This is an *Accepted Manuscript*, which has been through the Royal Society of Chemistry peer review process and has been accepted for publication.

Accepted Manuscripts are published online shortly after acceptance, before technical editing, formatting and proof reading. Using this free service, authors can make their results available to the community, in citable form, before we publish the edited article. We will replace this *Accepted Manuscript* with the edited and formatted *Advance Article* as soon as it is available.

You can find more information about *Accepted Manuscripts* in the **Information for Authors**.

Journal Name

ARTICLE

Butadiene from biomass, a life cycle perspective to address sustainability in the chemical industry

D. Cespi,[a] F. Passarini,[a,b] I. Vassura[a,b] and F. Cavani[a,b]

In the past decades, innovative approaches such as the Green Chemistry and Green Engineering came out in order to set the basic principles of more sustainable chemical industry. However, researchers need also a more scientific and quantitative tool to address the sustainability behind the application of those principles. Therefore, a multi-criteria approach based on life cycle thinking was proposed to investigate the production of 1,3-butadiene. Five indicators were selected to address sustainability: the Cumulative Energy Demand, the carbon footprint, the water depletion, a midpoint-oriented analysis method and an economic index. The use of renewable feedstock was evaluated in comparison with the traditional fossil-based route from naphtha. Two alternative pathways which use bio-ethanol were considered -the Lebedev and Ostromisslensky processes- evaluating the possibility to locate the plant in three different regions (EU, Brazil and US). Detailed analysis reveals how the use of bio-based feedstock leads to a significant lower consumption of fossil sources, despite of a higher exploitation of renewables resources which leads to a larger water withdrawals. Moreover, the assessment of global warming potential reveals how bio-routes are far to be considered carbon-neutral. In addition, ReCiPe single-score was used showing higher sustainability of the Lebedev process if compared with the traditional way. On the other hand, the two-step pathways (Ostromisslensky) result in worst scores. Economic evaluation was also applied. The index reveals how the direct conversion into 1,3-butadiene seems more suitable than the two-step, in particular in the case of US production.
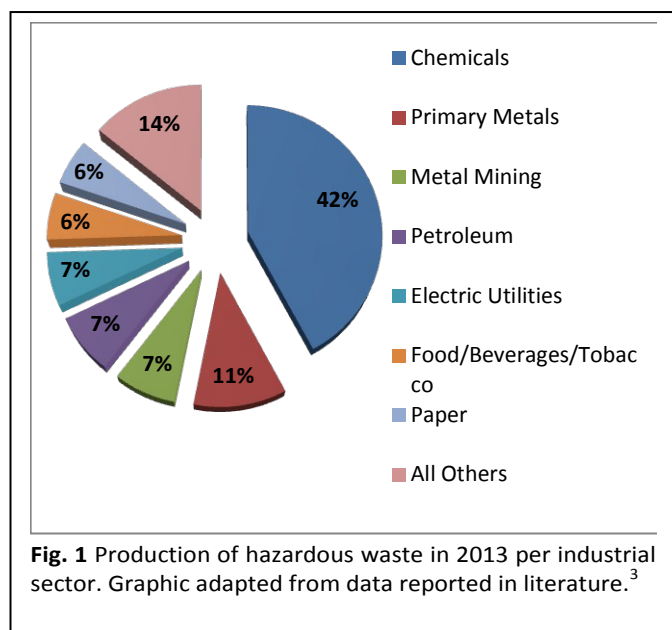
Introduction

A sustainable industry development is one of the main purpose of our society in order not to "compromise the ability of future generations to meet their own needs".[1] However, reaching this target seems to be far from easy in spite of all the efforts done by the community. Indeed, the US Energy Information Administration (EIA) evaluated that the industrial sector reached in 2010 a world energy consumption around 200 quadrillion Btu and it is expected to grow up to 307 quadrillion Btu in 2040 with an estimated average annual growth of 1.8% for the Non-OECD (Organisation for Economic Co-operation and Development) countries. Moreover, the production of chemicals (including feedstock) represents the major energy-intensive industry with a consumption around $4.2 \cdot 10^{10}$ GJ in 2010, almost the 20% of the total energy usage by the year.[2] Therefore, these numbers suggest that in order to reach targets promoted by sustainable development, Chemical Industry (CI), as well as the other energy-intensive sectors (e.g. iron and steel productions), needs to be re-thought in a more
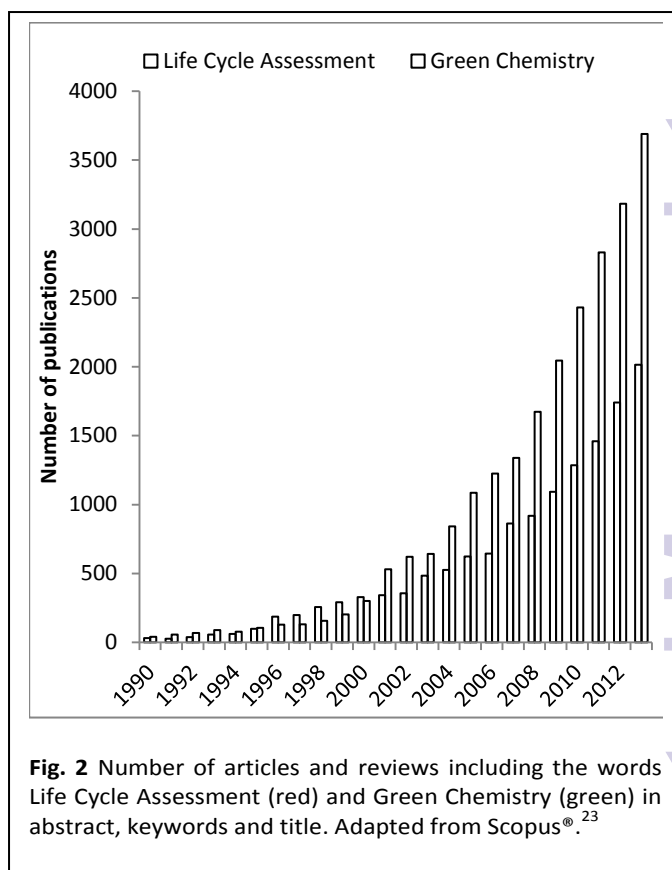
sustainable way. Furthermore, in addition to the resources depletion and the emissions of greenhouse gases associated with the energy consumption, CI is also characterised by the usage and the release of toxic substances, with clear repercussions on the waste streams. In 2013, chemical enterprises were responsible of the 42% of hazardous wastes released by the industrial sector in the United States (**Figure 1**).[3] For this reason during the past decades a new approach came out in chemistry and engineering, releasing the fundamental principles which constitute the basis of a more sustainable society. Green Chemistry (GC) and Green Engineering (GE) are considered as a new paradigm to drive future innovations in these fields. It is almost 20 years since GC principles were first released[4] and barely fifteen from the first GE definition reported in ACS (American Chemical Society) symposium book;[5] in this period, they spread all over the world thanks also to the efforts of several "Green Founders & Pioneers". In particular, the community's sensibility toward GC themes increased exponentially during the last years becoming the major topics of different subjects such as scientific journals,[6,7] book series,[8,9] centers and institutions,[10,11,12] international conferences and symposiums.[13,14,15]

[a.] Department of Industrial Chemistry "Toso Montanari", Bologna University, Viale del Risorgimento 4, 40136 Bologna (BO), Italy.
[b.] Centro Interdipardimentale di Ricerca Industriale - Energia e Ambiente, Via Angherà 22, 47900 Rimini (RN), Italy.

Fig. 1 Production of hazardous waste in 2013 per industrial sector. Graphic adapted from data reported in literature.[3]

However, the qualitative approaches suggested by GC and GE principles should be verified by researchers in order to assess their sustainability case by case. Therefore, several tools were developed by academia and industry. Among these, the *E-factor*[16,17] represents an easy and understandable way to address the environmental load associated with the industrial production. Together with Chemical Yield, Atom Economy and Process Mass Intensity, it belongs to the category called *green chemistry process metrics* and it is defined as the ratio between the amount of waste and the quantity of desired product.[18] The expression was developed in order to take into account all the substances involved in the synthesis such as reagents, solvents (including losses), auxiliaries and fuels. However, although the quantity of inorganic and organic substances in the waste streams are included in the calculation, the amount of water is voluntarily excluded, in order to avoid higher E-factor values and make the comparison easier.[19] However, this is not an absolute rule, e.g. in the pharmaceutical industry the use of a *complete* E-factor can be helpful, which includes water usages.[18] Although these benefits, some aspects in the use of E-factor have been questioned: i) the need of a clear definition concerning what is considered or not as a waste; ii) as suggested by Tufvesson et al.,[20] as the other green metrics (e.g. mass intensity), it does not make distinction between the different types of waste produced; iii) furthermore, it takes into account one environmental load, the production of waste, without providing other information regarding the potential effects associated with the use and the release of certain substances in the environment. Therefore, it seems necessary to use a dedicated software able to associate potential environmental burdens to each input and output of a chemical process. Among these, *EATOS* (*Environmental Assessment Tool for Organic Syntheses*),[21] released by Marco Eissen (Swiss Federal Institute of Technology Zürich - ETH) and Jürgen O. Metzger (Carl von Ossietzky Universität Oldenburg), deserves to be mentioned. Differently from the other green chemistry metrics, it evaluates the sustainability of a substance by comparing alternative synthesis routes on a laboratory scale. In fact, through mass balances, researchers identify all the reagents and auxiliaries involved in the processes as well as the recovery and waste streams, thus the software is able to express each environmental load in terms of several impact categories such as human toxicity, ecotoxicity, air pollution, resources claiming, etc. Moreover, it provides the function to

Fig. 2 Number of articles and reviews including the words Life Cycle Assessment (red) and Green Chemistry (green) in abstract, keywords and title. Adapted from Scopus®.[23]

estimate the E-factor value for each route. Although EATOS has many valid functions that can help in a screening analysis, it has been listed among other "simple models"[20] because of the restriction of its database (around 60 chemicals) and its limitation to the organic syntheses only. Furthermore, green metrics and tools such as EATOS are presently not standardised. In fact, in order to have a crucial effect on the community it is necessary to point the attention on the application of a standardised methodology well recognised internationally, which can be applied both to organic and inorganic chemistry as well as to the more innovative fields such as bio-based and nanomaterials. Given these motivations, the LCA (Life Cycle Assessment) represents a thorough methodology to address the environmental sustainability in the CI.

Moreover, as a confirmation of the relevance of such themes, starting from the 90s the interest of the scientific community toward both GC and LCA grew exponentially (**Figure 2**). As depicted, the increasing trend is almost the same even though since 2001 an inversion occurred, showing the greater importance of GC as a discipline able to drive and perform sustainability.

In particular, the use of bio-based feedstock, as suggested by 7th principle of Green Chemistry,[4] represents one of the most important scope of a green approach applied to the CI. Studies on this theme seem to be driven by several aspects. First, the possibility of a greenhouse gases reduction (strictly related with agricultural practices) and the replacement of non-renewable feedstock are the main drivers.[22] However, the improvement of the public confidence in the chemical industry thanks to the use of bio-products, the preservation of its competitiveness on a global market economy, also through new opportunities for these kind of materials, together with lesser legislative constraints (no REACH registration) are well recognised to be other possible reasons.[22]

Therefore, the aim of this manuscript is to assess potentialities of the renewable feedstock applications in order to develop a new

concept of a chemical industry based on GC principles. Thus, LCA methodology was used to analyse in depth the production from biomass of one of the major world chemical commodity, 1,3-butadiene (BD), focusing the attention on the main aspects that should be taken into account when a bio-based pathway is under study, such as: renewable and non-renewable resources consumption, energy requirements, CO_2 emissions and the damage categories affected by potential impacts.

Background

As outlined above BD is one of the major commodity on international scale with a forecast production around 12Mt in 2015, mainly settled in Asia which increased its productivity of almost 56% since 2008 (compared to an average world increase of 32%). [24] On the other hand, developed countries (such as Europe and US) have more conservative and stable market both in terms of manufacture and consumption. BD production trends are depicted in **Figure 3**. As well known, it plays a crucial role as a key chemical in the production of rubbers (53%), leading the market of vehicles tires, and copolymers (24%) globally. [24] Nowadays it is mainly produced by naphtha cracking, together with further co-products such as: ethylene, propylene, methane, hydrogen, light fuel oil and other commodities. Thermal cracking represents the most diffused technology worldwide. First developed in 1960s, it is essentially a high temperature pyrolysis (750-875°C) which occurs in the presence of steam. [25] Although both oil and natural gas derived feedstocks can be used, naphtha still represents the large raw material used on international scale (55%) followed by ethane (30%). [25,26]

Although thermal cracking is the largest widespread and consolidated technology to produce BD, it is also considered the most stressful process of the chemical industry both in terms of energetic and environmental burdens, with a consumption of 8% of the total primary energy and the release of 180-200 million tons of CO_2 worldwide approximately. [26] In addition, concerns regarding fossil reserves lead CI to necessary reconsiderations, turning to a bio-based supply chain in line with GC suggestion on the use of renewable rather than finite resources. In particular, industrial and scientific communities started to look at the possible exploitation of bio-ethanol as a renewable feedstock. [27,28,29,30] Indeed, it is considered one of the most promising molecular platform of the chemical industry for three main reasons: i) build-up of knowledge on production and conversion, ii) possibility of industrial scale-up and iii) existence of commercial bio-based processes. [31] In addition, its exploitation as a starting raw material, instead of as a fuel, seems the better way to valorise it from an economical and environmental point of view: possible greenhouse gases (GHG) reduction. [27]
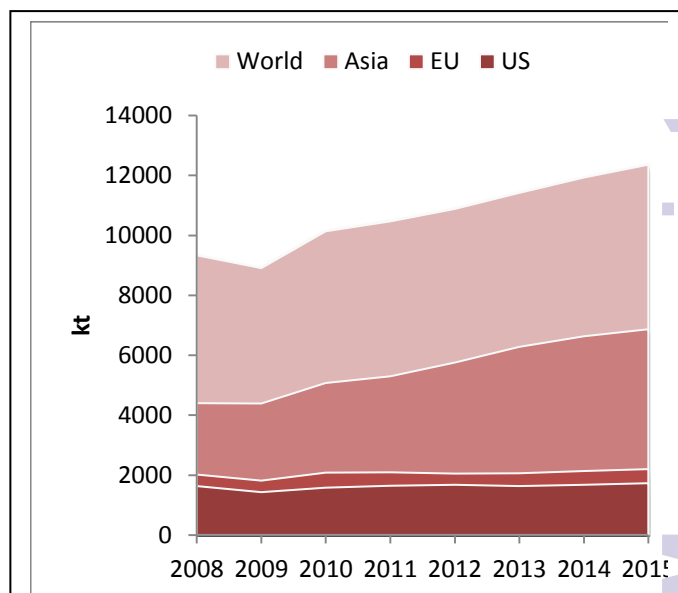

Fig. 3 1,3-butadiene production. Data source Nexant. [24]

Furthermore, another crucial aspect is its abundance: 2013 World ethanol production was estimated around 105 billion of liters and it is expected to grow up to $158 \cdot 10^9$ L by 2023 (**Figure 4**, dashed fill). [32] 2012 ethanol production distribution [33] reflects projections of 2023: US and Brazil will have a leader position on the market leaving to Europe and Asia the rest (**Table 1**). Moreover, values also reveal a strong correlation between producer and consumer countries, maybe as a cause of the main ethanol use: automotive fuel. However, its alternative usage as a potential carbon source to build chemicals is an open debate in scientific literature. In particular, although results achieved for several commodities (e.g. ethylene, ethyl acetate, acetaldehyde and ethylene oxide) do not present any particular advantages if compared with traditional fossil route, its application on the BD supply chain seems favourable in terms of i) lower environmental and cost performance indexes and ii) possible

Country	Production	Consumption
United States	45%	48%
Brazil	31%	25%
European Union	8%	9%
China	5%	6%
India	2%	2%
Thailand	1%	1%
Other	8%	9%

Tab. 1 Forecast production and consumption distribution of ethanol at 2023. Data source OECD-FAO. [32]
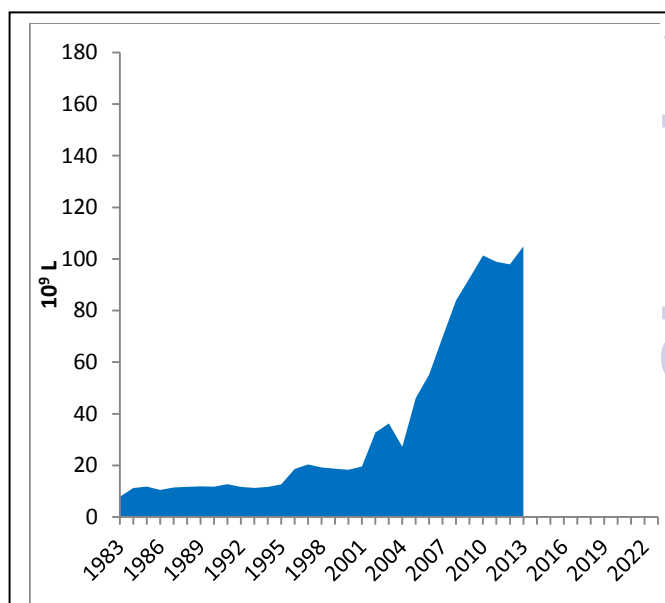
Fig. 4 World ethanol production outlook. Data source OECD-FAO. [32]

ARTICLE

Journal Name

reduction of 50% in greenhouse gases emissions.[29] The possibility to obtain small quantities of BD (1.5% yield) from low alcohol was first demonstrated by the Russian researcher Vladimir Nikolayevich Ipatiev in 1903 by passing ethanol over aluminium powder.[34] Twelve years after, Iwan I. Ostromisslensky discovered that larger amounts of BD were obtained using a mixture of ethanol and acetaldehyde in a two-steps pathway.[35] The synthesis occurs through the partial alcohol dehydrogenation to acetaldehyde and their recombination to obtain BD with a 18% yield, over alumina catalyst at 440-460°C. [35,36,37] Later in the 1930s, S.V. Lebedev proposed the direct ethanol conversion into BD using zinc oxide and alumina at 400°C.[38,39,40] Both pathways are represented in **Figure 5**. Although substantial improvements achieved in terms of yield (up to 70%),[41] only Russia undertook the industrialization of the Lebedev process (Sinteticheskii Kauchuk); on the contrary the Union Carbide and Carbon Chemicals Corporation preferred the two-steps or so-called Ostromisslensky process over tantalum oxide on silica.[36] Even though ethanol based routes represent the first process developed to synthesize BD on a large scale, the lower oil price together with the growth of ethylene production facilitated their replacement with the more consolidated cracking technology since 1970s.[36] However, BD price is expected to grow in the near future as a consequence of the abundance contraction on the market, due to the replacement of naphtha with ethane as feedstock in the cracking.‡ Therefore, new scenarios are going to be delineated and a return to ethanol based routes represents an already consolidated alternative.[36,37,42] In addition to the ethanol-based routes, other pathways were recently developed. Among these, the hydrogenation of succinic acid to 1,4-butanediol, followed by its conversion into BD, and the direct sugar fermentation deserve to be mentioned. Furthermore, preliminary economic analysis has shown that direct conversion of glucose seems to be the more attractive route.[24] However, all the uncertainties due to the early development stage make this solution still not competitive on industrial scale, especially if compared with Lebedev and Ostromisslensky processes, which seem the more suitable pathways in all the regions except Asia (e.g. Europe, North and South America).[24]

Methodology

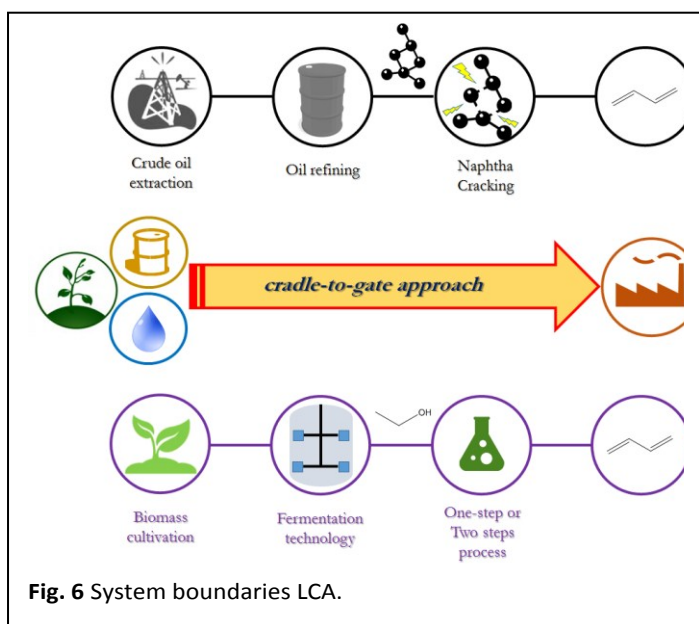The purpose of this manuscript is not to illustrate what LCA is,
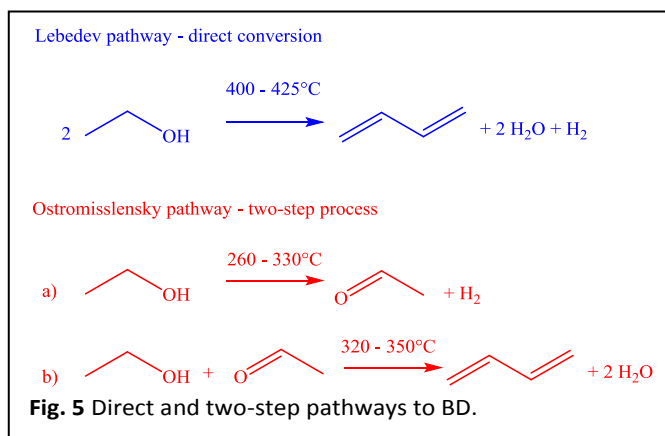

Fig. 6 System boundaries LCA.

Fig. 5 Direct and two-step pathways to BD.

indeed, literature already contains several educational methodology descriptions to understand well how it works.[20,43,44,45] However, since its application as a screening and assessment tool for the bio-based chemical industry is increasing,[46,47,48,49,50,51,52,53] due to the importance given by the international community to this sector, we propose a double aim. First, to provide a list of well recognised indicators to investigate this branch; then, to verify the feasibility of an industrial BD production from renewable feedstock. In fact, the usage of bio-ethanol as a chemical source in the BD synthesis was already investigated in literature showing potential benefits at early-stage. [29,42,54] In particular, it was evaluated how future developments in the biomass route could lead to a favourable "sustainability index ratio" (lower than 1) which suggests potential benefits of the renewable synthesis compared with the more traditional naphtha cracking.[42] Therefore, a more comprehensive analysis based on the use of LCA software (SimaPro)[55] and Ecoinvent database,[56] together with selected indicators of sustainability, seems necessary to investigate the bio-based routes to BD on an industrial scale. A *cradle-to-gate* approach was identified covering all the stages involved in the BD production chain: from raw materials extraction up to the industrial synthesis of product (industry gate), including all the need in terms of resources, auxiliaries and energies. BD utilization as building block was intentionally not included, due to the wide range of its exploitation on the market. A more comprehensive representation of LCA boundaries of both traditional and alternative routes is depicted in **Figure 6**. One ton of BD was selected as functional unit in order to build each model. Three different scenarios were created in order to simulate the fossil-based pathway and the renewable routes to BD. Below and in the supplementary information section a detailed description of each model is reported.

Allocation

Before starting the Life Cycle Inventory (LCI) description, the concept of allocation should be introduced. As depicted in the following parts, BD synthesis is far to be considered as a single output process, but better a multipurpose pathway which produces several co-products at the same time. Therefore, treating a multi-output process through LCA needs further considerations in order not to make mistakes. There are two possibilities. First, as suggested by literature,[57] a system boundaries expansion could be carry out to the co-products. However, this solution is not always easy due to large amount of time and energies needed to create new processes. Moreover, sometimes, the expansion constraints to introduce the concept of "avoided product or process", which is often ambiguous and can create misunderstandings. Therefore, in

these cases, apply the allocation criteria seems helpful. Allocation is introduced in order to allocate input, output and impacts to the target product only (in our case BD). Two different types of allocation are ordinarily used: physical or economic. In this study, a mass allocation based on BD and co-products mass yields was applied to each scenario. Given the allocation factors, SimaPro software[55] is able to complete this procedure automatically. Therefore, in order to make the inventory recreation process easier, in line with the target of sharing new databases, no allocated data were reported in the LCI listed in the text (manuscript and supplementary information). Allocation values to be applied are listed separated in the supplementary information (**Table S1-2-3**).

Traditional route to BD

Detailed flows analysis of the cracker processes were already carried out by Ren et al. [26] All the inputs and outputs of an average ethane and naphtha based technologies were evaluated, describing systems in terms of: raw materials, main products, energy requirements, losses and CO_2 emissions. As already discussed above, naphtha still represents the main feedstock in thermal cracking all over the world.[25,26] Therefore, naphtha based appliances was selected in order to simulate conventional BD synthesis. All the upstream stages which leads to naphtha, i.e. oil extraction and refining, were included in system boundaries using Ecoinvent database (v3.1)[56] to carry out the simulation. As well depicted in literature,[26] steam cracking plant can be usually divided into three sections. First, the pyrolysis chamber, in which naphtha after has been preheated at 650°C and then vaporised is cracked at 790-1100°C. Then is quenched at 550-650°C and a heat recovery occurs. After leaving the furnace the hot gas mixture is sent to the primary fractionation/compression where the fuel oil and BTX (benzene, toluene and xylene) are fractionated meanwhile the gas fraction is quenched and cleaned up from impurities (e.g. CO_2, acid gases and water). Finally, the mixture is sent to the last section in which different products are separated and recovered through distillation and extraction. First, C_2 compounds are recovered followed by C_3. Ethane and propane are recycled as feedstock, while ethylene, propylene, butadiene, other C_4 compounds and aromatics are recovered. Methane and hydrogen -after cryogenic separation- are used as pyrolysis fuels. As suggested by literature,[26] overall BD yield do not exceed 4.5% (wt%) making it evident that it is not the major cracking product if compared with ethylene (31.5%) or propylene (14.5%). Therefore, given the data about process efficiency reported above, an input of 22.2t of naphtha per t of BD results necessary. Moreover, basing on the value calculated by Ren et al.,[26] an average energy usage (given by the sum of energy loss and theoretical thermodynamic energy requirement) and CO_2 emission (released from fuel combustion and utilities usage) of 199.5GJ and a of 13.3t were evaluated respectively. A fully description of the LCI for the naphtha cracking route is reported in supplementary information section (**Table S1**).

Bio-based routes to BD

Lebedev process
As already outlined, since its first development in 1928 Lebedev pathway was subjected to continuous yield improvements from 21% up to 40% in 1940s.[24] Nowadays, a BD molar yield around 72% is reached with an ethanol conversion almost complete (99.8%).[58] Industrial process usually takes place in two stages, involving first the dehydration and catalytic dehydrogenation to BD, carried out in a fixed bed technology at 400-650°C after ethanol preheated,

followed by separation, purification and recovery procedures such as distillation, absorbers and wash columns.[24] Mixed oxide catalysts are generally used in a fixed pack. Process specifications already reported were evaluated by BASF SE using a multicomponent system composed by Hf:M1:M2 in a preferred range 1:(0.5-2.5):(0.3-1.5), where M1 and M2, represent active metals among the group Zr, Zn, Cu.[58] Due to the rediscovered interest of industries in direct ethanol conversion, also the scientific community started new projects with the aim of understanding well the reaction mechanism behind the catalytic process. One was recently published in literature,[30] in which it was shown that the true mechanism does not include the classical aldol condensation between two molecules of the intermediately formed acetaldehyde, but a direct reaction between acetaldehyde and an activated form of ethanol. Nevertheless, due to corporate confidentiality, no information about catalyst consumption and regeneration was introduced in the model. However, as already discussed in literature this seems not to influence overall results in a significant amount.[52,59] As for the naphtha cracking, direct ethanol conversion to BD implies a variety of multi-outputs such as acetaldehyde, methane (10-17% selectivity respectively) and a small amount of diethyl ether (around 1%).[58] Therefore, also in this case mass allocation was applied. No information regarding recovery performance was available. Therefore, we assumed that unreacted ethanol is burned realising CO_2. Data concerning energy and utilities consumptions were taken from Process Economics and Research Planning (PERP) report[24] and re-calculated normalizing on the functional unit. A more comprehensive list of the LCI is shown in supporting information section (**Table S2**).

Ostromisslensky process

The two-step pathway to BD takes place in distinct fixed bed reactors. After ethanol preheating, reaction flow is sent to the first catalytic bed in which conversion into acetaldehyde occurs at 260-330°C.[24] After a first recovery section, acetaldehyde and ethanol vapors are send to the second tubular reactor. Here BD synthesis is completed at 320-350°C.[24] Thereafter, several purification procedures take place in order to obtain product specifics and resource recovery. Daicel Corporation proposed a 56.5% BD yield with an ethanol conversion far from completeness (63.5%), using a mixed oxide metal system over silica (Ta_2O_5/MgO) and a mixed inlet flow composed by ethanol:acetaldehyde:H_2 (0.21:0.09:0.7).[60] In addition to the input evaluated by mass balance, a further ethanol amount was considered in the model in order to simulate the production of acetaldehyde and part of H_2 required by inlet flow composition. Their amounts were evaluated according with stoichiometry (**Figure 5-a**), assuming a complete ethanol conversion. Hydrogen does not take part to the reaction, thus it is recirculated in order to maintain catalyst in a partial-reduced form and obtain higher yield than under normal condition (without acetaldehyde and H_2 co-alimentation).[60] As in the previous cases, the large variety of co-products includes: ethylene (7.3%), n-butane (4.1%), n-butanol (0.9%) and butyraldehyde (0.1%) making the allocation procedure necessary. Further substances are produced according with the label "other" reported on patent. However, due to their unknown nature and to their small amount, we decided to neglect them. Energy and utilities needs were evaluated through PERP report.[24] As above, an incineration of the unreacted raw materials (ethanol and acetaldehyde) was assumed. Detailed LCI for the two-step route is reported in supporting information section (**Table S3**).

Ethanol source

As depicted in **Figure 6**, cradle-to-gate system boundaries were considered in the study, in order to include each stage which occurs from raw materials extraction up to BD synthesis. Therefore, as already done for the traditional route, bio-ethanol production chain was included in the system boundaries. However, differently from the other, several scenarios were created in order to simulate alternative ethanol sources. As reported in the text and depicted in **Table 1**, the main ethanol world suppliers are: US, Brazil and Europe. Therefore, basing on information reported in literature,[32] three different production chains were considered, assuming 100% corn-based ethanol for US, 100% sugarcane-based for Brazil and an equal mix of corn/wheat/rye/sugar beet-based ethanol in the case of Europe. Ecoinvent database (v3.1)[56] was used to fill in the inventories in order to simulate the cultivation phase of different crops (e.g. corn, sugarcane, rye and sugar-beet) and their transformation into ethanol through an average fermentation technology in each country. However, wheat-based ethanol is not included in database. Therefore, in order to complete the EU ethanol chain inventory, a scenario to simulate the use of wheat as starting material was creates using data already proposed in the case of France by Muñoz et al.[61] Supporting information collects a detailed description of the LCI for the ethanol from wheat route (**Table S4**). For the inventories of the other crops-based ethanol routes, please refer to Ecoinvent database report No. 17.[62]

Sustainable indicators

As outlined in the introduction, our intention is to propose several indicators to assess sustainability of bio-based chemicals at industrial scale. Therefore, each of them is described below, explaining the reasons why their selection and use are suggested.

- *Cumulative Energy Demand –CED,* defined as "the entire demand, valued as primary energy, which arises in connection with the production, use and disposal of an economic good",[63] was used to assess environmental burdens of commodities since early 1970s.[64] It is considered a valuable screening indicator of the overall impact of products[65,66] thanks to its ability to express a wide range of environmental burdens.[54] Moreover, according to the literature,[64] it shows high correlation with several LCA analysis methodologies given that they provide comparable impacts. Therefore, its usage to address environmental footprint of several products, such as raw materials,[67] is often recommended. In this study, CED method (v 1.09)[68] was selected to perform the analysis expressing results in terms of *GJ eq.*

- *Carbon footprint*, evaluated through the method developed by IPCC (Intergovernmental Panel on Climate Change) considering a 20-year time horizon,[69] estimates the emissions of greenhouse gases all over the life cycle considered, expressing it in terms of *ton of CO_2 eq.* Therefore, differently from CED, which is considered a resource-oriented indicator, carbon footprint belongs to the category of "impact-related" indicators since it evaluates the potential impact of a product to climate change.[64] This evaluation looks necessary to verify one of the major drivers which promote the development of a bio-based industry: GHG reduction.

- *Water depletion* was selected in order to assess direct and indirect consumptions within the entire cradle-to-gate boundaries. Having an estimation of the potential amount of water embodied inside a bio-based chemical is fundamental to understand how efficient the process is, in terms of one of the major natural resources. ReCiPe

method (v.1.11)[70] at midpoint level was selected to have an estimation of the water depletion ($m^3/ton\ BD$) of each pathway.

- *Single score*, carrying out a comparison between the scenarios taking into account different impact categories, represents a wider perception of sustainability. LCA software usually contain several different analysis methods. Among these ReCiPe (v.1.11)[70] was selected, due to the fact it is one of the main used and thanks to its ability to aggregate several midpoint categories in terms of eco-indicator (point - Pt) to show which scenario achieves worst results. Considering the purpose of the present work, five impact categories were selected within seventeen in order to address environmental burdens in terms of climate change, particulate matter formation, fossil fuel depletion, agricultural land occupation and terrestrial eco-toxicity.

- *Economic Index - EI* usually express sustainability just in terms of environmental implications seems not enough and further considerations should be taken into account. Economy is an integral part of the three spheres which compose the concept of sustainable development (together with environmental and social issues).[7] However, economy is an extremely complex aspect, which involves several relations between the parts. A simple and preliminary evaluation is here introduced. EI represents the ratio between the product price (BD) and the cost of the synthesis (utilities plus raw materials) allocated to the desired product. Below the EI expression is depicted

$$EI = \frac{P_z}{\left(\sum_{i=1}^{x} p_x * q_x\right) * A_z}$$

Where P_z is the price of product z ($), p_x represents the price of input x (raw materials and utilities) per unit ($/unit), q_x is the unit of each input (e.g. kg, kWh, etc.) and A_z the mass allocation factor for the desired product.

Results and discussion

Figure 7 shows scores achieved by each scenario in terms of CED. As well known, this indicator is composed by different categories which represent the depletion of non-renewable (fossil, nuclear and biomass) and renewable (biomass, wind-solar-geothermal and water) resources expressed in the form of GJ eq. Indeed, as declared in literature[68] "the intrinsic value of each resource is determined by the amount of energy withdrawn from nature". There is no strictly recommended way to represent CED results. Therefore, in line with the aim of the manuscript and following the suggestion to combine these categories as required to satisfy the calculation needs,[68] we chose to split cumulative scores with the purpose of showing burdens on non-renewable (*a*) and renewable (*b*) resources. As one might expect, the large amount of fossil fuels involved in the naphtha cracking leads this scenario to achieve the worst results in terms of non-renewable resources depletion. Indeed, around 79% of the global CED value is related to the huge consumption of oil and derivatives (feedstock and energy) to obtain naphtha. The remaining part is attributable to the energy requirements to run the cracking process. On the other hand, negligible impacts are associated to the renewable resources depletion, because of their restricted amount consumed. A comprehensive tree diagram showing contribution of the traditional route to CED is depicted in **Figure S1** (supporting information section). On the contrary, consumption of renewable resources

associated to the unconventional routes to BD is mainly driven by biomasses exploitation to obtain ethanol. Indeed, both Lebedev and Ostromisslensky routes show the same trend and contribution if compared in terms of the same regional supplier (**Figure S2**). The contribution analysis is helpful when a multitude of crops are used as starting raw material, as in the case of Europe. In this way, LCA can be used as a screening tool to assess the environmental footprint of each culture. As described above, LCIs of the European ethanol production were built following OECD-FAO suggestions assuming a non-equal distribution between crops. Corn and rye are used in the same proportions (around 1/6 of the total), while sugar beet was assumed equal to wheat and they represent 2/3 of the overall amount. However, although the first two reveal almost the same contribution to the category, contribution of wheat cultivation to the biomass depletion results higher (32%) and so less sustainable than sugar beet (24%). On the other hand, when monoculture is used it looks evident how cultivation supply chain is the major responsible of the renewable resources depletion category (BR and US examples). Therefore, in conclusion, European production chains for bio-BD reach better results with a lower environmental stresses on renewables. On the other side, the

intensive practices to replace natural habitat with sugarcane crops (as assumed in Brazilian scenario) seem to generate stronger impoverishment in terms of natural resources. **Figure S3** exhibits the network complexity behind LCA model. In particular, this analysis was launched to evaluate the phase with the higher contribution on the depletion of renewable resources for the sugarcane-based route to BD. Thicker the arrow (in red), higher the contribution to the impact category. As depicted, the left side has thicker arrows and it corresponds with all the activities connected to sugarcane cultivation, underlying their lower sustainability.

Furthermore, although also water withdrawal seems to influence renewable resources category, its contribution is lesser than crops cultivation and it will be discussed in detail later in the text.

The selection of different ethanol supply chains seems to have also relevant effects on the non-renewable resources. Indeed, various crops imply different farming practices, which entail diversities in energy requirements. From this point of view, the choice of sugarcane seems to be the most favourable, followed by the European mix, whereas corn-based ethanol looks the worst. Main cause is the large amount of fossil fuels used within the overall corn cultivation and drying (**Figure S4**). Obviously, this trend is the same for both bio-based pathways. Looking carefully at **Figure S5** ethanol supply chain seems have a double contribution to the non-renewable category (two red flows). However, the thinner arrow points out the contribution due to the ethanol excess necessary to fill up the acetaldehyde and H_2 required in the inlet mixture.

Another aspect which was taken into account in the study is the cradle-to-gate carbon footprint. **Figure 8** shows the outcomes of this evaluation. As a result of the lower number of step and the lesser amount of energy needs, sugarcane-based Lebedev process seems to achieve a better score in terms of CO_2 eq. emissions and, if compared with the conventional route, it contributes to the GHG mitigation target. On the other hand, the remaining Lebedev routes (EU and US) are not competitive enough to consider them as a valuable key-factor to fight climate change (**Table S5**). Furthermore, two out of three among the Ostromisslensky scenarios release an amount of GHG double than the naphtha cracking technology. The
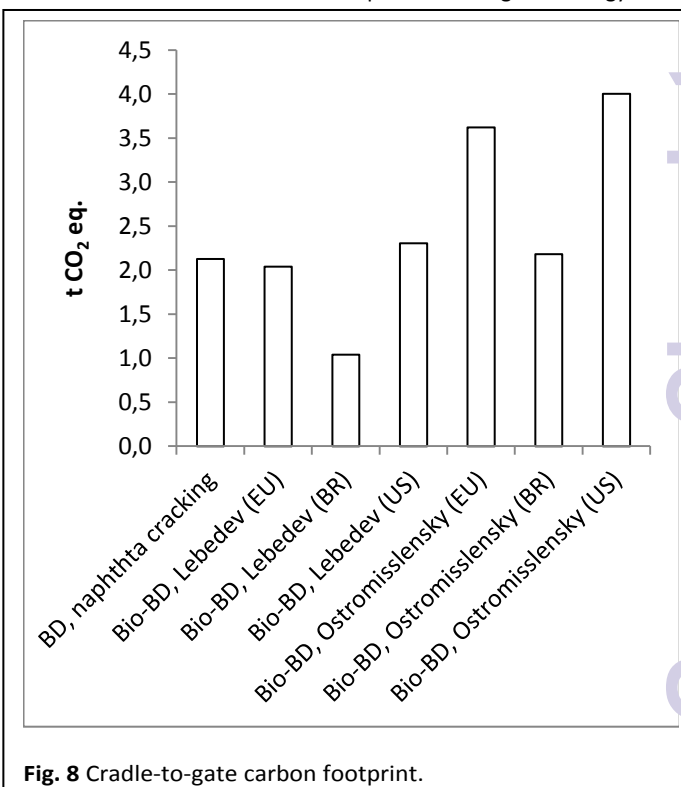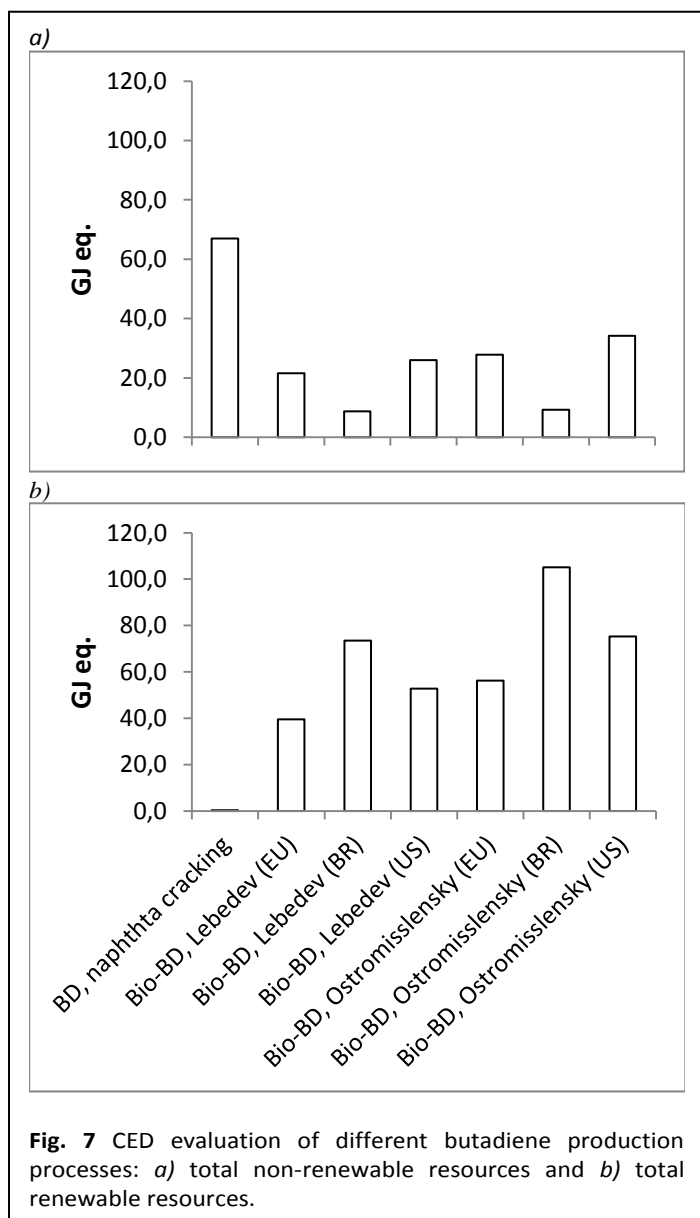

Fig. 7 CED evaluation of different butadiene production processes: *a)* total non-renewable resources and *b)* total renewable resources.

Fig. 8 Cradle-to-gate carbon footprint.

problem is still associated to the larger amount of resources involved in the harvesting, transportation and conversion of biomass into building blocks, in particular when dedicated crops are employed. The use of fertilizers to farm crops still remains one of the crucial aspect involved into climate change. An inventory analysis performed for the corn-based BD reveals how the release of N_2O has a contribution of 13% to CO_2 eq. emissions. Dinitrogen monoxide, derived from the use of N-based fertilizers, has a 300 times greater greenhouse effect than carbon dioxide. Therefore, also small quantities of this molecule have huge effects on the ecosystem. Another critical outcome is represented by the EU Lebedev process which results in 2.04 t of CO_2 eq. released per t of BD, not so far from the 2.13 t achieved by the conventional route. Therefore, these scores appear not sustainable enough to justify the usage of mix crops instead of fossil sources. A detailed contribution analysis (**Figure S6**) sets wheat-based ethanol as the main GHG source. Therefore, given literature forecasts which suggest an increase of the wood-derived ethanol at 2023,[32] a further scenario was built, substituting the wheat fraction with a residual wood-chips. The replacement leads to a significant reduction in GHG emissions (1.49 t of CO_2 eq.), much lower than the value achieved by other processes (**Table S5**). Therefore, the exploitation of lignocellulosic biomass should be considered as a viable solution, although the other conventional sources seem still dominate the world production at 2023.[32]

As outlined above, another crucial point, when bio-based chemicals are taken into account, is the water consumption associated to their production process. In this study, direct and indirect water withdrawals were considered in order to have a rough estimation of cradle-to-gate water footprint. **Figure 9** summarizes the main results achieved. As expected, unconventional bio-based pathways reach higher amounts than the consumptions involved in the naphtha supply chain. However, different crops present diversities in water withdrawals. Results show how using corn instead of sugarcane as a starting culture leads to a lower sustainability of the entire process. Indeed, moving from a corn-based (US) to sugarcane-derived BD (BR) a reduction around 30% of water

consumptions was estimated, respectively in the case of Ostromisslensky and Lebedev pathways. **Table S6** collects the results of the analysis, expressed them in $m^3/$ t of BD. Moreover, a further confirmation of the higher water needs for the EU scenario is given by its contribution analysis. Although corn represents just a small amount in the crops mixture (around 1/6), it constitutes the main contribution to the water consumption category (**Figure S7**).

Until now all the indicators introduced and discussed in this paper represent a good estimation of a single environmental issue. Only CED can be considered as a valuable marker of overall results, even if it is considered a more resource-oriented indicator. Therefore, in order to have a wider perspective of the overall potential impacts achieved by each scenario, ReCiPe was used as analysis method. As already stated, five impact categories were selected in order to cover the main environmental issues: climate change, sustainability of crops cultivation in terms of terrestrial eco-toxicity and agricultural land occupation, consumption of fossil resources and air quality, choosing a good indicator such as particulate matter formation. An aggregation of the selected midpoint categories, called also ReCiPe single-score, is depicted in **Figure 10** and results are summarised in **Table S7**. A wider comparison reveals how unconventional Lebedev routes reach lower score (points) than the more consolidated naphtha cracking technology. Lower score means less environmental burdens, therefore more sustainable scenarios. In particular, Brazilian sugarcane-derived BD achieves an overall impacts reduction of 60%. On the contrary, reductions reached by the US and EU scenarios are quite lower, around 25-28%
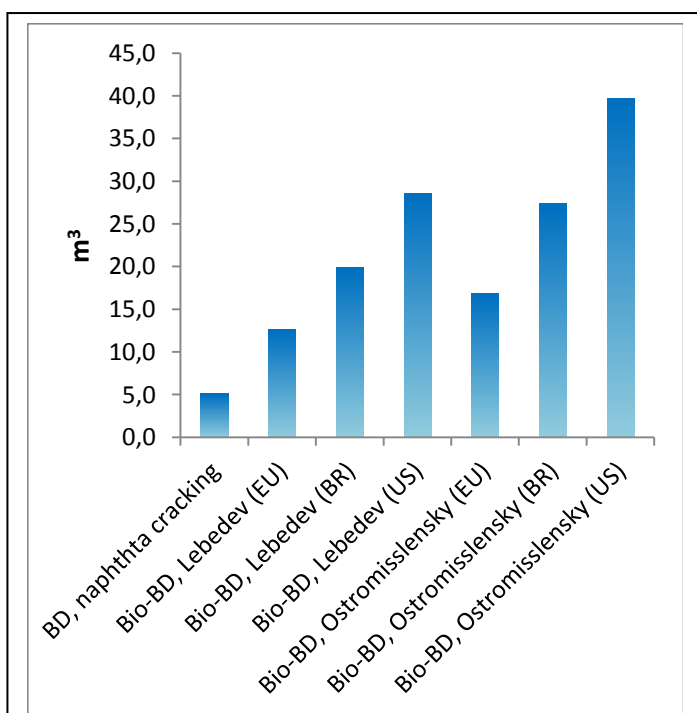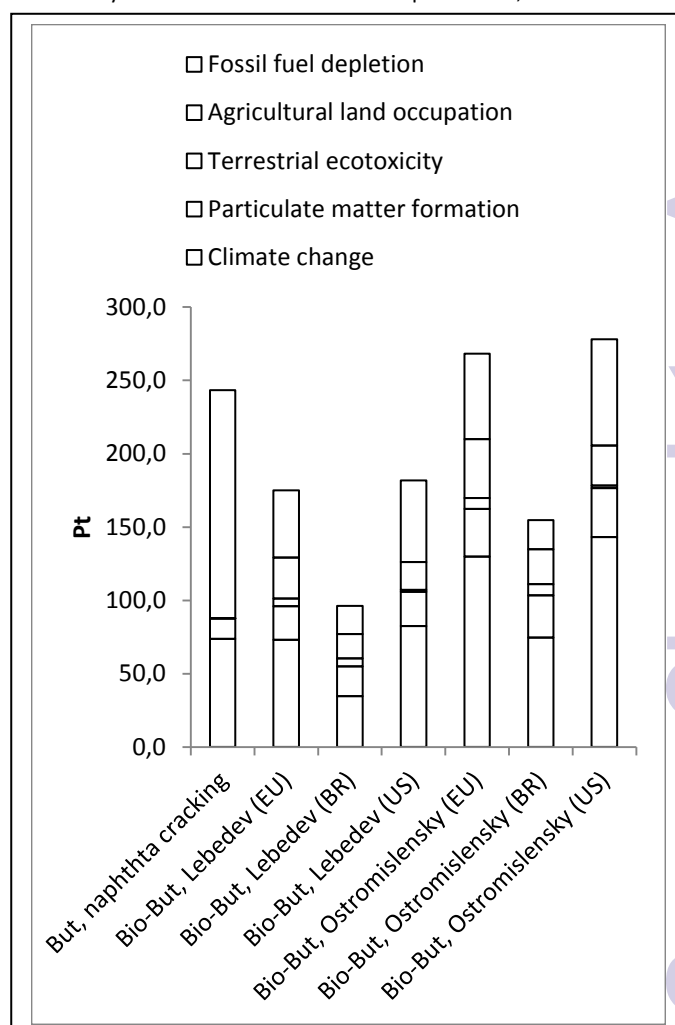
Fig. 9 Cradle-to-gate water consumption.

Fig. 10 Recipe single score of several butadiene production processes.

respectively, but anyway considerable.

However, while the Brazilian two-step process shows scores quite similar to the US and EU Lebedev scenarios (**Table S7**), **Figure 10** displays the higher environmental footprints of the other Ostromisslensky routes. In both cases, larger ethanol amount utilised in the overall chain leads to stronger burdens in terms of climate change and fossil fuels depletion. In both cases, energy requests behind maize drying procedures represent the major contributor, followed by heat requirements at industrial scale. Therefore, it appears evident how ethanol supply chain represents the major cause of potential impacts. However, it is not possible to imagine lower ethanol amounts, since its large usage is also necessary to cover acetaldehyde and hydrogen needs in order to consider the Ostromisslensky route as a 100% bio-based scenario. Indeed, in the case in which ethylene-derived acetaldehyde is considered (through partial oxidation, Wacker process), the 7th principle of Green Chemistry[4] is not maintained, losing the "green label". Moreover, further LCA analysis reveals how a fossil-based supply chain to acetaldehyde leads to lower sustainability if analysed using ReCiPe method (**Table S7** last column). Therefore, these scores are a further confirmation that a partial bio-based pathway should not be taken into account.

Potential impacts on particulate matter formation and agricultural land occupation are also not negligible, but they are discussed later in the manuscript.

As a confirmation of the CED results for the non-renewable resources, the dashed purple bars indicate the lower sustainability of the traditional route in terms of fossil fuels depletion category, due to the direct and embodied exploitation of the limited fossil reserves behind naphtha-based process, as well as the lower amount of non-renewable resources implied within the sugarcane-based scenario. Moreover, as a confirmation of the method relevance, results achieved previously in terms of GHG appear quite similar to the trend shown by ReCiPe analysis for the climate change category.

In order to give more relevance to the ReCiPe analysis and include a higher number of impact categories, an extension to further indicators was performed in order to evaluate the sustainability of cultivation practices. As outlined before, agricultural land occupation and terrestrial ecotoxicity were chosen for two main reasons: i) no marginal crops were considered in the study, due to the fact that dedicated cultures seem still driving the market;[32] ii) to evaluate negative effects of fertilizer and other substances used by farmers.

As shown by **Figure 10**, European and Brazilian scenarios (both Lebedev and Ostromisslensky) seem to have the major effect on terrestrial ecotoxicity category. Using a software tool, the main substances responsible of impacts are pointed out. As expected, chemicals released during the cultivation phase have the major contribution. Among these, aldrin and cypermethrin (stronger insecticides) as well as atrazine and isoproturon (herbicide) seem to affect negatively the cultivation of sugarcane and rye. The latter is responsible of almost the 80% of the impacts in the case of the EU production chain.

The bio-products(fuels and chemicals)/food competition is still an open debate in scientific and social communities. It was estimated that 500 kg of grain can be converted into 200 kg of ethanol, however the same amount of cereals can feed a person per one year.[72] Indeed, considering an average ethanol yield of 3,092 kg per hectare (estimated from values reported in literature per different cultures)[61] the production of 200 kg of ethanol employs around 647 m^2 that could be devoted to agricultural purposes. This not negligible value pressed to the introduction of agricultural land occupation as an indicator of sustainability.

Table S7 shows that the crops mix assumed in the case of EU has the higher impacts in terms of land occupation. A more complete contribution analysis reveals that wheat-based ethanol contributes to the category for the 37% (**Figure S9**). This result appears in line with literature,[61] which suggests a wheat to ethanol yield around 1,914 kg/ha: quite lower than the other crops (corn, sugarcane and sugar beet) and the average value too (3,092 kg/ha). For the same reason, comparable ethanol yields for corn and sugarcane lead US and BR scenarios to have similar scores. However, it appears clear that the major contribution is associated to use of rye. Although this crop constitutes around 17% of the total amount of biomass used as input in the EU scenario, its contribution to the category is around 40%. According to FAOSTAT,[73] the main reason is attributable to the cultivation yield estimated to be approximately 3.00kg/ha, quite lower than wheat (3.92kg/ha).

On the other hand, the use of fossil resources (as in the case of naphtha cracking) does not result in a great influence on land occupation and ecotoxicity. However, refinery and oil processing plants still have huge impacts both in terms of space and release of toxic substances. Therefore, a more conservative evaluation should consider these aspects when bio-based chemicals are under study.

Finally, particulate matter formation (PMF) category was introduced as air quality indicator. PMF was chosen for its chemical and toxicological importance. As well known, particles can be released directly into environment (primary particulate) or originated from subsequent reactions (secondary particulate). Moreover, a classification between physical and chemical sources can be carried out. Among chemical sources, combustion plays an important role. Therefore, each energy process which implies fuels combustion within its supply chain is responsible of direct or indirect particulate emissions. Hence, given what stated in the introduction regarding energy requirements of the chemical sector, PMF seems a valuable indicator of sustainability. **Table S8** collects main activities which have higher contribution to PMF category for each scenario. As shown, processes related to energy (including heat and electricity) produce higher contribution to PM (around 30%) when BD is obtained by conventional fossil route, although the remaining contribution is attributable to naphtha supply. On the other hand, in the case of bio-based routes, the consumptions within ethanol supply chain are the cause of the higher PMF impacts, reaching a 94% contribution in the case of one-step process and 95% for the Ostromisslensky pathway. Moreover, a detailed inventory analysis helps to understand the mechanisms behind particles formation, revealing that secondary particulate prevails since gases emissions (e.g. NO_x, SO_x and NH_3) show a higher contribution to PMF category.

Finally, a screening estimation of the economic aspects involved in the bio-based processes was carried out using EI indicator. Both unconventional routes were chosen as a base for the comparison for these reasons: first, naphtha cracking is a well-established technology and second, in line with the manuscript purpose, we decided to focus the study on the assessment of the potentialities of alternative green pathways. Results from the analysis are reported below in **Figure 11**.

A comparison between EU, BR and US scenarios was carried out, taking into account both direct ethanol conversion and two-step process. Economic data reported in literature[24] for 2013 were used to run EI simulation. Allocation factors based on mass yield for each process were used in order to refer indexes to the BD production only. Moreover, error bars were introduced showing how results
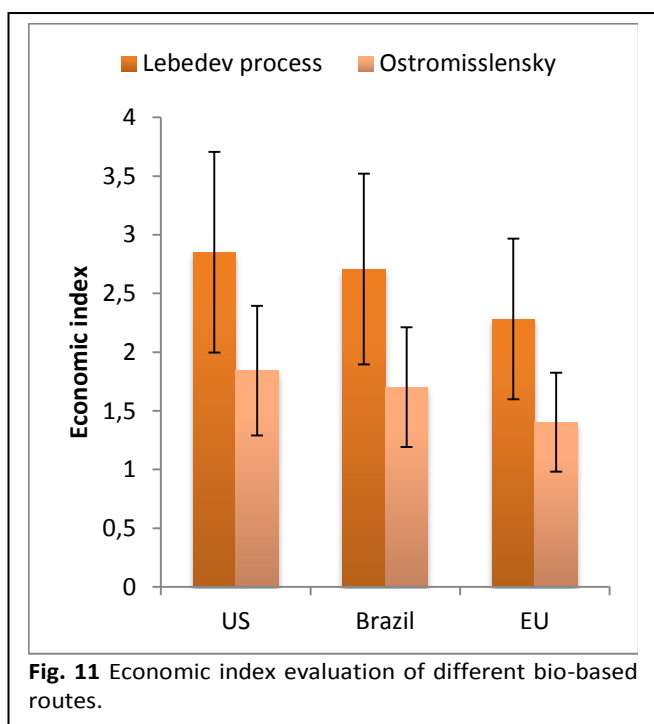
ARTICLE

Fig. 11 Economic index evaluation of different bio-based routes.

are influenced by the fluctuation of the product price. Two limited cases were considered: a minimal BD price of 1,750\$/t (considering an average value for the period 2007-2011) and the maximum price reached in 2013 of 3,250\$/t, both extrapolated from PERP review.[24] As expected from the equation, higher the ratio, more convenient the solution. Results achieved clearly show how Lebedev process prevails on Ostromisslensky pathway. Indeed, although energy and utilities requirements are quite similar for both processes, the larger ethanol amount used in the two-step pathway leads to lower economic sustainability. In addition, a more conservative analysis should take also into account the economic behind plant activities. In the case of the two-step pathway, reactions are carried out into two separate reactors.[24] This solution implies higher investment as well as major fixed costs due to both the maintenance operations and all the recirculation and vent procedures. Moreover, index denotes which is the more convenient region to set the plant. Analysis shows that North American location seems the more affordable in economic terms, followed by the Brazilian one. On the other hand, a production plant situated in Europe appears not convenient at all, especially if compared with the other countries considered. This sensible difference is mainly due to the prices of utilities and raw materials. In particular, given the abundance of Brazilian and North American ethanol its price is quite lower than in Europe. Furthermore, literature data[24] reveal that electricity, steam and cooling water are more expensive in EU countries. In the case of energy carriers in chemical plant (e.i. electricity and steam) the oil price as well as the cost of the other fossil fuels play a crucial role on final values.

Although the Asian BD market is expected to grow in the near future, no scenario describing China production was considered both in the environmental and economic evaluations. This is because literature already classified Lebedev and Ostromisslensky as "not convenient" processes, as a cause of the high ethanol price on chinese market. Therefore, these solutions appear still not competitive in Asia.[24] In conclusion, the use of EI index is strictly recommended as a support indicator to evaluate overall sustainability of biomass-based chemical production plant.

However, these kind of evaluations should carried out carefully, since differently from physical balances (energy and material), which remain constant for the same type of technology, economic flows are subjected to continuous fluctuations as a consequence of resources availability and of the political and social conditions.

Conclusions

In this manuscript, a multi-criteria approach was proposed with the aim of evaluating the sustainability of bio-based chemical processes. Resource- and impact-oriented indicators, as well as economic index were used in order to cover several aspects proposed by the concept of sustainability. LCA methodology on industrial scale level was applied to the production 1,3-butadiene, selected as target molecule due its relevance on the market. In line with 7th principle of Green Chemistry,[4] a comparison between traditional fossil-based process and alternative pathways starting from biomass were carried out. A general overview of the results emerged in the study reveals that the reduction in the performing of conventional route should be driven by the large consumption of non-renewable resources involved in naphtha cracking technology. Both CED and ReCiPe at midpoint level confirm this negative trend. Moreover, lower the abundance of fossil reserves, higher their price. However, bio-based productions are not always the best solutions. Outcomes show how water consumption and the depletion of natural resources must be considered when bio-based processes are under study. Furthermore, these aspects are strictly influenced by geography than other. In the case of the Brazilian scenario, an impoverishment of the renewable resources can provoke large damages on ecosystem and natural habitat. However, the relevance given to the exploitation of natural resources is strictly related to analysis method used and the calculation setup behind it. In the case of Brazilian-production BD, results achieved for the category non-renewable resources (CED) are higher than the values obtained for the EU scenario. On the other hand, ReCiPe single-score shows higher sustainability of the Lebedev pathways, in particular when a sugarcane-based route is considered. Therefore, it follows that it is necessary to include several analysis methods in the same evaluation in order to have a more comprehensive assessment of the potential impacts.

Furthermore, the idea that bio-based processes are carbon-neutral is not in line with the outcomes of the present study. Several activities involved in the biomass production chains are responsible for large GHG emissions. However, results show a favourable outcome in the case of Lebedev routes especially if residual wood is used as starting raw material.

However, in conclusion, two are the main aspects which came out from the study. First, results from a more broad evaluation of several environmental issues, carried out through ReCiPe single-score, disclosed that Lebedev process (in all regions considered) reaches lower burdens than conventional naphtha cracking route. On the other hand, both the environmental and economic evaluations performed for bio-based processes confirm the Lebedev pathway as a more valuable alternative than Ostromisslensky. Therefore, given these results, it is recommended focus future efforts and investments on direct ethanol conversion into BD, where possible.

Low crude oil price still represents the main barrier to the investments toward a more environmental-friendly chemical industry. However, the main aim of Green Chemistry, as well as of Green Engineering and other disciplines aimed to sustainability, is to move the attention of the community toward a society more

oriented on the environmental and social issues than driven exclusively by economic considerations.

Abbreviations

BD   1,3-butadiene

BR   Brazil

CED   Cumulative Energy Demand

CI   Chemical Industry

EATOS   Environmental Assessment Tool for Organic Syntheses

EIAUS   Energy Information Administration

EI   Economic Index

EU   Europe

FAO   Food and Agriculture Organization of the United Nations

GC   Green Chemistry

GE   Green Engineering

GWP   Global Warming Potential

IPCC   Intergovernmental Panel on Climate Change

LCA   Life Cycle Assessment

LCI   Life Cycle Inventory

OECD   Organisation for Economic Co-operation and Development

PERP   Process Economics and Research Planning

PMF   Particulate Matter Formation

US   United States of America

Notes and references

‡ Unconventional sources (e.g. shale gas) have contributed to the natural gas price reduction, now completely decoupled from oil price.[24] As a consequence ethane usage in the US cracking technology increased from 46% up to 65% during the period 2005-2011.[24] In addition to gas abundance, a lower capital cost and higher ethylene selectivity are promoting the transition, in spite of a lower BD yield if compared with naphtha cracking.[24,36,74] Therefore, according to literature,[74] the increasing substitution of naphtha by shale gas and other unconventional sources could result in a real opportunity to develop valuable bio-based routes to fulfill the overall BD and aromatic compounds request, which seems still growing.[24]

1   WCED, *Our common future, World Commission on Environment and Development*, Oxford University Press, Oxford, 1987.

2   US Energy Information Administration (EIA), *International Energy Outlook 2013 – with projections to 2040*, http://www.eia.gov/ieo/, (accessed September 2015).

3   Office of Pollution Prevention and Toxics - EPA (US Environmental Protection Agency), *2013 Toxics Release Inventory*, available on http://www2.epa.gov/toxics-release-inventory-tri-program/2013-toxics-release-inventory-national-analysis, (accessed September 2015).

4   P. T. Anastas and J. C. Warner, *Green Chemistry: Theory and Practice*, Oxford University Press, Oxford, 1998.

5   P. T. Anastas, L. G. Heine and T. C. Williamson, *Green Engineering*, American Chemical Society (ACS) symposium series 766, Washington, DC, 2000.

6   Royal Society of Chemistry publishing - *Green Chemistry*, http://pubs.rsc.org/en/journals/journalissues/gc#!recentarticles&adv, (accessed September 2015).

7   Taylor & Francis Online - *Green Chemistry Letters and Reviews,* http://www.tandfonline.com/toc/tgcl20/current#.VVmht_ntmko, (accessed September 2015).

8   P.T. Anastas, *Handbook of Green Chemistry*, Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim, ISBN: 978-3-527-33710-1 2013.

9   J.H Clarks, G. Kraus, A. Stanklevic, P. Seidl and C. Hu, *RSC Green Chemistry series*, Royal Society of Chemistry publishing, ISSNI: 1757-7039, DOI: 10.1039/1757-7047.

10   Center for Green Chemistry and Green Engineering http://greenchemistry.yale.edu/, (accessed September 2015).

11   The Center for Sustainable Chemistry - https://www.nottingham.ac.uk/chemistry/research/centre-for-sustainable-chemistry.aspx, (accessed September 2015).

12   The Berkeley Center for Green Chemistry - http://bcgc.berkeley.edu/, (accessed September 2015).

13   http://www.isgc2015.com/, (accessed September 2015).

14   http://www.gcande.org/, (accessed September 2015).

15   http://www.grc.org/programs.aspx?id=12560, (accessed September 2015).

16   R. A. Sheldon, *Chem. Ind.*, 1992, **23**, 903-906.

17   R. A. Sheldon, *Chem. Ind.*, 1997, **1**, 12-15.

18   F. Roschangar, R. A Sheldon and C. H. Senanayake, *Green Chem.,* 2015, **17**, 752–768.

19   M. Lancaster, *Green Chemistry: An Introductory Text*, Royal Society of Chemistry, Cambridge, 2002.

20   L. M. Tufvesson, P. Tufvesson, J. Woodley and P. Börjesson, *Int. J. Life Cycle Assess.*, 2013, **18**, 431-444.

21   http://www.metzger.chemie.uni-oldenburg.de/eatos/, (accessed September 2015).

22   P. Gallezot, *Chem. Soc. Rev.*, 2012, **41**, 1538-1558.

23   Scopus® - Copyright Elsevier B.V., http://scopus.com, (accessed September 2015).

24   NexantThinking™, *Bio-Butadiene PERP 2013S9*, Process Evaluation/Research Planning program.

25   H. Zimmermann and R. Walzl, *Ethylene, Ullmann's Encyclopedia of Industrial Chemistry*, Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim, 2009.

26   T. Ren, M. Patel and K. Blok, *Energy*, 2006, **31**, 425-451.

27   J. Rass-Hansen, H. Falsig, B. Jørgensen and C. H. Christensen, *J. Chem. Technol. Biot.*, 2007, **82**, 329-333.

28   R. A. Weusthuis, J. M. M. J. G. Aarts, J. P. M. Sanders, *Biofuel. Bioprod. Bior.*, 2011, **5**, 486-494.

29   J. A. Posada, A. D. Patel, A. Roes, K. Blok, A. P. C. Faaji and M. K. Patel, *Bioresource Technol.*, 2013, **135**, 490-499.

30   A. Chieregato, J. V. Ochoa, C. Bandinelli, G. Fornasari, F. Cavani and M. Mella, *ChemSusChem*, 2014, **7**, 1-13.

31   J. J. Bozell and G. R. Patersen, *Green Chem.*, 2010, **12**, 539-554.

32   OECD/Food and Agriculture Organization of the United Nations, *OECD-FAO Agricultural Outlook 2014-2023*, OECD Publishing, 2014.

33   EIA – US Energy Information Administration, *International energy statistics 2012*,

http://www.eia.gov/cfapps/ipdbproject/iedindex3.cfm?tid=79&pid=80&aid=1&cid=regions&syid=2008&eyid=2012&unit=TBPD, (accessed September 2015).

34 V. N. Ipatiev, *J. Russ. Phys.-Chem. Soc.*, 1903, **35**, 449–452.

35 I. I. Ostromisslensky, *J. Russ. Phys.-Chem. Soc.*, 1915, **47**, 1472–1506.

36 E. V. Makshina, M. Dusselier, W. Janssens, J. Degrève, P. A. Jacobs and B. F. Sels, *Chem. Soc. Rev.*, 2014, **43**, 7917-7953.

37 C. Angelici, B. M. Weckhuysen and P. C. A. Bruijnincx, *ChemSusChem*, 2013, **6**, 1595-1614.

38 S. V. Lebedev, FR 665917, 1929.

39 S. V. Lebedev, GB 331482, 1930.

40 S. V. Lebedev, *Zh. Obshch. Khim.*, 1933, **3**, 698–717.

41 Y. A. Gorin, *Zh. Obshch. Khim.*, 1946, 16, 283–294.

42 A. D. Patel, K. Meesters H. den Uil, E. de Jong, E. Worrell and M. K. Patel, *ChemSusChem*, 2013,**6**, 1724-1736.

43 C. Jiménez-González and M. R. Overcash, *Green Chem.*, 2014, **16**, 3392–3400.

44 D. Kralisch, D. Ott and D. Gericke, *Green Chem.*, 2015, **17**, 123-145.

45 D. Cespi, E. S. Beach, T. E. Swarr, F. Passarini, I. Vassura, P. J. Dunn and P. T. Anastas, *Green Chem.*, 2015, **17**, 3390-3400.

46 B. W. Vigon, D. A. Tolle, D. P. Evens, S. L. Freeman, K. K. Humphreys, C. F. Wend and R. Landucci, *Life Cycle Assessment of Biomass Conversion to Feedstock Chemicals*, Energy Conversion Engineering Conference, 1996.

47 B. G. Hermann, K. Block and M. K. Patel, *Environ. Sci. Technol.*, 2007, **41**, 7916-7921.

48 R. A. Urban and B. R. Bakshi, *Ind. Eng. Chem. Res.*, 2009, **48**, 8068-8082.

49 A. D. Patel, J. C. Serrano-Ruiz, J. A. Dumesic and R. P. Anex, *Chem. Eng. J.*, 2011, 160, 311-321.

50 B. Cok, I. Tsiropoulos, A. L. Roes and M. K. Patel, *Biofuels, Bioprod. Bioref.*, 2014, 8, 16-29.

51 P. P. Van Uytvanck, B. Hallmark, G. Haire, P. J. Marshall and J. S. Dennis, *ACS Sustainable Chem. Eng.*, 2014, **2**, 1098-1105.

52 D. Cespi, F. Passarini, G. Mastragostino, I. Vassura, S. Larocca, A. Iaconi, A. Chieregato, J.-L. Dubois and F. Cavani, *Green Chem.*, 2015, **17**, 343–355.

53 I. Tsiropoulos, A. P. C. Faaij, I. Lundquist, U. Schenker, J. F. Briois and M. K. Patel, *J. Cleaner Prod.*, 2015, **90**, 114–127.

54 A. D. Patel, K. Meesters H. den Uil, E. de Jong, K. Blok, and M. K. Patel, *Energy Environ. Sci.*, 2012, **5**, 8430-8444.

55 PRé Consultants, SimaPro, PhD version 8.0.4.30, Amersfoort, The Netherlands, 2014.

56 Ecoinvent Centre (formerly Swiss Centre for Life Cycle Inventories) (2014) Ecoinvent 3.1 Database.

57 M. A. Curran, *Life Cycle Assessment Handbook: A Guide for Environmentally Sustainable Products*, John Wiley & Sons, Inc. Hoboken, New Jersey, and Scrivener Publishing LLC, Salem, Massachusetts, 2012.

58 M. Feyen, K. Spannhoff, Müller U., X. Bao, W. Zhang, D. De Vos, H. Gies, T. Tatsumi, F. Xiao, Y. Toshiyuki and Y. Bilge, *WO Pat.*, 199349 A2, 2014.

59 D. Cespi, F. Passarini, E. Neri, I. Vassura, L. Ciacci and F. Cavani, *J. Cleaner Prod.*, 2014, **69**, 17–25.

60 T. Nakatani, Y. Tanaka and Y. Goto, *WO Pat.*, 125389 A1, 2013.

61 I. Muñoz, K. Flury, N. Jungbluth, G. Rigarlsford, L.M.i Canals and H. King, *Int. J. Life Cycle Assess.*, 2014, **19**, 109-119.

62 N. Jungbluth, M. Chudacoff, A. Dauriat, F. Dinkel, G. Doka, M. Faist Emmenegger, E. Gnansounou, N. Kljun, K. Schleiss, M. Spielmann, C. Stettler and J. Sutter, *Life Cycle Inventories of Bioenergy. ecoinvent report No. 17*, Swiss Centre for Life Cycle Inventories, Dübendorf, CH, 2007.

63 VDI – Verein Deutscher Ingenieure, *VDI-richtlinie 4600: Cumulative energy demand, terms, defiitions, methods of calculation*, Düsseldorf, Germany, 1997.

64 M. A. J Huijbregts, S. Hellweg, R. Frischknecht, H. W. M. Hendriks, K. Hungerbühler and A. Jan Hendriks, *Environ. Sci. Technol.*, 2010, **44**, 2189-2196.

65 M. A. J. Huijbregts, L. J. A. Rombouts, S. Hellweg, R. Frischknecht, A. JAN Hendriks, D. Van De Meent, A. M. J. Ragas, L. Reijnders and J. Struijs, *Environ. Sci. Technol.*, 2006, **40**, 641-648.

66 G. Wernet, C. Mutel, S. Hellweg and K. Hungerbühler, *J. Ind. Ecol.*, 2011, **15**, 96–107.

67 H. Sugiyama, U. Fischer, K. Hungerbuhler and M. Hirao, *AIChE J.*, 2008, **54**, 1037–1053.

68 R. Frischknecht, N. Jungbluth, H.-J. Althaus, C. Bauer, G. Doka, R. Dones, R. Hischier, S. Hellweg, S. Humbert, T. Köllner, Y. Loerincik, M. Margni and T. Nemecek, *Implementation of Life Cycle Impact Assessment Methods*. ecoinvent report No. 3, v2.0, Swiss Centre for Life Cycle Inventories, Dübendorf, 2007.

69 IPCC – Intergovernmental Panel on Climate Change, Climate Change 2013. *The Physical Science Basis. Fifth Assessment Report*, Cambridge University Press, United Kingdom, 2013.

70 M. Goedkoop, R. Heijungs, M. Huijbregts, A. De Schryver, J. Struijs and R. van Zelm, *ReCiPe 2008 – A life cycle impact assessment method which comprises harmonised category indicators at the midpoint and the endpoint level*, First edition (version 1.08), Ministry of Housing, Spatial Planning and the Environment (VROM), Netherlands, 2013.

71 R. Clift, *The challenge for manufacturing*, Engineering for sustainable development, J. McQuaid editor, London: The Royal Academy of Engineering, 1995.

72 N. Armaroli and V. Balzani, *Energy for a Sustainable World*, Wiley-VCH Verlag & Co. KGaA, Weinheim, Germany, 2011.

73 FAOSTAT, http://faostat3.fao.org/home/E, (accessed September 2015).

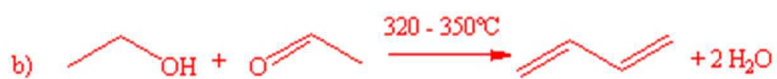74 P. C. A. Bruijnincx and B. M. Weckhuysen, *Angew. Chem. Int. Ed.*, 2013, **52**, 11980-11987.
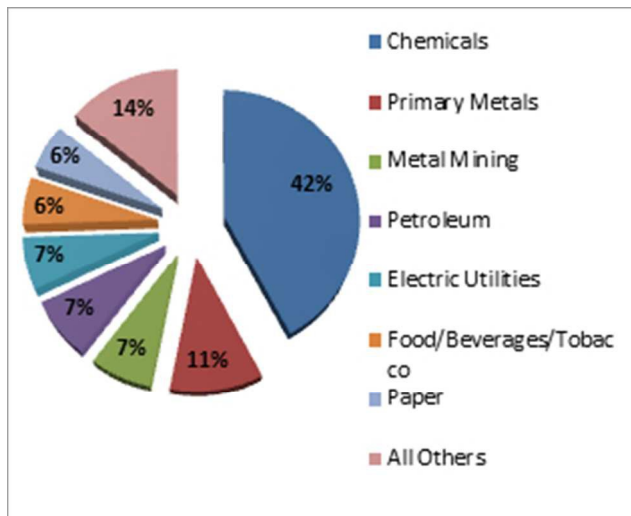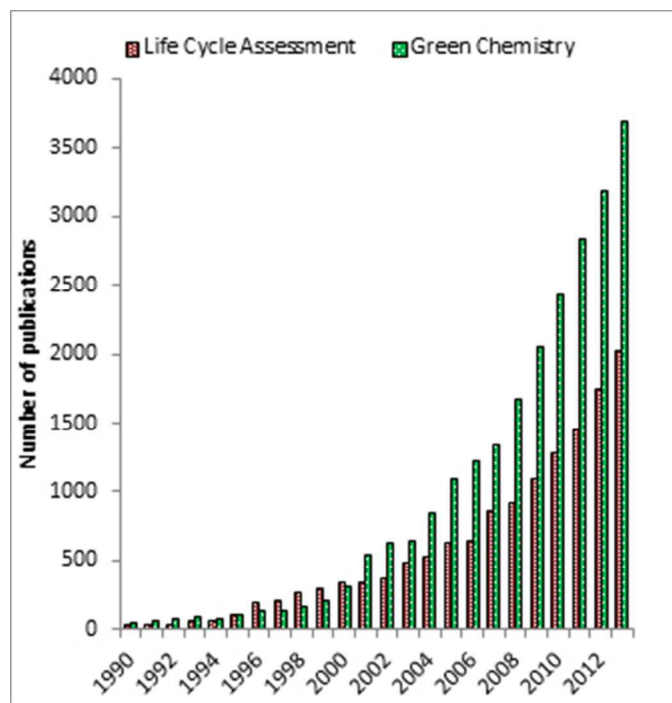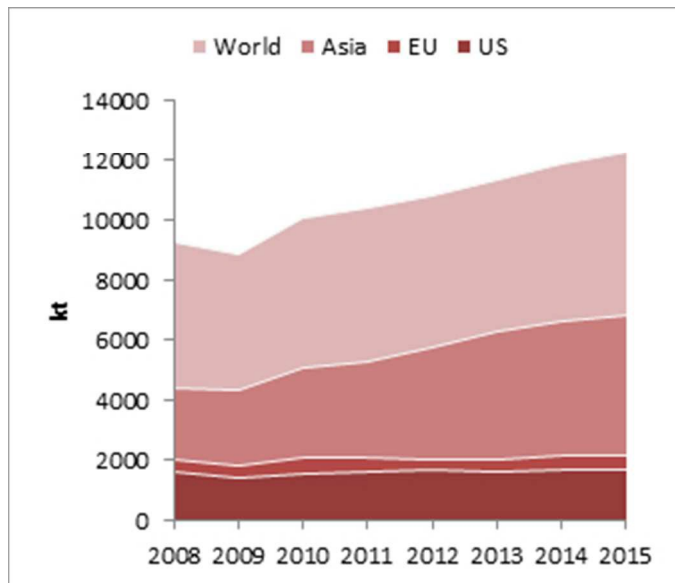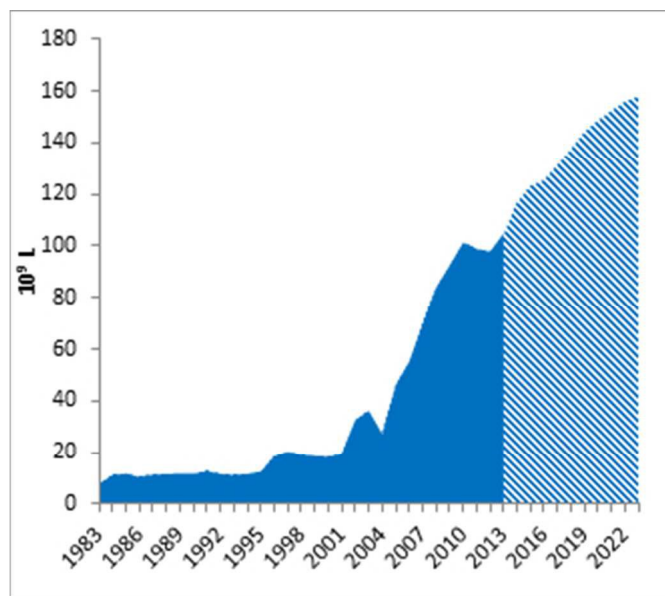
Lebedev pathway - direct conversion
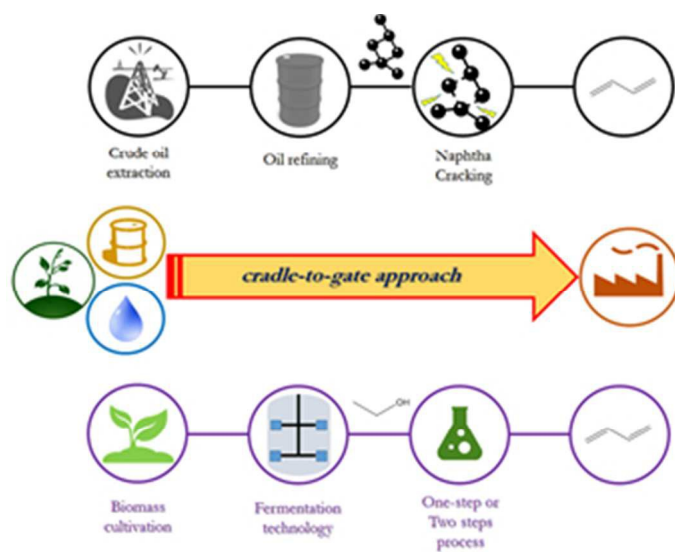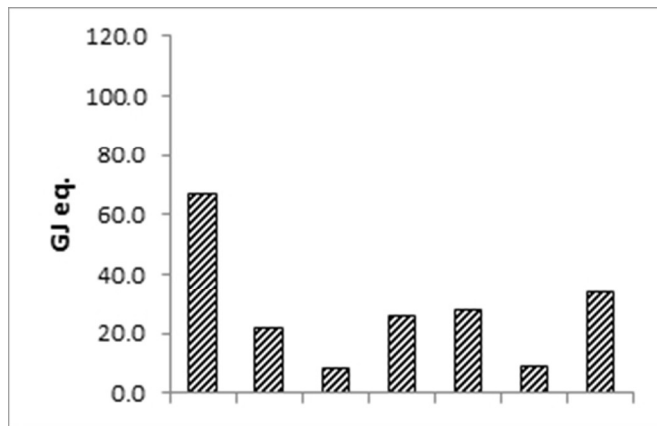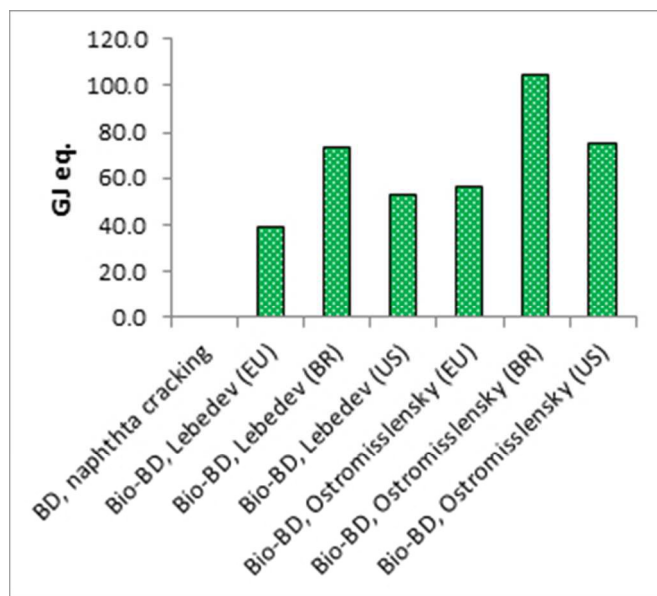
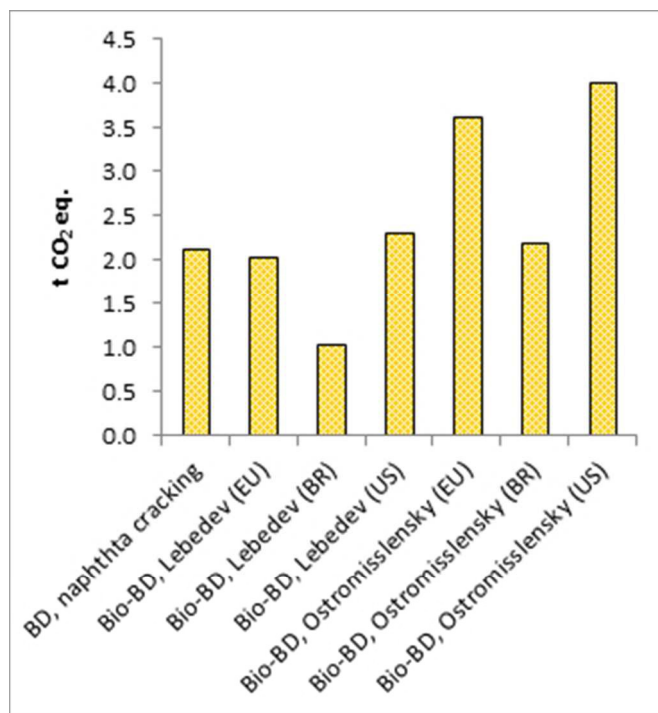$$2 \quad \diagdown\diagup\!\diagup^{OH} \xrightarrow{\text{400 - 425°C}} \diagup\!\diagup\diagdown\diagup + 2\,H_2O + H_2$$

Ostromisslensky pathway - two-step process

a) $\diagup\!\diagdown\diagup^{OH} \xrightarrow{\text{260 - 330°C}} O\!\!=\!\!\diagdown\diagup + H_2$

b) $\diagup\!\diagdown\diagup^{OH} + O\!\!=\!\!\diagdown\diagup \xrightarrow{\text{320 - 350°C}} \diagup\!\diagup\diagdown\diagup + 2\,H_2O$
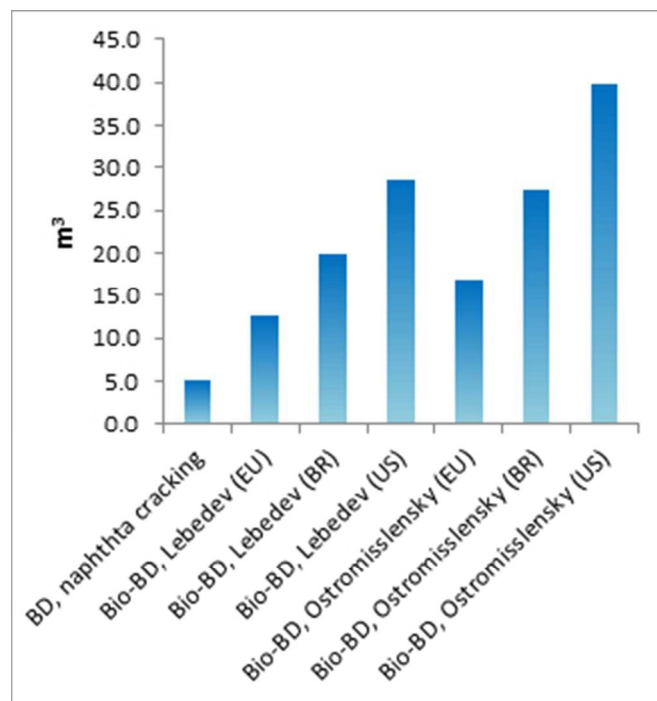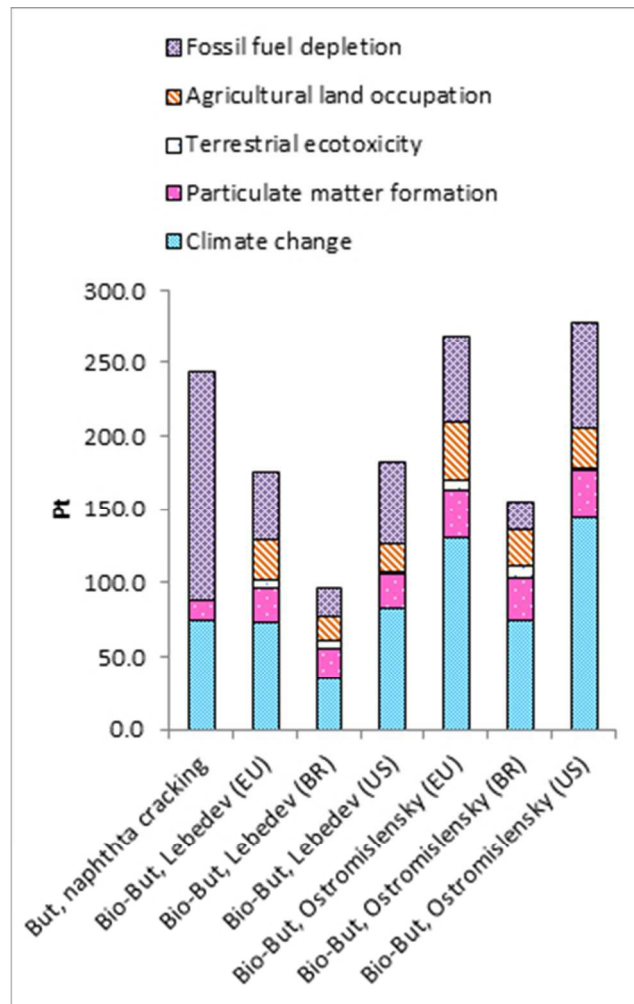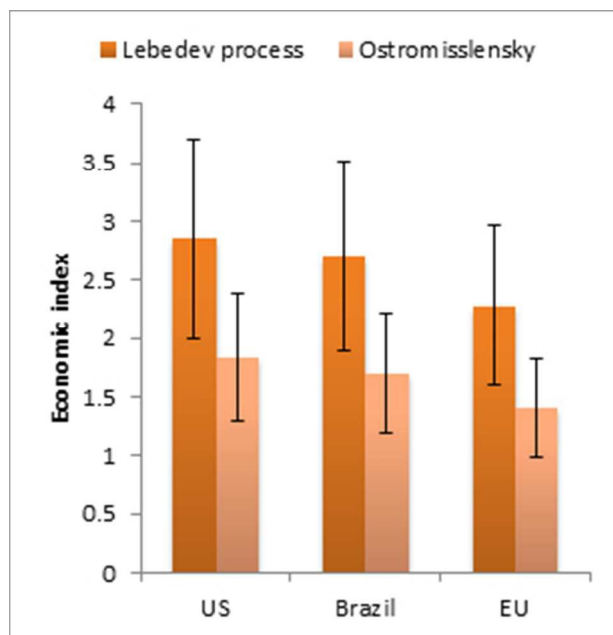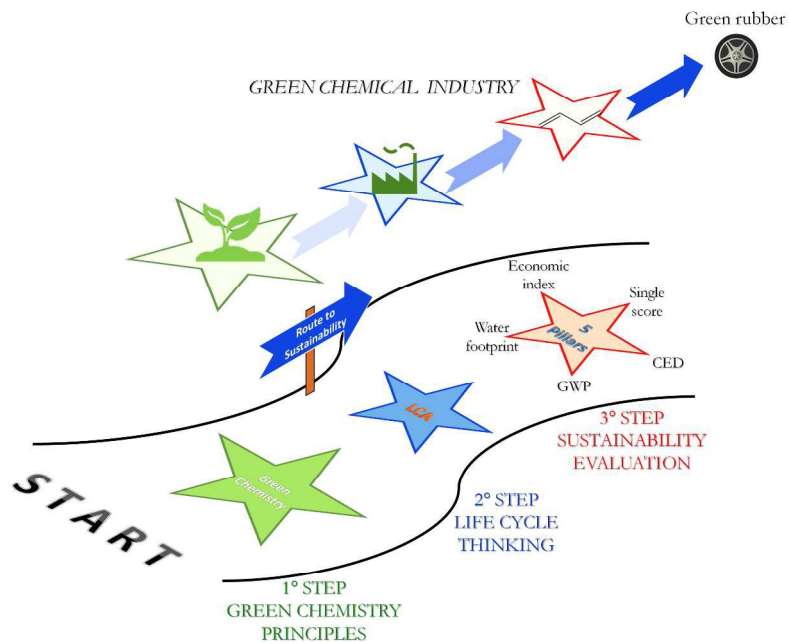
Supporting information

Substances	Amount	Unit
Inputs		
Naphtha	2.22E+01	t
Energy	2.00E+02	GJ
Co-products		
Ethylene	7.00E+00	t
Propylene	3.22E+00	t
Aromatics and C4	2.89E+00	t
CH_4	3.00E+00	t
H_2	2.22E-01	t
Other	2.44E+00	t
Outputs		
Losses&blackflows	2.44E+00	t
CO_2	1.33E+01	t
Allocation to be applied	4.5	%

Tab. S1 Naphtha cracking LCI to 1t of BD.

Substances	Amount	Unit
Inputs		
Ethanol[i]	2.06E+00	t
Electricity	9.86E-01	GJ
Cooling water	7.00E+01	t
Steam	2.66E+00	t
Co-products		
Fuel (Methane)	1.40E-01	t
Diethyl Ether	3.81E-02	t
Acetaldehyde	2.26E-01	t
Outputs		
CO_2	9.06E-03	t
Allocation to be applied	48.0	%

Tab. S2 Lebedev process LCI to 1t of BD.

Substances	Amount	Unit
Inputs		
Ethanol[i]	3.75E+00	t
Electricity	7.74E-01	GJ
Cooling water	5.00E+01	t
Steam	2.20E+00	t
Co-products		
Ethylene	8.51E-02	t
Butene	9.56E-02	t
n-Butanol	2.77E-02	t
Butyraldehyde	3.00E-03	t
Crothyl alcohol	1.92E-02	t
Outputs		
CO_2	2.10E+00	t
Allocation to be applied	38.0	%

Tab. S3 Ostromisslensky process LCI to 1t of BD.

[i]As described in the manuscript several alternatives to simulate ethanol production were considered depending on which country is chosen as supplier:

- United States - a **100%** *Ethanol, 95% in H_2O, from corn, at distillery/US U*
- Brazil - a **100%** *Ethanol, 95% in H_2O, from sugar cane, at fermentation plant/BR U*
- Europe – **1/6** *Ethanol, 95% in H_2O, from corn, at distillery/US U*, **1/6** Ethanol, 95% in H_2O, from rye, at distillery/RER U, **1/3** Ethanol, 95% in H_2O, from sugar beets, at fermentation plant/CH U and **1/3** Ethanol from wheat, Europe (inventory reported below).

Process input	Amount	Unit
Wheat grains conventional, Barrois, at farm/FR U	2.5	kg
Chemicals organic, at plant/GLO U	0.02	kg
Water, unspecified natural origin/kg	0.31	kg
Electricity, production mix RER/RER U	0.1	kWh
Heat, unspecific, in chemical plant/RER U	5.1	MJ
Transport, lorry >16t, fleet average/RER U	0.27	tkm

Tab. S4 LCI for 1 kg of ethanol from EU wheat.
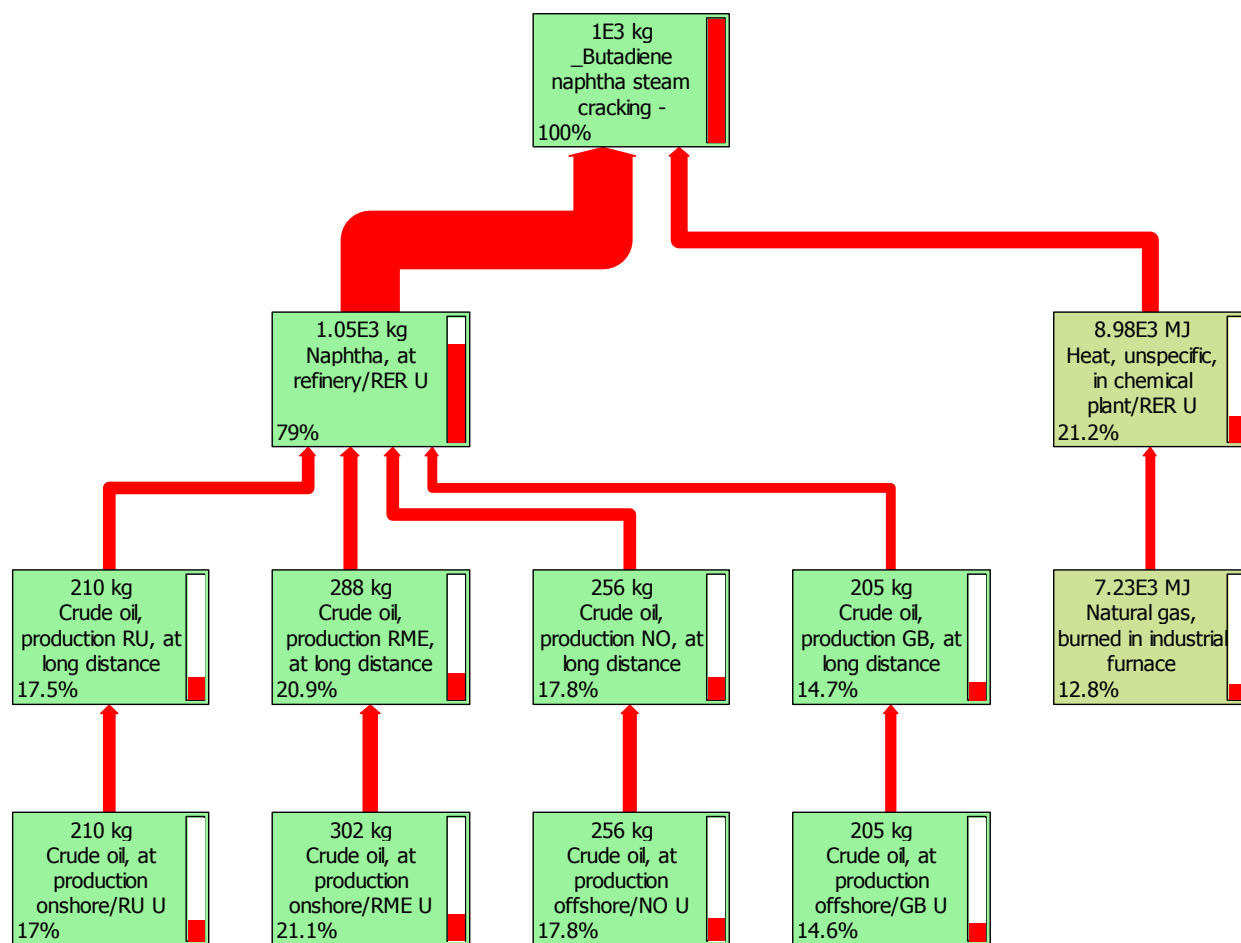
Fig. S1 Cumulative contribution to CED for naphtha cracking route to BD.
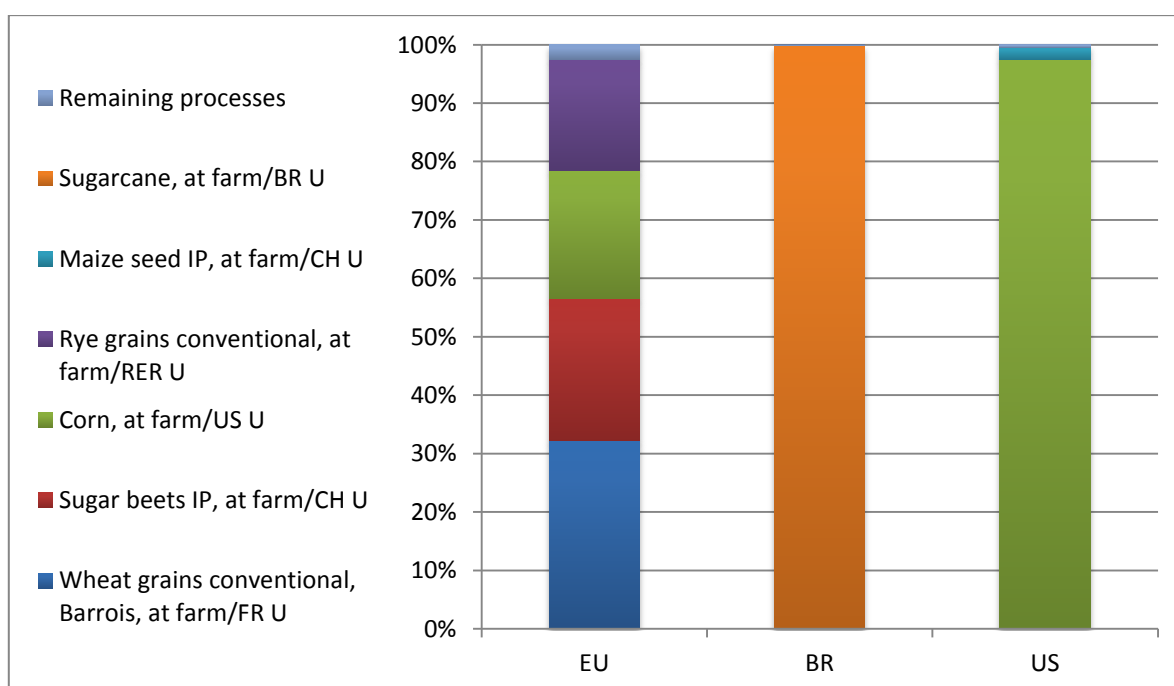
Fig. S2 CED contribution to the renewable biomass category for the unconventional BD routes.
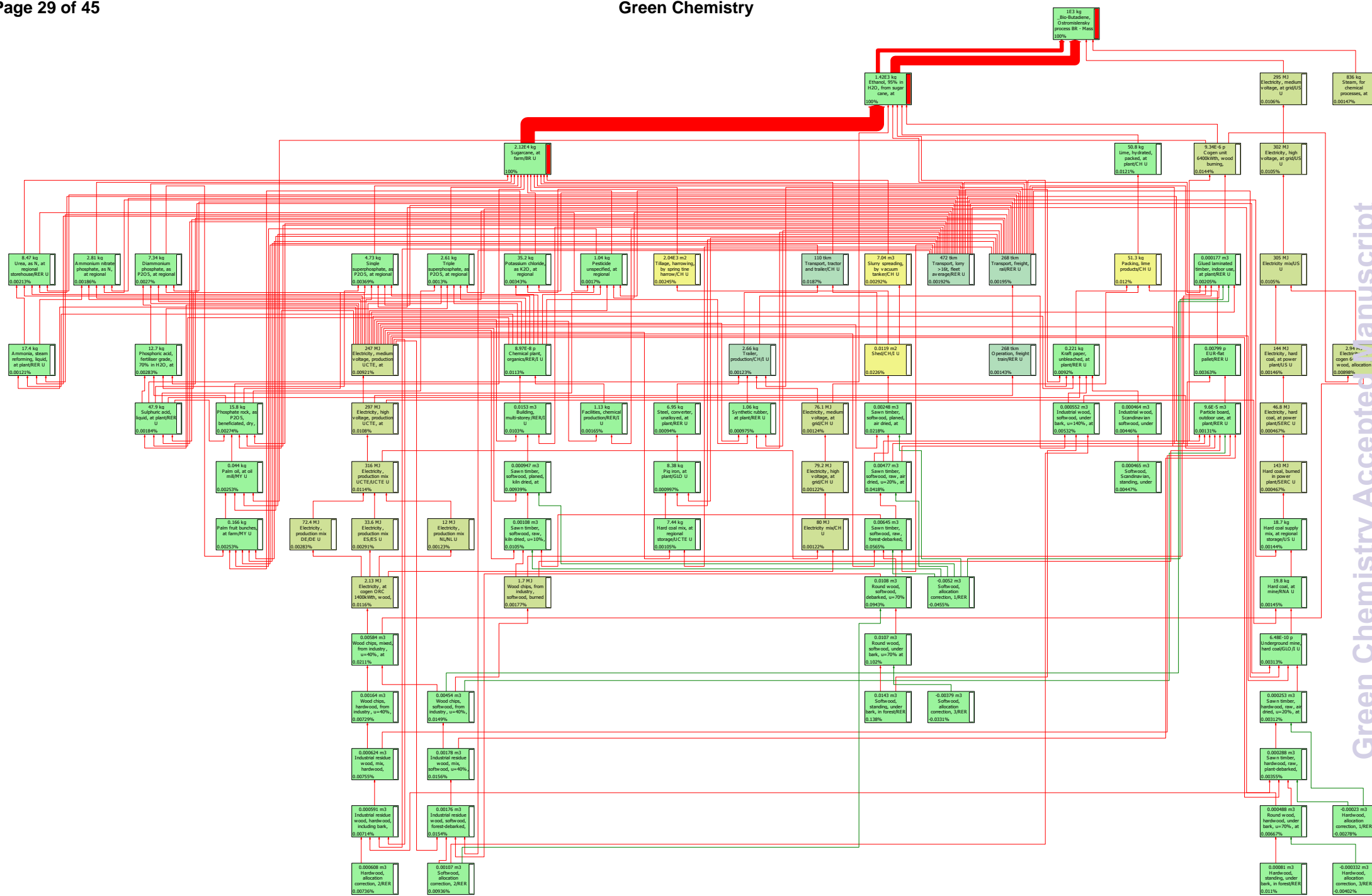
Green Chemistry

Fig. S3 CED contribution to the renewable biomass category for the unconventional BD route in Brazil, using network tool.
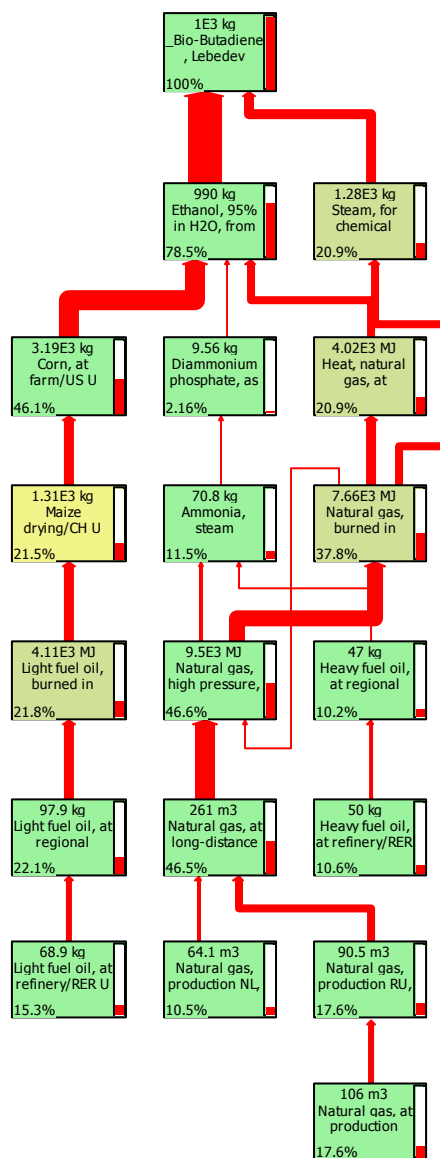
Fig. S4 CED contribution to the non-renewable fossil category, using network tool: Lebedev process in the United States.
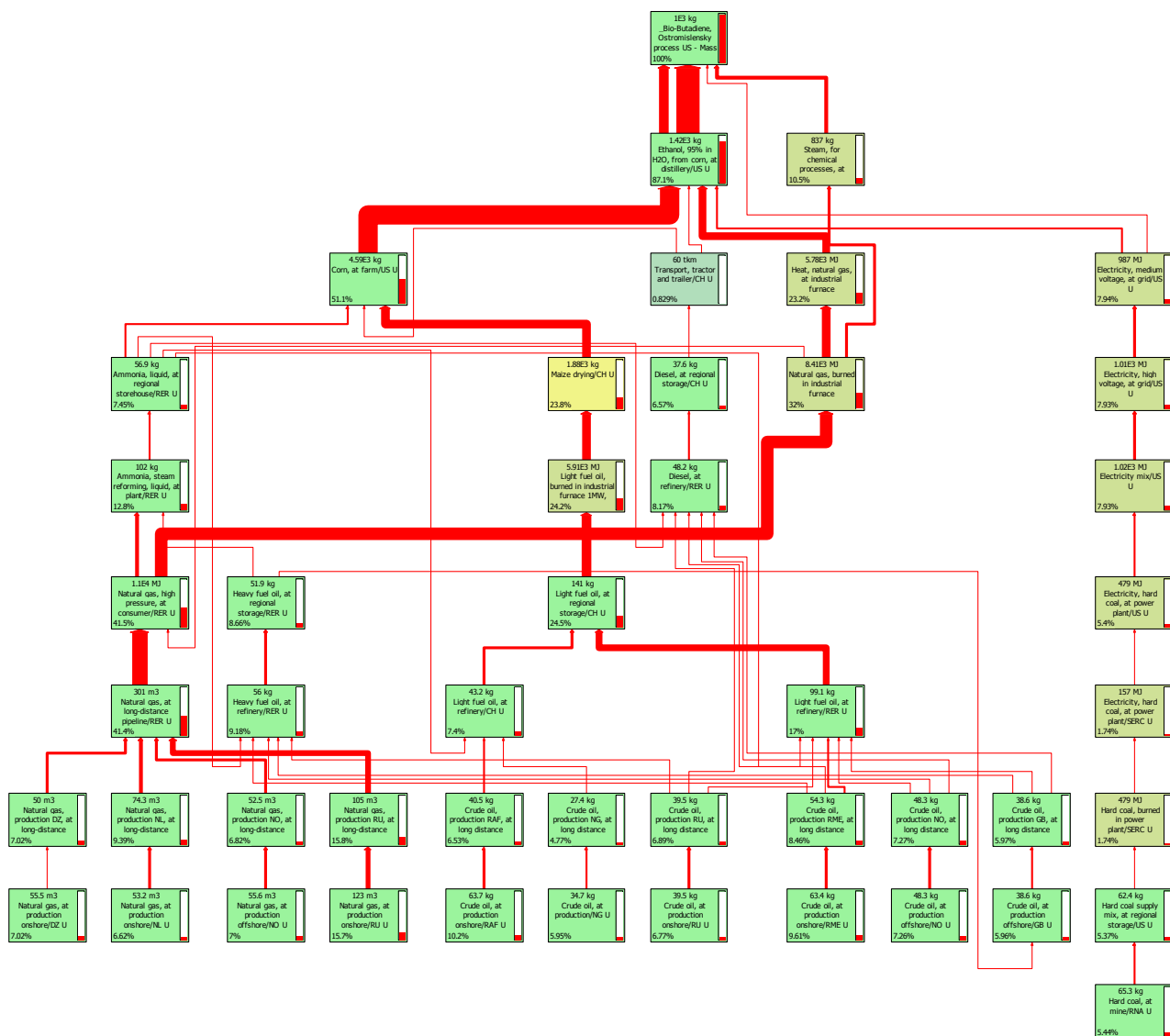
Fig. S5 CED contribution to the non-renewable fossil category, using network tool: Ostromisslensky process in the United States.
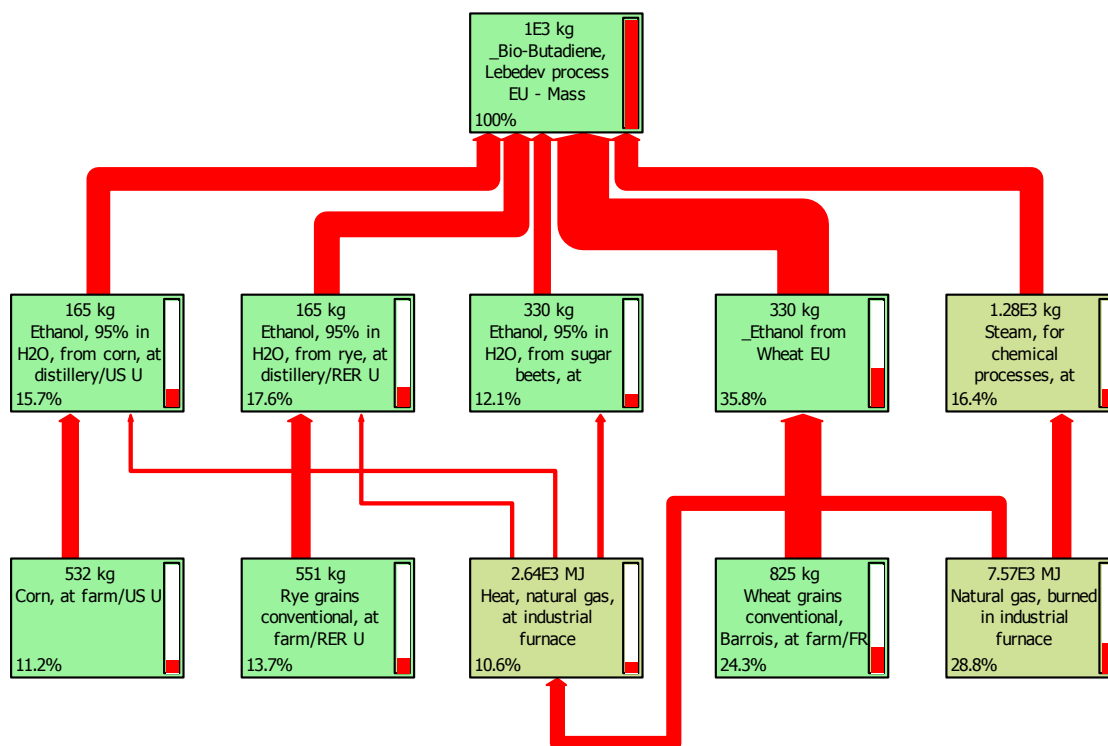
Fig. S6 GWP contribution through network tool for the Lebedev process in Europe.

BD, naphthta cracking	Bio- BD, Lebedev (EU)	Bio- BD, Lebedev (BR)	Bio- BD, Lebedev (US)	Bio- BD, Ostromiss lensky (EU)	Bio- BD, Ostromiss lensky (BR)	Bio- BD, Ostromiss lensky (US)	Bio-BD, Lebedev (EU) at 2023
2.13	2.04	1.04	2.30	3.62	2.18	4.00	1.49

Tab. S5 Results from the cradle-to-gate carbon footprint for each scenario in terms of t CO_2 eq.

BD, naphthta cracking	Bio- BD, Lebedev (EU)	Bio- BD, Lebedev (BR)	Bio- BD, Lebedev (US)	Bio- BD, Ostromisslensky (EU)	Bio- BD, Ostromisslensky (BR)	Bio- BD, Ostromisslensky (US)
5.12	12.63	19.95	28.57	16.81	27.34	39.73

Tab. S6 Results from the cradle-to-gate water consumption in m^3 per ton of BD.
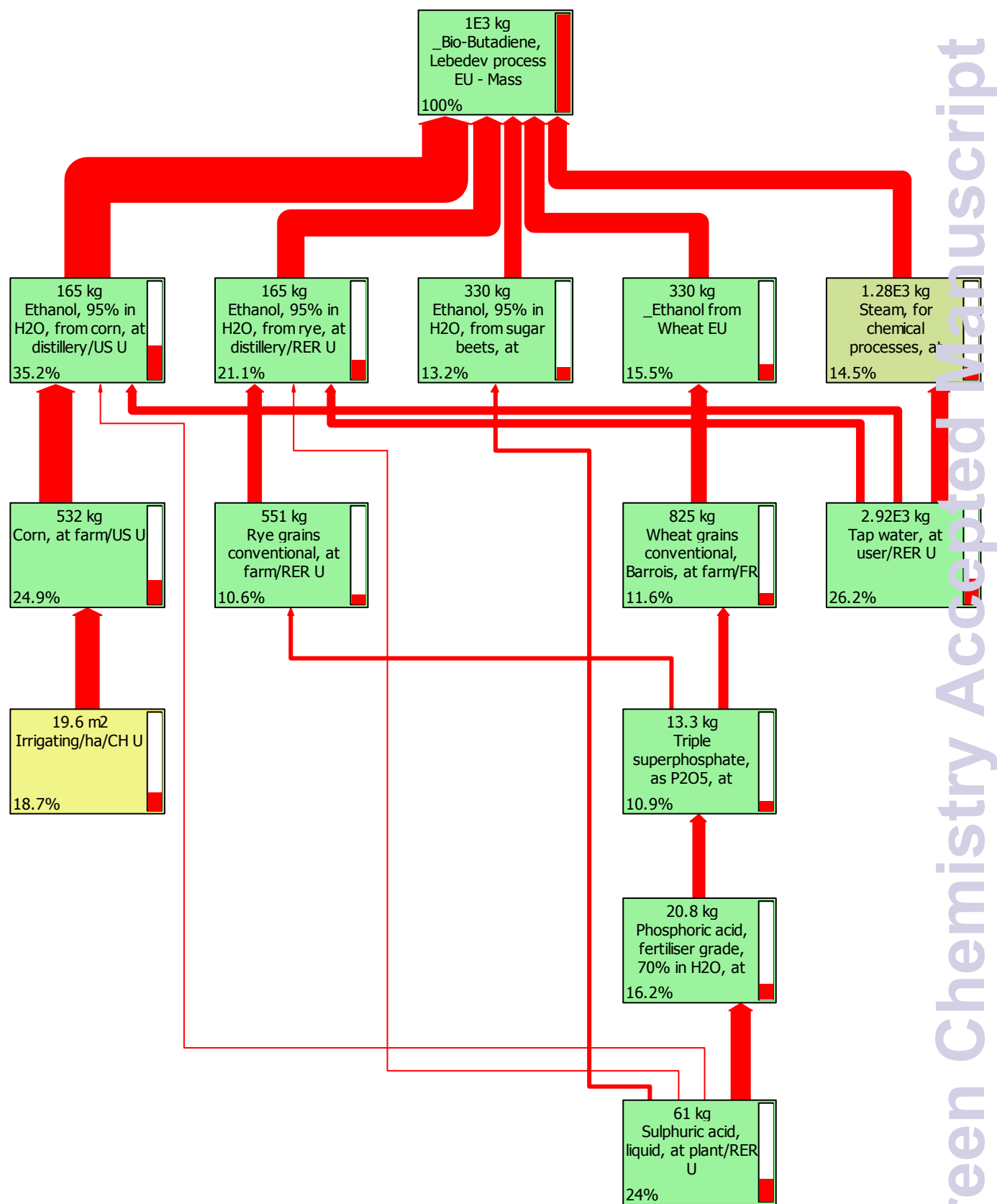
Fig. S7 Contribution to water depletion through network tool for the Lebedev process in Europe.

Impact categories - Pt	BD, naphthta cracking	Bio- BD, Lebedev (EU)	Bio- BD, Lebedev (BR)	Bio- BD, Lebedev (US)	Bio- BD, Ostromisslensky (EU)	Bio- BD, Ostromisslensky (BR)	Bio- BD, Ostromisslensky (US)	Bio-BD, Ostromisslensky (US)-NO 100% bio
Climate change	7.38E+01	7.31E+01	3.46E+01	8.23E+01	1.30E+02	7.45E+01	1.43E+02	1.59E+02
Particu. matter formation	1.39E+01	2.29E+01	2.04E+01	2.35E+01	3.25E+01	2.89E+01	3.33E+01	3.42E+01
Terrestrial ecotoxicity	9.28E-03	5.22E+00	5.29E+00	1.21E+00	7.51E+00	7.61E+00	1.74E+00	1.22E+00
Agricul. land occupation	1.60E-02	2.78E+01	1.67E+01	1.90E+01	4.00E+01	2.39E+01	2.73E+01	1.92E+01
Fossil fuel depletion	1.56E+02	4.60E+01	1.92E+01	5.58E+01	5.84E+01	1.98E+01	7.25E+01	1.22E+02
Tot	2.43E+02	1.77E+02	9.76E+01	1.84E+02	2.68E+02	1.55E+02	2.78E+02	3.36E+02

Tab. S7 Results from the ReCiPe aggregation procedure into single-score eco-indicator.
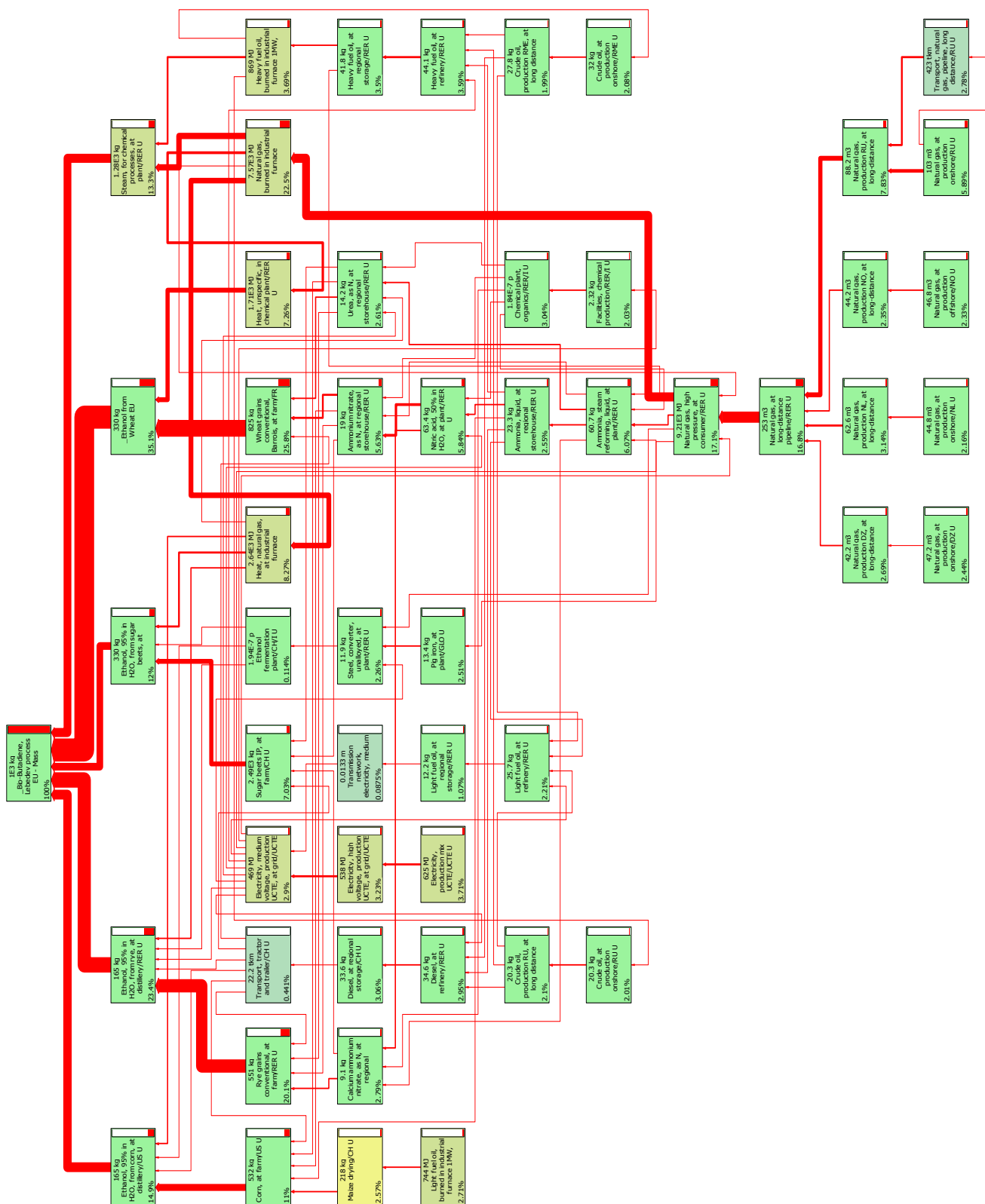
Fig. S8 Contribution to the ReCiPe single-score using network tool for the Lebedev process in Europe.
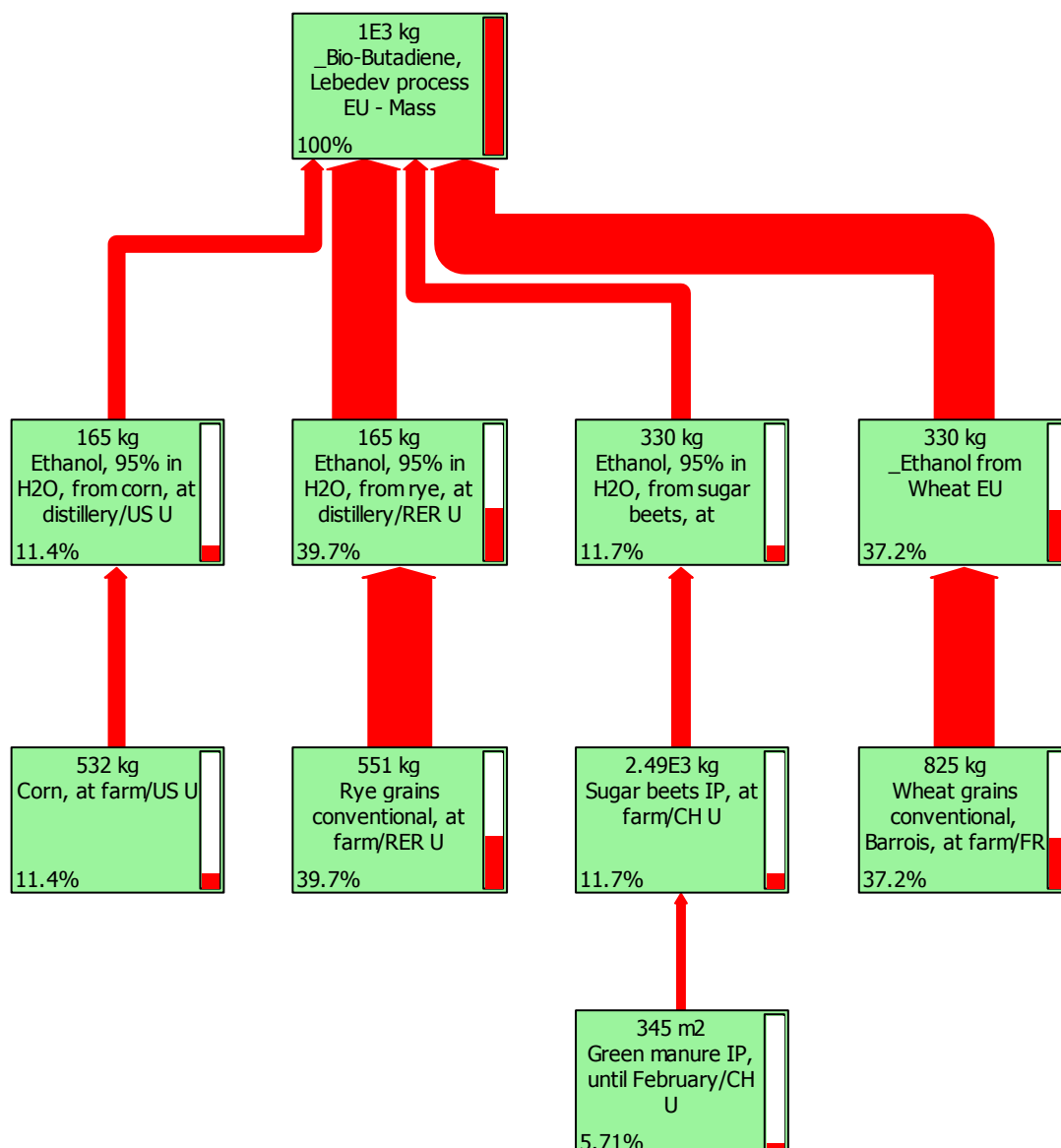
Fig. S9 Contribution to the agricultural land occupation through network tool for the Lebedev process in Europe.

Contribution to PMF	BD, naphthta cracking	Bio- BD, Lebedev (EU)	Bio- BD, Lebedev (BR)	Bio- BD, Lebedev (US)	Bio- BD, Ostromisslensky (EU)	Bio- BD, Ostromisslensky (BR)	Bio- BD, Ostromis lensky (US)
Process Energy	30%	6%	7%	6%	5%	5%	5%
Naphtha prduction	70%	0%	0%	0%	0%	0%	0%
Ethanol production	0%	94%	93%	94%	95%	95%	95%

Tab. S8 Contribution to PMF impact category.

```
                          ┌─────────────────┐
                          │ 1E3 kg          │
                          │ _Butadiene      │
                          │ naphtha steam   │
                          │ cracking -      │
                          │ 100%            │
                          └────────┬────────┘
            ┌──────────────────────┼──────────────────────────────┐
            │                      │                              │
   ┌────────┴────────┐                              ┌────────────┴────────┐
   │ 1.05E3 kg       │                              │ 8.98E3 MJ           │
   │ Naphtha, at     │                              │ Heat, unspecific,   │
   │ refinery/RER U  │                              │ in chemical         │
   │                 │                              │ plant/RER U         │
   │ 79%             │                              │ 21.2%               │
   └───┬─────────────┘                              └──────────┬──────────┘
```

| 210 kg Crude oil, production RU, at long distance 17.5% | 288 kg Crude oil, production RME, at long distance 20.9% | 256 kg Crude oil, production NO, at long distance 17.8% | 205 kg Crude oil, production GB, at long distance 14.7% | 7.23E3 MJ Natural gas, burned in industrial furnace 12.8% |

| 210 kg Crude oil, at production onshore/RU U 17% | 302 kg Crude oil, at production onshore/RME U 21.1% | 256 kg Crude oil, at production offshore/NO U 17.8% | 205 kg Crude oil, at production offshore/GB U 14.6% |