Crop residues as raw materials for biorefinery systems – A LCA case study

Francesco Cherubini [a,*], Sergio Ulgiati [b]

[a] Joanneum Research, Institute of Energy Research, Elisabethstraße 5, 8010 Graz, Austria
[b] Parthenope University of Naples, Department of Environmental Sciences, Centro Direzionale, Isola C4, 80143 Napoli, Italy

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ABSTRACT

Our strong dependence on fossil fuels results from the intensive use and consumption of petroleum derivatives which, combined with diminishing oil resources, causes environmental and political concerns. The utilization of agricultural residues as raw materials in a biorefinery is a promising alternative to fossil resources for production of energy carriers and chemicals, thus mitigating climate change and enhancing energy security. This paper focuses on a biorefinery concept which produces bioethanol, bioenergy and biochemicals from two types of agricultural residues, corn stover and wheat straw. These biorefinery systems are investigated using a Life Cycle Assessment (LCA) approach, which takes into account all the input and output flows occurring along the production chain. This approach can be applied to almost all the other patterns that convert lignocellulosic residues into bioenergy and biochemicals. The analysis elaborates on land use change aspects, i.e. the effects of crop residue removal (like decrease in grain yields, change in soil N_2O emissions and decrease of soil organic carbon). The biorefinery systems are compared with the respective fossil reference systems producing the same amount of products/services from fossils instead of biomass. Since climate change mitigation and energy security are the two most important driving forces for biorefinery development, the assessment focuses on greenhouse gas (GHG) emissions and cumulative primary energy demand, but other environmental categories are evaluated as well.

Results show that the use of crop residues in a biorefinery saves GHG emissions and reduces fossil energy demand. For instance, GHG emissions are reduced by about 50% and more than 80% of non-renewable energy is saved. Land use change effects have a strong influence in the final GHG balance (about 50%), and their uncertainty is discussed in a sensitivity analysis. Concerning the investigation of the other impact categories, biorefinery systems have higher eutrophication potential than fossil reference systems. Based on these results, a residues-based biorefinery concept is able to solve two problems at the same time, namely find a use for the abundant lignocellulosic residues and ensure a mitigation effect for most of the environmental concerns related to the utilization of non-renewable energy resources.

Therefore, when agricultural residues are used as feedstocks, best management practices and harvest rates need to be carefully established. In fact, rotation, tillage, fertilization management, soil properties and climate can play an important role in the determination of the amount of crop residue that can be removed minimizing soil carbon losses.

1. Introduction and aim

Concerns about sustainability and security of fossil fuel use, along with advances in biomass conversion technology, stimulated the interest in crop residue use as feedstocks for bioenergy purposes to partially meet our energy needs [1].

The term of "biorefinery", i.e. co-production of transportation biofuels, bioenergy and marketable chemicals from renewable biomass sources, is raising importance in the scientific community.

The biorefinery concept is analogous to today's petroleum refinery, which produces multiple fuels and products from petroleum. One of the main promoting factors for the future development of biorefineries can be seen in the efficient production of transportation liquid biofuels [2]. In fact, the energy demand in the transportation sector is growing steadily and the demand for renewable (bio-)fuels, which can only be produced from biomass (the only C rich material available besides fossils), grows accordingly [3]. A large number of world countries have targets for improving the shares of biofuels in the national transport sector. For instance, Europe aims at a share of biofuels equal to 5.75% in 2010 and 10% in 2020, according to the draft directive for renewable energy, while IEA

and IPCC expect a significant contribution of biofuels on transportation market in 2030 (10–20%) [4]. The most common biofuels produced today in the world are bioethanol, biodiesel and biogas (or biomethane). They represent the 1st generation biofuels and their LCA performances are investigated in several case studies [5–7]. 1st generation biofuels gave rise to some concerns (e.g. limited GHG savings, competition with food and feed industries) that are expected to be partially overcome by developing the so-called 2nd generation biofuels which are produced from a variety of biomass residues and nonfood crops [8]. These include the utilization of lignocellulosic materials, such as residues from agriculture, forestry and industry and dedicated lignocellulosic energy crops. Few LCA studies on 2nd generation biofuels are currently available and they generally reveal better environmental performances than 1st generation biofuels [9,10].

Concerning the state of the art of biobased products, they are currently obtained from basic biomass components like starch, oil, and cellulose. In addition, chemicals like lactic acid and amino acids are produced and used in the food industry. Other biobased products include adhesives, cleaning compounds, detergents, dielectric fluids, dyes, hydraulic fluids, inks, lubricants, packaging materials, paints and coatings, paper and box board, plastic fillers, polymers, solvents, and sorbents.

However, most of these biofuels and biochemicals are produced in single production chains and not within a biorefinery framework, and usually require materials in competition with the food and feed industry. Their exploitation is thereby limited. An alternative can be represented by lignocellulosic materials. In fact, lignocellulosic feedstocks can be supplied either from dedicated crops or as residues from agricultural, forestry and wood industry. This feedstock is made of three main components (cellulose, hemicellulose, and lignin) which can be refined into different final products using a set of jointly applied technological processes. Among the different possible feedstocks, agricultural residues are a widespread lignocellulosic biomass source available in many countries. Available residues are estimated to be 10^{10} Mt worldwide, corresponding to an energy value of 47 EJ [11]. Among them, cereal residues are the largest source (about 3.8×10^9 tons), making up two thirds of the total available amount [12]. Therefore, crop residues are considered possible renewable biomass sources in countries with large available land area. However, there is an ongoing debate on the effective possibilities of crop residue removal from agricultural field, since such removal affects processes like soil organic matter turnover, soil erosion, crop yields, N_2O emissions from soils and others. Effects of collection of crop residues are strongly affected by local conditions (climate, soil type, crop management) and are described in several papers [1,12–14]. By contrast, LCA implications in terms of environmental impacts due to straw removal are still uncertain: there are few references on these effects in the literature and the patterns are not consistent across references [11].

This study aims at addressing this topic performing a thorough LCA of a biorefinery system which converts crop residues (corn stover and wheat straw) into bioethanol, bioenergy, and biochemicals (phenols). This approach can be applied to almost all the other patterns that convert lignocellulosic residues into bioenergy and biochemicals. The assessment takes into account residue collection, processing, transport, conversion and final use of products, along with the related methodological issues such as land use change effects. Since climate change mitigation and energy independence are the main driving forces for future biorefineries, results have a special focus on GHG and energy balance. Other environmental impact categories are estimated according to the CML classification method. Results of the biorefinery systems are compared with those of the respective fossil reference systems, which produce the same amount of products and services from fossil sources.

2. Goal, scope and methodological issues

2.1. Goal definition

This work performs a LCA of two biorefinery systems which produce bioethanol, electricity, heat and phenols from two types of agricultural residues, corn stover and wheat straw. According to the classification method for biorefinery systems [15], these concepts can be labeled:

C5/C6 sugars, biogas, lignin/pyrolytic oil biorefinery for bioethanol, electricity and heat and chemicals from lignocellulosic residues.

This system is a combination of several conversion technologies which are jointly applied in order to produce biofuels and material products from lignocellulosic biomass, within a biorefinery approach. The functional unit of the assessment is the amount of agricultural residues treated per year by each biorefinery system (both with corn stover and wheat straw as feedstock), i.e. 477 kilotons$_{dry}$/a. The biorefinery systems are compared with fossil reference systems which produce the same amount of products/services from fossils. The reference use for the cultivated land is residue left in the field, i.e. ploughed back to the soil.

This study is modelled by means of the LCA software tool SimaPro 7.1 (http://www.pre.nl/simapro/default.htm) and selected literature references are used to estimate input flows, specific emissions and land use change effects. Results have a special focus on GHG and energy balance, but other environmental impact categories are estimated as well. The GHG balance accounts for emissions of GHGs like CO_2, CH_4, and N_2O, expressed as CO_2 equivalents using equivalence factors with a 100 year time horizon. The energy balance includes the cumulative primary energy demand, distinguished into non-renewable energy (fossil and nuclear), renewable energy (biomass) and other renewable energy (mainly hydropower, but also solar, wind, etc.). In addition, the Energy Return on Investment (EROI) is calculated; this is an index given by the ratio between energy out (i.e. the energy content of the products) and the non-renewable energy in (i.e. all the non-renewable energy inputs, direct and indirect, required along the full life cycle) [16]. The other environmental impact categories are estimated according to the CML classification method (CML 2 baseline 2000 V. 2.03). This is a problem-oriented Life Cycle Assessment method developed by the Institute of Environmental Sciences of the University of Leiden. The most uncertain parameters are finally discussed in a sensitivity analysis.

2.2. System boundaries and definition of the fossil reference systems

In Fig. 1, the simplified system boundaries for the biorefinery and fossil reference systems are shown. The biorefinery chain starts at the top of the diagram using agricultural residues which are made with carbon fixation from the atmosphere via photosynthesis. At the end, the biorefinery system supplies products and services. All input and output flows occurring along the full chain, for collecting the residues, processing the feedstock into biofuel, transporting and storing of feedstocks, distributing and final use of biofuels are accounted for using a life cycle perspective. By contrast, the fossil reference system starts with consumption of non-renewable sources (i.e. fossil oil and natural gas), and its main life-cycle stages are the following: extraction and conveyance of raw materials, production of the raw fossil fuel, refining, storage, distribution and combustion. Since production of the biomass feedstock requires a raw material previously dedicated to other purposes (i.e. left in the field to enhance soil fertility), the reference system also includes an alternative raw material use (residues
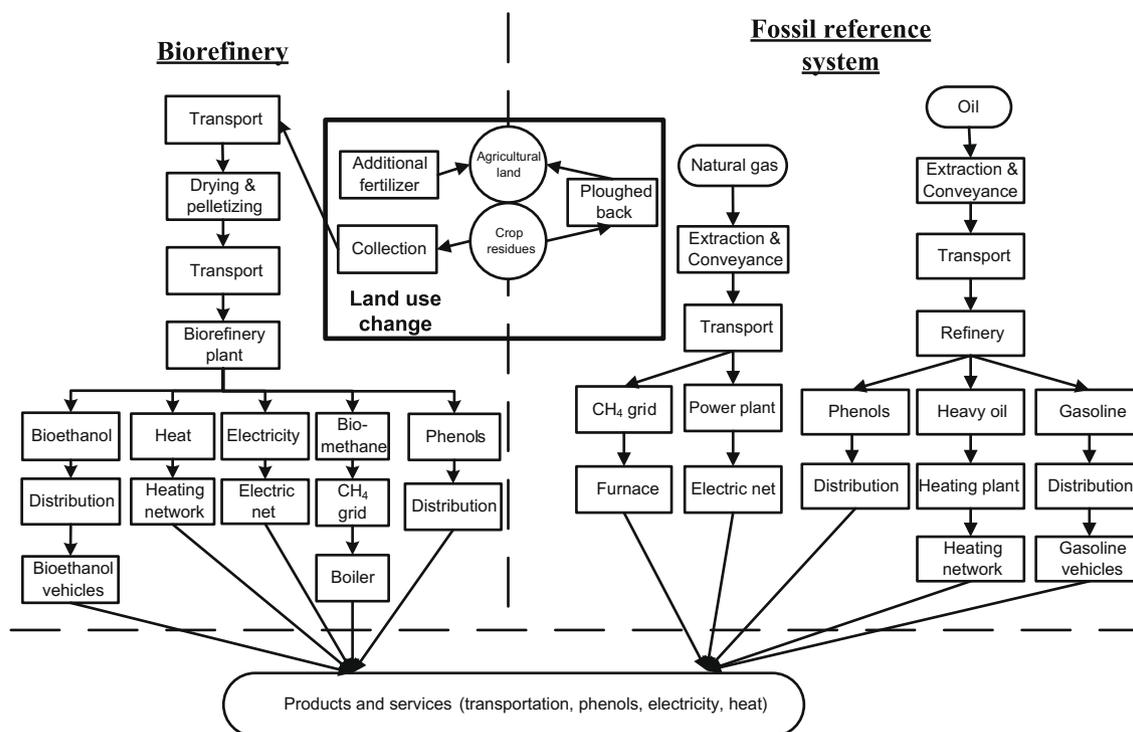
Fig. 1. Comparison between the production chains of the biorefinery and the fossil reference systems.

ploughed back to the soil), and the LCA effects of such land use change are accounted for in the assessment.

The fossil reference systems produce the same amounts of products and services of the biorefinery systems from the following sources:

- gasoline for the transportation service;
- electricity from natural gas;
- heat from heavy oil;
- phenols from oil refinery; and
- heat from natural gas (instead of heat from biomethane).

The fossil-derived alternatives to biorefinery products are listed in Table 1. In the right part of the table, their specific GHG and energy demand factors are shown with the respective databases. These values, multiplied by the final quantities of products, are used for estimating the total GHG emissions and cumulative primary energy demand of the fossil reference system.

The definition of the fossil reference system is extremely important as it has a direct influence on the estimation of the GHG savings of the biorefinery system. For instance, electricity can be assumed to be produced from oil, natural gas, coal or other sources, all of which have different GHG emission factors. In this assess-

ment, natural gas derived electricity is assumed (in order to take into account the fossil best available technologies) and it has a GHG emission factor of 0.73 kg CO_2-eq./kW h (average among Austrian natural gas power plants), while coal derived electricity has a factor much higher, i.e. about 1.05 kg CO_2-eq./kW h (average among Austrian coal power plants) (ETH-ESU 96). The GHG emission savings of the biorefinery systems would therefore be larger if coal electricity is displaced.

2.3. Agricultural residues as raw materials

Agricultural residues like corn stover and wheat straw are categorized as lignocellulosic biomass sources. Lignocellulosic biomass has three major components: cellulose, hemicellulose, and lignin. Cellulose $(C_6H_{10}O_6)_n$ has a strong molecular structure made by long chains of glucose molecules (C6 sugar). Cellulose (30–50% of total lignocellulosic dry matter) is much more difficult to hydrolyze and set free individual glucose monomers than starch, and this conversion requires strong conditions of temperature and pressure.

Hemicellulose $(C_5H_8O_5)_n$ is a relatively amorphous component that is easier to break down with chemicals and/or heat than cellulose; it contains a mix of C6 and C5 sugars and it is the second main

Table 1
GHG emissions and cumulative energy demand of the conventional (fossil) alternatives to biorefinery products.

Biorefinery product	Fossil alternative	Unit	GHG emissions g CO_2-eq./unit	Total energy MJ/unit[a]	Database
Transportation (bioethanol)	Transportation (gasoline)	km	198	3.14	Ecoinvent
Electricity from CHP	Electricity from natural gas[b]	kW h	731	11.9	ETH-ESU 96
Heat from CHP	Heat from oil[c]	kW h	425	5.88	ETH-ESU 96
Heat from biomethane	Heat from natural gas[d]	kW h	289	4.85	ETH-ESU 96
Phenols	Conventional phenols	g	3.5	0.12	Ecoinvent

[a] Mainly non-renewable energy (99%).
[b] Average among natural gas power plants in Austria.
[c] Industrial furnace (Europe).
[d] Industrial furnace >100 kW.

component of lignocellulosic biomass (20–40% of total feedstock dry matter).

Lignin $(C_9H_{10}O_2(OCH_3)_n)$ is essentially the glue that provides the overall rigidity to the structure of plants and trees and is made of phenolic polymers. While cellulose and hemicellulose are polysaccharides that can be hydrolyzed to sugars and then fermented to ethanol, lignin (15–25% of total feedstock dry matter) cannot be used in fermentation processes, but it may be useful for other purposes (chemical extraction or energy production). The chemical composition of corn stover and wheat straw is reported in Table 2. There are some differences between these feedstocks which influence the quantities of final products and, as a consequence, the final environmental performances of biorefinery systems. Both corn stover and wheat straw are assumed to be collected from the field, baled, loaded on trucks, converted to pellets and then used as raw materials in the biorefinery plant. The feedstock is assumed to be transported from the source (i.e. the field) to pellet production facilities (20 km) and then to biorefinery plants (100 km). All the agricultural inputs required to grow the crops are not accounted for because they are assumed to be completely allocated to the grains.

The removal of agricultural residues from fields may give rise to some concerns concerning soil quality, decrease in soil organic carbon (SOC), soil erosion, crop yields and other environmental implications. All the possible benefits and disadvantages of crop residue collection for bioenergy use are still under discussion [12,17,18]. This paper addresses these issues in the following section, where the land use change effects are estimated.

2.4. Land use change effects

The use of biomass may lead to a change in carbon stored above and below ground and in general these changes are not considered in the GHG balance of bioenergy systems, unless few exceptions [19,20]. Generally, organic C is stored in three different pools: vegetation (including roots), litter and soil. When changing land utilization, these storage pools can change until a new equilibrium is reached. This is an important aspect because of the large quantities of carbon in soil organic matter: these pools of carbon are so large that even relatively small percentage increases or decreases in their size can have relevance in the GHG balance. The dynamics affecting soil carbon pools are very site-specific and highly dependent on former and current agronomic practices, climate, and soil characteristics [21].

The issue of land use change (LUC) effects induced by agricultural residue collection was already investigated in the scientific literature [14,18]. In this assessment, estimation of land use change effects is based on a recent study that modelled the effects of crop rotation and straw removal frequency on two different soil types [11]. Results show that the differences across rotations are generally more important than those related to straw management for a given rotation: the removal of straw implied limited consequences on field emissions.

As already mentioned, the reference land use considered in this assessment is agricultural land where corn stover and wheat straw are left on the ground and ploughed back to the field. When these residues are collected and used as raw materials in biorefineries, the main GHG implications related to such land use change are the following:

- Decrease in crop grain productivity yields, because of a lower net mineralization of N in soils. This corresponds to a straw fertilizer value of 1.5–4.5 kg N/t dry straw, which is lower than the total N content of the straw (6 kg N/t dry straw). The implications on GHG balances of bioenergy systems consist in an increase of synthetic fertilizer application to balance the nutrient removed with the straw and the decrease in crop yields, which must be addressed [11]. The decrease in grain yields can be seen as a consequence of indirect land use change: the "missing" cereals will be produced somewhere else (by an expansion of agricultural land) or will be supplied by an increase of fertilization.
- Decrease in N_2O emissions from land with increasing crop residue removal. The reason is that straw return to soil increases soil's denitrification potentials and its capacity to produce N_2O [22]. This means that the additional fertilizer enhances N_2O soil emissions at a lower rate.
- Decrease in soil organic carbon (SOC) due to a change in soil carbon stocks, in comparison with the reference land use (i.e. residues left in the field). This leads to a loss of soil carbon which is emitted as CO_2.

The manufacture of additional fertilizer and methane soil emissions (as a result of N fertilizer application) must be also accounted for as land use change effects. Further information about N_2O emissions from agricultural soils can be found in [2,23]. All these GHG effects induced by land use change (GHG_{LUC}) can be summarized as follows:

$$GHG_{LUC} = \Delta SOC + CH_4 + FM + N_2O$$

where ΔSOC is the change (either increase or decrease) in SOC, CH_4 the soil methane emissions from fertilizer use, FM the GHG emissions for the manufacture of the additional fertilizers used to maintain crop yields, and N_2O is the soil N_2O emission induced by the additional N fertilizer.

The way by which these aspects are addressed is explained hereinafter.

2.4.1. Corn stover

The removal of corn stover from the field causes a reduction in SOC which is estimated to be 0.35 tons C/ha per year. This value comes from a study dedicated to wheat straw collection, where the Authors estimate an annual range of SOC decrease of 0.2–0.35 tons C/ha [11]. In this assessment, the upper value of this range is assumed because corn stover has a higher yield than wheat straw, and its removal causes a lower C input to the soil. Average corn grain yield in Austria is 8.2 tons$_{dry}$/ha per year (time period: 2000–2007) [24] and, with a residue/grain ratio of 1.1 [25],

Table 2
Chemical composition of the crop residues used as biorefinery raw materials. Sources: corn stover EERE 2009 (biomass sample type: Corn Stover Zea Mays Stalks and Leaves w/o cobs #55) [41]; wheat straw EERE 2009 (biomass sample type: Wheat straw (*Triticum aestivum*) Thunderbird Whole Plant #154) [41].

Parameter	Unit (dry)	Corn stover	Wheat straw
Water	%	15.0	15.0
LHV	MJ/kg	18.5	17.6
Cellulose	%	38.1	32.6
Glucan (C6)	%	38.1	32.6
Hemicellulose	%	25.3	22.6
Xylan (C5)	%	20.2	19.2
Arabinan (C5)	%	2.03	2.35
Galactan (C6)	%	0.74	0.75
Mannan (C6)	%	0.41	0.31
Lignin	%	20.2	16.8
Acids	%	4.84	2.24
Extractives	%	4.78	12.9
Ash	%	8.59	10.2
C	%	46.7	43.9
H	%	5.49	5.26
O	%	38.4	38.7
N	%	0.67	0.63
S	%	0.1	0.16

the corn stover production is estimated to be 9.02 tons$_{dry}$/ha per year. In order to supply 477 kilotons$_{dry}$ to the biorefinery plant, 52.8 kha of corn cultivated land are required. An amount of 18.5 kilotons C/a is therefore lost from SOC to the atmosphere and 67.9 kilotons CO_2/a are emitted.

Concerning the decrease in grain yields, the removal of corn stover influences crop productivity. For each ton per hectare of the previous crop's residue removed, grain yield of the current crop is reduced by 0.13 tons/ha, and biomass yield by 0.29 tons/ha [18]. Such a decrease is compensated by an increase in N–P–K fertilization which must be applied to the field. These amounts are reported in Table 3 (upper part).

In case of residue retention in the field, the environmental burdens of fertilizers are completely assigned to the grains, but when corn stover is collected, the resulting difference in fertilizer applications is completely assigned to the stover. Manufacture of this additional fertilizers is responsible for an emission of 5.96 kilotons CO_2-eq./a (Ecoinvent database).

Concerning N_2O emissions from additional fertilizer use, these emissions are lower than those estimated through IPCC factors [25]. These factors estimate that 1.325% of N in N fertilizer is released as N in N_2O. This corresponds to an emission of 26.7 kilotons CO_2-eq./a. However, when agricultural residues are removed, there is a decrease in N_2O emissions equal to 0.01–0.05 kg N/t$_{dry}$ of residue removed, due to the fact that the N applied is not so much as the N content of the stover removed [11]. An average value of 0.03 kgN/t$_{dry}$ is assumed, which results in a reduction of N_2O emissions equal to 13.3 kilotons CO_2-eq./a. Therefore, the final N_2O soil emissions are equal to 13.4 kilotons CO_2-eq./a. The application of N fertilizer is also responsible of the following emissions:

- soil emission of CH_4, which is estimated to be 10 g/kgN [23]: 494 tons CO_2-eq./a of CH_4 are therefore emitted to the atmosphere;
- volatilization of N as NH_3, at a rate of 10% of total N of synthetic N application; and
- leaching to groundwater as nitrate (30% of total N applied).

While the first emission contributes to total GHG emissions, the others affect other environmental impact categories like acidification and eutrophication.

The final GHG implications of LUC effects can be summarized as:

$$GHG_{LUC} = \Delta SOC + CH_4 + FM + N_2O = 67.9 + 0.49 + 5.96 + 13.4$$
$$= 87.8 \text{ kt } CO_2\text{-eq.}/a$$

Fig. 2 shows the decreasing trend of SOC. According to IPCC factors, the initial soil C stock is assumed to be about 75 tons C/ha (parameters: cold temperate/moist; high clay activity soil; long term cultivated land; full tillage; high C inputs to soil without manure) and the reduction down to 68 tons C/ha is modelled by means of the software tool RothC [26] (by setting a SOC decrease of 0.35 tons C/ha per year in 20 years).

It should be noticed that the data on which the estimation of ΔSOC is based have a high degree of uncertainty, because the impact of residue collection on soil dynamics are highly variable and depend on specific local factors. This topic is therefore discussed in the sensitivity analysis.

2.4.2. Wheat straw

Concerning wheat straw, its removal from the field contribute to increase global warming potential by 1 tons CO_2-eq./ha on average, due to an annual C loss of 0.27 tons C/ha [11]. Average wheat grain yield in Austria is 4.34 tons$_{dry}$/ha (time period: 2000–2007) [24] and, with a residue/grain ratio of 1.6 [25], wheat straw production is equal to 6.94 tons$_{dry}$/ha. In order to meet biorefinery feedstock demand, 68.7 kha of wheat cultivated land are required: 68 kilotons CO_2/a are therefore emitted.

Grain yields are negatively affected by straw removal because of a lower net mineralization of N in soils. The yield losses range between 0.05 and 0.15 tons$_{dry}$/ha for each tonne of straw removed [11]. Such a decrease is compensated by an additional application of N–P–K fertilizers (see Table 3, lower part).
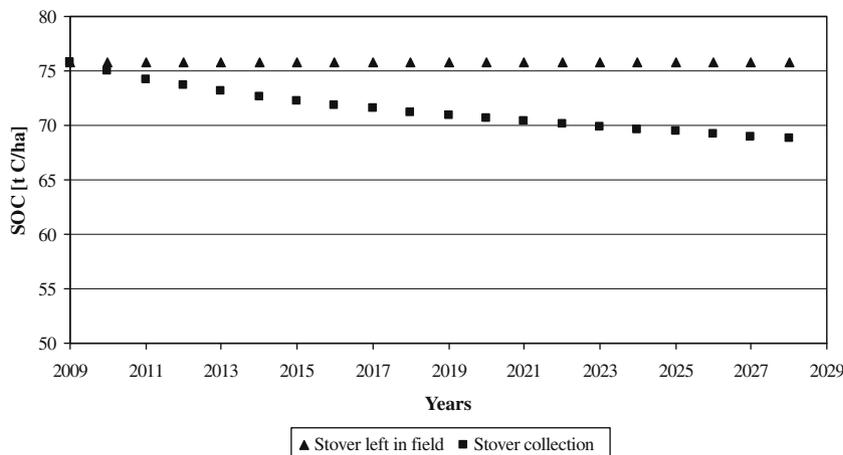
Table 3
Application rates of N–P–K fertilizers (kg/ha per year).

	Left in the field	Removed	Difference
Corn stover			
N	166[a]	207[b]	41
P	46	57	11
K	90	112	22
Wheat straw			
N	185[c]	206[d]	21
P	94	105	11
K	77	86	9

[a] [18].
[b] Estimated with proportion to the N removed with the stover.
[c] [42].
[d] [11].

Fig. 2. Decrease in SOC in corn fields due to corn stover removal.

As in the case of corn stover, the environmental burdens from additional fertilizer manufacture are completely assigned to wheat straw. They are estimated to be 4.12 kilotons CO_2-eq./a.

In addition, similarly to the previous case, soil N_2O emissions due to N fertilizer application are reduced of 13.3 kilotons CO_2-eq./a, while 329 tons CO_2-eq./a of CH_4 are released. Emissions of NH_3 and nitrates are estimated as well. The total GHG emissions due to land use change are therefore the following:

$$GHG_{LUC} = \Delta SOC + CH_4 + FM + N_2O = 68.0 + 0.33 + 4.12 + 4.48$$
$$= 76.9 \text{ kt } CO_2\text{-eq.}/a$$

The decreasing trend in SOC when wheat straw is collected is similar to that of corn stover illustrated in Fig. 2. In this case, the reduction of SOC from 75 tons C/ha to 69.5 tons C/ha has a decreasing rate of 0.27 tons C in 20 years. This time frame is in line with IPCC guidelines, which indicate in 20 years the payback time (or effect time), which is the standard inventory time period for many bioenergy crops.

2.5. Biorefinery conversion steps

After collection and processing (i.e. drying and pelletizing), the crop residue is transported to the biorefinery plant where it is converted to bioethanol, bioenergy and biochemicals (e.g. phenols). The conversion steps to which corn stover and wheat straw pellets are subjected are the following (see process scheme in Fig. 3):

- pretreatment (uncatalyzed steam explosion) of the raw material in order to depolymerize hemicellulose and separate lignin [27,28];
- enzymatic cellulose hydrolysis to glucose monomers [29,30];
- fermentation and distillation of sugars to bioethanol [30];
- anaerobic digestion of wastewaters [31,32];
- flash pyrolysis of lignin followed by phenol separation from the resulting pyrolytic oil [33,34]; and
- final combustion (for heat and power production) of process residues, fraction of lignin that is not pyrolyzed, pyrolytic char and the remaining pyrolytic oil after phenol extraction [35,36].

The feedstock undergoes a pretreatment step (uncatalyzed steam explosion), which occurs at a temperature range of 160–260 °C, with a reaction time of 2 min. During this stage, the C5 sugars in hemicellulose are hydrolyzed to xylose and arabinose with an efficiency of 85% [30]; arabinose is assumed to have the same conversion efficiency of xylose. Cellulose is hydrolyzed to glucose in a following enzymatic step with an efficiency of 90%; the remaining C6 polymers, galactan and mannan, are hydrolyzed to galactose and mannose with an efficiency of 82% and 89%, respectively [30]. A fraction of cellulose (9%) is set aside for bacteria cultivation. All the sugar monomers are then sent to fermentation while all the residues, together with lignin, undergo thermochemical treatment (combustion or pyrolysis). Concerning sugar fermentation, which occurs in a Simultaneous Saccharification and Co-Fermentation mode (SSCF, with simultaneous fermentation of C5 and C6 sugars), ethanol conversion yields are 92.5% from C6 sugars and 85% from C5 sugars on a molecular basis [30].

Bioethanol is finally distilled with an efficiency of 98%. Residues of these two steps are in water solutions and are anaerobically digested in order to produce biogas. These wastewaters have a total dry matter content of 85 kilotons$_{dry}$ and generate biogas at an average rate of 6 GJ/t$_{dry}$ [31]. The produced biogas has a higher heating value of 24 MJ/m^3 and methane content of 60%. Methane emissions to the atmosphere during digestion are estimated to be 3.47 mg/MJ
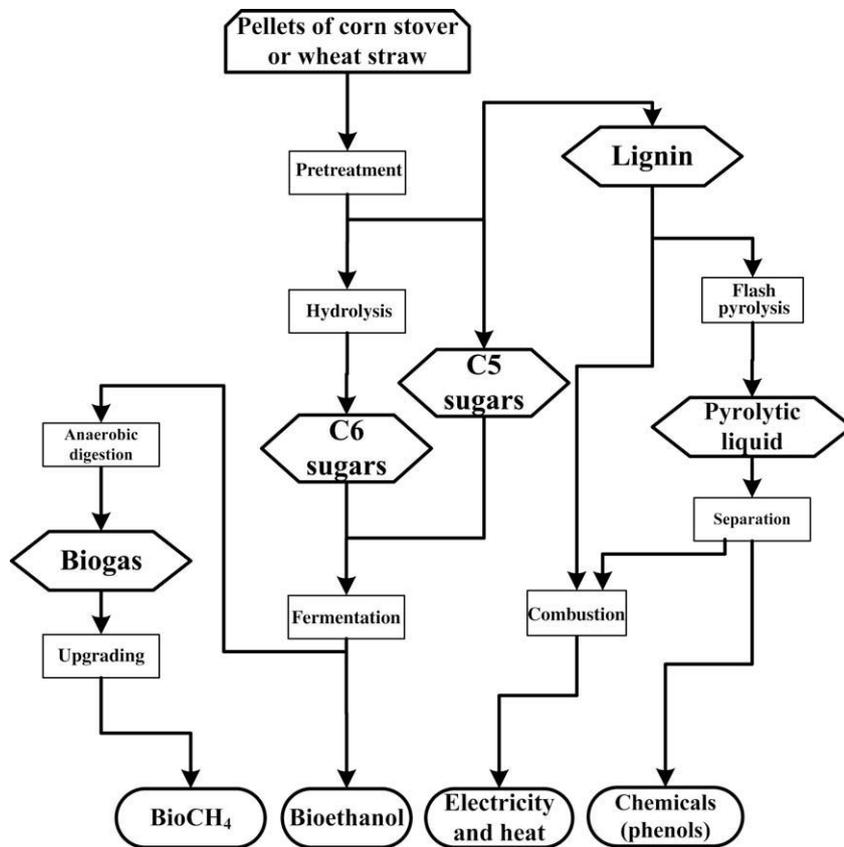

Fig. 3. Simplified process scheme of the biorefinery conversion plant.

and the upgrading of biogas to biomethane (having a CH_4 content greater than 97%) by removing impurities and CO_2, needs 5% of the energy content of the biogas itself [37]. The remaining digestate is disposed of in a wastewater treatment plant.

Concerning thermochemical treatments, 20% of lignin is subjected to flash pyrolysis, resulting in 75% pyrolytic oil (higher heating value 16 MJ/kg) and 25% charcoal (higher heating value 14 MJ/kg) [33]. The pyrolytic oil is a mix of different chemical compounds having an average phenol content of 32.3% [33], which can be recovered at an efficiency of 50% [38].

The remaining pyrolytic oil after phenol separation is combusted with charcoal and the remaining lignin fraction (higher heating value 22.9 MJ/kg) and other residues (mainly unconverted sugar polymers, with a higher heating value assumed equal to 15.6 MJ/kg) to generate electricity and heat with an efficiency of 25.5% and 44%, respectively [39]. Ashes are disposed of to a monitored landfill.

This biorefinery system has an electricity demand of 0.83 GJ/t dry feedstock [30], plus 0.03 GJ/GJ pyrolytic oil produced in flash pyrolysis [39] and 0.54 GJ/t dry matter in wastewater for biogas production and upgrading to biomethane [37]. The heat demand of the plant is 0.40 GJ/GJ bioethanol produced [39] and 110 MJ/t dry matter in wastewaters [31]. These energy needs are completely met by heat and power produced by combustion of lignin and residues. Information concerning auxiliary material used comes from [30].

2.6. Distribution and final use

Bioethanol is distributed to fuelling stations (transport distance assumed: 100 km) where it is used to fuel passenger cars at a specific consumption of 2.45 MJ/km. Emissions for combustion of bioethanol in cars are estimated according to Halleux et al. [40]. Biomethane is fed to the national natural gas grid, by which it is delivered to final applications where it can replace natural gas in all its existing applications. It is assumed that biomethane will be burnt in a boiler and the resulting emissions are estimated. It should be noted that, since the combustion of these biofuels (e.g. lignin and residues, bioethanol, and biomethane) releases CO_2 which has a biological origin, it is not accounted for as a GHG. Phe-

nols are transported for 50 km and used for producing resins; they are finally disposed of via incineration.

3. Results and discussion

Table 4 reports the quantities of products produced by the biorefinery systems having corn stover and wheat straw as raw materials. For electricity and heat from CHP the net values are shown, i.e. the plant energy requirements are already subtracted: for instance, when corn stover is used as raw material, the biorefinery plant requires 77% of the electricity and 99% of the heat produced via CHP from process residues. The variation in the volume of final products is given by the compositional difference of these lignocellulosic biomass feedstocks: as already shown in Table 2, the shares of cellulose, hemicellulose and lignin change between the feedstocks.

The largest quantities of products are produced from corn stover, thanks to a higher C content, a larger fraction of carbohydrates and lignin and a lower amount of oxygen and useless components like ashes, acids, and extractives.

The fossil reference systems, used for comparison of environmental impacts, produce the same amount of products/services, as reported in Table 4, from fossil sources.

3.1. GHG balance

Results of the GHG balance are reported in Table 5, both for biorefinery systems and their respective fossil reference systems.

Both biorefinery systems have lower total GHG emissions than the fossil reference systems (137 vs. 296 kilotons CO_2-eq./a for corn stover and 130 vs. 255 kilotons CO_2-eq./a for wheat straw). While for both CO_2 and CH_4 emissions there is a decrease in total emissions, emissions of N_2O are larger in the biorefinery systems than in the fossil reference systems. This is due to the application of Nitrogen fertilizers in agricultural soil, which stimulates N_2O soil emissions.

Concerning GHG emission savings, they are estimated using different parameters: per year, per input biomass and per hectare of agricultural land required to supply the feedstock. When results are normalized per input biomass, information about the possible savings from 1 ton of dry feedstock are provided (0.33 tons CO_2-eq./t for corn stover and 0.26 tons CO_2-eq./t for wheat straw). This indicator is particularly important because renewable biomass is a finite resource. On the other hand, when savings are expressed per ha of dedicated agricultural land, results are related to a fundamental limiting factor, the available land (3 tons CO_2-eq./ha for corn stover and 1.8 tons CO_2-eq./ha for wheat straw). This measure should be always used when agricultural or lignocellulosic crops are used. In these cases, the GHG benefits per unit of land are a superior indicator from a land-use efficiency perspective. However, it should not be neglected that in case of agricultural land (corn

Table 4
Final products produced from the biorefinery using corn stover or wheat straw as raw materials.

Product	Unit/a	Biorefinery-Corn stover	Biorefinery-Wheat straw
Bioethanol	10^6 km	1208	1083
Heat (from biomethane)	TJ	243	350
Electricity (from CHP)	TJ	183	90.2
Heat (from CHP)	TJ	2.17	3.74
Phenols	kt	1.75	1.46

Table 5
GHG emissions and savings of the biorefinery systems in comparison with their respective fossil reference systems.

	Unit/a	Corn stover	Fossil reference system	Wheat straw	Fossil reference system
GHG emissions					
Total	kt CO_2-eq.	137	296	130	255
CO_2	kt CO_2-eq.	107	280	113	242
N_2O	kt CO_2-eq.	26.3	6.51	13.3	5.79
CH_4	kt CO_2-eq.	3.89	10.5	3.88	7.7
GHG savings					
Per year	kt CO_2-eq.	159		125	
Per year	%	53.7		49.0	
Per t_{dry} feedstock	t CO_2-eq./t_{dry}	333		262	
Per hectare	t CO_2-eq./ha	3.01		1.82	

stover and wheat straw), land has a prior main use, i.e. the production of corn and wheat for food/feed purposes. The possibility to show GHG savings using different parameters is extremely important when assessing the effectiveness of policy decisions on biomass energy in terms of their GHG balance. It is important to carefully set the functional unit and the normalization parameters, so that all GHG consequences of such decisions are included. Enhancing benefits with one indicator may result in an opposite information when other parameters are used, and such tradeoffs can only be adequately addressed if all the possible parameters are taken into account.

Contributions to total GHG emissions of the biorefinery systems are shown in Fig. 4. Change in soil carbon pools and production of pellets play the largest role in determining the final GHG balance, while smaller contributions are due to production of plant auxiliary materials, emissions from biorefinery plant activities (mainly combustion of residues for heat and power production), transport and distribution and final use.

Concerning the fossil reference systems with which the biorefineries are compared, the largest fraction of total GHG emissions is originated from gasoline (81% for the reference system of corn stover and 84% for that of wheat straw), followed by electricity from natural gas (10% and 3%), heat from natural gas (7% and 11%) and then others.

3.2. Energy balance

The primary energy demand of the biorefinery and fossil reference systems is shown in Fig. 5. Results reveal that the biorefinery system needs a higher cumulative primary energy supply than the fossil reference system, but it is mainly based on renewable energy (i.e. the energy content of the feedstock itself): the non-renewable
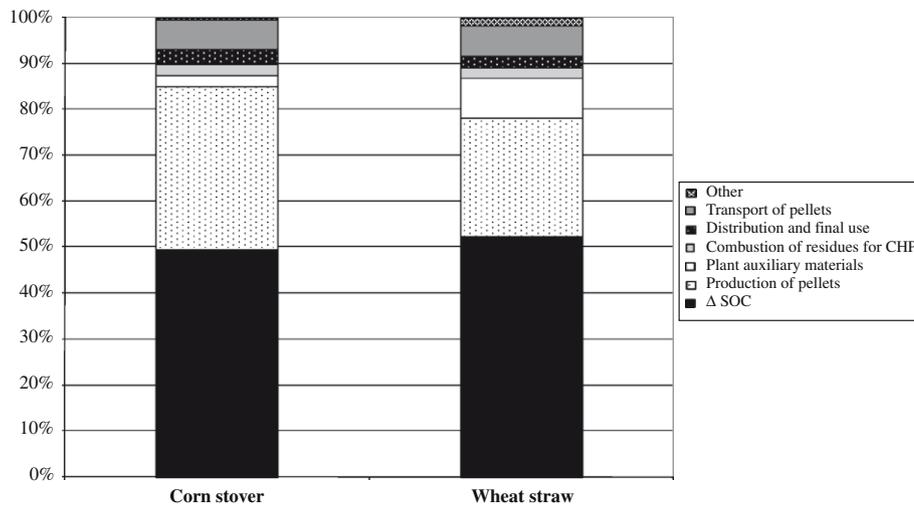

Fig. 4. Contributions to the total GHG emissions of the biorefinery systems. LUC effects are disaggregated: N_2O and CH_4 emissions from soil and production of additional fertilizers are included within the group "production of pellets".
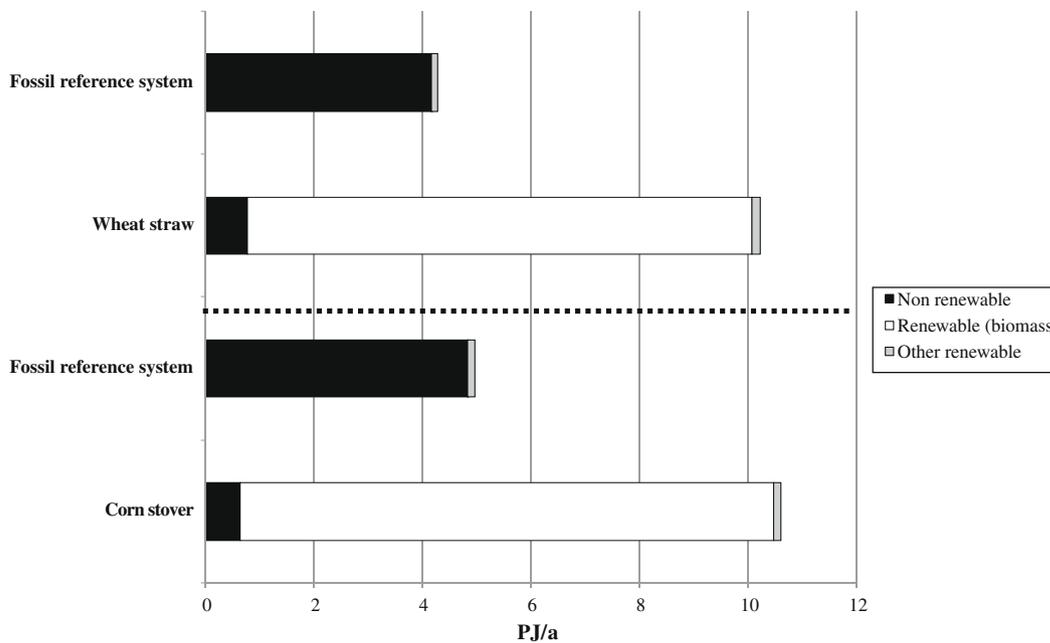

Fig. 5. Cumulative primary energy demand of the biorefinery and fossil reference systems.

energy demand of the reference system is drastically reduced by the biorefinery system, thus saving fossil energy sources. The estimated non-renewable energy savings are about 4.2 PJ/a, which corresponds to 8.8 GJ/t_{dry} and 79 GJ/ha, for corn stover and 3.39 PJ/a, equal to 7.1 GJ/t_{dry} and 49 GJ/ha for wheat straw.

The EROI (Energy Return On Investment) is the ratio between energy out (i.e. the energy content of the products) and the non-renewable energy in (i.e. all the non-renewable energy inputs, direct and indirect, required along the full life cycle). When the EROI is equal to or lower than 1, that product becomes an "energy sink", and can no longer be used as a primary source of energy. The biorefinery system with corn stover as raw material has an EROI index equal to 5.2, while when wheat straw is used the index decreases to 4.0: this means that the energy output of these systems contains from 4 to 5 times the non-renewable energy invested.

3.3. Other impact categories

Besides GHG and energy balances, the investigated biorefinery systems were analyzed under other environmental impact categories. Results were calculated using the method "CML 2 baseline 2000 V. 2.03" for impact assessment evaluation.

Results are shown in Table 6, where each biorefinery system is compared with the respective fossil reference system. Biorefinery systems have lower impacts in all categories except eutrophication: it is mostly given by N fertilization, which causes leaching of nitrates to groundwater. Emissions induced by fertilizer application also influence other environmental categories, like terrestrial and fresh water ecotoxicity, acidification, human toxicity, and others.

These results demonstrate that even if a biorefinery system achieves relevant GHG and fossil energy savings, it may cause additional environmental impacts than fossil based systems in other impact categories. Despite most policy makers and initiatives assigning the highest priority to climate change mitigation strategies, other environmental impacts cannot be disregarded in order to avoid decisions based on partial, and sometimes even worthless, indications.

3.4. Sensitivity analysis

After estimation of the final LCA results, an investigation of the effects of variation in key parameters to the outcome of the assessment should be always performed. The aim is to establish a required degree of confidence in the results of the study relative to its overall goal. In particular, the objective of this step is to review the results of the analysis, identify the parameters which have the largest influence on the final results and check the accuracy of the data. Afterwards, these key parameters are changed according to different data sources or assumptions, and the outcomes compared. In this assessment, the most uncertain parameter is the factor assumed for estimating the decrease in soil carbon pools for corn stover collection. As already discussed, such a decrease is a key parameter which strongly affects the final GHG balance of the biorefinery system.

Table 6
Results of the CML impact assessment method.

| Impact category	Unit	Biorefinery corn stover	Fossil reference system	Biorefinery wheat straw	Fossil reference system
Abiotic depletion	kt Sb eq	0.30	2.09	0.35	1.78
Global warming (GWP100)	kt CO_2-eq	137	296	130	255
Ozone layer depletion (ODP)	kg CFC-11 eq	8.31	29.7	8.86	26.9
Human toxicity	kt 1,4-DB eq	24.7	192	25.6	167
Fresh water aquatic ecotox.	kt 1,4-DB eq	2.54	17.4	2.90	14.8
Marine aquatic ecotoxicity	Mt 1,4-DB eq	17.7	51.2	20.1	44.5
Terrestrial ecotoxicity	kt 1,4-DB eq	0.22	0.60	0.28	0.54
Photochemical oxidation	kt C_2H_4	0.06	0.28	0.05	0.25
Acidification	kt SO_2 eq	0.93	1.16	0.78	1.03
Eutrophication	kt PO_4-eq	0.52	0.17	0.39	0.15
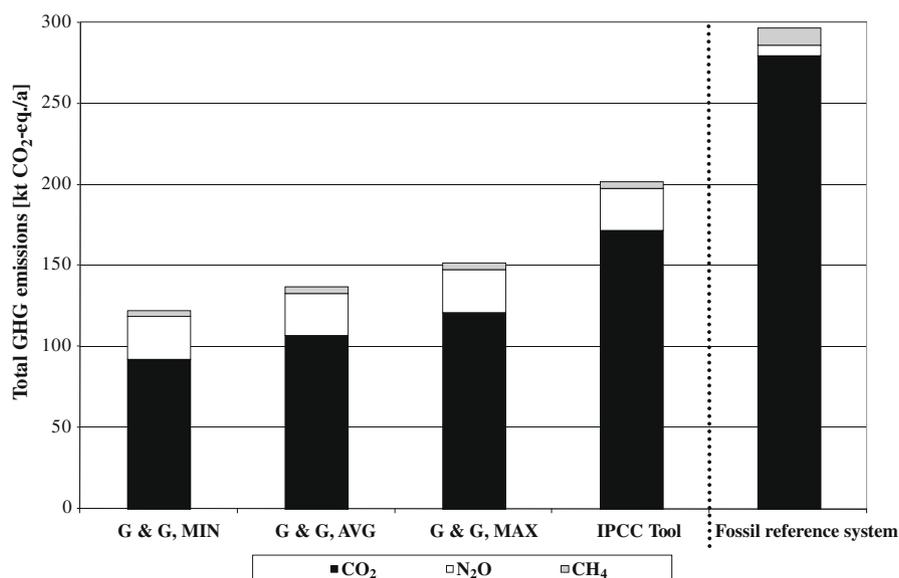
Fig. 6. Total GHG emissions of the biorefinery system based on corn stover using different decrease rates of SOC.

According to literature references, it has been assumed that removal of corn stover reduces soil carbon pool at a rate of 0.35 tons C/(ha a). This value is the upper limit of the range 0.2–0.35 t C/(ha a) reported for wheat straw in a recent study [11]. This choice is based on the considerations that corn stover has larger yield than wheat straw (and then the reduction in soil carbon content is expected to be higher) as well as on the fact that differences across rotations are generally more important than those related to residue management for a given rotation (and therefore soil carbon losses can be minimized). However, in this section, results based on different soil carbon decrease rates are also investigated and compared. The following soil carbon decrease factors are assumed:

- 0.2 tons C/(ha a), minimum value from Gabrielle and Gagnaire (G & G), 2008 [11];
- 0.275 tons C/(ha a), average value from Gabrielle and Gagnaire (G & G), 2008 [11];
- 0.35 tons C/(ha a), maximum value from Gabrielle and Gagnaire (G & G), 2008 (and assumed in the above analysis) [11];
- 0.61 tons C/(ha a), as derived from the IPCC Soil Carbon Tool based on IPCC factors (country: Austria; climate region: cold temperate moist; native soil type: high clay activity mineral; full tillage; from medium to low inputs).

This latter parameter is greater than others because it does not take into account the mitigation in soil carbon decrease ensured by crop rotation.

Results are shown in Fig. 6, where the above mentioned factors of soil carbon decrease were applied. In all cases, GHG emissions of the biorefinery systems are lower than those of the fossil reference system with which they are compared.

However, best management practices and above ground residue harvest rates need to be established for minimum amount of stover that must be retained on the soil to maintain or increase SOC, minimizing erosion and protecting soil quality and productivity. This very complex issue must be addressed regionally if not on a field or even subfield basis. Rotation, tillage and fertilization management, soil properties and climate will all play major roles in determining the amount of crop residue that can be removed in a sustainable system.

4. Conclusions

The use of biomass as raw materials for bioenergy and biochemical production is encouraged by the need for a secure energy supply, a reduction of fossil CO_2 emissions and a revitalization of rural areas. Biomass energy and material recovery is maximized when a biorefinery approach is considered, in which many technological processes are jointly applied. The use of crop residues as raw materials for biorefinery showed great potentials in the production of bioenergy and chemical products able to replace fossil derived products and services, on condition that the environmental impact effects of the removal are minimized. The Life Cycle Assessment study depicted in this work demonstrate that significant GHG and fossil energy savings are achieved when the biorefinery system is compared with a fossil reference system. GHG savings are in the range of 50% while non-renewable energy savings go beyond 80%. When the savings are related to the agricultural land used to produce corn and wheat, the use of crop residues in biorefinery can save from 1.8 to 3 tons CO_2-eq./ha. Even if the biorefinery has higher primary energy demand than the fossil reference system, it is mainly based on renewable energy (i.e. the energy content of the processed feedstock) and non-renewable energy is saved. The provision of biomass with sustainable practices is then a crucial point

to ensure a renewable energy supply to biorefineries. Land use change effects, manufacture of additional fertilizers (required to maintain crop yields) and supply of raw materials play the biggest role in the final GHG balance. In the sensitivity analysis, the uncertainty in the estimation of soil C losses from corn stover collection is discussed. Concerning the potential impacts on other environmental categories, biorefinery systems are responsible of higher eutrophication potential than the fossil reference systems. This means that even if a reduction in GHG emissions and fossil energy consumption is achieved, it should not be disregarded that higher environmental impacts (like acidification and eutrophication) may be caused. This aspect cannot be ignored by policy makers, even if they have climate change mitigation objectives as main goal.

In conclusion, the use of agricultural residues as raw materials in this biorefinery is an effective option for reducing environmental concerns related to fossil resources: biorefinery systems can mitigate climate change, reduce dependence on imported fossil fuels and enhance cleaner production chains based on local and renewable sources. However, this assessment also evidences that an exact determination of the GHG savings of biorefinery systems is complex, due to the large uncertainty in some basic assumptions (like land use change effects) which depend on local and climate conditions. Ranges in final results can be even more widened by applying different combinations of biomass feedstocks, conversion routes, fuels, end-use applications, and methodological assumptions. Notwithstanding the difficulties and uncertainties in the estimation of land use change effects, any change (both decline and increase) in C stock of any pool should be always taken into consideration when estimating the GHG balance of a biorefinery system.

When agricultural residues are used as feedstocks, best management practices and above ground residue harvest rates need to be established for minimum amount of stover that must be retained on the soil to maintain SOC, minimizing erosion and protecting soil quality and productivity. This very complex issue must be addressed regionally if not on a field or even subfield basis. Rotation, tillage and fertilization management, soil properties and climate will all play important roles in determining the amount of crop residue that can be removed in a sustainable system. Therefore, when agricultural residues are collected from fields and used for bioenergy production, the effects of the removal on that particular soil type cannot be neglected and the GHG implications (i.e. lower yields, N_2O emissions from land and decline in soil carbon pools) should be accounted for when compiling the overall GHG balance of the biorefinery system.

References

[1] Andrews SS. Crop residue removal for biomass energy production: effects on soils and recommendations, White paper USDA; 2006. <http://www.soils.usda.gov/sqi/management/files/AgForum_Residue_White_Paper.pdf>.
[2] Cherubini F. From oil refinery to biorefinery: production of energy and chemicals from biomass. Ital Biol (Biol Ital) 2009;5:44–59.
[3] GBEP – Global Bioenergy Partnership. A review of the current state of bioenergy development in G8 + 5 countries, GBEP Secretariat, Food and Agriculture Organization of the United Nations (FAO), Rome 2007; 2007. <ftp://ftp.fao.org/docrep/fao/010/a1348e/a1348e00.pdf>.
[4] EBS – European Biomass Statistics 2007. A statistical report on the contribution of biomass to the energy system in the EU 27. Belgium (Brussels): European Biomass Association (AEBIOM); 2007.
[5] Punter G, Rickeard D, Larivé JF, Edwards R, Mortimer N, Horne R, Bauen A, Woods J. Well-to-Wheel evaluation for production of ethanol from wheat. A report by the LowCVP fuels working group, WTW sub-group, FWG-P-04-024; October 2004.
[6] Kim S, Dale BE. Life cycle assessment of various cropping systems utilized for producing biofuels: bioethanol and biodiesel. Biomass Bioenergy 2005;29:426–39.
[7] Blottnitz von H, Curran MA. A review of assessments conducted on bio-ethanol as a transportation fuel from a net energy, greenhouse gas, and environmental life cycle perspective. J Cleaner Prod 2007;15:607–19.
[8] Cherubini F, Bird N, Cowie A, Jungmeier G, Schlamadinger B, Woess-Gallasch S. Energy and GHG-based LCA of biofuel and bioenergy systems: key issues, ranges and recommendation. Resour, Conserv Recy 2009;53:434–47.

[9] Jungmeier G, Lingitz A, Spitzer J, Hofbauer H, Fürnsinn S. Wood to biofuels: feasibility study for a biofuel plant in the Austrian province of Styria. In: Proceedings of the 15th European Biomass Conference and Exhibition – From Research to Market Deployment, Berlin, 7–11 May; 2007.

[10] Stoeglehner G, Narodoslawsky M. How sustainable are biofuels? Answers and further questions arising from an ecological footprint perspective. Bioresour Technol 2009;16:3825–30.

[11] Gabrielle B, Gagnaire N. Life-cycle assessment of straw use in bio-ethanol production: a case study based on biophysical modelling. Biomass Bioenergy 2008;32:431–41.

[12] Lal R. Crop residues as soil amendments and feedstock for bioethanol production. Waste Manage 2008;28:747–58.

[13] Lal R, Kimble LM, Follet RF, Cole CV. The potential of US cropland to sequester carbon and mitigate the greenhouse effect. Chelsea, MI: Ann Arbor Press; 1998.

[14] Lal R. World crop residues production and implications of its use as a biofuel. Environ Int 2005;31:575–84.

[15] Cherubini F, Jungmeier G, Wellisch M, Willke T, Skiadas I, Van Ree R, et al. Towards a classification approach for biorefinery systems. Biofuels, Bioprod Biorefining 2009, in press.

[16] Hammerschlag R. Ethanol energy return on investment: a survey of the literature 1990-present. Environ Sci Technol 2006;40(6):1744–50.

[17] Mann L, Tolbert V, Cushman J. Potential environmental effects of corn (*Zea mays* L.) stover removal with emphasis on soil organic matter and erosion. Agri, Ecosyst Environ 2002;89:149–66.

[18] Wilhem WW, Johnson JMF, Hatfield JL, Voorhees WB, Linden DR. Crop and soil productivity response to corn residue removal: a literature review. Agron J 2004;96:1–17.

[19] Jungmeier G, Schwaiger H. Changing carbon storage pools in LCA of bioenergy – A static accounting approach for a dynamic effect. Life cycle assessment on forestry and forestry products, Cost Action E9, Brussel, Belgium; 2000. p. 101–15.

[20] Cowie AL. Greenhouse gas balance of bioenergy systems based on integrated plantation forestry in North East New South Wales, Australia. Case study for IEA Bioenergy Task 38 on GHG balance of biomass and bioenergy system; 2004. <http://www.ieabioenergy-task38.org/projects/task38casestudies/index1.htm>.

[21] Larson E. A review of LCA studies on liquid biofuels for the transport sector. Scientific and Technical Advisory Panel of the Global Environment Facility (STAP) workshop on Liquid Biofuels, 29 August to 1 September 2005, New Delhi, India; 2005.

[22] Cai Z, Laughlin RJ, Stevens RJ. Nitrous oxide and dinitrogen emissions from soil under different water regimes and straw amendment. Chemosphere 2001;42:113–21.

[23] Delucchi MA, Lipman T. A lifecycle emissions model (LEM): lifecycle emissions from transportation fuels, motor vehicles, transportation modes, electricity use, heating and cooking fuels, and materials. Appendix C: Emissions related to cultivation and fertilizer use. Davis, CA, USA: Institute of Transportation Studies, University of California; 2003.

[24] Cherubini F. Life cycle assessment of biorefinery systems based on lignocellulosic raw materials – Concept development, classification and

environmental evaluation. PhD thesis, Graz, Austria: Graz University of Technology – Joanneum Research; 2009.

[25] IPCC. Guidelines for national greenhouse gas inventories. Volume 4: Agriculture, forestry and other land use; 2006.

[26] Skjemstad JO, Spouncer LR, Cowie B, Swift RS. Calibration of the Rothamsted organic carbon turnover model (RothC ver.26.3), using measurable soil organic carbon pools. Aust J Soil Res 2004;42:79–88.

[27] Sun Y, Cheng J. Hydrolysis of lignocellulosic materials for ethanol production: a review. Bioresour Technol 2002;83(1):1–11.

[28] Lynd LR. Overview and evaluation of fuel ethanol from cellulosic biomass: technology, economics, the environment, and policy. Annu Rev Energy Environ 1996;21:403–65.

[29] Palmqvist E, Hahn-Hägerdal B. Fermentation of lignocellulosic hydrolysates. I: inhibition and detoxification and II: inhibitors and mechanisms of inhibition. Bioresour Technol 2000;74(1):17–33.

[30] Hamelinck NC, van Hooijdonk G, Faaij APC. Ethanol from lignocellulosic biomass: techno-economic performance in short-, middle- and long-term. Biomass Bioenergy 2005;28:384–410.

[31] Berglund M, Börjesson P. Assessment of energy performance in the life-cycle of biogas production. Biomass Bioenergy 2006;30:254–66.

[32] Romano RT, Zhang R. Co-digestion of onion juice and wastewater sludge using an anaerobic mixed biofilm reactor. Bioresour Technol 2008;99(3): 631–7.

[33] Zhang Q, Chang J, Wang T, Xu Y. Review of biomass pyrolysis oil properties and upgrading research. Energy Convers Manage 2007;48:87–92.

[34] Meister JJ. Modification of lignin. J Macromol Sci Polym Rev 2002;42(2):235–89.

[35] Senneca O. Kinetics of pyrolysis, combustion and gasification of three biomass fuels. Fuel Process Technol 2007;88(1):87–97.

[36] Gani A, Naruse I. Effect of cellulose and lignin content on pyrolysis and combustion characteristics for several types of biomass. Renew Energy 2007;32(4):649–61.

[37] Gemis. Global Emission Model for Integrated Systems, Version 4.5. Data Set on Bioenergy for Heat, Electricity and Transportation Biofuel Systems, Joanneum Research, Graz, Austria; 2009. LCA software tool website: <http://www.oeko.de/service/gemis/en/index.htm>.

[38] Scholze B. Long-term stability, catalytic upgrading, and application of pyrolysis oils – Improving the properties of a potential substitute for fossil fuels. PhD dissertation, Hamburg University; 2002.

[39] De Feber MAPC, Gielen DJ. Biomass for greenhouse gas emission reduction, Task 7: Energy Technology Characterization. ECN-C-99-078; 2000.

[40] Halleux H, Lassaux S, Renzoni R, Germain A. Comparative life cycle assessment of two biofuels: ethanol from sugar beet and rapeseed methyl ester. Int J LCA 2008;13(3):184–90.

[41] EERE. Biomass feedstock composition and property database, biomass program, US Department of Energy, Energy Efficiency and Renewable Energy; 2009. <http://www.1.eere.energy.gov/biomass/feedstock_databases.html> [last visited 06.06.09].

[42] Hamelinck C, Koop K, Croezen H, Koper M, Kampman B, Bergsma G. Technical specification: greenhouse gas calculator for biofuel, SenterNovem, Ecofys; 2008 <http://www.senternovem.nl/mmfiles/Technicalspecificationv2. 1b20080813_tcm24-280269.pdf>.