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ARTICLE

Bio-chemicals from lignocellulose feedstock: sustainability, LCA and the green conundrum

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This article discusses the environmental sustainability of bio-based or green chemicals and highlights various factors determining their "level of greenness". Life Cycle Assessment was introduced as a systems-wide approach that considers all processes from extraction of natural resources to various bio-conversion steps that leads to the final product. Three bio-chemicals are selected in the investigation: methanol, formic acid, and acetone. The results suggest that the environmental benefits anticipated from renewable resources to produce green chemicals should be reviewed as a case by case basis. Sensitivity analysis was carried out to demonstrate that a 10% increase in biomass output and its availability (per unit land area) receives more CO_2 savings than a 10% increased yield in the bio-conversion methods. More importantly, land use change may impose a dramatic consequence on the total CO_2 emissions for lignocellulose utilization.

1. Introduction

The chemical industry has grown in size and technological maturity throughout the centuries and has come under pressure to be more sustainable. One of the emerging trends observed in the 21st century is the switch from using non-renewable fossil resources to renewable ones for producing chemicals and materials. Awareness towards the level of environmental sustainability has globally spread throughout various industries, and along with this paradigm shift, the use of biomass as feedstock for producing fuels and chemicals is perceived as a means for "going green".[1-4] Lactic acid and citric acid are two examples of bio-based commodity chemicals with many applications. The more important of the two is lactic acid due to the rapidly growing application of polylactate as a bioplastic.[5] Other growing sectors in this area are bio-ethanol and bio-methanol.[6-8] Various other advancements in biotechnology saw the production of lactic acid from lignocellulose-derived sugars[9] and A-B-E (acetone-butanol-ethanol) production from rice straw.[10]

Lignocellulosic biomass is considered here as a potential sustainable resource for the production of bio-chemicals due to their global abundance.[11-12] These renewable feedstocks are synthesized via photosynthetic processes that convert atmospheric carbon dioxide and water into sugars.[13] Lignocellulosic feedstock constitute fibrous materials and are more difficult to convert than the first generation renewable feedstocks – sugars, starches and vegetable oils - but its use solves the social issue pertaining to food versus fuel.[2,8] These renewable feedstocks are mainly from agricultural wastes or by-products, such as straw from wheat or rice crops, or stover that are left on the fields after harvesting corn grains. These feedstocks are composed primarily of carbohydrate polymers (cellulose and hemicellulose) and a complex matrix of phenolic polymers known as lignin. Small concentrations of other compounds (proteins, acids, salts, minerals) are also present.[14]

The three major polymeric components of lignocellulose can be classified into: cellulose (30-50%), hemicellulose (15-30%), and lignin (10-25%). Cellulose $(C_6H_{10}O_6)_n$ has a linear structure made of repetition of glucose molecules linked by β-1-4 glycosidic bonds and its crystalline form is difficult to be chemically hydrolized.[3,14,15] Hemicellulose $(C_5H_8O_5)_n$, on the other hand, contains both C5 sugars (e.g. xylose and arabinose) and C6 sugars (galactose, glucose, and mannose) resulting in a relatively amorphous solid structure which is easier to break down and depolymerize.[16] Lignin is essentially the glue that provides the overall rigidity to the structure of plants. It is a three-dimensional aromatic polymer of lignols connected by C-C and C-O-C links. The empirical formula describing the composition of lignin is $C_9H_{10}O_2(OCH_3)n$, where n varies from 0.94 for softwood to 1.40 for hardwood.[17-18] An example of sugar compositions of rice straw, wheat straw, corn stover, and sugarcane bagasse is shown in Table 1.

Table 1: Compositions of various lignocellulose feedstock [14]

Feedstock	Glucose	Xylose	Mannose	Galactose	Arabinose
Sugarcane bagasse	38.1	23.3	-	1.1	2.5
Rice straw	41.0-43.4	14.8-20.2	1.8	0.4	2.7- 4.5
Wheat straw	38.3-39.3	21.9-22.5	1.5-1.9	2.6 – 2.8	4.6- 4.8
Corn Stover	39.0	14.8	0.3	1.1	2.5

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† Electronic Supplementary Information (ESI) available: Life cycle inventory and system boundary of biomass-to-chemical production

The transition to exploit the potential of renewable resources comes with new technological, ecological and sustainability challenges.[1,8,19] In order to effectively convert lignocellulose feedstock to liquid fuels or commodity chemicals, they first have to be depolymerized and (partially) deoxygenated. In his review, Sheldon[2,3] explained two ways for basically achieving this: thermochemical and hydrolytic (see Fig. 1).

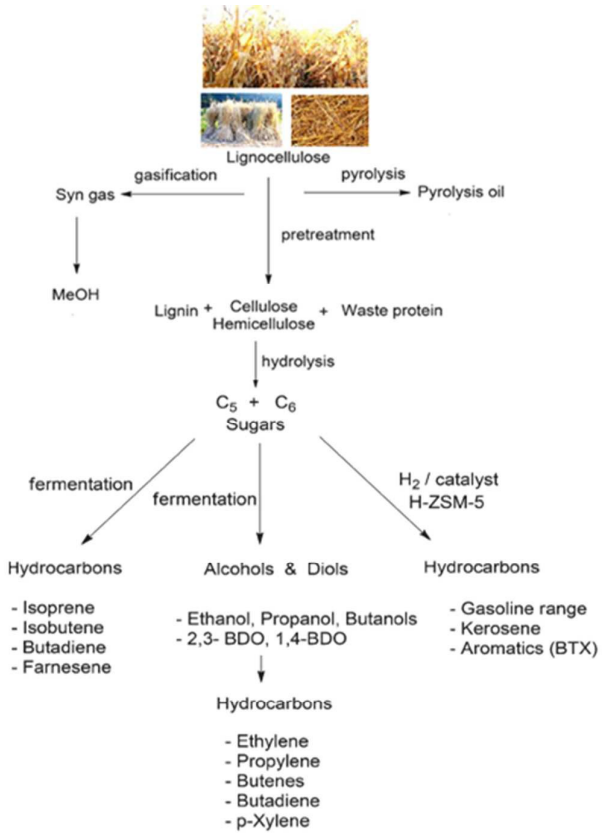

Fig. 1. From lignocellulose to various bio-chemicals [adapted from Sheldon[3]].

1.1 Pretreatment

The efficiency of pretreatment methods is imperative to the success of utilizing cellulosic materials for the production of bio-chemicals. The first challenge is to disarray lignin to make cellulose and hemicellulose accessible for further uses. The four fundamental types of pretreatment techniques available are physical, chemical, physicochemical and biological methods.[20-21] Among the various methods employed, physical and chemical pre-treatment has been successfully used for extraction of sugars. Acid pretreatment involves the use of concentrated or diluted acids, typically H_2SO_4, to break the rigid structure of lignocellulosic materials. In one example, Cao and Aita[22] obtained 66% cellulose by pretreating bagasse with ammonium hydroxide (28% v/v) to a temperature of 160◦C for 1 hour. In another case, Lin et al.[23] described improvements in the yields of glucose and xylose by adding dilute chemical reagents (e.g., H_2SO_4, HCl, CH_3COOH, HCOOH, NaOH, KOH) in the ball milling pretreatment of corn stover. Pretreatments that combine both chemical and physical methods are referred to as physico-chemical processes. Some of these methods include: steam explosion, SO_2 or CO_2 catalyzed steam explosion and ammonia fiber explosion.[24] A comprehensive review of physical, chemical, physicochemical and biological pretreatment methods can be found in Sarkar et al.[14]

1.2 Bio-conversion methods

Bio-conversion techniques have received a lot of research attention to effectively make the most use of C5 and C6 sugars.[1-3,20,24-26] The final step for the conversion of sugars can be done via fermentation, saccharification, thermochemical conversion, or a combination of methods.[8] The maximum utilization of all sugar fractions is essential to obtain an economic and viable conversion biotechnology. A few approaches for the gasification of biomass for bio-methanol production have already been developed. Process details of bio-methanol production via the gasification of sugarcane bagasse can be found in Renó et al.[6] and Hamelinck and Faaij.[27] Research efforts from China have actively focused on technologies for bio-methanol production via biomass gasification in interconnected fluidized beds[28] and catalytic gasification.[29] Xiao et al.[30] reported the successful lab-scale production of bio-methanol using rice straw as the biomass feedstock. Their analysis involved the simulation of methanol synthesis via biomass gasification in interconnected fluidized beds. The reported methanol yield reached 0.308 kg per kg rice straw.

Yoo et al.[31] reported the production of cellulosic ethanol and furfural via two-stage hybrid fractionation. During the first stage, zinc chloride ($ZnCl_2$) was utilized to selectively solubilize hemicellulose; next, the remaining solids were converted into ethanol using commercial cellulase and *Saccharomyces cerevisiae* or recombinant *Escherichia coli*. Also, Alonso et al.[32] described the catalytic conversion of hemicellulose and cellulose to furfural and levulinic acid by using γ-valerolactone (GVL) as the solvent. The authors demonstrated how the lower boiling point of furfural (b.p. 441 K), as compared to GVL (b.p. 481 K), enabled it to be continuously removed by distillation. By passing through the intermediate formation of hydroxymethylfurfural, the cellulose is then converted to levulinic acid.[25] In a more recent example, the production of formic acid (FA) from wheat straw in $NaVO_3$–H_2SO_4 aqueous solution with molecular oxygen (O_2) was studied. The resultant conversion was 47% of FA and 7.3% of acetic acid.[33] (Figure 2).

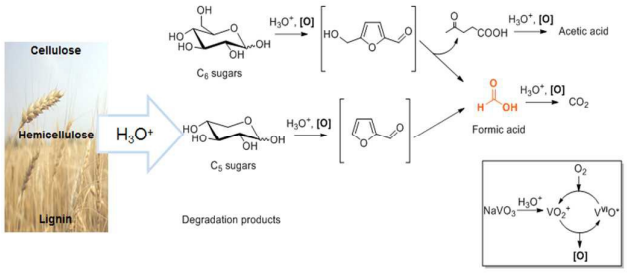

Fig. 2. From wheat straw (in $NaVO_3$–H_2SO_4 aqueous solution with molecular oxygen) to formic acid and acetic acid [33]

Among the bio-processes that involve the conversion of fermentable sugars into higher value chemicals it is worth mentioning the revival of the A-B-E process (Fig. 3), due to growing concerns about the volatility of oil supply and the potential of butanol, one of the main outputs of the process, as biofuel. In an example described by Moradi et al.,[10] 1 kg of rice straw was successfully converted into 44 g of butanol and 17 g of acetone using *Clostridium acetobutylicum* for the enzymatic transformation.

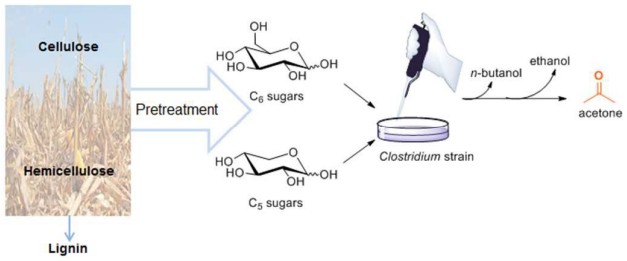

Fig. 3. From lignocellulose to bio-acetone via A-B-E process[10]

A comprehensive review of other bio-conversion technologies, namely for the production of bio-ethanol, is already reported elsewhere.[5,8,18] As a summary, the combined goals of effective pretreatment and bio-conversion processes are: i) selection of suitable lignocellulose feedstock; ii) high yield of useful sugars (C5, C6) extracted; iii) avoid losses and/or any degradations of sugars extracted; iv) efficient or high conversion of sugars to the final bio-products; v) and overall, minimize energy demands and unwanted by-products.[1,13,19,34,35]

2. Life cycle assessment

Along with the increasing transition from a fossil to bio-based economy, the sustainability of bio-based or green chemicals have on numerous occasions became a subject of debate. Questions surrounding the environmental sustainability of bio-based products have been highlighted in several articles.[35-40] The levels of "greenness" of bio-chemicals have been addressed by Bakshi[41], where the interlinked complexities and challenges faced by a changing chemical industry striving towards the goals of sustainability were discussed. Seeking sustainability has resulted in various environmental assessment methods. In their review of bio-based chemical production, Hatti-Kaul et al.[42] stressed the need for the evaluation of environmental impacts of these products from a life cycle perspective. Life Cycle Assessment (LCA) considers a larger boundary that aims to include all processes from extraction of natural resources to various manufacturing stages that leads to the final product. As deliberated by Jiménez-González at al.,[19] LCA methodology provides a holistic approach beyond the boundaries of a one stage manufacturing system, and traces the flows of material usage from its source or "cradle". Developed about 30 years ago, LCA has positioned itself as a valuable environmental assessment tool in chemical and pharmaceutical industries.[43-45]

While the use of renewable resources becomes an important objective, life cycle thinking helps in sorting out the underpinning complications of the material's production chain. This approach is motivated by the realization that by expanding the boundary of assessment, the possibility of shifting the environmental problem outside the system can be prevented.[39-42] Starting from agriculture, the understanding of the process chain and material transformation at each stage, mass and energy balances are all essential in LCA.[35] Emissions released to the environment such as acidic gases (SO_2, NO*x*), greenhouse gases (CO_2, CH_4, N_2O) and others such as VOC, NH_3, PM, are quantified at each stage for the final evaluation of the product's potential environmental impacts. Specific potential environmental consequences (classified as 'impact categories') such as global warming, acidification and Photochemical Ozone Creation Potential (POCP) are the resultant outcome of LCA investigations.[6,35,46] Figure 4 illustrates the overall concept behind LCA and its outcome.

Life cycle assessment has been actively applied in biorefinery technologies.[47-49] Henderson et al.[50] investigated the manufacture of the pharmaceutical intermediate 7-aminocephalosporanic acid (7-ACA). In their assessment, a renewable bio-based process was compared against a previous synthetic route to generate the life cycle environmental impacts of both. Hottle et al.[51] presented the environmental impact comparisons of three bio-based polymers, polylactic acid (PLA), polyhydroxyalkanoate (PHA), and thermoplastic starch (TPS) with five common petroleum derived polymers. In a more recent study, Hong et al.[52] applied LCA comparing corn-based and cassava-based ethylene production scenarios. Their results showed that bio-based ethylene contribute significantly to respiratory inorganics, land occupation, and global warming.

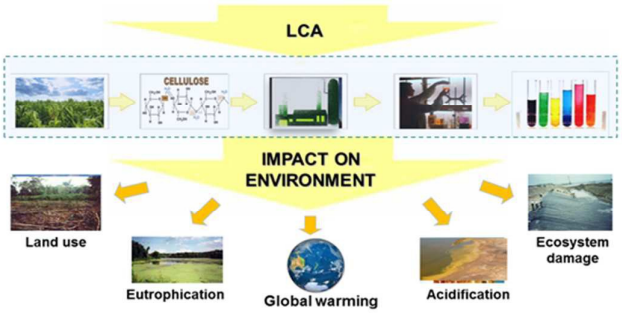

Fig 4. LCA concept and the associated environmental impacts

2.1 LCA case study

In our work, three bio-chemicals are selected – bio-methanol, bio-formic acid, and bio-acetone – due to their importance in chemical and pharmaceutical industry. Apart from its use as an important solvent, methanol is a versatile platform chemical used for making formaldehyde, acetic acid, and a wide variety of other products. Lately, methanol has also played an important role in a bioprocess involving methylotrophs, microorganisms that can use one-carbon sources (e.g. methanol) for their growth.[53] Formic acid (FA), the simplest carboxylic acid, is an important material widely used in industry. Besides the traditional use in chemical, agricultural, and pharmaceutical industries, formic acid is being considered as an efficient H_2 storage molecule, as well as, new C1 chemical building block.[54] Lastly acetone, one of the most versatile solvents, is used not only for cleaning and decontamination protocols, but also for the production of cosmetics, household and personal care products, and pulp and paper processing.[55]

To the best of our knowledge, the last two chemicals are less studied from a life cycle perspective. This paper presents a life cycle "cradle-to-gate" assessment of the following six cases of lignocellulose feedstock to bio-chemicals:

1. Rice straw to bio-methanol (RS-Methanol)
2. Bagasse to bio-methanol (bagasse-Methanol)
3. Rice straw to acetone (RE-Acetone)
4. Stover to formic acid (stover-FA)
5. Wheat straw to acetone (WS-Acetone)
6. Wheat straw to formic (WS-FA)

The functional unit, used as the basis of comparison, is defined as **1 kg bio-chemical** produced at the factory gate. The case studies are adapted from several reports and articles, including biomass gasification from Brazil[6,27,56] and China[30], biotechnology process designs[57-58], and several other lab-scale experimental studies.[10,33] The details of each case are compiled in Table 2. Two life cycle system examples are illustrated in Figs. 5 and 6.

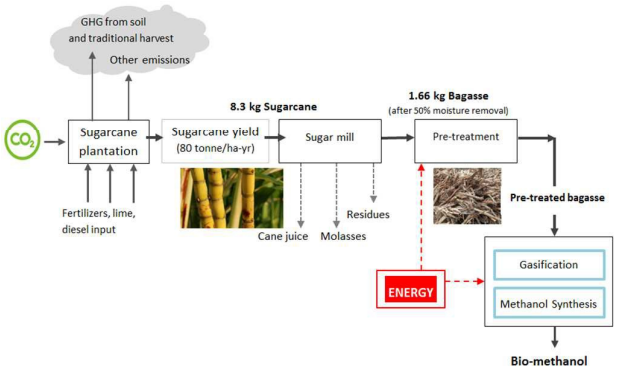

Fig 5. Life cycle flow diagram of sugarcane cultivation, bagasse generation from sugar mill, pre-treatment, and bio-methanol

Table 2: Lignocellulose-to-chemicals case studies

Feedstock	Bio conversion process	Yield of bio-chemical	Remarks/references
Sugarcane bagasse	Methanol produced from sugarcane bagasse by BTL (Biomass to Liquid) route. Main process steps: pretreatment, gasification, gas clean-up, syngas conditioning, final methanol synthesis and purification.	1 kg methanol from 1.66 kg of treated, dry bagasse	Case study from Brazil for scale of 656 m^3/day bio-methanol production. Gas and solids flow rates modelled with the help of CSFMB[a] software. Life cycle emissions for sugarcane cultivation, traditional harvesting and sugar milling, including energy inputs for gasification and related emissions are included. [6,56]
Rice straw	Methanol produced from rice straw via gasification in interconnected fluidized beds. Production process includes raw syngas purification, catalytic synthesis, and methanol distillation.	0.308 kg methanol per kg rice straw[b]	Case study from China.[30] Done with the help of Aspen Plus simulation software
Rice straw	Concentrated phosphoric acid pretreatment and hydrolysis of rice straw followed by fermentation *via Clostridium acetobutylicum*. Production of ABE (acetone, butanol, ethanol)	17 g acetone /kg rice straw[b] produced	Lab-scale experimental study.[10] All life cycle input-output co-allocated to acetone by mass output fraction.
Wheat straw	Conceptual process design of ABE (acetone, butanol, ethanol) fermentation. Self-supply of steam and electricity demands for the process via co-generation of surplus energy. Typical yield: 0.3 kg ABE from 1 kg sugar with 3:6:1 mass ratio.		Designed for 167 k-tonne/year ABE by ECN (Energy Research Center), the Netherlands.[57] All life cycle input-output of wheat and straw[c] production co-allocated to acetone by mass output fraction.
Wheat straw	Production of formic acid from wheat straw in $NaVO_3$–H_2SO_4 aqueous solution with molecular oxygen (O_2). The conversion resulted in efficiencies of 47% (based on carbon, 75.2% based on mass) of formic acid	47% yield of FA from wheat straw[c]	Lab-scale experimental study.[33] All life cycle input-output of wheat and straw collection co-allocated to acetone by mass output fraction.
Corn Stover	Production of formic acid via a process adapted from the Biofine technology.	1 kg formic acid[d] from 1.7 kg stover[e]	The Biofine is a patented process with substantial commercial potential.[58] All life cycle input-output co-allocated to acetone by mass output fraction.

[a] Comprehensive Simulator of Fluidized and Moving Bed Equipment

[b] Input-output data for rice cultivation, rice-to-straw ratio, and rice straw collection from NREL.[59]

[c] Input-output data for wheat cultivation, wheat-to-straw ratio, and straw collection from NREL.[59]

[d] Based on theoretical calculations assuming optimal sugar yield

[e] Input-output data for corn cultivation, corn-to-stover ratio, and stover collection from NREL.[59]

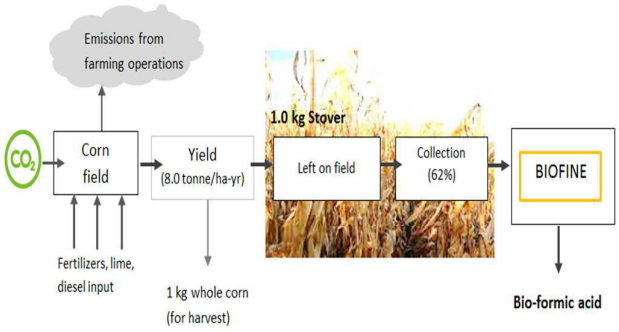

Fig 6. Life cycle flow diagram of corn cultivation, stover collection from fields (after corn harvest), drying, and final formic acid production via Biofine process

In all LCA cases, the production pathways are tracked stage-by-stage: i) crop cultivation starting from agricultural; ii) crop yields (per tonne/ha-yr) of corn, sugarcane, wheat, and rice; iii) fraction of production via gasification lignocellulose feedstock (waste or by-products) from each crop (stover from corn, bagasse from sugarcane, and straws from wheat and rice); iv) pretreatment requirements for the breaking down of lignocelluloses structure, followed the extraction of sugars; v) final conversion to bio-products (bio-methanol, bio-formic acid, bio-acetone).

Life cycle inventory

Information and inventory data for each case starts from agriculture. Input-output data, known as life cycle inventory (LCI), forms the backbone of the LCA investigation. LCI database are widely available (e.g., NREL, EcoInvent, etc.).[59,60] In this procedure, input materials and energy used during biomass cultivation (diesel, water, fertilizers) and the associated emissions to the environment (SO_2, NOx, NH_3, CO, CO_2, CH_4, N_2O, VOC, PM, etc.) and wastewater are all accounted for. Furthermore, mass flows linked to energy demands are included in the assessment (e.g., CO_2 emissions due to energy demands). It is important to remind to those unfamiliar with LCA studies that changing the geographical locations for the same case study will generate a different set of inventories. This in turn critically influences the environmental impact results. For example, 1 kg of untreated bagasse from Brazil[6] generates emissions equal to 0.987 g N_2O, 2.20 g NOx and 0.258 g NH_3; the same quantity of bagasse from Australia, results in 1.10 g N_2O, 3.50 g NOx and 0.265 NH_3 g emissions.[47] The main difference is due to the use of coal for power generation in Australia.

One of the advantages of utilizing biomass is the ability to store carbon via the process of photosynthesis during their growth and cultivation. The amount of CO_2 absorbed by each crop is taken into account and co-allocate by mass to the respective lignocellulose feedstock. LCI data are extracted from NREL[59] for all information pertaining to CO_2 sequestration and emissions from the production of corn, wheat and rice, as well as, the residual lignocellulose feedstock from each respective crop (stover from corn, and straws from wheat and rice). Input-output data for sugarcane cultivation, harvest, and the amount of bagasse obtained from sugar milling was provided by Renó.[6] Details of "cradle-to-gate" LCA of fossil-based methanol, formic acid and acetone are supplemented by EcoInvent.[60] All LCI information are contained in the Supplementary Information section. Other examples of life cycle cradle-to-gate systems can also be found in the Supporting Information section.

3. Environmental impact results and discussions

Irrespective of a fossil or bio-based chemical synthesis, in LCA it is necessary to quantify the environmental impacts from the flow of materials and resources utilized from the source of extraction till the end of final product output.[19,35,50,61] The following environmental impacts can be generated: global warming potential (measured as kg CO_2-eq), acidification (kg SO_2-eq), eutrophication (kg phosphate-eq), human toxicity (kg DCB-eq), Photochemical Ozone Creation Potential (kg ethylene-eq), and water use in total m^3. The environmental impacts, displayed as Figures 7 – 12, are each compared against fossil-based methanol, formic acid and acetone.

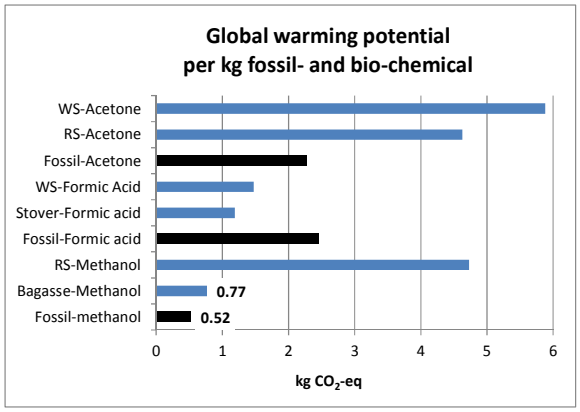

Fig 7. Global warming potential

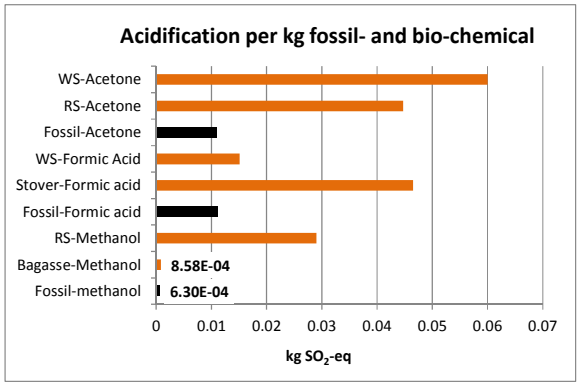

Fig 8. Acidification

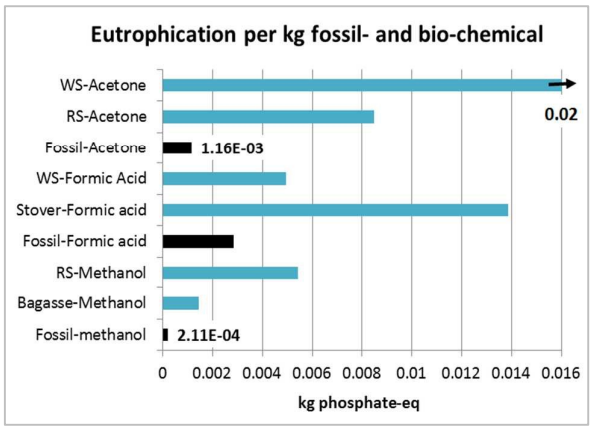

Fig 9. Eutrophication

The graphs of GWP displayed for bio-products (Fig. 7) has factored in emissions from agricultural processes[62,63] as well as CO_2 sequestration, feedstock collection and handling. Included are also downstream processes (i.e., sugar extraction and final conversion). With the exception of WS-FA acid and stover-FA, the rest of the global warming impacts – from resources to final bio-chemicals – are relatively higher than their fossil-based counterparts. The results imply that the environemntal benefits of bio-based products are subjective to a case-by-case basis. From a life cycle prespective, fossil-based acetone exhibits an environmental advantage over bio-acetone produced from both rice straw and wheat straw. In our work, *ca.* 8.5 kg wheat straw is required per kg acetone[57], resulting in ~ 5.87 kg CO_2-eq/kg WS-Acetone.

Paddy fields are large contributors of nitrous oxide (N_2O) and methane (CH_4) – two significant greenhouse gases.[64] In the investigation of methane emissions from rice fields in China, Yan et al.[65] reported an annual release of around 5.82 to 9.57 million tonnes CH_4 for an area of 31.3 million hectares dedicated to rice cultivation. This explains the significant global warming results of RS-Acetone and RS-Methanol (Fig. 7 again). Bio-methanol from bagasse results in more CO_2 savings than bio-methanol from rice straw. Without traditional harvest which causes the release of greenhouse gases[66], the result of bagasse-methanol would reduce from 0.77 to ~ 0.3 kg CO_2-eq/kg, nearly 40% reduction of CO_2-eq as compared to fossil-methanol.

The other results augment the fact that agricultural practices have environmental impacts of their own which cause different environmental stresses resulting mostly from the use of herbicides and pesticides.[59] Nitrogen (N) fertilizers play an important role in agricultural systems in terms of crop yield. Emissions of NOx and NH_3 are the consequences of N-fertilizers applications in agricultural lands. Measured in LCA, these environmental impact models are classified as acidification (Fig. 8) and eutrophication (Fig. 9). WS-Acetone scored highest in these two impacts, caused largely by the sheer amount of lignocellulose feedstock (8.5 kg) required per bio-acetone. Eutrophication is generally associated with the environmental impacts of excessively high nutrients (i.e. N and P), which are released from soil to atmosphere after fertilizations, during biomass growth, and after harvesting.[67] Intensive application of N and P fertilizers causes environmentally detrimental impacts to terrestrial ecosystems.[68] Environmental studies of N losses have already been reported elsewhere, focusing largely on ammonia volatilization, NOx emission, and nitrate leaching.[69-71]

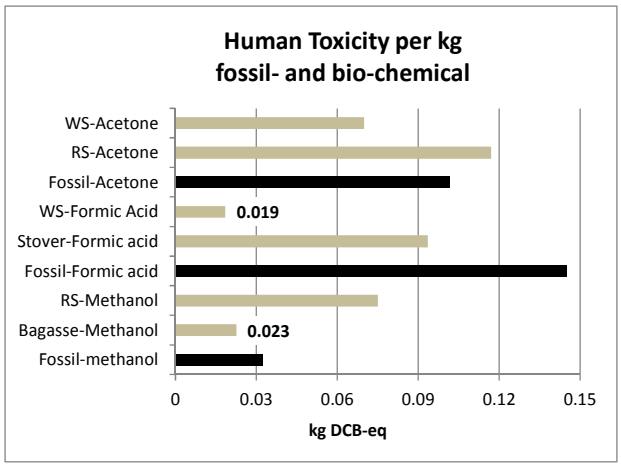

Fig 10. Human toxicity

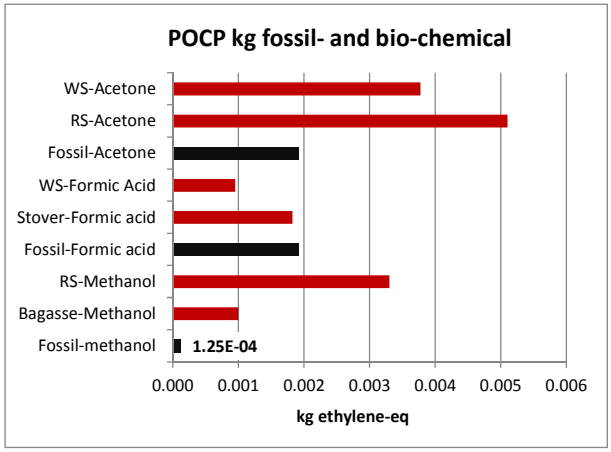

Fig 11. Photochemical Ozone Creation Potential (POCP)

Human Toxicity involves the assessment of toxic substances in the frame of LCA. In this case, bio-based formic acid proves to have an environmental advantage over fossil-formic acid (Fig. 10). The higher human toxicity potential for fossil-based formic acid was mainly contributed by the generation of heat via the combustion of natural gas during its production. During the combustion of natural gas, emissions comprising of hydrocarbons and other substances are released,[60] which contribute to the high human toxicity results.

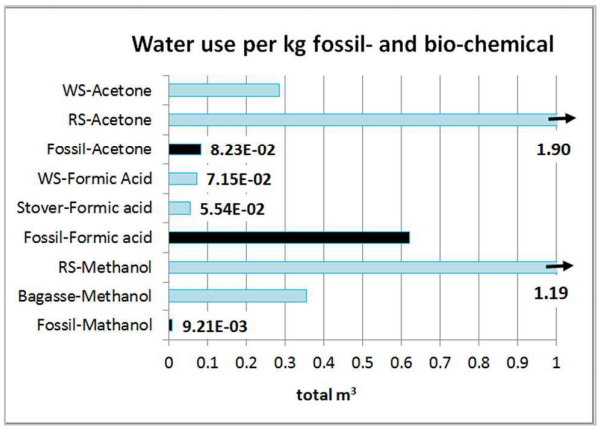

Fig 12. Water use

Photochemical oxidation, also referred as summer smog, is the result of reactions between NO*x* and hydrocarbons or volatile organic compounds (VOC).[7] The release of these substances from the widespread use of N-fertilizers in rice fields have created severe environmental problems[71,72] leading to the significantly higher POCP results exhibited by RS-based acetone and methanol (Fig. 11). Chen et al.[71] suggested reducing the use of N-fertilizers by one-third to mitigate this environmental impact, but this will however cause a reduction in rice yield.

Water use impacts are categorized into those required for the manufacture of fossil-based chemicals, as well as, water needed in agriculture for biomass production. Water used for irrigation purpose in agriculture is rather significant, especially for rice crops.[73,74] This is reflected in the impacts of Fig. 12.

4. Further discussions and analysis

The nature of the results from our work is echoed in various other LCA cases.[48-50] Liang et al.[75] reiterated that the use of cellulose-based feedstocks do not always sanctify long-term sustainability; the life cycle assessment of their usage may lead to increased impacts such as global warming, eutrophication, and freshwater use. Among the most important environmental compartment, reductions and/or emissions of CO_2 have garnered foremost attention in lignocellulose-biomass utilization.[6,30,35,39,42,48-52] Lately, sustainable land use has also become an emerging topic in biomass utilization.[8,11,34,37,38]

4.1 CO_2 from biomass utilization

Despite the ability to absorb CO_2 via photosynthesis, this benefit is overshadowed by greenhouse emissions caused by farming activities[62,63], harvesting methods (specifically for sugarcane[6]), and other processes involved in biomass production.[59] The GWP impacts per kg of lignocellulosic feedstock alone are less than those shown in Fig. 7. They are: 0.56 kg CO_2-eq per kg wheat straw (left on field), 0.72 kg CO_2-eq per kg rice straw (left on field), 0.43 kg CO_2-eq per kg (untreated) bagasse and merely 0.1 kg CO_2-eq per kg stover (left on field). However, based on the number of processing steps, accompanied by the accumulated quantity of feedstock needed, the series of environmental impacts intensifies along the life cycle production chain.

Considerable amounts of greenhouse gases released for the LCA of (2-Methyl tetrahydrofuran) 2-MeTHF was also reported in Khoo et al.[35] The environmental benefits of utilizing stover to produce 2-MeTHF were negated by CO_2 emissions from various farming and further processing activities. The quantity of lignocellulosic biomass required is determined by a few factors. The contents of cellulose and hemicellulose in lignocellulose feedstocks vary considerably between different genus of biomass, seasonal events and other parameters.[8,14,24] In the case study by Khoo et al.,[35] bio-based levulinic acid was first produced as the intermediate before the final conversion to 2-MeTHF. Once the C6 sugars wt% is identified from a target lignocellulosic residue (e.g. corn stover, glucan content 37.1 wt%), the following formula was applied to estimate the quantity of biomass required to produce 1 kg of 2-MeTHF:

$$\text{Biomass required [kg]} = \frac{1}{Glucan\ wt\%\ x\ \frac{MW\ LA}{MW\ C_6H_{12}O_6}\ x\ \eta P\ x\ \eta NWL} \quad \text{Eqn.1}$$

Where

LA: Levulinic acid

ηP: efficiency of bio-conversion = 70% by mass

ηNWL: efficiency of hydrogenation process = 63% by mass

From Eqn 1., the required quantity of 10 kg stover to produce kg 2-MeTHF intensified the amount of greenhouse gases up to 5.6 kg CO_2-eq.

4.2 Sensitivity analysis

Crop and bio-conversion yields, land use

Due to continuing advancements in agricultural science[76] and bio-technologies,[1,2,22,32] the outlook of both lignocellulose yields (due to improvements in crop output/ha)[8] and bio-conversion efficiencies are expected to increase. One such effort is carried out by the Crop Physiology Laboratory at the University of Illinois, U.S. According to the researchers, up to 10-20% agriculture yield increase (per ha-yr) can be made possible by intelligent intensification and cultivation management.[76] This improvement implies that 10-20% more stover will be made available (per hectare) for biorefineries. To test these possible outcomes, sensitivity analysis is carried out for the LCA of some selected bio-chemicals considering a conservative 10% increment in the availability of lignocellulose feedstock for use (from the same area of agricultural land); and separately, 10% increase in bio-conversion yields.

Producing more bio-products will directly or indirectly demand dedicating more agricultural land for growing biomass

resources.[12,77] The total Land Footprint (in hectares-year) needed in the production of a bio-based product (e.g. bio-ethanol) can be found in Khoo.[8] Dissimilar to Land Footprint, Land Use Change is another important aspect of biomass utilization. This means that LUC may impose a dramatic consequence on the total CO_2 emissions for biomass-lignocellulose utilization, and deserves further analysis.

Land Use Change

In general, organic carbon (C) is stored in different pools such as above and below ground residues, dead wood, litter and soil. Any changes to land utilisation or LUC (Land Use Change) affects the Carbon pool storages.[34,78] As an example, Schubert[79] reported emissions of 1230 kg CO_2/ha-yr for both wheat and corn for LUC from grassland to cropland. In another important example, the widespread promotion of bio-products made from sugarcane and bagasse came with an additional environmental burden – the demand for the biomass resource led to the clearing of forestland for the expansion of sugarcane plantations in Brazil. It was reported that during the years 1996–2006 land conversions to grow more sugarcane led to more greenhouse gas emissions due to deforestation.[80] In a more in-depth analysis, Song et al.[81] examined the effect of climate change caused by deforestation in Brazil. Across the study area of 1.59 million ha/yr the authors estimated the associated carbon emissions caused by the clearing of forest land was 0.18 Pg C/yr. This translates to about 0.415 million kg CO_2 per ha of deforestation. In this assessment, the total life cycle CO_2, inclusive of the greenhouse gas emissions from LUC, is calculated as follows:

Total CO_2 per kg bio-chemical = GWP_1 + [LF(ha) x $CO_{2(LUC)}$] Eqn. 2

Where

GWP_1 : life cycle kg CO_2-eq/kg bio-chemical

LF: Land footprint (in ha-yr/bio-chemical)

$CO_{2(LUC)}$: total greenhouse gas emissions per area LUC (kg/ha-yr)

In Eqn. 2, GWP_1 follows the total life cycle results of kg CO_2-eq (as reported in Fig. 7), and the detailed descriptions of Land Footprint can be found in Khoo.[8] Values of $CO_{2(LUC)}$ are taken from reports.[79,81]

Eutrophication impacts due to N and P

The impacts of fertilizer use, namely N and P, also deserve further attention as they are a global concern to terrestrial ecosystems.[68,71.] Different rates of N and P application will affect crop yields, which in turn determine the amount of lignocellulose resources available for making bio-chemicals. Information pertaining to the different application rates of N and P for corn, wheat, rice and sugarcane; vs. the corresponding crop yields, are compiled in the Supporting Information section.

4.3 Further Results: sensitivity analysis and others

The results of 10% increased yields of both lignocellulose resources and bio-conversions, as well as LUC, are displayed as Fig. 13. RS-acetone is omitted from the analysis due to its various significant environmental impacts. The sensitivity analysis results for Eutrophication impacts are displayed in Fig. 14.

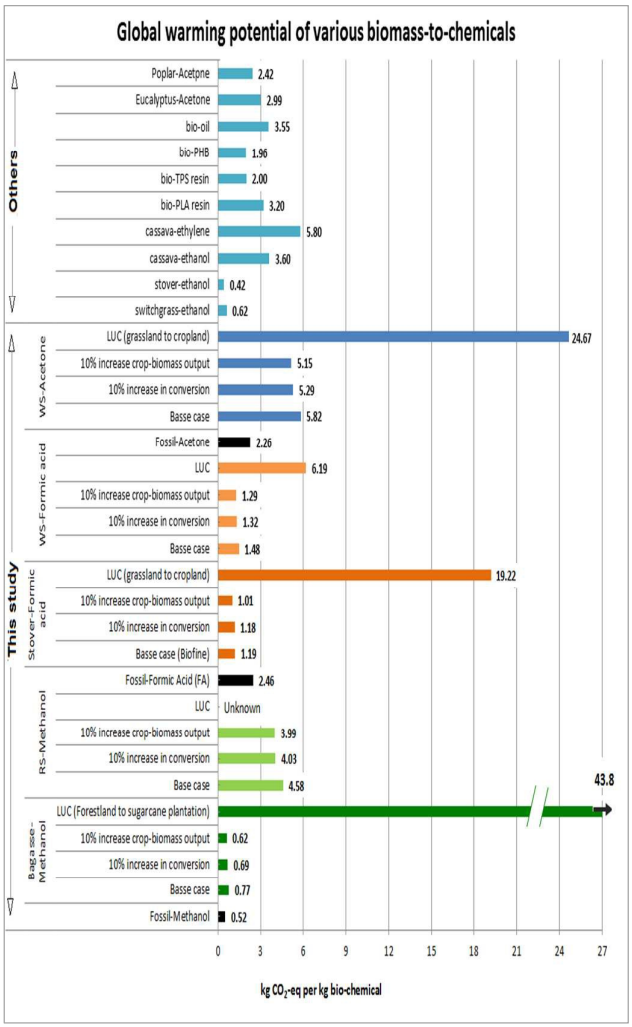

Fig 13. CO2-eq results of various bio-based chemicals

The graphs also display the total CO_2 emissions (in kg/kg) of bio-chemicals from various other reports: cassava-ethanol,[48] cassava-ethylene,[49] TPS and PLA resins,[51] bio-polyhydroxybutyrrate (PHB),[82] acetone from poplar and eucalyptus,[83] ethanol from stover and switchgrass,[84] and bio-oil from palm.[85]

It is highlighted again that the potential environmental advantages anticipated from using biomass to produce chemicals or other materials have to be thoroughly reviewed case by case.[19,27,30,33,48-52] In some cases, the global warming results score as low as *ca.* 0.5 kg CO_2-eq/kg (bio-ethanol and methanol from bagasse) to over 4.5 kg CO_2-eq/kg for methanol from rice straw, acetone from wheat straw, and ethylene from cassava.[49] Fig. 13 also demonstrates that, from a life cycle perspective, 10% increase in biomass output and its availability (per unit land area) for biorefinery processing receives more CO_2 savings than a 10% increased yield in the bio-conversion methods.

With LUC (land use change) considered in the LCA, the results are intensified by a magnitude of ~5 times for WS-acetone, ~19 times for stover-formic acid, and an astounding 57 times for bagasse-methanol. Land use change is one of the largest contributors to greenhouse gas emissions, as deliberated by climate scientists.[37,81,86-89] The clearing of land for meeting increased biomass demand is especially alarming where deforestation is concerned. From 2005 to 2010, the average carbon density of cleared forests in the Amazon basin increased at a rate of 7 Mg C/ha-yr, suggesting that LUC has been progressively encroaching into densely forested land areas.[81]

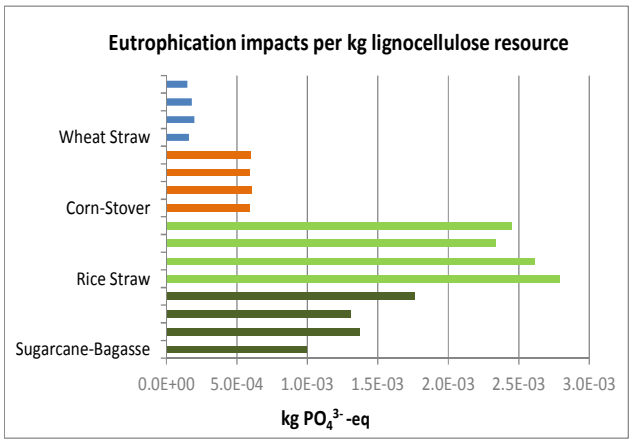

Fig 14. Eutrophication impacts due to different application rates of N and P

Eutrophication impacts (per kg lignocellulose) due to varying N and P applications are displayed in Fig. 14. Since N and P use only applies to agriculture, the results are allocated according to 1 kg lignocellulose feedstock, without considering those released from other process stages such as energy use. Sustainable management of N and P to produce optimal yields can found in the combined disciplines of agro-ecology, crop sciences and bioresource technology.[42,68,71,79.]

4. Concluding remarks

This paper suggests that the environmental benefits anticipated from renewable resources to produce chemicals or materials should be reviewed thoroughly. A life cycle approach or LCA ensures that resource usage is captured, and offers the advantage of making sure that environmental damages will not be shifted across the production chain.[19,46-50] It should also be highlighted that LCA system boundaries and locations where the particular biomass resources are grown will not generate the same amount of emissions.[6,,47,57-60] In LCA, system boundaries represent the perimeter of exchanges between a process chain and the environment; within which, dissimilar input-output data from a respective geographical area will tend to influence the environmental impact results in the production chain leading to 1 kg bio-chemical. Further work is suggested for developing a database of input-output information that can provide ease of use for LCA, as well as an 'averaging' of impacts for bio-chemicals.

Biomass resources are especially favoured for their their ability to absorb CO_2 via photosynthesis. Our results show that this benefit is overshadowed by greenhouse emissions caused by agricultural activities, harvesting, and other downstream processes involved before leading to 1 kg bio-chemical. Sanders et al.[90] projected that in the year 2050, a considerable quantity of base chemicals, at least 30% by weight, will be produced from biomass. This expected demand may in turn require more land utilization. The life cycle global warming impacts of bio-chemicals are estimated to intensify substantially if land use change (LUC) is included in the analysis, especially when deforestation is considered.

Increasing the efficiency of bio-conversion technologies for bio-based chemical production remains a challenge for a plethora of target molecules.[2-3,41-42] With the continuing development and updating of different bio-chemical conversion technologies, biorefineries are expected to play the role of efficient and highly integrated systems to meet the new demands of bio-based chemicals of the 21st century.[1-5,18] That said, this milestone is accompanied by proper selection of appropriate biomass resources considering useful sugar contents, high biomass output per land area, and sustainable agricultural management.[66,70,76,79] Above all, the need for investigating the environmental impacts from a life cycle perspective – which includes land utilization – is imperative to determine the environmental sustainability of bio-based chemicals.

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References

1 D. Esposito, M. Antonietti, *Chemical Society Reviews*, 2015, **44**, 5821.

2 R.A. Sheldon, *Catalysis Today*, 2011, **167**, 3.
3 R.A. Sheldon, *Green Chemistry*, 2014, **16**, 950.
4 P. Gallezot, *Chemical Society Reviews*, 2014, **41**, 1538.
5 S.T. Yang, H.A. El-Enshasy, N. Thongchul, *Bioprocessing Technologies: Biorefinery for Sustainable Production of Fuels, Chemicals and Polymers*, Wiley, Hoboken, 2013.
6 M.L.G. Renó, E.E.S. Lora, O.J., Venturini, J.C.E. Palacio, *20th International Congress of Mechanical Engineering*, Brazil, 2009.
7 B. Gabrielle, N. Gagnaire, *Biomass and Bioenergy*, 2008, **32**, 431.
8 H.H. Khoo, *Sustainable Renewable Energy Reviews*, 2015, **46**, 100.
9 M.A. Abdel-Rahman, Y. Tashiro, K. Sonomoto, *Journal of Biotechnology*, 2011, **4**, 156.
10 F. Moradi, H. Amiri, S. Soleimanian-Zad, M.R. Ehsani, K. Karimi, *Fuel*, 2013, **112**, 8.
11 R. Lal, *Environment International*, 2005, **31**, 575.
12 H. Kahr, J. Wimberger, D. Schürz, A. Jäger, *Energy Procedia*, 2013, **40**, 146.
13 F. Cherubini, *Energy Conversion and Management*, 2010, **51**, 1412.
14 N. Sarkar, S.K. Ghosh, S. Barnnerjee,, A. Aikat, *Renewable Energy*, 2012, **37**, 19.
15 F.M. Girio, C. Fonseca, F. Carvalheiro, C.L. Duarte, S. Marques, R. Bogel-qukasik, *Bioresource Technology*, 2010, **101**, 4775.
16 K. Karimi, S. Kheradmandinia, M.J. Taherzadeh, *Biomass and Bioenergy*, 2006, **30**, 247.
17 R. Kumar, C.E. Wyman, *Biotechnology Progress*, 2009, **25**, 302.
18 J.A. Malero, J. Iglesias, A. Garcia, *Energy and Environmental Science*, 2012, **5**, 7393.
19 C. Jiménez-González, D.J.C. Constable, C.S. Ponder, *Chemical Society Reviews*, 2012, **41**, 1485.
20 M.P. Tucker, K.H. Kim, M.M. Newman, Q.A. Nguyen, *Applied Biochemistry and Biotechnology*, 2003, **105**, 165.
21 R. Singh, A.J. Varma, R. Seeta-Laxman, M. Rao, *Bioresource Technology*, 2009, **100**, 6679.
22 S. Cao, G.M. Aita, *Bioresource Technology*, 2013, **131**, 357.
23 Z. Lin, H. Huang, H. Zhang, L. Zhang, L. Yan, J. Chen, *Applied Biochemistry and Biotechnology*, 2010, **162**, 1872.
24 V. Menon, M. Rao, Progress in Energy and Combustion Science, 2012, **38**, 522.
25 B. Girisuta, L.P.B.M. Janssen, H.J. Heeres, *Green Chemistry*, 2006, **8**, 701.
26 T. Hasunuma, F. Okazaki, N. Okai, K.Y. Hara, J. Ishii, A. Kondo, *Bioresource Technology*, 2013, **135**, 513.'
27 C.N. Hamelinck, A.C. Faaij, *Journal of Power Sources*, 2002, **1**, 1.
28 Y. Zhang, J. Xiao, L. Shen, *Industrial & Engineering Chemistry Research*, 2009, **48**, 5351.
29 J. Wang, J. Chang, X. Yin, Y. Fu, *Journal of Fuel Chemistry and Technology*, 2005, **33**, 58.
30 J. Xiao, L. Shen, Y. Zhang, J. Gu, *Industrial & Engineering Chemistry Research*, 2009, **48**, 9999.
31 C.G. Yoo, M. Kuo, T.H. Kim, *Process Biochemistry*, 2012, **47**, 319.
32 D.A. Alonso, S.G. Wettstein, M.A. Mellmer, E.I. Gurbuz, J.A. Dumesic, *Energy and Environmental Science*, 2013, **6**, 76.
33 M. Niu, Y. Hou, S. Ren, W. Wu, K.N. Marsh, *Green Chemistry*, 2015, **17**, 453.
34 F. Cherubini, A.H. Strómman, *Bioresource Technology*, 2011, **102**, 437.
35 H.H. Khoo, V. Isoni, L.L. Wong, J. Tan, P.N. Sharratt. *Resources, Conservation, Recycling*, 2015, **95**, 174.
36 D.S. Powlson, A.B. Riche, I. Shield, *Annals of Applied Biology*, 2005, 146, 193.
37 I.D.C. Macedo, J.E.A. Seabra, J.E.A.R. Silva, *Biomass and Bioenergy*, 2008, **32**, 582.
38 R. Rathmann, A. Szklo, R. Schaeffer, R. *Renewable Energy, 2010,* **35,** 14.
39 D. Khatiwada, J. Seabra, S. Silveira, A. Walter, *Energy Policy*, 2012, **47**, 384.
40 L. Reijnders, *Energy Policy*, 2006, **34**, 863.
41 B.R. Bakshi, Current Opinion in Chemical Engineering, 2011, **1**, 64.
42 R. Hatti-Kaul, U. Törnvall, L. Gustafsson, P. Börjesson, P. *Trends in Biotechnology*, 2007, **25**, 119.
43 E.T.H Vink, K.R. Rábago, D.A. Glassner, P.R. Gruber, *Polymer Degradation and Stability*, 2003, **80**, 403–419.
44 R.A. Urban, B.R. Bakshi, *Industrial & Engineering Chemistry Research*, 2009, **48**, 8068.
45 C. Jiménez-González, A.D. Curzons, D.J.C. Constable, V.L. Cunningham, *Clean Technologies and Environmental Policy*, 2005, **7**, 42.
46 D. Kralisch, D. Ott, D. Gericke, *Green Chemistry*, 2015, **17**, 123.
47 M.A. Renouf, M.K Wegener, *Prod. Aus. Soc. Sugarcane Tech.*, 2007.
48 Papong, P. Malakul, *Bioresource Technology*, 2010, **101**, 112.
49 J. Hong, *Bioresource Technology*, 2012, **113**, 3.
50 R.K. Henderson, C. Jiménez-González, C. Preston, D.J.C. Constable, J.M. Woodley, *Industrial Biotechnology*, 2008, **4**, 180.
51 T.A. Hottle, M.M. Bilec, A.E. Landis, *Polymer Degradation and Stability*, 2013, **98**, 1898.
52 J. Hong, Y. Zhang, X. Xu, X. Li, *Biomass and Bioenergy*, 2014, **67**, 304.
53 J. Schrader, M. Schilling, D. Holtmann, D. Sell, M.V. Filho, A. Marx, J.A. Vorholt, *Trends in Biotechnology*, 2009, **27**, 107.
54 W. Supronowicz, I.A. Ignatyev, G. Lolli, A. Wolf, L. Zhao, L. Mleczko, *Green Chemistry*, 2015, **17**, 2904.
55 L. Jiménez, J.C. García, I. Pérez, J.L. Ferrer, A. Chic, *Bioresource Technology*, 2001, **79**, 23.
56 H. Liu, B.M. Gibbs, *Fuel*, 2003, 82, 1591.
57 C.M.D. Montaño, *4th International Bioenergy Conference and Exhibition*, Finland, 2009.

58 D.J. Hayes, S. Fitzpatrick, M.H.B. Hayes, J.R.H. Ross, *Biorefineries - Industrial Processes and Products: Status Quo and Future Directions*, 2006, Chapter 7, Wiley-VCH Verlag GmbH & Co. KGaA.
59 NREL (National Renewable Energy Laboratory), *US Life cycle inventory database*, www.nrel.gov/lci
60 EcoInvent, *Life cycle database*, Zurich, Switzerland, www.ecoinvnt.org
61 G. Geisler, T. Hofstetter, K. Hungerbühler, *International Journal of Life Cycle Assessment*, 2003, **9**, 101.
62 H.M.G. van der Werf, J. Petit, *Agriculture, Ecosystems & Environment*, 2002, **93**, 1.
63 C.S. Snyder, T.W. Bruulsema, T.L. Jensen, P.E. Fixen, *Agriculture, Ecosystems & Environment*, 2009, **133**, 247.
64 S. Ahmad, C. Li, G. Dai, M. Zhan, J. Wang, S. Pan, C. Cao, *Soil & Tillage Research*, 2009; **106**, 54.
65 X. Yan, T. Ohara, H. Akimoto, Z. Cai, *Journal of Geophysical Research*, 2003, **108**, 4505.
66 E.B de Figuiredo, N. La Scala Jr., *Agriculture Ecosystem Environment*, 2011, **141**, 77.
67 S. Kim, B.E. Dale, R. Jenkins, *International Journal of Life Cycle Assessment*, 2009, **14**, 160.
68 D. Tilman, K.G. Cassman, P.A. Matson, R. Naylor, S. Polasky, *Nature*, 2002, **418**, 671.
69 K.R. Brye, J.M. Norman, L.G. Bundy, S.T. Gower, *Journal of Environmental Quality*, 2001, **30**, 58.
70 A. Emissions, *Journal of Environmental Quality*, 2008, **37**, 515.
71 C. Gao, B. Sun, T.L. Zhang, *Pedosphere*, 2006, **16**, 253.
72 L. Xie, M. Liu, B. Ni, X. Zhang, Y. Wang, *Chemical Engineering Journal*, 2011, 167, 342.
73 T.P Tuong, S.I. Bhuiyan, *Agricultural Water Management*, 1999, 40, 117.
74 S.J. Zwart, W.G.M. Bastiaanssen, *Agricultural Water Management,* 2004, 69, 115.
75 S. Liang, M. Xu, T. Zhang, *Bioresource Technology*, 2012, **125**, 312.
76 F. Below, J. Haegele, *Department of Crop Sciences, University of Illinois at Urbana-Champaign, Springfield, Illinois*, 2013.
77 S. Bringezu, M. O'Brien, H. Schütz, *Land Use Policy*, 2012, **29**, 224.
78 H.Y. Kwon , S. Mueller, J.B. Dunn, M.M. Wander, *Biomass and Bioenergy*, 2013, **55**, 299.
79 R. Schubert, *World in Transition: Future Bioenergy and Sustainable Land Use,* Earthscan, London, UK, 2010.
80 G. Sparovek, A. Barretto, G. Berndes, S. Martins , R. Maule, *Mitigation and Adaptation Strategies for Global Change*, 2009, **14**, 285.
81 X.P. Song, C. Huang, S.S. Saatchi, M.C. Hansen, J.R. Townshend, *PLoS One*, 2015, **10**, DOI: 10.1371/journal.pone.0126754
82 K.G. Harding, J.S. Dennis, H. von Blottnitz, S.T.L. Harrison, *Journal of Biotechnology*, 2007, **130**, 57.
83 M. Gallardo, *Industrial Ecology, Dept. Energy Process Engr., Norwegian University of Science and Technology (NTNU), Norway*, 2011.
84 S. Spatari, Y. Zhang, H.L. Maclean, *Environmental Science and Technology*, 2005, **39**, 9750.
85 Y.H. Chan, S. Yusup, A.T. Quitain, R.R. Tan, M. Sasaki, H.L. Lam, Y. Uemura, *Energy Conversion and Management*, 2015, in print.
86 T. Searchinger, R. Heimlich, R.A. Houghton, F. Dong, A. Elobeid, J. Fabiosa, S. Tokgoz, D. Hayes, T.H. Yu, *Science*, 2008, **319**, 1238.
87 K. Hergoualc'h, L.V. Verchot, *Mitigation and Adaptation Strategies for Global Change*, 2014, **19**, 789.
88 L. Marelli, F. Ramos, R. Hiederer, R. Koeble, Joint Research Centre, Institute for Energy, Renewable Energy Unit, European Commission, Report no. EUR 24817 EN, 2011.
89 H.Y. Kwon , S. Mueller, J.B. Dunn, M.M. Wander, *Biomass and Bioenergy*, 2013, **55**, 299.
90 J.P.M. Sanders, J.H. Clark, G.J. Harmsen, H.J. Heeres, J.J. Heijnen, S.R.A. Kersten, W.P.M van Swaaij, J.A. Moulijn, *Chemical Engineering and Processing*, 2012, **51**, 117.