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RESEARCH ARTICLE

Nitrogen and biofuels; an overview of the current state of knowledge

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Abstract Biofuels are forms of energy (heat, power, transport fuels or chemicals) based on different kinds of biomass. There is much discussion on the availability of different biomass sources for bioenergy application and on the reduction of greenhouse gas emissions compared to conventional fossil fuels. There is much less discussion on the other effects of biomass such as the acceleration of the nitrogen cycle through increased fertilizer use resulting in losses to the environment and additional emissions of oxidized nitrogen. This paper provides an overview of the state of knowledge on nitrogen and biofuels. Increasing biofuel production touch upon several sustainability issues for which reason sustainability criteria are being developed for biomass use. We propose that these criteria should include the disturbance of the nitrogen cycle for biomass options that require additional fertilizer inputs. Optimization of the nitrogen use efficiency and the development of second generation technologies will help fulfill the sustainability criteria.

Keywords Bioenergy · Biofuels · Emission · Environment · Effects · Nitrogen · Nitrous oxide

Introduction

Energy use is one of the main drivers of developments in our society. The availability and use of energy strongly influences transportation, food and water, industrial development, economic growth and human welfare. Biomass is the oldest resource of energy used by mankind and has been the main source of energy until no less than a century ago. Biomass is storage of (solar) energy and can be committed as and when required. In principle biomass can replace the current fossil fuels without changing the infrastructure. Biomass can be used to produce synthetic or substitute natural gas (SNG or Green gas), transportation fuels as diesel, ethanol and even gasoline type of fuels and fuels that can be used in power plants. This is a main advantage over other sustainable options. As with fossil fuels, however, the need to produce sustainable energy from biomass requires emission and waste control, as

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the composition of biomass and the resulting losses to the environment with current production and conversion technologies are not much different.

Because of the inherently low efficiency of the photosynthetic process and the production of phytomass, energy supply from this source has low power densities, and hence high land demands. Recent estimates of the global terrestrial net primary productivity (NPP) average approximately 120 Gton of dry biomass that contains some 1,800 10^{18} Js (EJ) of energy (Smil 2004). In principal there is globally enough annual growth of new biomass to cover up to four times the human annual energy use. However, in order to grow, collect and use biomass in a sustainable way to satisfy the human energy hunger, a well regulated and optimized process is needed.

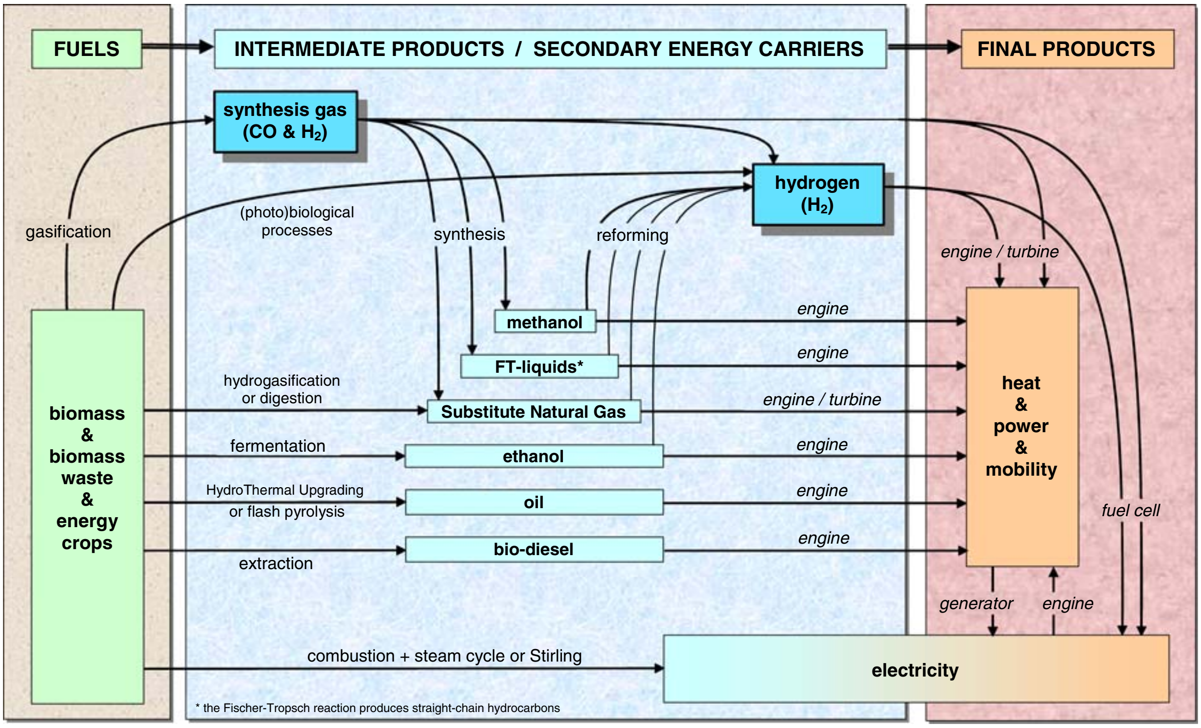
Biofuels are forms of energy (heat, power, transport fuels or chemicals) based on different kinds of biomass. Recently the EU adopted new targets for sustainable energy and greenhouse gas (GHG) emission reductions: 20% reductions and 20% contribution of sustainable sources and a 10% share of biofuels in the transportation sector in 2020. China has set a target of increasing renewable energy use from the present 10–20% of the total energy consumption by 2020 to meet the increasing demand and reduce the greenhouse effect. It is evident that biomass as transport fuel, electricity and heat production and Substitute Natural Gas will be a major component necessary to reach these targets. Bioenergy provides about 10% of the world's total primary energy supply. Most of this is used for domestic heating and cooking and is produced locally. Bioenergy represented 78% of all renewable energy produced. About 97% of biofuels are made of solid biomass. The share of biomass in the European energy use in 2006 was 6%. China is the largest user of biomass as a source of energy, followed by India, the US and Brazil; in China the contribution was 13% (www.globalbioenergy.org). There is a major challenge to reach the targets in a sustainable way and there is much discussion on the availability of different biomass sources for bioenergy application. A recent OECD study estimates that 50% of the current global energy use (450 EJ) is potentially available in 2050 for bioenergy (OECD 2007). Taking an overall energy efficiency of 35% for biofuels production in the whole chain, the study expects a contribution of 10% to the fuel use in 2050. This means that the targets on biofuels in different regions of the world will not easily be met and there will therefore be a need to increase biomass production. There is a major concern about the cultivation of biomass for energy mainly because of the competition with food, the related destruction of tropical rain forests and the concerns about the potential negative effect on the greenhouse gas (GHG) balance (e.g., OECD 2007; Bergsma et al. 2007; Biello 2008; Elsayed et al. 2003; Scharlemann and Laurance 2008; Crutzen et al. 2008; Searchinger et al. 2008; Fargione et al. 2008). However, there has been little concern over the changes in the nitrogen cycle and the related negative environmental impacts. The increase of reactive nitrogen production and the loss of to the environment has caused a range of environmental problems amongst other eutrophication, greenhouse gas emission, biodiversity loss, water and air pollution. Reactive nitrogen cascades through the environment contributing to these issues sequential over time until it is fixed (e.g., Galloway et al. 2003, 2008; Erisman 2004). Increased biomass production requires more fertilizer inputs, which will accelerate the nitrogen cycle. Current predictions of fertilizer production and use do not include this additional need (e.g., Erisman et al. 2008).

The purpose of this paper is to discuss the nitrogen and related GHG issues of using biomass as an energy source and transportation fuel and to use our knowledge to provide recommendations for sustainable use of biomass to replace fossil fuels. First an overview is given of the nitrogen relevant processes in relation to biomass for energy use. Based on literature values an attempt is made to quantify the major nitrogen issues. This section is followed by a discussion whether current Life Cycle Analysis studies address these issues adequately or not, followed by conclusions about the nitrogen issues.

Biomass use for energy and overview of nitrogen relevant processes

Biomass can be used to produce a wide range of products for energy use in several ways. Fig. 1 provides an overview of the different technological and product routes. In general the following products can be distinguished:

- Solid fuels (torrefaction) and liquid fuels (pyrolysis) as biomass upgrading or pre-treatment options



* the Fischer-Tropsch reaction produces straight-chain hydrocarbons

Fig. 1 Scheme showing the biomass technological and product routes (Boerrigter and van der Drift 2004)

- Electricity and heat (firing, co-firing, gasification)
- Transportation fuels:
  - Pure plant oil (rapeseed)
  - Biodiesel (fatty acid methyl ester, FAME, or fatty acid ethyl ester, FAEE) from rapeseed (RME), soybeans (SME), sunflowers, coconuts, oil palm, recycled cooking oil
  - Bio-ethanol (E100, E85, E10, ETBE) from grains or seeds (corn, wheat, potato), sugar crops (sugar beets, sugar cane) or lignocelluloses biomass (wheat straw, switch grass, short rotation woody crops)
  - Fischer-Tropsch diesel and Dimethyl ether (DME) from lignocelluloses waste wood, short-rotation woody crops (poplar, willow), switch grass
  - Hydrogen produced from syngas or produced through algae
  - Methanol from syngas
- Synthetic (or Substitute) natural gas (SNG) and/or biogas (from digestion)
- Chemicals

Currently, first and second generation biofuels are distinguished. The basis for this difference is the potential competition with food (seeds, beans pure plant oil) and the improved energy efficiency and GHG balance. First generation biofuels are produced from food crops with a limited reduction of GHG emissions and second generation is produced from waste streams, non-food part of crops and have at least a reduction of 50% GHG emissions. There are however many possible combinations of type of biomass, conversion technology and end products, which all have their own environmental pressures, energy efficiencies, greenhouse gas balances and interlinkages. We can group these as different bioenergy chains with their different environmental and socio-economic impacts, as shown in Fig. 1 for the technological routes. The efficiency in terms of energy balance and environmental performance varies among the different chains and increases with a shift from first to second generation biofuels. There is room for improvement of the efficiency by further development of the technology. For the different bioenergy chains, and especially for the feedstock

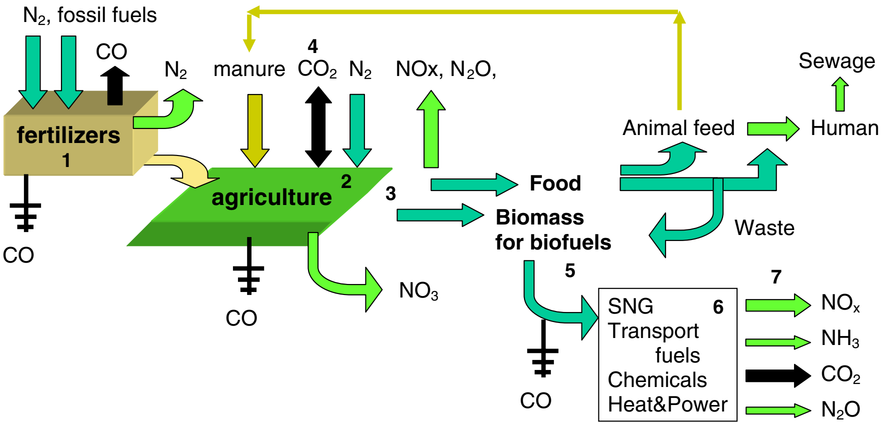


Fig. 2 Scheme showing the interaction between inputs and outputs (SNG = Substitute Natural Gas). See text for explanation of the *numbers*

that is used, the interactions between nitrogen and GHG emissions are similar to those for food production in agriculture when energy crops or crop residues are considered. The soil-crop-agricultural practice combination determines, to a large extent, the nitrogen losses. One exception is when biogas or energy from manure is produced, because then the additional cycle of animal food and manure plays a role in the interlinkages, making it more complex. The way the biomass is eventually converted into energy makes the difference in the GHG balance compared to food production. Figure 2 shows the relationships between nitrogen and GHG. The main interactions result from:

1. Fertilizer production from fossil fuels
2. Biomass cultivation and fertilizer use
3. Energy use for harvesting and transport
4. Carbon emission from the land (deforestation, land use change) and sequestration
5. Pre-treatment, transport of biomass
6. Production of fuel either directly from biomass, or indirectly through the food/animal/manure chain
7. Use of fuel, including credits from substitution of market products by site-products generated during biofuel-production

Overall, Life Cycle Assessment studies show that the energy consumption and related emissions of GHG from farm-cultivation of biocrops and from distribution and transport are small (<10%) compared to the cultivation and production and use of fuel, including possible credits arising from the use of side products (e.g., Delucchi 2006; Quirin et al. 2004). Besides being an issue with respect to CO$_2$ emissions, transport of biomass is also an important cost-factor. It is to be expected that there will be infrastructural constraints for the use of biomass, in particular for the production of electricity. Carbon emissions from direct or indirect land use change have the potential to off-set GHG saving from the use of biofuels, but available data are still very uncertain and focus on the assessment of CO$_2$ fluxes rather than nitrogen. Our assessment will therefore mainly focus on No. 1, 2, 5, 6 and 7. In the next paragraphs we will quantify the interlinkages of fertilizer production and application, fuel production and use. Conclusions drawn will provide the most important interlinkages and the means to quantify them.

Fertilizer production, application and biomass yield

Fertilizer production

In the past fertilizer production was mainly based on gasification of coal. Currently natural gas is used to produce the ammonia, which is the main base material for fertilizers. Today, fertilizer production consumes approximately 1.2% of the world's energy (5% of the natural gas use) and is responsible for approximately 1.2% of the total emission of the GHG. The GHGs in term of CO$_2$-equivalents consisted of 0.3% of pure CO$_2$, 0.3% as N$_2$O and 0.6% as flue gas CO$_2$ (Kongshaug 1998). Increased focus on energy issues during the last 25–30 years has already caused a positive downward trend both for energy consumption and GHG emissions (Smil 2001). In

2000 the energy needed to produce one ton of NH_3 in the most efficient plants was 26 GJ (Smil 2001). FAO reported values from 40 (natural gas) to 50 $GJ.ton^{-1}$ (coal). The amount of ammonia produced in 2004 was 142 Mton for which about 5700 PJ was needed (1.2% of worlds energy use of 450 EJ). If a carbon efficiency of 100% is assumed (literature states 98–99%), about 17 ton $C.TJ^{-1}$, CO_2 produced for global ammonia synthesis amounted to 350 Mton. 82% is for fertilizer use: 287 Mton CO_2 (or 2.5 kg CO_2/kg fertilizer–N).

Approximately 82% of the natural gas is used as base material for ammonia, while 18% is used as fuel. Including the energy credit, 88% of the net energy consumption is used as ammonia synthesis feed. The energy loss for production of electrical energy is not included (50% for Combined Cycle and 65% for Steam Turbine). Average net consumption for European plants is assumed to be 39 GJ/t N (28 GJ/t N for ammonia synthesis and 11 GJ/t N as net fuel). 30 years ago, the best plants operated with approximately 47 GJ/t N (28 GJ/t N as feed and 19 GJ/t N as net fuel). The energy improvement has consequently also reduced total CO_2 emission. A modern ammonia plant, given credit for energy export should be charged by a net emission of ~2.0 t CO_2/t NH_3–N, of which ~1.75 t CO_2/t N is pure CO_2 gas generated from feedstock. The average European CO_2 formation in ammonia plants is 2.2 t CO_2/t N, while 30 years ago the net CO_2 emission was around 2.7 t CO_2/t N (Kongshaug 1998).

In order to produce fertilizer ammonia has to be oxidised to nitric acid, which forms the basis of ammonium nitrate fertilizer. Oxidation of ammonia generates 700–1,300 ppm of the GHG nitrous oxide (N_2O) in the tail gas. Increases in combustion pressure from 1 to 5 bar has slightly increased the N_2O emission. The global N_2O emission for nitric acid plants is estimated to be 70 Tg CO_2 eq. (EDGAR database). A good average for the European nitric acid plants is 0.03 t N_2O/t N, corresponding to 9.3 t CO_2-eq/t N (Kongshaug 1998).

More extensively used is urea fertilizer, which has a much lower N_2O emission of 1–4 t CO_2-eq/t N. Table 1 shows an overview of different estimates of CO_2 and N_2O emissions of fertilizer production. The largest share of GHG emission with fertilizer production is from N_2O. Currently there are secondary and tertiary catalytic converters available that can reduce the N_2O emission by more than 90% (e.g., www.ecn.nl). Within the Clean Development Mechanism (CDM) under the Kyoto Protocol several plants are being equipped with these converters. Therefore it is expected that the N_2O emissions will decrease in the coming years.

Fertilizer application

The nitrogen cycle is drastically changed though human creation of reactive nitrogen and its losses to the environment, causing a cascade of effects (Galloway et al. 2003; Erisman 2004). Fertilizer application is one of the major components in this process leading to direct and indirect losses of reactive nitrogen in to the environment. Because of the limited nitrogen efficiency especially at increasing rates of fertilizer application, losses become larger. Losses can be in the form of nitrates to the groundwater, ammonia emissions, N_2O

Table 1 Overview of direct CO_2 and N_2O emissions of fertilizer production in the literature

Fertilizer	kg CO_2/kg N in product	kg N_2O/kg N in product	Total kg CO_2 eq/kg N in product	Reference
AN	1.5–2.8	0.013–0.017	3.0–7.1	Wood and Cowie (2004)
CAN	2.6–3.2	0.013–0.020	3.0–9.6	Wood and Cowie (2004)
Urea	0.9–4.0		0.9–4.0	Wood and Cowie (2004)
UAN	1.3–3.4	0.0073–0.0075	2.0–5.7	Wood and Cowie (2004)
N	2.0–2.7	0.03	11.3–12.0	Kongshaug (1998); Smil (2001)
N	3.02	0.00964	6.07	JEC (2004)
N	3.5	0.0164	8.6	Seinfeld et al. (2006)
N	3.9			Elsayed et al. (2003)
N	3.2	0.018	8.8	Börjesson and Berghund (2007)

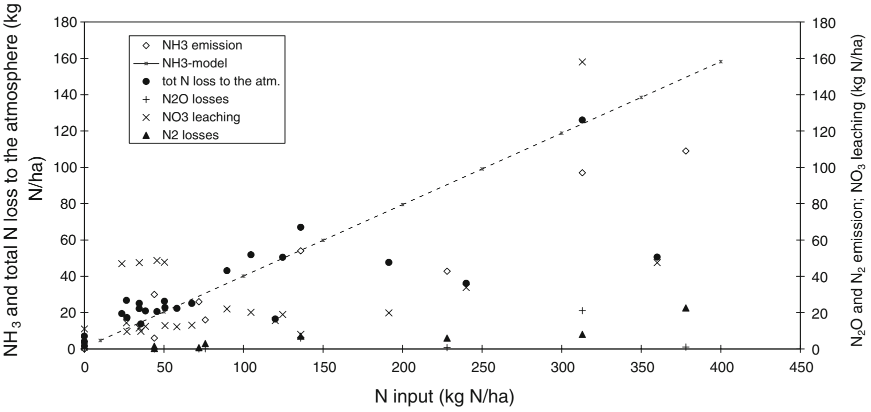
emissions and nitrogen oxide emissions to the air. On the positive side, CO_2 uptake by the plant increases because of the increase in biomass. This is, however, not a linear effect and there is a maximum level of nitrogen addition after which the uptake becomes lower (see e.g., Sinclair and Horie 1989). CO_2 is also sequestered in the soil through the addition of fertilizer. From a global analysis of the fate of anthropogenic nitrogen, Schlesinger (2009) concluded that the sink for N in trees and soils appears to be small, but large enough to support an important sink for carbon. The net GHG emission balance for fertilizer application is difficult to quantify because of the large variations in soil, crops, climatic and environmental conditions and management of the fields. It becomes even more complex if the animal manure cycle is introduced in a system (e.g., to eventually produce biogas, heat and power).

The application of fertilizer yields higher biomass and thus food and biofuels. Several models exist to determine the yield and N content of crops, showing a steady increase in yield and nitrogen content in the plant up to a certain optimum fertilizer level after which a decrease is shown (see e.g., the Nitrogen Crop Response Model (http://www.qpais.co.uk/nable/nitrogen.hm#info)). Based on data from the literature here we estimate the net return of energy using fertilizer. At the economic optimum (that is marginal monetary costs of additional N-input equal marginal crop yield benefit) nitrogen rate of 192 kg $N.ha^{-1}$ (winter wheat in Europe), it is possible to produce 9.3 tonnes of grain per hectare. When no nitrogen fertilizer was added the yield would be: 2.07 t $grain.ha^{-1}$, a factor 4.5 lower. For wheat and oil seed rape the yield of non-grain (non-tradable) plant parts increase from 4 to 7 tons per ha with increasing N-input from 20 to 110 kg $N.ha^{-1}$, however the response of the (tradable) grain yield was stronger for wheat than the oil seed (Dreccer et al. 2005). Addition of 170 $kg.ha^{-1}$ N-fertiliser increases the energy yield of a grain crop from 60 to 120 $GJ.ha^{-1}$ (Yara 2006). The energy needed to produce 170 kg of N-fertiliser was estimated at around 8 GJ, giving an energy production efficiency of 700–1,500% (Yara 2006). This example illustrates the value of fertilizer addition to increase energy yields of potential energy crops. However energy efficiencies will depend on crop type and fertilizer production process.

Along with the yield curves, very limited studies consider all the multi-media (soil, water, air) nitrogen losses that come along with increased fertilization. Recently it became clear that the strong increase in fertilizer for food crop and ethanol based maize production along the Mississippi river in the US increased the leaching and run-off of nitrate causing dead zones in the Gulf of Mexico (Biello 2008). In Europe, the US and China increase in fertilizer use has increased the levels of nitrogen in the environment to a large extent (e.g., Galloway et al. 2003, 2008; Erisman et al. 2008; Ju et al. 2004). A compilation of some literature of nitrogen losses from mixed systems is shown in Fig. 3. There is a clear increase of emissions with increase of fertilizer/manure application rates. This increase is scattered and certainly not linear, particularly because emissions of (predominantly) nitrous oxide, nitrate to groundwater and surface water are complementary to different environmental and physical factors as well as non-linear crop uptake.

The emissions of NH_3 are the largest part of the airborne emissions and generally (depending on the

Fig. 3 Compilation of N losses as function of N-input from the literature (Jarvis and Pain 1997; Kudeyarov and Bashkin (1984); Menzi 2003)



type of management and regional conditions larger than NO_3 leaching to the groundwater. The emission factors for NH_3 are about 0.6–9% of the fertilizer and 20–30% of the manure application, whereas the N_2O emissions generally range between 1 and 3% of the N added (IPCC 2006). Recently, Crutzen et al. (2008) derived N_2O emissions based on the annual atmospheric concentration growth and they estimate that the total N_2O emission should be 3–5% of the reactive nitrogen production. This top down approach received many comments because initially the numbers were compared to the IPCC estimates of 1–2% loss of nitrogen applied. However, all the direct/indirect bottom-up IPCC estimates should be added to derive a comparable number to the top down estimate. Recycling of N through livestock production and human sewage is accounted for in a separate part of the IPCC calculation. A recent bottom up modelling estimate of agricultural N_2O emissions from USA and global agricultural fields compared the values estimated by the Crutzen et al. top–down approach (Del Grosso et al. 2008). They found that their bottom up approach produced estimates of N_2O emissions that fell between the range of estimates using the Crutzen et al. top down approach, 0.9 compared to 0.8–1.4 Tg N_2O–N from USA agricultural soils and 5.8 compared to 4.2–7.0 Tg N_2O–N for global agricultural soils. When the other sources, such as industry, estuaries, etc. are added to the agricultural emissions, the bottum-up calculation being the sum of all sources yield similar results as the top–down approach by Crutzen et al (2008). Nitrogen oxide (NO_x) emissions from field applications in Europe and elsewhere are much lower than other emissions and irrelevant in comparison to the emissions from combustion of fossil fuel.

Crop production for food or biofuels leads to a different net-exchange of CO_2 if fertilizer is applied and when land use changes. The net exchange depends a.o. on the original carbon stock, the nitrogen stock, fertilizer application rate, the climatic and environmental conditions, the management of the field and the return of crop residues (see e.g., McLaughlin et al. 2002). Additionally, increase of soil carbon can occur also downstream the N cascade where nitrogen deposition to unfertilized areas can enhance carbon sequestration (e.g., Magnani et al. 2007; de Vries et al. 2008; Sutton et al. 2008). Soil carbon will eventually saturate and re-release is possible. Furthermore, if wood is used, deforestation might lead to initial CO_2 release from soil carbon (Fargione et al. 2008). Finally, as shown by Sinclair and Horie (1989) there is a relation between crop N-content and CO_2 uptake from the atmosphere. Most LCA studies assume no soil/plant carbon contribution (+ or −) to GHG emissions as the relations are too complex. It is generally assumed that this effect is small compared to other GHG and N interactions, but good data are scarce due to the high complexity of the processes. However, both effects (carbon losses in situ and carbon sequestration off site) can potentially be of the same order of magnitude as the carbon in fossil fuel saved. For example, an in situ loss rate of 0.5 t C ha^{-1} $year^{-1}$ would already amount to about 2,000 kg CO_2-eq ha^{-1}, comparable to the 2,500 kg CO_2-eq. saved by producing bio-diesel from rapeseed assuming a grain yield of 1,200 kg C ha^{-1}. On the other hand, assuming that 10% of the nitrogen volatilizing from the soil as NH_3 or NO_x, transported and deposited in remote regions will lead to the formation of new organic matter and assuming a C/N ratio of 25 in such regions (being a very conservative estimate, see Magnani et al. 2007) could completely off-set the in situ losses of carbon (Leip et al. 2007; de Vries et al. 2008).

Fuel production and use

Apart from the biomass production in relation to fertilizer use the next main issue for biomass is the fuel production and use efficiency. The efficiency determines the net-gain of GHG emissions compared to conventional fuels. Additional emissions of NO_x might be expected because the fuel-N is higher and/or no de-NO_x installations are used for small scale applications and because more energy (combustion) is needed to produce one unit of electricity or transport. There are some very detailed LCA studies and overview studies that can be used to provide an assessment of the current and future situation in terms of GHG emissions. For nitrogen there is very limited information. Most LCA studies consider the whole cycle from biomass production up to use, with the exception of JEC (2004) who split the well to tank and the tank to wheel analysis for transport fuels. The analysis shows that the GHG emissions from biomass options for transport fuels from well to tank is

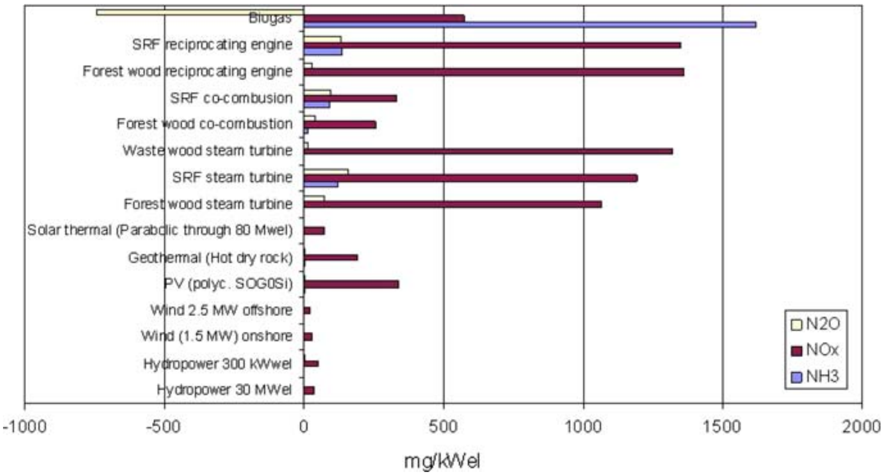


Fig. 4 LCA nitrogen emissions from biomass options to produce heat and power (Pehnt 2006)

generally smaller than the tank to wheel contribution. This implicates that for GHG the focus should be on the fuel conversion, whereas for nitrogen losses the focus should be much more on the well to tank part.

Weisser (2007) recently made an overview of LCA's of different electric supply technologies. He shows that renewables are an order of magnitude lower in GHG emissions than conventional technologies based on fossil fuels. Eight studies on biomass were included and they show a large range in emissions (35–100 gCO_2-eq/kWh), but compared to coal (average 1,000 gCO_2-eq/kWh) and natural gas (550 gCO_2-eq/kWh) this is on the average a huge reduction.

The direct nitrogen emissions from different options to produce heat and power are given by Pehnt (2006), one of the very few studies providing these data. The data are plotted in Fig. 4. The pattern for eutrophication is rather different: electricity generating systems excluding biomass are considerably better than the reference mix based on fossil fuels, but biomass systems are well above the reference mix (exception: systems with co-combustion of forest wood). This is due in particular to the fact that the NO_x emissions of small systems are higher. A special case is the manure based biogas system, which is above the reference mix owing to the ammonia emissions resulting from the animal manure of the agricultural system.

Environmental impacts of biofuel production

The global biofuel/bioenergy system may influence the global environment in a variety of ways. The direct impacts of agriculture on the environment include modification of land for agricultural purposes and by-products of production such as methane and nitrous oxide. Activities such as biomass processing, distribution and preparation use fossil or biofuels, fuel wood, refrigerants, and other inputs that generate wastes. Indirect impacts include the effects of energy, materials, and pollution entailed in constructing and maintaining equipment, transportation and storage facilities, and other infrastructure used in food production and related activities, and in supporting the populations involved in them. Of course, it is especially difficult to quantify such indirect impacts, to attribute them consistently to particular activities, and to ascertain whether alternative uses of resources would have resulted in greater or lesser impacts. The current increased use of biofuels is likely to be a counterproductive approach to mitigate global warming because the fuel energy gained from different biofuel crops might be offset against the nitrogen inputs and associated N_2O emissions from these crops. N_2O is a 300 times more effective greenhouse gas than CO_2 and therefore, a small increase in N_2O emissions resulting from additional fertilizer use can easily offset large CO_2 reductions through the replacement of fossil fuels by biofuels (see e.g., Crutzen et al. 2008).

The overview studies by Quirin et al. (2004), von Blottnitz et al. (2004, 2006), Delucchi (2006), Farrell et al. (2006) and Bergsma et al. (2007) provide the summary of all the LCA studies conducted so far, which are mainly focussed on GHGs. LCAs are almost universally set in European or North American context (crops, soil types, agronomic practices, etc.). All studies are relatively narrow engineering analyses that assume one set of activities replaces another (Delucchi 2006). The studies conclude that the different energy and GHG balances as well as their further environmental impacts and costs estimations vary greatly as the result of the different assumptions made regarding cultivation, the conversion and valuation of co-products. However, for a comprehensive assessment of the non-GHG environmental impact induced by biofuel targets, which also depends on the scope of biofuel use in future societies, this kind of LCA studies are not adequate (Porder et al. 2009).

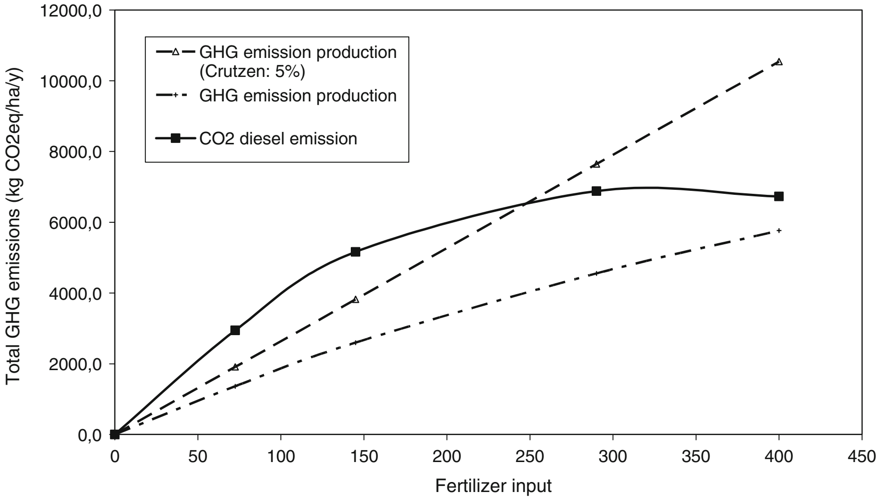
In general it is concluded that the disadvantage of biofuels from energy crops are the higher level of eutrophication, acidification and ozone depletion associated with their use due to the nitrogen compounds released from agricultural production (OECD 2007; Scharlemann and Laurance 2008). The difference with GHG is that these environmental impacts act locally or regionally, whereas GHG emissions contribute globally. It is therefore important to consider the location of the losses of NO_3 and the emissions of NO_x, NH_3, particles, etc. Local impacts can be due to NO_3 losses to the groundwater leading to groundwater pollution and leaching or run-off to lakes and rivers increasing eutrophication and to local high deposition of nitrogen to nature areas or exposure of humans to NO_x and/or particles. NO_x emissions for applications without (non) selective catalytic reductors or de-NO_x are important to consider. These will be especially relevant for the de-centralized production of heat and power from biogas and the small scale production of biofuels, where it is not cost effective to apply Selective Catalytic Reduction (SCR) for emission reduction.

The net biofuel GHG emissions are smaller than those of fossil fuels, especially when second generation crops and technology are used (up to 80% smaller emissions). For first generation the gain is much smaller: 20–40%. The largest part is CO_2 from the combustion engine, but N_2O from fertilizer production and application can be a considerable part, ranging from 0.1 g N_2O/MJ for straw to 0.012 g N_2O/MJ for wheat ethanol (Elsayed et al. 2003). Applying a regression model to biofuel production globally, Smeets et al. (2009) conclude that N_2O emissions typically contribute between 10 and 80% of the total GHG emissions due to biofuel production. According to Smeets et al. (2009) robust options for GHG saving based on first generation biofuel cultivation are sugar cane for ethanol (GHG reduction range 62 to 103%; reduction can exceed 100% because of avoided emissions through use of co-products) and palmfruit for diesel (range 39 to 75%); the GHG saving potential for the options wheat for ethanol (−53–107%), corn for ethanol (−72–13%) and rape seed for diesel (−76–72%) are very uncertain in view of lower crop yields and larger variation of N_2O emission from the various land-use systems for these crops.

We calculated the contribution of different emissions to the total GHG emissions as an illustration of the importance of fertilizer and the resulting N_2O emissions in the GHG balance. The outcome is very variable because it depends on the type of crop, amount and type of fertilizers used, soil type and condition, etc. However, when using rapeseed oil as a replacement for fossil fuel diesel at different fertilizer inputs it can be determined that at very high inputs of 400 kg.ha^{-1} the net reduction of GHG is only 10%, at lower fertilizer input it can be up to 50% reduction (Fig. 5). The largest part is due to the N_2O from fertilizer production and application. Through the application of reduction technologies these can be reduced with 90% yielding better performances in terms of net GHG emission reductions, even though this would increase cost and thus competitiveness of biofuels and/or GHG mitigation measures. For this case conservative estimates for N_2O emissions from application are used. When using the total (direct and indirect) emission estimate for N_2O and also the upper estimate derived by Crutzen et al. (2008) as an extreme case of N_2O emissions in our scenario we can determine the point where the net reduction of GHG becomes negative. Fig. 5 shows the results. It shows that with the estimate of Crutzen et al. (2008) the GHG emissions are equal for fossil diesel and rapeseed at fertilizer inputs of 250 kg.ha^{-1}, whereas with the other estimate of N_2O emissions the break-even point is reached above 400 kg.ha^{-1}. This exercise shows the importance of taken N_2O into account in these studies.

It also shows the uncertainty that is still associated with estimating the net GHG effect of biofuels. What CO_2 reduction will finally be achieved by setting, for example a target for biofuels in the transport sector, depends also very much on the environmental and

Fig. 5 Comparison of break-even points for GHG savings using two estimates of N_2O emissions



farming conditions into which the cultivation of the biofuel crops will be set. A study of Leip et al. 2008 on the distribution of the cultivation of crops in the European landscape show that rapeseed tends to be cultivated on high-quality soils on which also high direct N_2O fluxes (of 5 kg N_2O–N ha^{-1} year^{-1} and more) have been simulated using the mechanistic model DNDC. Much of the N_2O emitted on these soils stems from the mineralization of soil organic carbon and thus contributes also significantly to direct CO_2 losses from the soils. Using these data, a break-even between GHG emissions and biofuel production at even lower fertilizer application rates than 250 kg N ha^{-1} is possible in some situations (Leip et al. 2008). Nevertheless, high N_2O fluxes occur also if other (food) crops are being cultivated on those soils. The situation is different for other crops such as sugar beets that are used for the production of bio-ethanol. Sugar beet is a highly productive crop that is capable of a much higher biofuel yield at a lower rate of nitrogen fertilization. However, in the future second generation crops such as switchgrass Miscanthus (or mixed prairie as discussed by Tilman et al. 2006) will be used for biofuel production. These can change the nitrogen analysis greatly because they may require little fertilization, are perennials, and have tremendous biomass yield with a very high C to N ratio. Three situations can be distinguished with different effect on the nitrogen and GHG emissions: (1)- current agriculture converted to biocrops (land needed elsewhere for food); (2) unused grounds (marginal or not) as new land for crops (fertilizer needed, especially for marginal land), and (3) current agricultural practice with waste streams for energy (higher nitrogen soil losses: more fertilizer needed). It is not possible to provide recommendations for the optimum land use as it will need a decision on the need for food or other applications and the effect of local conditions on the production and environmental consequences. When determining the land use and selecting the crops at least also the full nitrogen cycle has to be taken into account as well as GHG, phosphorus, etc.

Concluding remarks on Nitrogen, biofuels and climate change

Cultivation of energy crops is generally viewed as controversial because of uncertainty with respect to net GHG-savings and its potential competition with land use for biodiversity and food. As shown in this study the net GHG saving effect is highly uncertain and depends on what crops are grown, where they are grown, N-fertilisation levels and assumed N_2O emission factors. N_2O is an important nitrogen component for the net greenhouse gas balance of biofuels. Some studies show that the contribution of N_2O emissions from fertilizer production and application make the GHG balance for certain biofuels small positive or even negative for some crops compared to fossil fuels. These studies indicate that N_2O emissions might be a factor 2–3 higher than estimated up until now from many field trials. This shows that there is still large uncertainty in the calculation of the net GHG balance, but the case-by-case balance depends very much on the C/N ratio of the crop used for producing the biofuel but also on the environment within which the crop is cultivated and the agricultural management practices. The GHG emission resulting from fertilizer production is dominated by N_2O and provide a large source. Currently catalysts are available to reduce these emissions with more than 90% and are being implemented.

Many present energy crops are not robust GHG savers when compared to the current fossil fuel use. Including GHG-emission or savings related to fertilizer production, N-related carbon sequestration, on farm use of the produced biofuels, can double total savings and emissions, and make the resulting net saving highly uncertain for many energy crops (Leip et al. 2007). Others state that these non-robust GHG saving crops could become robust in the future, as GHG-emissions of fossil fuels may increase due to exploitation of low grade crude fossils fuels, like tar sands. There might also be other arguments to develop a market for biofuels, such as the security of the energy supply, the independence of politically unstable or economically weak regions for energy supply, stimulation of new markets leading to economic growth, farmer support, etc. There is also discussion on the potential of increased non-point N-losses to the environment for sequestering carbon and by this reducing net CO_2-emission. Although there is evidence for additional carbon sequestration in agricultural soils and also forests due to nitrogen inputs, nitrogen is believed to enhance CO_2-losses from wetlands and estuaries (Bobbink pers com.). New developments are needed to increase biomass production while limiting nitrogen (and other) losses by e.g., increasing biological nitrogen fixation for non-legumes plants by introducing the gluconacetobacter bacteria (Cocking 2005) or by introducing slow release fertilizers or nitrogen management techniques (Erisman 2004).

Net increases of NO_x emission during production and combustion of biofuels as compared to fossil fuels are a reason for regional concern for additional air pollution that needs to be balanced against the climate benefits. In terms of GHG balances, the best option for bioenergy is large scale electricity production. The efficiency might be twice that of using biomass for biofuels and the nitrogen emissions can be controlled with existing Selective Catalytic Reduction technology that are too costly for small scale facilities. With a strong increase of biomass use for electricity by small scale facilities NO_x might therefore become a serious issue.

All in all, there is a need to more systematically quantify and weigh the greenhouse and eutrophication effects of nitrogen (Miller et al. 2007). However, perhaps the biggest concern regarding biofuels is its potential competition with food and feed crops and with biodiversity. If economic gains per hectare or per unit of labor for cultivation of energy crops can exceed those gains for food and feed crops, they will inevitably oust food and feed. Competition between food/feed and energy crops can also push agricultural activities further into yet semi-natural land with high value for biodiversity and carbon stocks. It can also lead to changes in the production intensity for food/feed crops and therewith the nitrogen cycle. Only strong government regulations will ensure that energy crops remain restricted to marginal crop land. There are several sustainability issues and nitrogen is just one of them. A set of sustainability criteria applied to biomass use, including the disturbance of the nitrogen cycle, needs to be developed. Optimization of the nitrogen use efficiency and the development of second generation technologies will help fulfill the sustainability criteria.

Risk and opportunities of climate policies and nitrogen policies

- Decentralised biofuel production leads to higher NO_x emissions; large scale production (de-NO_x SCR) and fuel use (catalytic converters) do not yield higher NO_x
- (Co-)digestion of agricultural waste is a widely promoted option to produce biogas and/or heat and power. However, there is a competition between using waste from agriculture (and food industry) for animal feed, energy/biofuels and as a source of soil carbon. Furthermore, it might be sustainable with respect to energy production, but when focussed on GHG reduction only, it is more effective to only use manure digestion without addition crops (eg. maize).

- Increased biomass production yields higher N emissions in the existing cascade (similar to food production nitrogen cascade). High yield perennial crops using less fertilizer are preferred.
- 2nd generation biofuels are favourable in relation to energy/GHG balances. However, the competition with animal feed (or food in general) needs continuous attention in view of the risk of more rapid extension of agricultural land into rainforest areas.
- Overall we should focus on 2nd generation crops and aim to improve the nitrogen use efficiency and technology of fuel production and use.

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