12×10 ⁻⁵	3.05×10 ⁻⁵	-2.59×10 ⁻⁵

Scenario 3: Combustion-Best

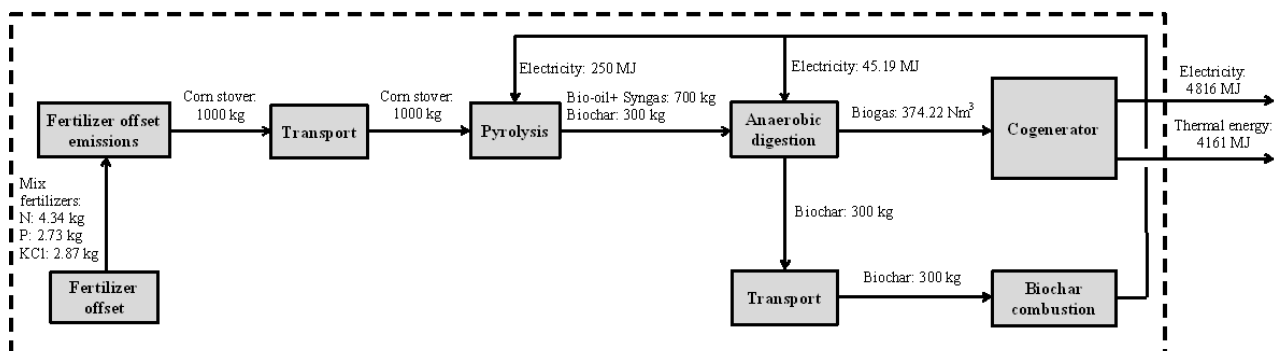


Fig. 1

This item was downloaded from IRIS Università di Bologna (<https://cris.unibo.it/>)

When citing, please refer to the published version.

Scenario 6: Amendment-Best

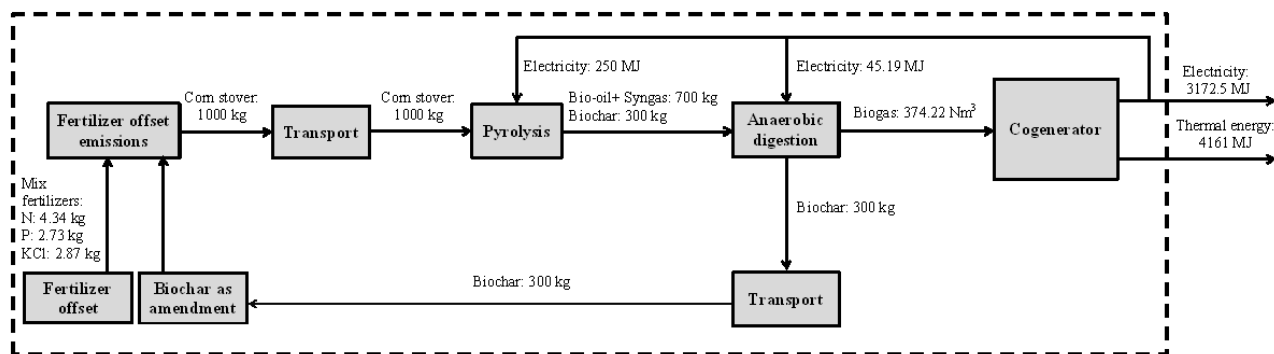
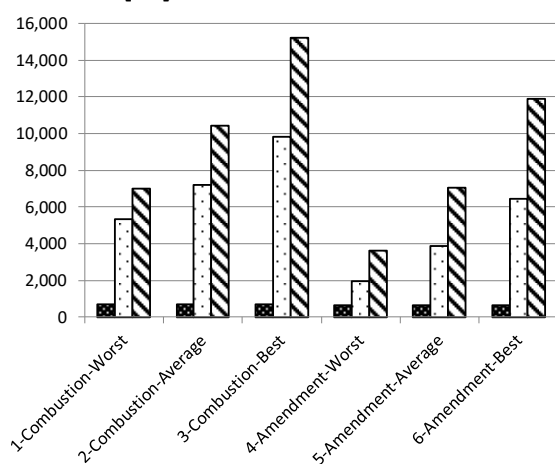


Fig. 2

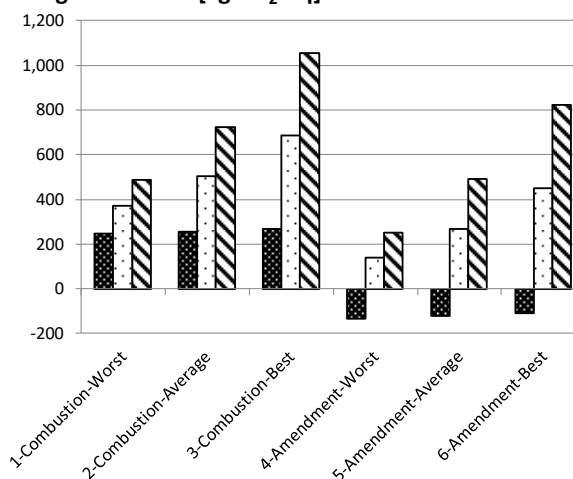
This item was downloaded from IRIS Università di Bologna (<https://cris.unibo.it/>)

When citing, please refer to the published version.

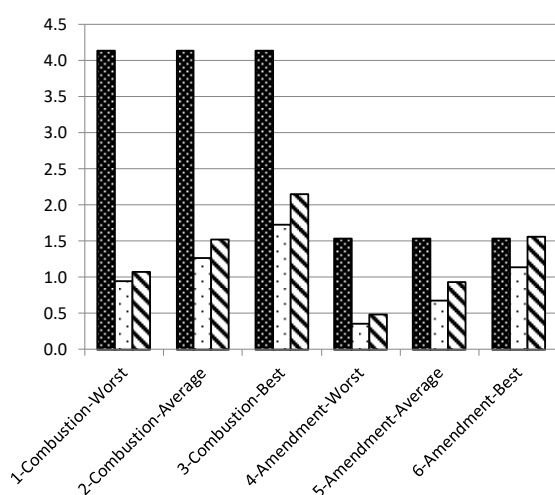
Primary Energy from non-renewable resources [MJ]



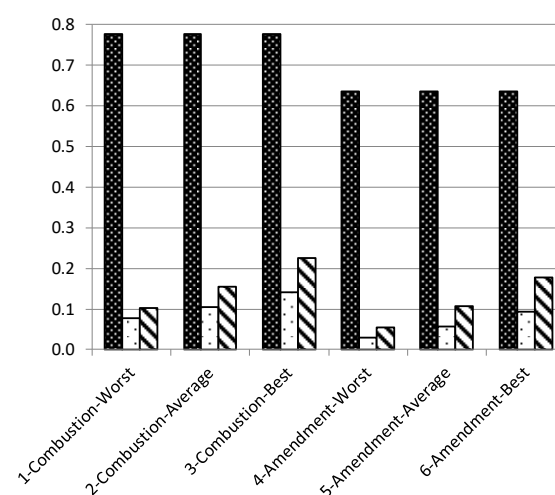
Global Warming Potential, excluding biogenic carbon [kg CO₂-eq]



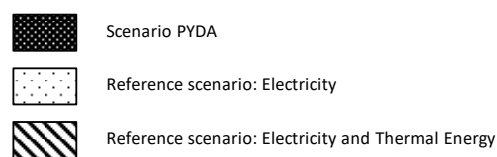
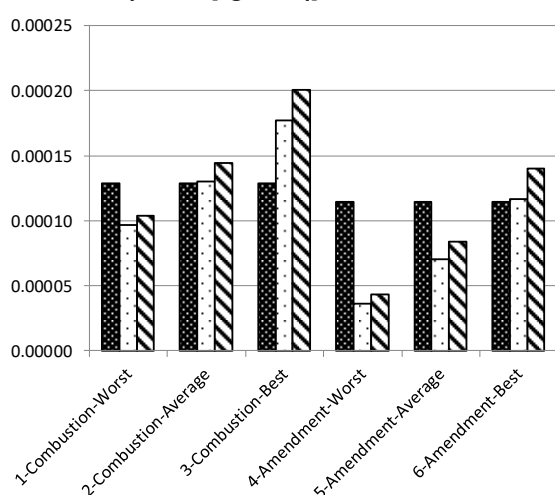
Acidification Potential [kg SO₂-eq]



Eutrophication Potential [kg PO₄³⁻-eq]



Abiotic Depletion [kg Sb-eq]



This item was downloaded from IRIS Università di Bologna (<https://cris.unibo.it/>)

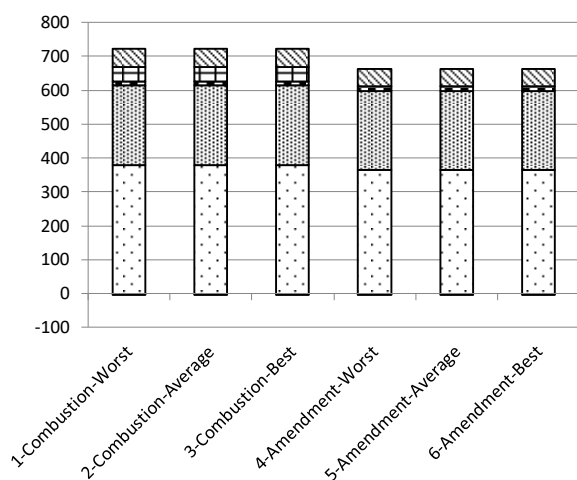
When citing, please refer to the published version.

Fig. 3

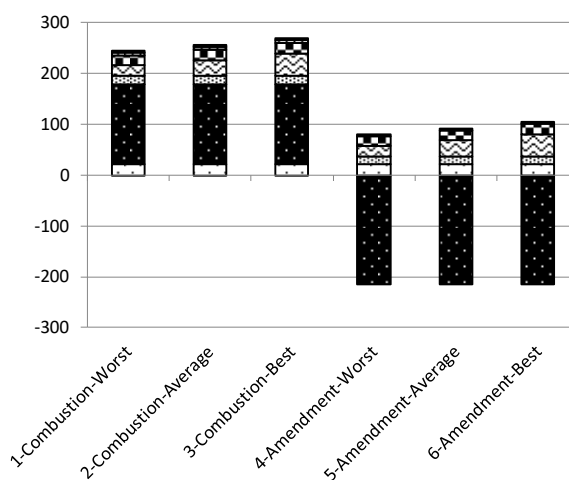
This item was downloaded from IRIS Università di Bologna (<https://cris.unibo.it/>)

When citing, please refer to the published version.

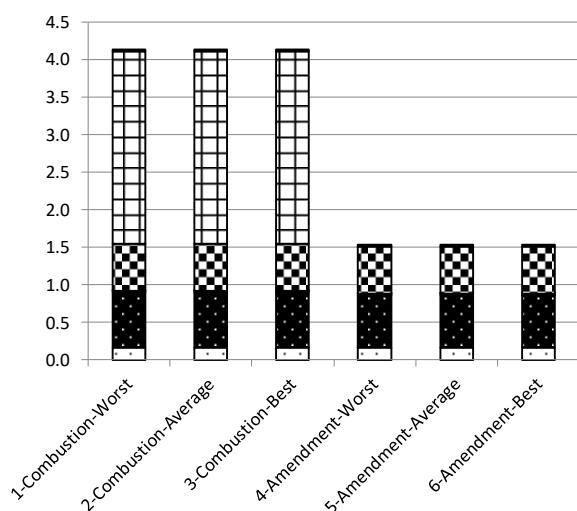
Primary Energy from non-renewable resources [MJ]



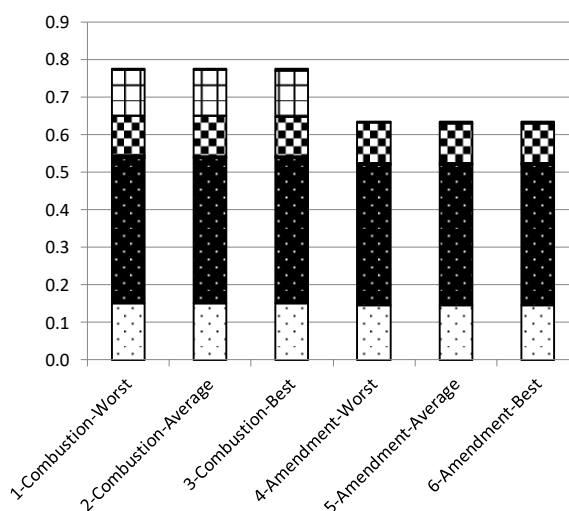
Global Warming Potential, excluding biogenic carbon [kg CO₂-eq]



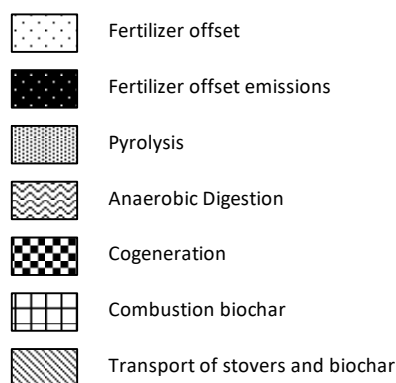
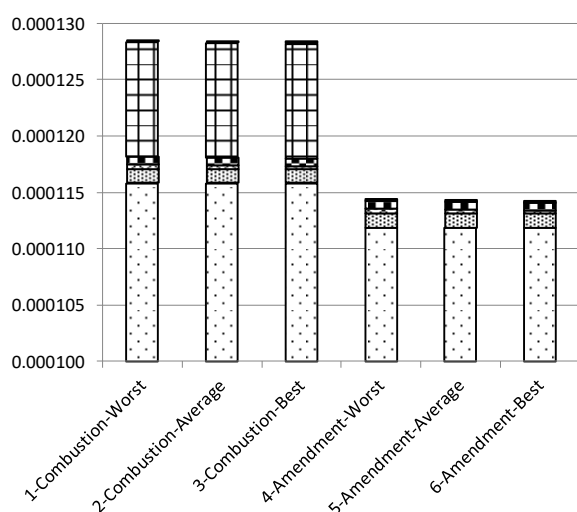
Acidification Potential [kg SO₂-eq]



Eutrophication Potential [kg PO₄³⁻-eq]



Abiotic Depletion [kg Sb-eq]



This item was downloaded from IRIS Università di Bologna (<https://cris.unibo.it/>)

When citing, please refer to the published version.

Fig. 4

This item was downloaded from IRIS Università di Bologna (<https://cris.unibo.it/>)

When citing, please refer to the published version.