

Article

## Exergetical Evaluation of Biobased Synthesis Pathways

Philipp Frenzel <sup>1</sup>, Rafaela Hillerbrand <sup>2</sup> and Andreas Pfennig <sup>1,\*</sup>

<sup>1</sup> Institute of Chemical Engineering and Environmental Technology, TU Graz, Inffeldgasse 25/C/II, Graz 8010, Austria; E-Mail: philipp.frenzel@rwth-aachen.de

<sup>2</sup> Department of Values, Technology and Innovation, TPM—Faculty of Technology, Policy and Management, Delft University of Technology, Jaffalaan 5, BX Delft NL-2628, The Netherlands; E-Mail: r.c.hillerbrand@tudelft.nl

\* Author to whom correspondence should be addressed; E-Mail: andreas.pfennig@tugraz.at; Tel.: +43-316-873-7463; Fax: +43-316-873-7469.

Received: 13 January 2014; in revised form: 26 January 2014 / Accepted: 27 January 2014 /

Published: 29 January 2014

---

**Abstract:** The vast majority of today's chemical products are based on crude oil. An attractive and sustainable alternative feedstock is biomass. Since crude oil and biomass differ in various properties, new synthesis pathways and processes have to be developed. In order to prioritize limited resources for research and development (R & D), their economic potential must be estimated in the early stages of development. A suitable measure for an estimation of the economic potential is based on exergy balances. Different structures of synthesis pathways characterised by the chemical exergy of the main components are evaluated. Based on a detailed evaluation of the underlying processes, general recommendations for future bio-based synthesis pathways are derived.

**Keywords:** biomass; bio-based products; exergy analysis; synthesis pathways

### Nomenclature:

$E$	molar exergy (J/kmol)
$E_{\text{chem}}$	molar chemical exergy (J/kmol)
$E_{\text{chem,el},i}$	molar chemical exergy of an element (J/kmol)
$\dot{E}_{\text{in}}$	exergy flux of entering stream (J/s)
$\dot{E}_{\text{loss}}$	exergy loss (J/s)
$E_{\text{mix}}$	molar mixing exergy (J/kmol)

Cont.

$\dot{E}_{\text{out}}$	exergy flux of leaving stream (J/s)
$E_{\text{phys}}$	molar physical exergy (J/kmol)
$\dot{E}_{\text{util,in}}$	exergy flux of entering utilities (J/s)
$\dot{E}_{\text{util,out}}$	exergy flux of leaving utilities (J/s)
$f_{\text{alloc}}$	allocation factor (–)
$\Delta_r G^\circ$	molar Gibbs energy of formation (J/kmol)
$H$	molar enthalpy (J/kmol)
$m_{\text{feedstock}}$	mass of feedstock (kg)
$m_{\text{product}}$	mass of product (kg)
$m_{\text{by-products}}$	mass of by-products (kg)
$N_{\text{el}}$	number of elements (–)
$p$	pressure (Pa)
$S$	molar entropy (J/kmol K) / selectivity (–)
$T$	temperature (K)
$w_{\text{aq}}$	weight fraction of aqueous solution (kg/kg)
$X$	conversion (–)
$\eta_{\text{mass}}$	mass efficiency (–)

## 1. Introduction

The chemical industry requires a carbon source for the production of the chemical goods. Today, approximately 80% of the feedstock is crude oil. A further 10% are other fossil raw materials like natural gas or coal. The remaining 10% is based on biomass [1].

Due to the continuously rising price of fossil raw materials [2] and the international efforts to limit greenhouse-gas emissions [3,4], alternative feedstocks are becoming more attractive. One alternative feedstock is biomass that is easily accessible and available in sufficient quantities [5,6].

Since the chemical structure and the properties of biomass differ significantly from those of crude oil, it is not possible to directly substitute direct biomass for crude oil. New synthesis pathways and corresponding underlying processes will have to be developed. Currently, different approaches for utilizing biomass are investigated (e.g., [7–14]) and it is not clear which of the approaches will be most successful.

In this paper, bio-based synthesis pathways are evaluated. Most of the bio-based synthesis pathways are in an early stage of development in which only little information about the processes is available. In order to control the limited resources for research and development (R & D), an early evaluation of the economic potential of the synthesis pathways is required. To perform such an early evaluation, sufficient economic data are usually not available. An evaluation with material and energy balances alone, however, does not suffice because energy balances cannot distinguish between different forms

of energy. By accounting of both enthalpy and entropy flows in the form of exergy, it is possible to assess the quality and, hence, the economic value of different energy forms [15]. Exergy balances are thus applied for evaluation of the considered synthesis pathways in this paper. The aim is to identify principle aspects from the exergetic point of view, which will have to be considered in the design and development of new synthesis pathways.

## 2. Methods

In the following, the basic equations for calculation of exergy flows, the system boundary required for the accounting of exergy flows and the according measures are introduced.

The molar exergy content of a material flow is composed of three terms [16], namely the chemical exergy  $E_{\text{chem}}$ , the physical exergy  $E_{\text{phys}}$ , and the mixing exergy  $E_{\text{mix}}$ :

$$E = E_{\text{chem}} + E_{\text{phys}} + E_{\text{mix}} \quad (1)$$

In general, exergy is the work that can be obtained by bringing a substance through a reversible process into equilibrium with the environment [17]. Thus, exergy has to be defined with respect to a reference environment.

Chemical exergy is the exergy content of a substance at reference conditions regarding temperature and pressure. The molar chemical exergy of a component is given by the sum of molar Gibbs energy of formation  $\Delta_f G^\circ$  and molar standard exergy values  $E_{\text{chem,el},i}$  that depend on the composition of the environment:

$$E_{\text{chem}}^\circ = \Delta_f G^\circ + \sum_{i=1}^{N_{\text{el}}} \nu_{\text{el},i} E_{\text{chem,el},i} \quad (2)$$

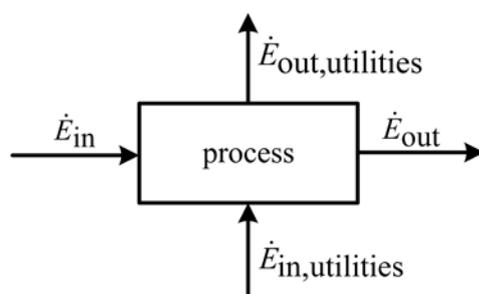
where  $N_{\text{el}}$  is the number of different elements and  $\nu_{\text{el},i}$  denotes the stoichiometric coefficient of each element in the substance [17]. Physical exergy is the exergy content of a substance due to differences with the environment regarding temperature and pressure. It can be calculated as a sum of enthalpy and entropy differences with the environment:

$$E_{\text{phys}} = H(T, p) - H_0(T_0, p_0) - T_0[S(T, p) - S_0(T_0, p_0)] \quad (3)$$

where  $H$  is the molar enthalpy and  $S$  the molar entropy of a substance at temperature  $T$  and pressure  $p$ . The subscript 0 denotes the state of the environment. Mixing exergy is usually smaller than chemical and physical exergy and can generally be neglected.

The calculation of exergy depends on a reference environment. In this paper, the reference model of Szargut *et al.* is used for the composition of the environment [17]. Regarding reference temperature and pressure standard conditions are used, because in this case, the Gibbs energy of formation also can be used at standard conditions for calculation of the chemical exergy.

For an assessment of systems with exergy balances, an appropriate measure is required. The measure is based on the system depicted in Figure 1.

**Figure 1.** Entering and leaving exergy flows of a chemical process.

The difference that results in balancing of all entering and leaving exergy flows is denoted as exergy loss  $\dot{E}_{loss}$ :

$$\dot{E}_{loss} = \sum_i \dot{E}_{in,i} - \sum_j \dot{E}_{out,j} + \sum_k \dot{E}_{util,in,k} - \sum_l \dot{E}_{util,out,l} \quad (4)$$

where  $\dot{E}_{in}$  and  $\dot{E}_{out}$  denote the entering and leaving material flows and  $\dot{E}_{util,in}$  and  $\dot{E}_{util,out}$  the entering and leaving utilities.

By applying Equation (4), a synthesis pathway or a process can be judged based on a single number. In order to allow comparability, the measure is given specifically based on a functional unit. In this paper, the functional unit is one kilogram of product. According to Kim and Overcash, in 20% of the processes, valuable by-products are produced [18]. In these cases, the exergy losses have to be allocated to main and by-products. This is a typical issue in life cycle assessments (LCA) according to DIN 14,044, so that solutions can be found in this field [19–23]. As suggested by Marvuglia *et al.* and Schmidt, the allocation should be carried out by causal connections that are based on physical or chemical principles [24,25]. Hence, a casual allocation is possible if the exergy losses of a single unit operation can be assigned distinctly to the product. If both product and by-products occur in one unit operation, a causal-based allocation is not possible without deeper understanding. In this case, a non-casual allocation is chosen based on the respective mass flows [26–28]. To this end, the allocation factor  $f_{alloc}$  is defined, with which the exergy losses are weighted according to weight fraction of the product:

$$f_{alloc} = \frac{m_{product}}{m_{product} + m_{by-products}} \quad (5)$$

where  $m_{product}$  denotes the mass of product and  $m_{by-product}$  the mass of by-products that leave the process.

The exergy analyses based on the descriptions above are carried out in the simulation toolbox called ExergySim we developed. To this end, the underlying processes of the synthesis pathways have been modelled in this toolbox. The process models are based on process descriptions taken from literature. Essential assumptions and the associated references of the process models are depicted in Table 1. Processes that already have been developed years ago are usually well described in Ullmann's Encyclopedia of Industrial Chemistry [29]. In these cases, detailed information about reaction conditions, conversions, feed compositions and downstream processing can be found.

For missing information like the provision of heat, exergetically advantageous assumptions have been made. Some processes are in a stage of development in which no complete process descriptions are publicly available. If the basic technical feasibility of a process has already been demonstrated, this information is often available in patents. These patents usually describe only a certain segment of a process, like a catalyst of the reaction or a suitable downstream processing. For missing information, exergetically advantageous assumptions have also been made or assumptions have been adopted from similar processes. In an even earlier stage of development of a process, only information about the reactions is available. For these reactions that are usually only tested in laboratories, process flow sheets usually do not exist. Nevertheless, in order to carry out an evaluation, hypothetical processes with typical unit operations for separation of the reaction mixture are assumed. To ensure a general comparability of the considered processes, heat and material flows are integrated identically e.g., with respect to temperature differences for heat transfer as well as purge flows. Properties of the pure components are taken from the Design Institute for Physical Properties database [30].

**Table 1.** Basic data and references for the modeled processes.

Process	Reaction	References
glucose → ethanol	$C_6H_{12}O_6 \rightarrow C_2H_6O + 2CO_2$ $X_{ethanol} = 1$ $T_r = 308 \text{ K}$ $p_r = 1 \text{ bar}$ $w_{aq} = 0.8 \text{ kg/kg}$	[31]
ethanol → ethylene	$C_2H_6O \rightarrow C_2H_4 + H_2O$ $2C_2H_6O \rightarrow (C_2H_5)_2O + H_2O$ $X_{ethanol} = 0.98$ $S_{ethylene} = 0.97$ $T_r = 625 \text{ K}$ $p_r = 40 \text{ bar}$	[32]
ethylene → ethylene oxide	$C_2H_4 + 0.5 O_2 \rightarrow C_2H_4O$ $CH_4 + 2 O_2 \rightarrow CO_2 + 2H_2O$ $X_{oxygen} = 0.35$ $S_{ethyleneoxide} = 0.80$ $T_r = 501 \text{ K}$ $p_r = 16 \text{ bar}$	[33,34]
ethylene oxide → 1,2-ethanediol	$C_2H_4O + H_2O \rightarrow C_2H_6O_2$ $X_{ethyleneoxide} = 1$ $T_r = 363 \text{ K}$ $p_r = 20 \text{ bar}$	[35]
glucose → 1,2-ethanediol	$C_6H_{12}O_6 + 3H_2 \rightarrow C_2H_6O_2$ $C_6H_{12}O_6 + H_2 \rightarrow C_6H_{14}O_6$ $X_{glucose} = 0.72$ $S_{1,2-ethanediol} = 0.06$ $T_r = 433 \text{ K}$ $p_r = 50 \text{ bar}$ $w_{aq} = 0.8 \text{ kg/kg}$	[36]

Table 1. Cont.

Process	Reaction	References
glucose → lactic acid	$C_6H_{12}O_6 \rightarrow C_3H_6O_3$ $X_{\text{lactic acid}} = 0.95$ $T_r = 323 \text{ K}$ $p_r = 1 \text{ bar}$ $w_{\text{aq}} = 0.8 \text{ kg/kg}$	[37]
plant oil → ethylene	$X_{\text{plantoil}} = 0.945$ $S_{\text{ethylene}} = 0.41$ $T_r = 773 \text{ K}$ $p_r = 1 \text{ bar}$ other by-products (mass fractions): propylene (0.14), carbon monoxide (0.05), carbon (0.06), methane (0.08), ethane (0.03), <i>n</i> -butane (0.13), <i>p</i> -xylene (0.04), benzene (0.04), hydrogen (0.01) degrees of freedom: carbon dioxide, water	[38]
plant oil → ethylene	$C_{57}H_{104}O_6 + 9 H_2 \rightarrow 27 C_2H_4 + C_3H_8O_3 + 3 H_2O$ $X_{\text{plantoil}} = 1$ $T_r = 500 \text{ K}$ $p_r = 1 \text{ bar}$	structure-destroying (simplified)
plant oil → 1-octadecene	$C_{57}H_{104}O_6 + 9 H_2 \rightarrow 3 C_{18}H_{36} + C_3H_8O_3 + 3 H_2O$ $X_{\text{plantoil}} = 1$ $T_r = 370 \text{ K}$ $p_r = 1 \text{ bar}$	structure-preserving (simplified)

### 3. Selection of Representative Synthesis Pathways

In principle, many different bio-based synthesis pathways are conceivable. The synthesis pathways differ in the type of bio-based feedstock, their intermediates as well as their products. This raises the question as to which combination of feedstock, intermediates and products is advantageous in terms of economic potential. As basis for such an evaluation, some representative synthesis pathways are chosen that will be evaluated.

The properties of biomass and crude oil differ significantly, especially in their chemical composition. Crude oil and other fossil raw materials consist mainly of carbon and hydrogen and essentially no oxygen. The element ratios of conventional products like the bulk plastics polyethylene, polypropylene, polystyrene are very similar to their fossil raw material and contain mostly no oxygen as well. In contrast to that, the oxygen content of biomass is up to roughly 50 wt %. To produce conventional products from biomass, the oxygen content, *i.e.*, the O:C-ratio has to be adjusted along the synthesis pathway. The material adjustment is less, if products and raw materials are similar in element composition. Two approaches are conceivable in order to design synthesis pathways with little material adjustments: On the one hand, alternative bio-based raw materials can be used, the oxygen content of which is low and, thus, their composition is similar to today's conventional products. On the other hand, new products can be targeted with higher oxygen content and element ratios more similar to typical bio-based raw materials.

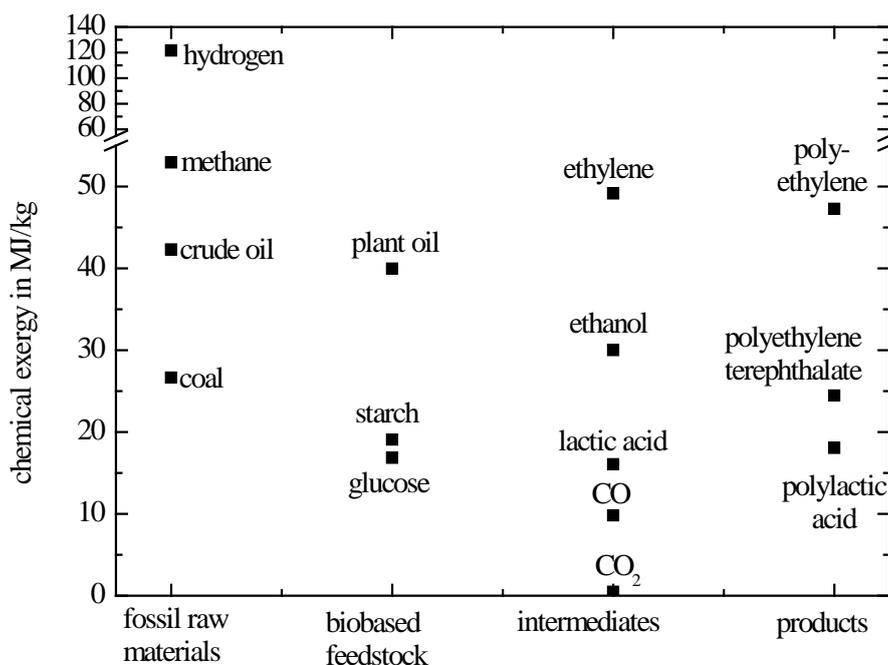
Alternative raw materials of the first approach are lignin or plant oil. The oxygen content of both lignin and plant oil is low and, thus, they differ only slightly from today's conventional products in this aspect. However, the depolymerisation of lignin and the selective usage of defined fragments as raw material are difficult because of its complex structure [39]. Plant oil consists of triglycerides which are already used today in large quantities for the production of bio-diesel [40] and chemical products like detergents.

Examples for the second approach, *i.e.*, the adjustments of the product to its raw material, are polyethylterephthalat and new bio-based polymers like polylactic acid and polyhydroxybutyrate, polymers with high oxygen content similar to that of glucose.

In order to evaluate the economic potential of these different routes, exergy balances can be used according to the exergoeconomic approach. As a first step, the often largest contribution to exergy, namely the chemical exergy, is regarded. Chemical exergy is a measure not only of the effects due to chemical composition but also of the effects of the molecular structure. Because the chemical exergy characterizes the value of components, it can be taken as a first indicator for evaluating the material adjustments within a synthesis pathway.

In Figure 2, the chemical exergy of crude oil, bio-based raw materials and conventional as well as bio-based polymers is depicted. Additionally, the chemical exergy of further reagents and by-products is shown.

**Figure 2.** Chemical exergy of fossil and biobased raw materials, intermediates and conventional and biobased polymers.



It is evident that the chemical exergy of components is high, if their oxygen content is low and *vice versa*. Because of its low oxygen content, the chemical exergy of crude oil is relatively high. Likewise, ethylene that is a typical crude-oil based intermediate has a high chemical exergy as well as the conventional polymers depicted in Figure 2. Therefore, the chemical exergy of the main components involved in typical synthesis pathways of petrochemistry is relatively similar. In contrast

to that, the chemical exergy of bio-based precursors like glucose or starch is significantly lower. Processes for conventional products with a low oxygen content based on biobased feedstock thus have to make up for this difference. If, on the other hand, polymers with a chemical exergy similar to glucose are produced from biomass, the synthesis pathways would again be horizontal like classical crude-oil based synthesis pathways.

Thus, different routes of synthesis pathways are possible that can be characterized by the chemical exergy of the components involved. Four characteristic routes can be identified:

- Horizontal routes: Chemical exergy and oxygen content of all main components involved is nearly the same.
- Routes increasing in chemical exergy: Chemical exergy of the product is higher, and oxygen content is lower compared to the feedstock.
- Routes decreasing in chemical exergy: Chemical exergy of the product is lower, and oxygen content is higher compared to the feedstock.
- Routes first increasing, then decreasing or first decreasing, then increasing in chemical exergy: Chemical exergy and oxygen content of the product and the feedstock is similar, but chemical exergy of intermediates is higher and their oxygen content is lower or *vice versa*.

To investigate the effect of the different routes, the role of the chemical exergy is examined. According to Equation (2), the chemical exergy of a component is closely linked to the Gibbs energy of formation, from which the Gibbs energy of reaction can be calculated for a given stoichiometry. Frenzel *et al.* have shown that the Gibbs energy of reaction needs to be negative or at most slightly positive in order to obtain processes with low overall exergy losses, because otherwise chemical equilibrium will reach only a low yield leading to high separation effort and large recycle streams [41]. For synthesis pathways, where the chemical exergy of the product is higher than that of the feedstock, either a further exergy-rich reactant has to be added or a low-exergy by-product has to be eliminated. Both options are associated with disadvantages: To generate exergy-rich reactants like hydrogen, additional exergy is required. By elimination of low-exergy by-products like carbon dioxide or water, only a part of the feedstock is available for the product. In the opposite case, where the chemical exergy of the product is lower compared to the feedstock, either a further low-exergy reactant has to be added or an exergy-rich by-product has to be eliminated and, therefore, the amount of the main feedstock required is reduced. To account for the effects of elimination of by-products and addition of further reactants a mass efficiency is defined, which shows how well the feedstock is utilized in the main product:

$$\eta_{\text{mass}} = \frac{m_{\text{product}}}{m_{\text{feedstock}}} \quad (6)$$

where  $m_{\text{feedstock}}$  is the mass of the feedstock and  $m_{\text{product}}$  that of the main product.

Thus, with reactions with additional products or reactants, it is possible to develop synthesis pathways where the exergy of the essential step is increasing or decreasing without thermodynamic limitations and where the mass efficiency allows judging the effect of the additional components. In the following, representative synthesis pathways are chosen, which correspond to the routes mentioned above.

The bio-based feedstock of the considered synthesis pathways are glucose and plant oil. As end products, polyethylene, polyethylene terephthalate and polylactic acid are chosen. Polyethylene is a plastic with the highest production volume worldwide and without any oxygen. Polyethylene terephthalate is a polyester with a high production volume as well but with a significant oxygen content. Polylactic acid is also an oxygen containing polyester which can substitute polyethylene terephthalate [42]. The polymers polyethylene and polyethylene terephthalate are based on monomers which are conventionally produced from crude oil. Because the bio- and crude-oil based synthesis pathways compete with each other, corresponding synthesis pathways from crude oil to these polymers are chosen as a benchmark.

The chosen precursors and polymers cover substances with different exergy and oxygen content, so that the characteristic routes of the synthesis pathways discussed above can be mapped in principle. The structure of the synthesis pathways which are examined is depicted in Table 2. The chemical composition of crude oil is assumed to be 86.5 wt % carbon, 12.5 wt % hydrogen and 1 wt % oxygen [43]. Plant oil is approximated with triolein, a triglyceride with three oleic acid side groups.

**Table 2.** Structure of the synthesis pathways.

Feedstock	Products		
	PE	PET	PLA
crude oil	horizontal	decreasing	-
plant oil	horizontal	-	-
glucose	decreasing	horizontal, first increasing and then decreasing	

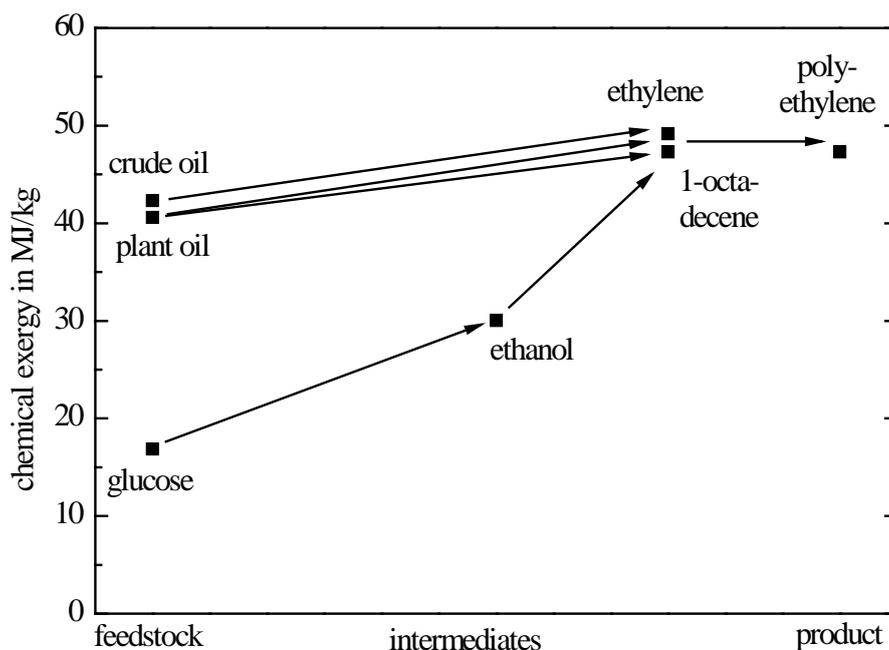
#### 4. Results and Discussion

In the following, the exergy losses of the entire synthesis pathways will be discussed. The discussion addresses several goals: First, the effects of the different characteristic routes of the synthesis pathways are indicated. Structures of synthesis pathways are identified that promise a high exergetic potential. Secondly, particularities of individual processes are indicated, where the insights based on exergy losses can be transferred to other processes. Thirdly, the applicability of exergy balances as an analysis tool is examined for processes that are in an early stage of development.

The first end product is polyethylene for which four synthesis pathways are considered. The structures of the synthesis pathways are depicted by the chemical exergy of the raw materials, intermediates and the end product in Figure 3. Each arrow represents a process that is modelled separately.

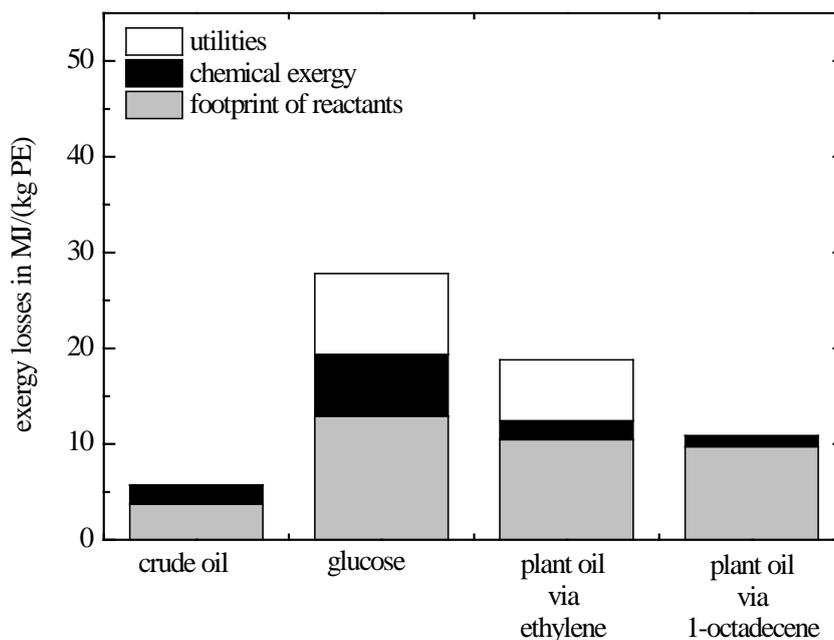
Polyethylene contains no oxygen and, therefore, its chemical exergy is high. The typical monomer of polyethylene is ethylene, on which three of the four synthesis pathways are based. Today, ethylene is typically obtained from crude oil. The chemical exergy of the main components of this synthesis pathway is nearly identical. Therefore, the course of this synthesis pathway is horizontal. The situation is similar to synthesis pathways starting from plant oil, the chemical exergy of which is high as well. On the one hand, the alkyl substituents of plant oil can be cracked to ethylene by gasification. Therefore, the course of this synthesis pathway is horizontal. On the other hand, it has been assumed that the alkyl substituents of the triglycerides can be preserved and converted to polyethylene directly. Because the chemical exergy of the intermediate 1-octadecene is also high, the course of this synthesis pathway is horizontal as well. The fourth synthesis pathway starting from glucose has an increasing course because the chemical exergy of glucose is significantly lower than that of ethylene or polyethylene.

**Figure 3.** Structure of the considered synthesis pathways to polyethylene.



The exergy losses related to polyethylene for the whole synthesis pathways are depicted in Figure 4. The total exergy losses are separated into three parts: exergy losses regarding chemical exergy, use of utilities, and provision of raw materials and reactants that are indicated as footprints. The values for the footprints are taken from Frenzel *et al.* [44].

**Figure 4.** Specific exergy losses of the considered synthesis pathways to polyethylene.



The conventional synthesis pathway starting from crude oil has the lowest exergy losses of all considered synthesis pathways. In this case, the footprint refers to obtaining ethylene from crude oil. In the subsequent polymerisation, chemical exergy is destroyed in an exothermal reaction. In this exothermal reaction, sufficient heat is released to cover the external heat demand in this process.

The exergy losses of the glucose-route are significantly higher compared to the crude-oil route. The reason for that is the large input of raw materials required to obtain one unit of polyethylene. According to Figure 3, the synthesis pathway from glucose to ethylene consists of two separate processes. In both processes, the specific chemical exergy of each product is increased compared to their respective reagents. As mentioned above, this is achieved either by adding exergy-rich reactants or low-exergy by-product has to be eliminated. Here, in the first process, carbon dioxide is released during the fermentation of glucose to ethanol, and in the second process, the production of ethylene from ethanol water is eliminated. These effects are described by the mass efficiency according to Equation (6). For the synthesis pathway of glucose to ethylene, the mass efficiency is only 0.27. That means to obtain one kilogram of ethylene, 3.7 kg of glucose are required associated with a correspondingly high footprint.

Besides the footprint of the raw materials, further exergy losses occur within the two processes. Regarding exergy losses in biotechnology processes, two aspects can be identified for the production of ethanol from glucose. On the one hand, biotechnology processes are usually carried out at moderate temperatures and ambient pressure. Therefore, the exergy losses associated with adjustment of reaction conditions are typically low. On the other hand, the product needs to be separated from a diluted aqueous solution. In this case, the downstream processing caused exergy losses of 3.2 MJ/(kg ethanol) and, hence, more than half of the total exergy losses of this process. In context of the entire synthesis pathway from glucose to polyethylene, this exergy loss is even magnified, because the mass efficiency from the intermediate ethanol to polyethylene is significantly lower than unity. Thus, not only the footprints of the primary raw materials like glucose are multiplied, but also the losses of the previous process steps within a synthesis pathway. These effects are characteristic for synthesis pathways where the exergy is increasing and, therefore, transferable to other similar synthesis pathways.

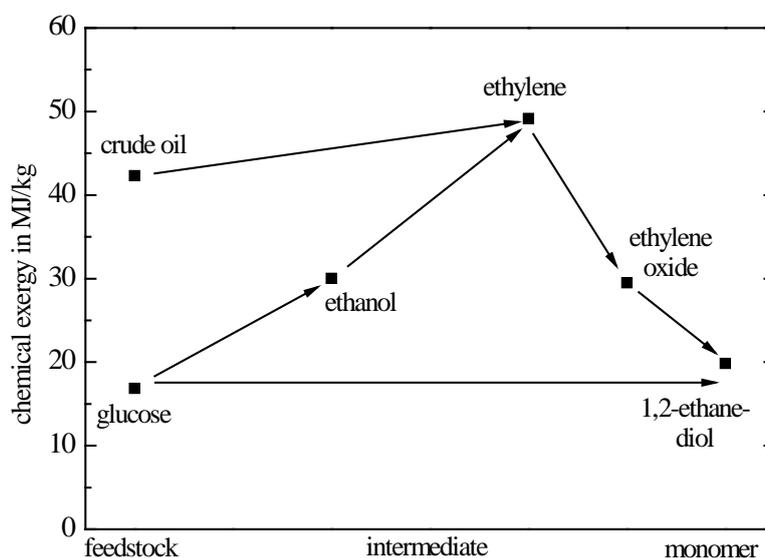
The exergy losses of the horizontal synthesis pathway starting out from plant oil are significantly lower compared to the synthesis pathway starting from glucose. The reason for this is the better utilization of the raw materials and the improved associated mass efficiency according to Equation (6). Starting from plant oil, two horizontal synthesis pathways are considered. The difference between these synthesis pathways is how well the structure of the plant oil is preserved. In the first synthesis pathway, plant oil is cracked to the C<sub>2</sub>-building block ethylene. Because polyethylene consists of long carbon chains, it seems reasonable to utilize and, therefore, preserve the alkyl substituents instead of cracking them. This is achieved if 1-octadecene is used exemplarily as intermediate in the second synthesis pathway from plant oil. The exergy losses depicted in Figure 4 for this synthesis pathway are based on a hypothetical process and represent a lower limit. A direct comparison of both synthesis pathways shows that the exergy losses regarding raw-material footprint and chemical exergy are similar. Because both the minimal reaction temperature required for a high conversion and the intensity of the underlying endothermic reaction are significantly lower, if the alkyl substituents are preserved, the exergy losses regarding the utilities are lower compared to the synthesis pathway via ethylene. Today, no suitable catalyst is available for this kind of reaction. In order to use these savings, potential new catalysts need to be developed in the future that allow a direct, structure-preserving conversion of the feedstock.

Thus, all synthesis pathways considered above leading to an end product—the chemical exergy of which is higher than that of the starting material—can be associated with high exergy losses.

The second end product considered here is polyethylene terephthalate, a high-volume polyester. Because of its high oxygen content of 33%, the chemical exergy of polyethylene terephthalate is significantly lower compared to polyethylene. Polyethylene terephthalate is based on two monomers: 1,2-ethanediol and terephthalic acid.

The considered synthesis pathways to 1,2-ethanediol are depicted in Figure 5. As in Figure 4, the structure of the synthesis pathways is depicted following the chemical exergy of the main components.

**Figure 5.** Structure of the considered synthesis pathways to 1,2-ethanediol that is one monomer of polyethylene terephthalate.



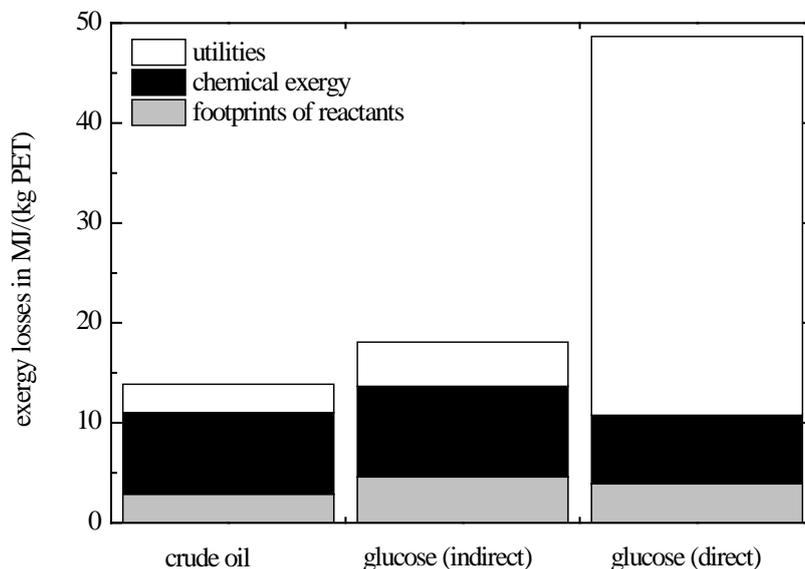
Today, 1,2-ethanediol is produced from crude oil via ethylene. Subsequently, ethylene is oxidized, first with oxygen to ethylene oxide and afterwards with water, because of which the exergy of this synthesis pathway is decreasing. A further synthesis pathway starts from glucose and leads to 1,2-ethanediol via ethylene as well. Because the chemical exergy of ethylene is higher than that of glucose and 1,2-ethanediol, the exergy along this synthesis pathway is first increasing and then decreasing. In the following, this synthesis pathway is indicated as an indirect synthesis pathway. An alternative is the hydrogenation of glucose to 1,2-ethanediol. Because 1,2-ethanediol is obtained from glucose directly, this pathway is indicated as a direct synthesis pathway.

For these synthesis pathways to polyethylene terephthalate, it is assumed that the second monomer—terephthalic acid—is obtained in all cases from crude-oil based *p*-xylene because this is the usual process for its production today.

The exergy losses related to polyethylene terephthalate for these synthesis pathways are depicted in Figure 6. Today's synthesis pathway for production of polyethylene terephthalate leads to the lowest exergy losses. The exergy losses of the indirect synthesis pathway starting from glucose are of the same order of magnitude. In contrast to that, the exergy losses of the direct synthesis pathway from glucose are significantly higher due to the high exergy losses to produce 1,2-ethanediol from glucose where the data have been taken from literature. This process is currently in an early stage of development, and especially, conversion and selectivity achieved by the catalyst are low. According to Palkovits *et al.*, conversion of glucose of 72%, and selectivity to 1,2-ethanediol of only 6% have been

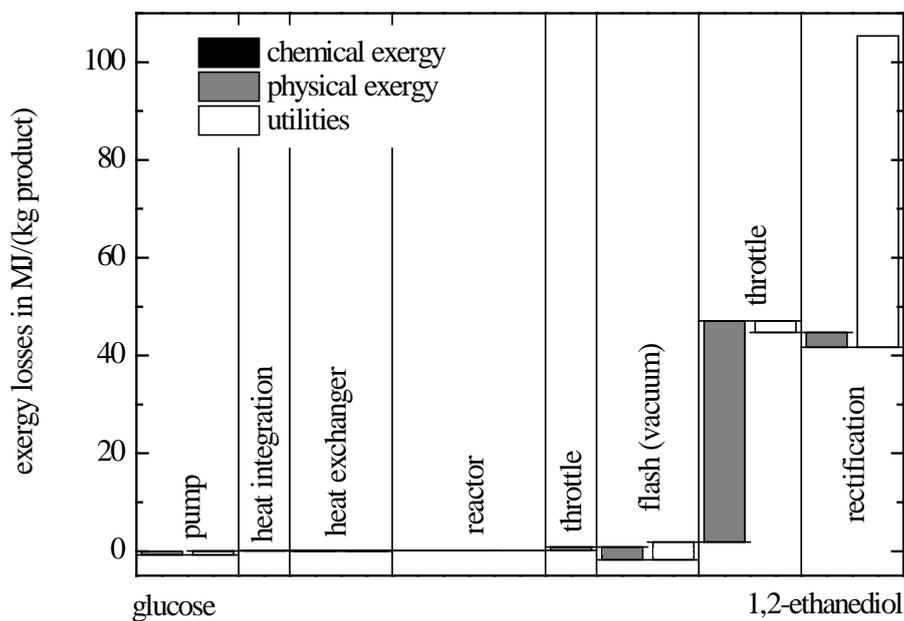
reached [36]. Besides 1,2-ethanediol, further by-products occur like glycerol, xylitol or sorbitol. The by-product with the highest fraction is sorbitol, which is why here sorbitol is taken as placeholder for all by-products occurring for simplicity. The exergy losses are allocated between the main product 1,2-ethanediol and this by-product based on their mass flows. Because of this allocation, the associated feedstock footprint is low for 1,2-ethanediol, although due to the low selectivity, only a small part is converted to the desired product.

**Figure 6.** Specific exergy losses of the considered synthesis pathways to polyethylene terephthalate.



Besides the exergy losses caused by the feedstock, additional losses occur in the chemical process that are depicted in Figure 7 for the respective exergy contributions according to Equation (1) and each unit operation. To improve the clarity of the figure, only exergy changes above 0.1 MJ/(kg product) are shown.

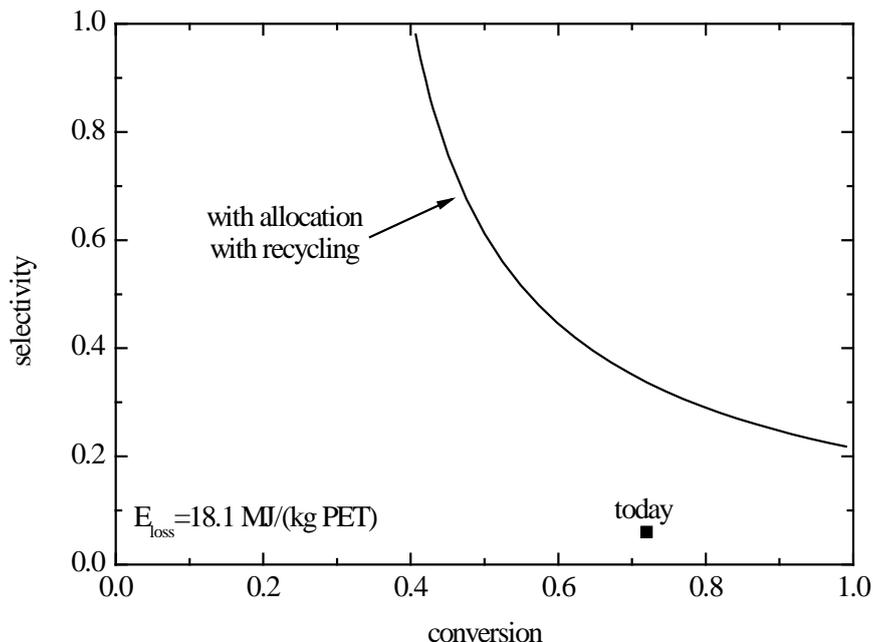
**Figure 7.** Exergy losses caused in the process for the production of 1,2-ethanediol from glucose.



The exergy losses caused by setting of the reaction conditions like the temperature of 433 K and the pressure of 50 bar and carrying out of the reaction itself are actually relatively low. Because the reaction is carried out in a diluted aqueous solution, the separation of the reaction mixture is associated with high exergy losses. In a vacuum flash, glucose that is not converted is separated from water and 1,2-ethanediol. A subsequent separation of water and 1,2-ethanediol is carried out in a distillation column, where 1,2-ethanediol is the bottom product. The exergy losses can be reduced, if a higher product concentration would be achieved, for which a catalyst would be required that allows a higher selectivity or conversion. In order to formulate specific objectives for the catalyst development, the saving potential can be estimated from the corresponding exergy balances.

Here, a combination of selectivity and conversion is used to characterize the improvement. In the corresponding diagram (Figure 8), it can be indicated at which combination of these variables the exergy losses of the direct synthesis pathway are identical to those of the indirect synthesis pathway. The exergy losses are based on allocation of the by-products and the recycling of the reactants that are not converted in the reactor. By allocation, the product-specific exergy losses can be reduced according to Equation (5). A further reduction of exergy losses caused by the footprint of the reactants is achieved if non-converted reagents are recycled.

**Figure 8.** Selectivity and conversion for the direct synthesis pathway from glucose to polyethylene terephthalate at which the exergy losses are identical to that of the indirect pathway. The value for today is based on Palkovits *et al.* [36].



On the one hand, this parameter study shows that the minimal selectivity to 1,2-ethanediol needs to be 20% if a complete conversion is possible in order to achieve the exergy losses of the benchmark. On the other hand, the minimal conversion needs to be 40% if a catalyst is found that avoid any side reactions. In reality, some combinations of intermediate values on these lines would need to be achieved.

As a case study, it was assumed that only the selectivity is modified as to reach the break even, *i.e.*, a selectivity of 35% and a conversion of 72%. A comparison of the separate exergy contributions

shows that the exergy losses stemming from the footprint are then nearly identical for both variants. In contrast to that, the losses according to the chemical exergy are lower for the direct variant. These results are specific to a comparison of direct and indirect synthesis pathways if the overall stoichiometry is different. Assuming an ideal stoichiometry, three molecules of 1,2-ethanediol can be obtained from glucose if the direct synthesis pathway is followed. For the indirect pathway, the yield amounts only to two molecules of the product desired.

The minimal exergy losses of the direct synthesis pathway for a complete conversion and avoiding of any side reactions is 14.1 MJ/(kg PET). This value is of the same order of magnitude as the exergy losses of the crude-oil route. Therefore, in principle, it is possible to carry out bio-based synthesis pathways with exergy losses being comparable to today's crude-oil pathways. From this, a need for further research can be derived, with the goal to optimize catalysts for bio-based synthesis pathways, because from the exergetical point of view, significant potential has been identified. Polyethylene terephthalate and its monomers are typical products of the petrochemistry; thus, the conversions and selectivities of the crude-oil route are high and the associated exergy losses are low as expected.

The third product considered in this study is polylactic acid, a typical bio-based polymer. Polylactic acid is a polyester, the oxygen content of which is high and the chemical exergy low. In this paper, only one synthesis pathway to polylactic acid is considered. Polylactic acid is obtained from glucose via lactic acid that is obtained by fermentation. The fermentation of glucose to lactic acid is very efficient; hence, the conversion is nearly unity. By-products occur only in small quantities with less than 0.5%, which is why they can be neglected in this consideration [37]. According to Figure 2, the chemical exergy of the main components involved in this synthesis pathway is nearly the same and, therefore, the course of this synthesis pathway is horizontal. The exergy losses caused for the production of one kilogram of polylactic acid including the footprint of the feedstock amounts to approximately 10 MJ. This low value is mainly related to the high conversion and selectivity of the reaction which have already been achieved today; thus, the feedstock is well utilized and the separation of the reaction mixture is relatively simple. Because both polylactic acid and polyethylene terephthalate are polyesters, the properties of which are similar, they can substitute each other in principle [42]. Compared to bio-based synthesis pathways to polyethylene terephthalate, the exergy losses of the pathway to polylactic acid are lower assuming today's achievable conditions. Thus, by utilizing appropriately adapted monomers, bio-based synthesis pathways are possible today, the exergy losses of which can compete with their crude-oil based counterpart.

## 5. Conclusions

In a first step, synthesis pathways can be characterized by the chemical exergy of their main components. In order to identify the economic potential of the different courses derived from these characteristics, specific synthesis pathways are evaluated by detailed exergy balances. Based on the exergy analysis of the different typical routes, general statements can be derived.

The examinations have shown that the exergy losses of synthesis pathways—the course of which is horizontal—can be low. Such synthesis pathways starting from glucose lead to intermediates and products with low chemical exergy and high oxygen content. For the production of biomass, arable land is required that is limited and competes with the food industry [45]. The arable land area required

for the production of biomass is lower if products of higher oxygen content are aimed at [44]. Since both land use and exergy losses are relevant cost factors for the production of bio-based chemicals, the economic potential of horizontal synthesis pathways points towards low-exergy products with higher oxygen content.

Products that satisfy these properties already exist today. These polymers are usually based on monomers that can be obtained from crude oil very efficiently. Exergy analyses have shown that bio-based synthesis pathways are possible that can compete with the crude-oil counterparts when suitable catalysts are available. Such catalysts have to be developed in the future. Since a development of appropriate catalysts will not always be possible, new monomers should be developed as well that can be obtained from biomass more efficiently. To that end, the chemical structure of biomass should be preserved to minimize losses in chemical exergy. From these new monomers, either variants of known polymers or completely new polymers can be obtained. It will not always be possible to satisfy the desired properties from substances with high oxygen content. Therefore, low-oxygen polymers are also required in the future. Analogously to the considerations above, bio-based synthesis pathways to low-oxygen products should use low-oxygen, raw material-like plant oil. In order to minimize material adjustments and associated exergy losses, the chemical structure, especially of the alkyl substituents, should be preserved. Also, in this case, the corresponding synthesis pathways and the underlying processes and catalysts have yet to be developed. To that end, exergy balances are a suitable tool to evaluate the economic potential of a new synthesis pathway even at an early stage of development.

### Conflicts of Interest

The authors declare no conflict of interest.

### References

1. Keim, W.; Röper, M. *Rohstoffbasis im Wandel: Positionspapier*; DECHEMA: Frankfurt, German, 2010 (in German).
2. Energy Information Administration (EIA). Spot Prices for Crude Oil and Petroleum Products, Washington. Available online: [http://www.eia.gov/dnav/pet/pet\\_pri\\_spt\\_s1\\_d.htm](http://www.eia.gov/dnav/pet/pet_pri_spt_s1_d.htm) (accessed on 24 December 2013).
3. Intergovernmental Panel on Climate Change (IPCC). *Fourth Assessment Report: Climate Change*; Cambridge University Press: Cambridge, UK, 2007.
4. UNFCCC. National Communications from Parties included in Annex I to the Convention: Greenhouse Gas Inventory Data from 1990 to 1998. In Proceedings of *the United Nations Framework Convention on Climate Change*, Lyon, France, 11–15 September 2000.
5. Perlack, R.D.; Wright, L.L.; Turhollow, A.F.; Graham, R.L.; Stokes, B.J.; Erbach, D.C. *Biomass as Feedstock for a Bioenergy and Bioproducts Industry: The Technical Feasibility of a Billion-Ton Annual Supply*; ADA436753; U.S. Department of Energy, U.S. Department of Agriculture: Oak Ridge, TN, USA, 2005.
6. Smeets, E.; Faaij, A.; Lewandowski, I.; Turkenburg, W. A bottom-up assessment and review of global bio-energy potentials to 2050. *Progr. Energ. Combust.* **2007**, *33*, 56–106.

7. Weusthuis, R.A.; Aarts, J.M.; Sanders, J.P. From biofuel to bioproduct: Is bioethanol a suitable fermentation feedstock for synthesis of bulk chemicals? *Biofuels Bioprod. Bioref.* **2011**, *5*, 486–494.
8. Bozell, J.J.; Petersen, G.R. Technology development for the production of biobased products from biorefinery carbohydrates—The US Department of Energy’s “Top 10” revisited. *Green Chem.* **2010**, *12*, 539–554.
9. Cherubini, F.; Strømman, A.H. Chemicals from lignocellulosic biomass: Opportunities, perspectives, and potential of biorefinery systems. *Biofuels Bioprod. Bioref.* **2011**, *5*, 548–561.
10. Haveren, J.V.; Scott, E.L.; Sanders, J. Bulk chemicals from biomass. *Biofuels Bioprod. Bioref.* **2008**, *2*, 41–57.
11. Corma, A.; Iborra, S.; Velty, A. Chemical routes for the transformation of biomass into chemicals. *Chem. Rev.* **2007**, *107*, 2411–2502.
12. Ragauskas, A.J.; Williams, C.K.; Davison, B.H.; Britovsek, G.; Cairney, J.; Eckert, C.A.; William J. Frederick, J.; Hallett, J.P.; Leak, D.J.; *et al.* The path forward for biofuels and biomaterials. *Science* **2006**, *311*, 484–489.
13. Werpy, T.; Petersen, G. *Top Value Added Chemicals from Biomass*; U.S. Department of Energy: Oak Ridge, TN, USA, 2004.
14. Bender, M.H. Potential conservation of biomass in the production of synthetic organics. *Resour. Conserv. Recycl.* **2000**, *30*, 49–58.
15. Tsatsaronis, G. Recent developments in exergy analysis and exergoeconomics. *Int. J. Exergy* **2008**, *5*, 489–499.
16. Munsch, M.; Mohr, T.; Futterer, E. Exergetische analyse und bewertung verfahrenstechnischer prozesse mit einem flow-sheeting-programm. *Chem. Ing. Tech.* **1990**, *62*, 995–1002.
17. Szargut J.; Morris, D.; Steward, F. *Exergy Analysis of Thermal, Chemical and Metallurgical Processes*; Springer: New York, NY, USA, 1989.
18. Kim, S.; Overcash, M. Allocation procedure in multi-output process: An illustration of ISO 14041. *Int. J. Life. Cycle Assess.* **2000**, *5*, 221–228.
19. *Umweltmanagement-Ökobilanz-Grundsätze und Rahmenbedingungen*; Beuth: Berlin, Germany, November 2009; DIN EN ISO 14040:2006.
20. *Umweltmanagement-Ökobilanz-Anforderungen und Anleitungen*; Beuth: Berlin, Germany, October 2006; DIN EN ISO 14044:2006.
21. Ekvall, T.; Finnveden, G. Allocation in ISO 14041-A critical review. *J. Clean. Prod.* **2001**, *9*, 197–208.
22. Frischknecht, R. Allocation in life cycle inventory analysis for joint production. *Int. J. Life Cycle Assess.* **2000**, *5*, 85–95.
23. Heijungs, R.; Frischknecht, R. A special view on the nature of the allocation problem. *Int. J. Life Cycle Assess.* **1998**, *3*, 321–332.
24. Marvuglia, A.; Cellura, M.; Hijungs, R. Toward a solution of allocation in life cycle inventories: The use of least-squares techniques. *Int. J. Life Cycle Assess.* **2010**, *15*, 1020–1040.
25. *Stoffstromanalysen in Ökobilanzen und Öko-Audits*; Schmidt, M., Schorb, A., Eds.; Springer: Berlin, Germany, 1995.

26. Azapagic, A.; Clift, R. Allocation of environmental burdens in co-product systems: Product-related burdens (part 1). *Int. J. Life Cycle Assess.* **1999**, *4*, 357–369.
27. Bösch, M.; Hellweg, S.; Huijbregts, M.; Frischknecht, R. Applying cumulative exergy demand (CExD) indicators to the ecoinvent database. *Int. J. Life Cycle Assess.* **2007**, *12*, 181–190.
28. Frischknecht, R. Allokation in der Sachbilanz bei Starrer Kuppelproduktion. In *Ökobilanz-Allokationsmethoden*; Eidgenössische Technische Hochschule Laboratorium für Technische Chemie Gruppe Sicherheit & Umweltschutz: Zürich, Switzerland, 1998; pp. 42–53.
29. Ullmann, F. *Ullmann's Encyclopedia of Industrial Chemistry*, 6th ed.; Wiley-VCH Verlag: Weinheim, Germany, 2001.
30. *Design Institute for Physical Properties*; DIPPR Project 801: Evaluated Process Design Data; American Institute of Chemical Engineers: New York, NY, USA, 2010; available online: <http://www.aiche.org/dippr/projects/801> (accessed on 28 January 2014).
31. Kosaric, N.; Duvnjak, Z.; Farkas, A.; Sahn, H.; Bringer-Meyer, S.; Goebel, O.; Mayer, D. Ethanol; In *Ullmann's Encyclopedia of Industrial Chemistry*; Wiley-VCH Verlag: Weinheim, Germany, 2001.
32. Chematur Technologies, Ethylene from Ethanol, 2009. Available online: [http://www.chematur.se/sok/download/Ethylene\\_rev\\_0904.pdf](http://www.chematur.se/sok/download/Ethylene_rev_0904.pdf) (accessed on 25 October 2013).
33. Herzog, K.; Mross, W.O.; Plueckhan, J.; Boehning, K.-H.; Schwarzmann, M. Verfahren zur Herstellung von Ethylenoxid, EP557833A1, 1 September 1993.
34. Jennings, J.R.; Hayden, P.; Allchurch, A.J. Herstellung von Ethylenoxid, DE69111811T2, 26 December 1990.
35. Syed, N. Ethylene Glycol: SRI Consulting, 2009. Available online: [http://jpr.janes.com/pdfs/RP2I\\_toc.pdf](http://jpr.janes.com/pdfs/RP2I_toc.pdf) (accessed on 9 December 2013).
36. Palkovits, R.; Tajvidi, K.; Procelewska, J.; Rinaldi, R.; Ruppert, A. Hydrogenolysis of cellulose combining mineral acids and hydrogenation catalysts. *Green Chem.* **2010**, *12*, 972–978.
37. Chahal, S. Lactic Acid. In *Ullmann's Encyclopedia of Industrial Chemistry*; Wiley-VCH Verlag: Weinheim, Germany, 2001.
38. Idem, R.O.; Katikaneni, S.P.R.; Bakhshi, N.N. Thermal cracking of canola oil: Reaction products in the presence and absence of steam. *Energy Fuel* **1996**, *10*, 1150–1162.
39. Azadi, P.; Inderwildi, O.R.; Farnood, R.; King, D.A. Liquid fuels, hydrogen and chemicals from lignin: A critical review *Renew. Sustain. Energy Rev.* **2013**, *21*, 506–523.
40. Balat, M.; Balat, H. A critical review of bio-diesel as a vehicular fuel. *Energ. Convers. Manag.* **2008**, *49*, 2727–2741.
41. Frenzel, P.; Fayyaz, S.; Hillerbrand, R.; Pfennig, A. Biomass as feedstock in the chemical industry—An examination from an exergetic point of view. *Chem. Eng. Sci.* **2013**, *36*, 233–240.
42. Bos, H.; Meesters, K.; Conijn, S.; Corre, W.; Patel, M. Accounting for the constrained availability of land: A comparison of bio-based ethanol, polyethylene, and PLA with regard to non-renewable energy use and land use. *Biofuels Bioprod. Biorefin.* **2012**, *6*, 146–158.
43. Banks, R.; King, P. *Chemistry and Physics of Petroleum*, 5th ed.; Wiley-VCH: Chichester, UK, 1984.
44. Frenzel, P.; Hillerbrand, R.; Pfennig, A. Increase in energy and land use by a bio-based chemical industry. *Chem. Eng. Res. Des.* **2014**, doi:10.1016/j.cherd.2013.12.024.

45. Pfennig, A. Supporting debottlenecking of global human processes by applying appropriate balances. *Biotechnol. J.* **2007**, *2*, 1485–1496.

© 2014 by the authors; licensee MDPI, Basel, Switzerland. This article is an open access article distributed under the terms and conditions of the Creative Commons Attribution license (<http://creativecommons.org/licenses/by/3.0/>).