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Definition, Calculation and Comparison of the "Biomass Utilization Efficiency (BUE)" of Various Bio-based Chemicals, Polymers and Fuels

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Contents

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1 Executive summary – definition and results

1.1 Summary

This paper defines, introduces and applies a new term, the "Biomass Utilization Efficiency (BUE)". This is a new and relatively simple approach to evaluate and compare different bio-based chemicals, materials and fuels based on the input-biomass, the used conversion process and the end product. A BUE analysis can answer the following questions: How efficiently is biomass utilized? What share of the biomass is ending up in the final product?

To summarise the role of the Biomass utilization efficiency (BUE) in the context of existing methods, it is obvious that this new metric has an emphasis on the best combination of biomass feedstock, process and bio-based product that is absent from existing calculations routinely used by research and process chemists and engineers. At present, waste minimisation during a manufacturing process is addressed through the choice of methods and optimisation of conditions. However, it is now clear that inherent waste, produced by aerobic fermentation for example, is easily overlooked when it concerns the conversion of biomass into chemical intermediates or fuels.

Biomass utilization efficiency (BUE) helps create awareness about alternative approaches for producing bio-based products. The difference in material efficiency between direct acetic acid production (anaerobic fermentation) and ethanol oxidation is clear (BUE_H = 90% compared to 60%). The same also applies to other examples covered in this paper. As demand for renewable resources rises, the efficiency of (bio)-chemical transformations will come under greater scrutiny. We anticipate the relevance and importance of insightful BUE calculations will increase as the bio-based chemical industry adapts to growing economic and material competition for resources.

Finally, this paper shows that it is important to use the right molecule with the right process in the right application. Molecules that have low oxygen content are more suitable for energetic purposes whereas molecules with higher oxygen content (and additional functional groups) are more suitable to create material with specific chemical properties. This oxygen-associated "functionality of biomass can reduce the steps of making a chemical and in that way reduce also the energy needs for the final molecule production" (Diels 2015). To put it differently, the use of oxygenated biomass only makes sense for material use (bio-based products). The only exception might be octane enhancers of the combustion process but those additives can also be grouped under the umbrella of material use of biomass.

Even though they were not a part of the scope of this paper, phenolic lignins should also be very suitable to create materials under the points we just mentioned above. Special cases are molecules such as succinic acid, which capture CO_2 in their molecular formula.

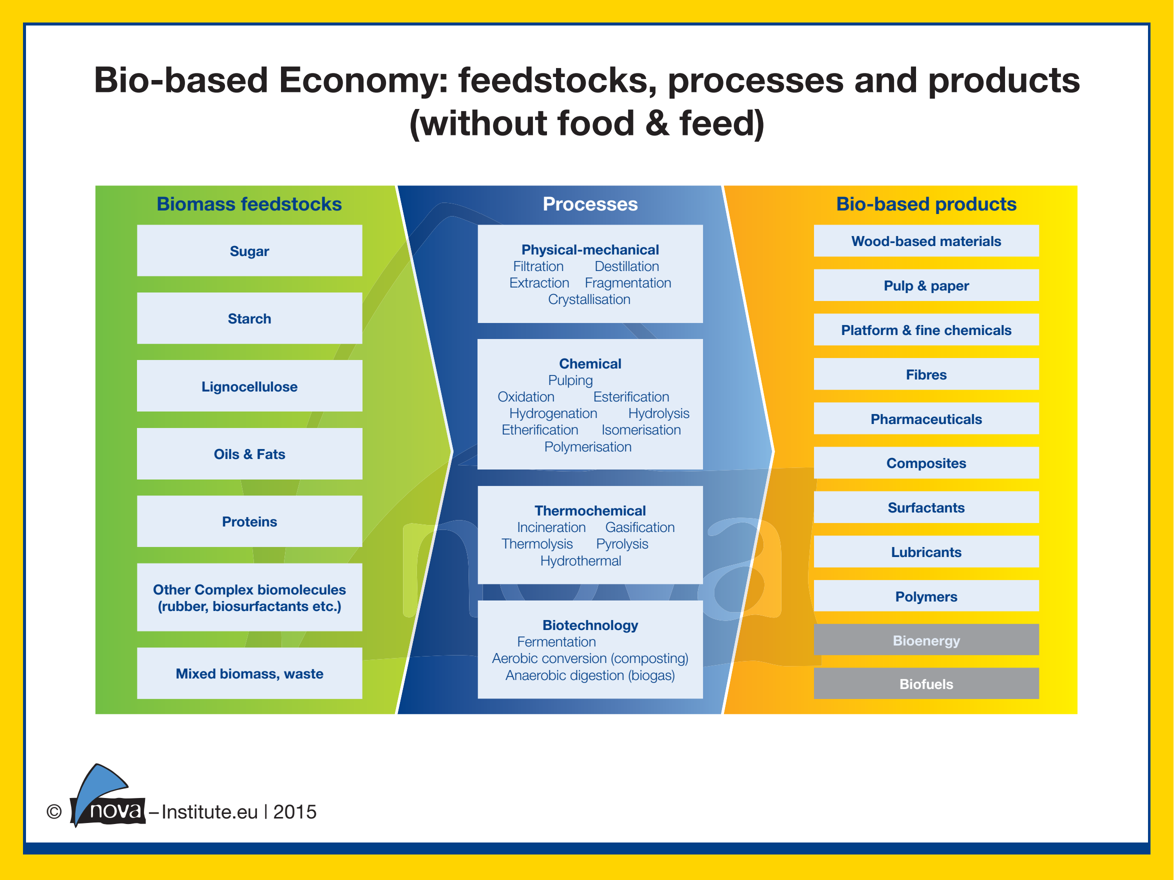

Figure 1: Bio-based economy: biomass feedstocks, processes and bio-based products.

Here, one has the additional, ecological benefit of reducing a greenhouse gas. Moreover, the formula we apply does not take into account that the CO_2 created by e.g. making ethanol from biomass could possibly be used to also make value added products like e.g. methane in a biorefinery approach.

In some cases a full environmental assessment shows different results. The BUE method does not take into account the energy use and environmental impacts related to bio-feedstock supply.

1.2 Introduction

Biomass can be used for the production of a large number of chemicals and materials as well as fuels (see Figure 1). There is a variety of approaches to determine the sustainability of different utilization routes for different kinds of biomass, processes and final products such as Life Cycle Assessment (LCA), Carbon Footprint, Techno-economic evaluation (TEE) or determination of carbon efficiencies. Each of these methodologies has its own pros and cons.

This paper defines, introduces and applies a new term, the "Biomass Utilization Efficiency (BUE)". This is a new and relatively simple approach to evaluate and compare different bio-based chemicals, materials and fuels based on the input-biomass, the used conversion process and the end product. A BUE analysis can answer the following questions: **How efficiently is biomass utilized? What share of the biomass is ending up in the final product?**

The BUE approach can be used to give a rough estimation of which type of biomass and process routes should be used for either fuels or materials, and also which combination of biomass and (bio)chemical process route is more efficient in producing different materials. Moreover, we calculate what fraction of the atoms, originally contained in the biomass are ending up in the product. We define these percentages in the end product as "biomass-derived". This term has to be clearly distinguished from the term "bio-based" (see box "Definitions").

Our approach is (of course) not supposed to replace an LCA, Carbon Footprint or TEE but instead provides additional, simplified insight into the amount of biomass resources needed to produce different bio-based chemicals and materials. Biomass Utilization Efficiency (BUE) is used to systematically analyse what share of the original biomass ends up in the final product. This depends on the kind of biomass feedstock, the process and the final product. Determining the percentage of carbon, hydrogen and oxygen ending up in the product provides additional information and a new criterion for the sustainable utilization of consumable biomass.

1.3 Definition and relevance of BUE

One advantage of the BUE in comparison to more intricate approaches such as LCA and TEE is that it can be quickly and easily applied. Whereas LCA and TEE need a considerable amount of data to start the analysis, the BUE calculation only requires the input-biomass, the chemical equation, the process efficiency (in case of BUE_L and BUE_H) and the target product.

A second advantage of this approach, when comparing it to carbon efficiency determination, is that it takes into account the main components of the biomass and the respective product. By also considering the fate of, for example, oxygen, which is important in many functional groups, especially in biomass composed of carbohydrates, one can analyse, if its chemical complexity is transferred to the product. This means that more interesting functionalities might be possible in the constructed product, for example by conserving the specific functional groups for polymer-crosslinking purposes. Moreover, it gives a rough estimation of energy consumption for the synthesis in a more straightforward approach than calculating exergies (Frenzel et al. 2014).

On its own, the Biomass Utilization Efficiency (BUE) is a quick and simple indicator to evaluate which product makes best use of the inherent biomass complexity and comparing the different categories, for example the theoretical percentage of reactant ending up in the product (BUE_S) and the highest yield currently being published (BUE_H), adds another layer of information. The comparison between BUE_S and BUE_H indicates whether one's efforts should be concentrated on selecting a different biomass-product combination or if one should focus one's attention on further improving the process itself, by choosing a different catalyst to improve selectivity of the reaction or downstream process for example.

Finally, the Biomass Utilization Efficiency (BUE) is linked to the land efficiency and is able to differentiate between dedicated new bio-based pathways and building blocks and drop-in solutions. In general, dedicated bio-based building blocks show higher BUEs compared to drop-in solutions, mainly because the chemical complexity of the biomass is transferred to the final product to a greater extent.

Definitions

Biomass utilization efficiency (BUE)
is hereafter defined as percentage of initial biomass ending up in the end product based on the molar mass of the reactant (= biomass) and target bio-based product. The BUE can be further subdivided in four specific categories:

BUE_S
The stoichiometric or alternatively theoretical BUE_S describes the percentage of reactant ending up in the product only based on the chemical reaction itself.

BUE_L and BUE_H
For determining the BUE-low and BUE-high, realistic yields for the described synthesis route were determined by a literature survey and industry experts. The BUE_L is the lowest yield and the BUE_H is the highest yield currently published.

BUE_E
The energetic BUE is calculated slightly differently; here the HHV of the product is divided by the HHV of the reactant. To calculate the energetic potential the heating values of the reactant and its products were compared using the realistic higher heating values of the feedstock needed to produce 1 g of product divided by the HHV of 1 g of educt.

bio-based product:
product wholly or partly derived from biomass

biomass:
material of biological origin, excluding material embedded in geological formations and/or fossilized. Examples: (whole or parts of) plants, trees, algae, marine organisms, micro-organisms, animals, etc. (EN 16575).

Bio-based product pathways with a higher BUE need smaller areas of cultivation for the same output compared to pathways with a lower BUE, which shows the BUE has a direct correlation with the land efficiency and the amount of land necessary to produce a certain product. For example, to produce the same amount of PE and PLA from sugar cane, you need almost twice the cultivation area for PE than PLA (different BUE for PLA and PE see Chapter 1.5).

The clearly defined and easy to calculate BUE can serve as a first guideline to evaluate the efficiency of a certain biomass transformation and can be linked to sustainable criteria such as efficient use of land. This is useful in the development of roadmaps for R&D as well as incentives for biomass utilization after the year 2020. At the very least it will contribute to the discussions around which methods and parameters might help to evaluate the sustainability of different pathways of biomass utilization.

The following Chapter 1.4, will give an example of a BUE calculation and a BUE-overview of more than 30 bio-based products follows in Chapter 1.5.

1.4 Example bioethanol

To demonstrate the BUE approach in detail, we have chosen bioethanol because it can be used as either a fuel or a platform chemical to build bio-based polymers such as PE.

Ethanol can be made by fermentation of sugar, resulting in the following chemical reaction:

$C_6H_{12}O_6 \rightarrow 2\ C_2H_5OH + 2\ CO_2$
1 glucose → 2 ethanol + 2 carbon dioxide
180 g/mol → 2 x 46 g/mol + 2 x 44 g/mol

In order to get the BUE$_S$, the theoretical biomass utilization efficiency, one would divide the weight of the product ethanol (2 times 46 g/mol) by the weight of the biomass, in this example glucose (= 180 g/mol). Consequently, this division results in a BUE$_S$ of 51.1%.

In reality, other competing side reactions can also occur. Furthermore, the downstream processing technology for separation and purification can yield less than 100% of the desired product if the process is not yet as technologically advanced as other biomass-process-product combinations. This means that a biomass-process-product combination might have a good theoretical BUE compared to another, but has a lower BUE$_H$, because less R&D has taken place on optimization, e.g. on the DSP, fermentation conditions/media or used catalyst.

In the case of ethanol, the BUE$_S$ and BUE$_H$ don't differ too much because glucose fermentation is a well-known, old and refined process and ethanol can be produced with a 92.3% yield. To calculate the BUE$_H$, the yield is multiplied by the BUE$_S$. In this example, this is 0.923 times 0.511 to give 0.472 equalling a BUE$_H$ = 47.2%.

Apart from the highest published realistic yield (= BUE$_H$), we also wanted to take into account a range of yields, described by the BUE$_L$. The reasoning behind this value is that, especially for newly developed processes, different methodological approaches (e.g. biotechnological fermentation with different microorganisms) exist in parallel and consequently, an industry standard is not yet established. When ethanol is produced from cellulosic biomass, various pre-treatment approaches exist; a BUE$_L$ of 34.6% can be given.

For the calculation of the BUE$_E$, the HHV of the ethanol (product) equalling 29.7 kJ/g is divided by the 2.12 g glucose needed for the production of 1 g ethanol times the glucose HHV of 15.6 kJ/g resulting in 34.6 kJ. This totals a BUE$_E$ of 85.8%. It is also interesting to note how the different BUEs relate to each other. As described above, the BUE$_S$ will always be higher than the BUE$_L$ and BUE$_H$. In contrast, it is possible and logical that the BUE$_E$ can be higher than the BUE$_S$. This is because only the C and H of the product are relevant for the energy content, and hence BUE$_E$, whereas for chemicals and materials, and hence BUE$_L$/BUE$_H$, C, H and O have to be taken into account (see Table 1).

The calculations show that bioethanol has a high efficiency if used as a fuel (BUE$_E$ of 85.8%), but as a starting point for chemicals and plastics bioethanol is less suitable, the efficiency is only in the range of 35–47% (see Table 1).

Table 1: Comparison of atom efficiency; BUE$_S$, BUE$_H$ and BUE$_L$ of bioethanol production from glucose.

Percentage of C, H, O of total mass of biomass (upper row)	**C**	**H**	**O**	**BUE$_S$ (in %)**	**BUE$_H$ / BUE$_L$ (in %)**	**BUE$_E$ (in %)**
Glucose ($C_6H_{12}O_6$ = 180 g/mol)	40.0	6.7	53.3			
Percentage of biomass-derived C, H, O in end product (lower row)						
Bioethanol (2 x C_2H_6O = 92 g/mol)	66.7	100.0	33.3	**51.1**	**47.2 / 34.6**	**85.8**

1.5 Results for more than 30 selected feedstock-process-product combinations for chemicals, polymers and fuels

Table 2 and Figure 2 show the results of the BUE calculations for more than 30 feedstock-process-chemicals/polymers, which were done by nova-scientists together with different external experts. The range of the BUEs lie between 100% and less than 3%. The chemicals are ranked according to their BUE$_H$ from the most efficient product to the least efficient, to give a realistic picture of which bio-based products use biomass the best, at the time this paper was written. The BUE$_L$, BUE$_S$ and BUE$_E$ are also given. The results show that materials made from vegetable oils, such as lubricating oils, alkyl polyglycosides, and cellulose-derivatives end up on top of the list, having the highest BUE$_H$s. This can be explained because not only are a high proportion of the C, H and O in the original molecule converted into the end product, but the existing functional groups of the biomass are not broken down. This means that by preserving the chemical complexity, the process will require less energy and/or the yield of product can be improved by using fewer reaction steps.

Figure 3 explains the calculation of BUE from another perspective – the share of oxygen in different raw materials (CO_2, biomass, fossil resources) and final products. Where products bear a similar elemental composition to the feedstock, the BUE$_H$ can be expected to be high. Acetic acid (direct fermentation) and lactic acid are good examples of this. If there is little similarity between the elemental composition of the feedstock and the product, it can be anticipated that the BUE$_H$ will be low. Polyethylene made from bio-ethanol illustrates this point and the difference between the BUE$_H$ of polyethylene and PLA underpins the need to consider biomass utilisation when selecting materials for the design and manufacture of bio-based products.

To show the different areas of application and the versatility of a BUE analysis, various examples of how these BUE values can be interpreted are given below in detail.

Table 2: Biomass Utilization Efficiency (BUE) for different bio-based feedstocks, processes and products: chemicals, polymers and fuels (sorted by BUE_H in descending order).

BIOMASS ORIGIN	PRODUCT	BUE_S STOICHIOMETRIC PERCENTAGE OF USED BIOMASS ENDING UP IN DESIRED PRODUCT (IN %)	BUE_L LOWEST REALISTIC PERCENTAGE OF USED BIOMASS ENDING UP IN DESIRED PRODUCT (IN %)	BUE_H HIGHEST REALISTIC PERCENTAGE OF USED BIOMASS ENDING UP IN DESIRED PRODUCT (IN %)	BUE_E PERCENTAGE OF INITIAL ENERGY ENDING UP IN THE PRODUCT (GROSS HHV)
Vegetable oil	Vegetable oil fuel	100.0		100.0	
Cellulose	Cellulose derivates	100.0	95.0	100.0	
Starch	Starch polymers	100.0		100.0	
Vegetable oil	Biodiesel (biomass also yields 9.9% glycerol which can also be valorized)	100.0	72.7	98.0	72.0 – 98.0
Glucose	Lactic acid	100.0	85.0	97.0	
Glucose	Alkyl polyglycoside	100.0	90.0	96.0	
Vegetable oil	PA11 (when heptanal and glycerol are also valorized)	100.0	89.0	94.0	
Glucose	BDO	100.0	76.9	90.0	
Glucose	Acetic acid (one-step process)	100.0	80.0	90.0	
Glucose	Succinic acid	100.0	80.6	90.0	
Cellulose	Regenerated cellulose	100.0		88.0	
Glucose	MEG (direct synthesis)	100.0	61.0	81.0	
Vegetable oil	Lubricating and hydraulics oils	100.0		80.0	
Vegetable oil	HVO/NExBTL	84.6		77.6	80.8
Glucose	PLA	80.0	67.1	76.6	
Glucose	HMF	70.0	60.9	64.4	
Glucose	PBS	95.5	50.4	63.0	
Glucose	Acetic acid (production with ethanol intermediate)	66.7		60.0	
Glucose	PEF	55.6	51.2	54.8	
Glucose	FDCA	86.7	51.2	54.1	
Vegetable oil	PA11 (from ricinoleic acid)	61.4	49.5	52.2	
Glucose	PDO	84.4	40.2	50.7	
Glucose	Bioethanol	51.1		47.2	85.8
Glucose	P3HB	47.8		40.1	
Cellulose	Bioethanol	56.8	34.6	38.1	59.2
Glycerol	Acrylic Acid	78.3		31.3	
Glucose	Ethylene	31.1		28.6	
Glucose	PE	31.1		28.6	
Glucose	MEG (via ethylene)	31.1		28.6	
Glucose	BTL (octane)	31.1		26.8	88.2
Cellulose	Biomethane	34.8		20.3	71.0
Glucose	Isoprene	45.4	13.7	14.5	
Cellulose	BTL (synfuel: CH2)	34.6		12.1	32.2
Glucose	PET	53.3		11.4	
Glucose	pX	92.2	9.6	10.2	
Glucose	TPA (pX oxidation)	59.0	9.4	10.0	
Glucose	TPA (via acylic acid+isoprene)	92.2	2.9	3.1	

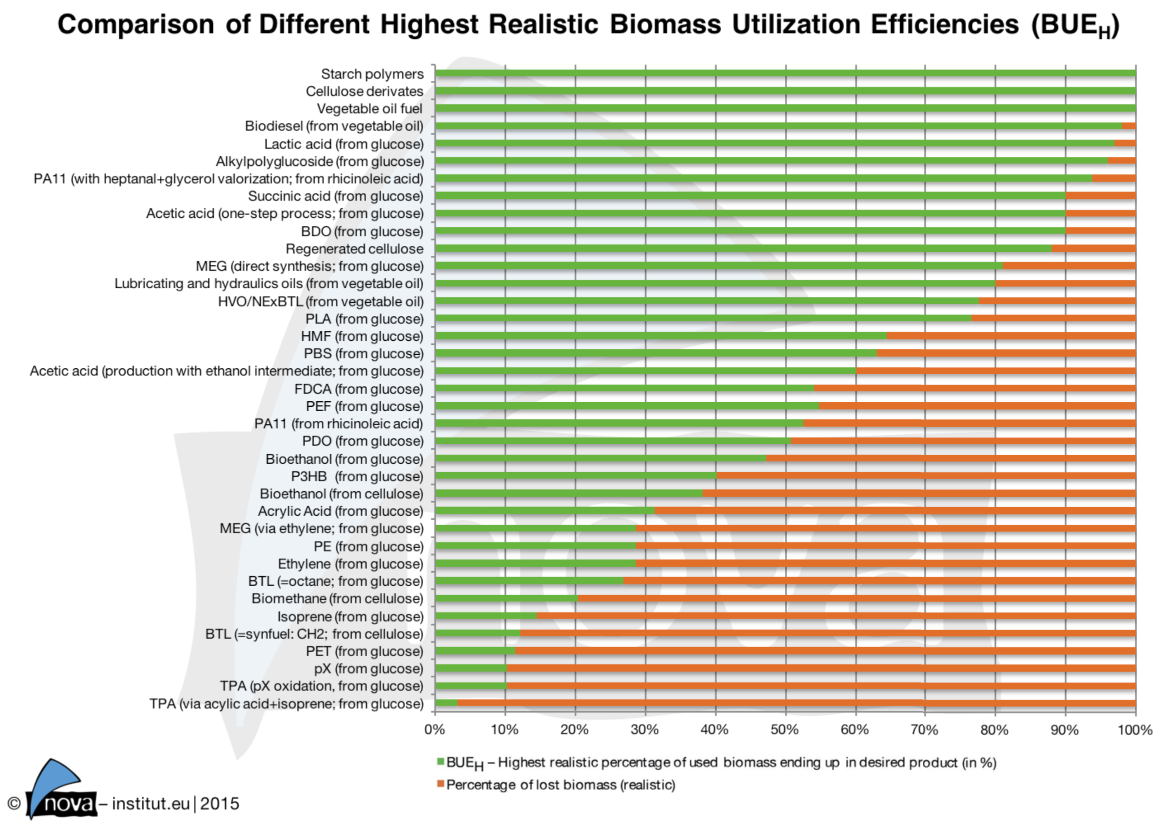

Figure 2: Highest Realistic Biomass Utilization Efficiency (BUE_H) for different bio-based feedstocks, processes and products: chemicals, polymers and fuels.

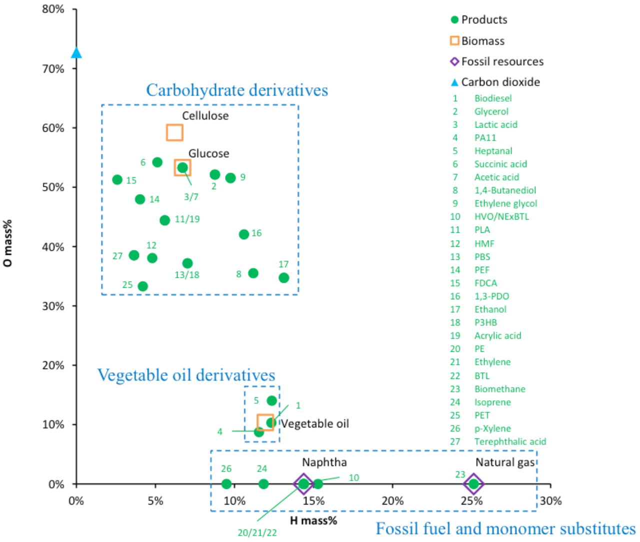

Figure 3: Relative amounts of hydrogen and oxygen atoms in feedstocks and downstream products. For complex mixtures (vegetable oil and naphtha) idealised stoichiometries have been used.

1.6 Implications of BUE_H

As shown in the table above (Table 2), bio-based polymers with high biomass utilization efficiencies already exist.

1.6.1 PLA and SA have a high BUE_H and therefore exhibit a highly efficient material use of biomass

Using this approach we show that oxygen-rich and carbonated molecules such as PLA (polylactic acid) and SA (= succinic acid) can be made very efficiently from biomass (for example glucose). In layman's terms, this can be explained as follows: the sugar molecule contains C_6, H_{12} and O_6 (6 carbon atoms, 12 hydrogen atoms and 6 oxygen atoms) and the atoms are just rearranged in the PLA molecule. Therefore, the atom economy is very efficient.

Based on stoichiometry (= BUE_S), 100% glucose reacts to lactic acid, thereby rendering its production very effective. With a BUE_H of 97% its production is the most cost-effective, in a real world setting, compared to other building blocks such as SA, 1,4-BDO or AA, which all have yields of ca. 90% at the time this paper was written.

When comparing these data with ethylene (see paragraph below), their BUEs are still remarkably good. This is because in LA, SA, 1,4-BDO and AA, oxygen is still present in the final molecules, while in ethylene all the oxygen is removed and replaced by carbon and hydrogen, making the overall process less efficient from the BUE point of view. Another factor is that some molecules, lactic acid, succinic acid and acetic acid, often are part of a microorganism's natural metabolism. Therefore, the fermentation of glucose to the aforementioned building blocks may have been optimized by evolution and, in contrast to ethylene (which requires the ethanol intermediate in the fermentation), the reaction only occurs in one step. This reduces the possibility that multiple incomplete reactions adding up to further reduce the yield of the reaction. With fewer process steps the total energy consumption can be expected to be reduced as well.

1.6.2 Comparison of BUE_S with BUE_H reveals where production processes should be optimized

The phenomenon of more synthetic steps reducing the overall BUE can also be observed for PA11 (= polyamide 11) production. Here, the use of six reactions reduces the realistic efficiency of PA11 production from ricinoleic acid from a stoichiometric BUE of 61.4% to a BUE_H of 52.2%. In this case though, some of the intermediates such as glycerol and heptanal have a market of their own. When their molecular weight is also considered, the BUE_L is increased because 93.8% of the initially used biomass ends up in valorizable products.

In contrast, LA is produced in one step by fermentation of sugar, therefore, the stoichiometric and realistic BUEs differ only by ca. 10%. This is not the case for 1,3-PDO. In theory, 84.4% of the glucose biomass is converted into 1,3-propanediol, according to the stoichiometry of the reaction. But from the literature it seems that the production is not yet as efficient as only 40.2–50.7% of glucose reacts to 1,3-PDO in a real life setting.

Analyzing the bio-polymers, the afore-mentioned effects carry through, meaning that PLA has the highest BUE. Both the stoichiometric value (80%) and the realistic value (77.6%) are significantly higher than those for P3HB (realistic: 40.1%) and PE (realistic: 28.6%). For P_3HB, the lower values can be explained by the fact that the reactant's C, H and O content are not efficiently used, hence the atom economy is low. For example, one third of the glucose-derived oxygen is lost due to CO_2 as by-product.

1.6.3 PE has a low BUE_H indicating biomass is not used efficiently to form PE

A major part of the overall low BUE_H of PE is again the inefficient use of glucose for the production of ethylene. The drop-in chemicals ethylene and consequently PE have a rather low BUE_H with 28.6% (Figure 3). This can be explained by the fact that the ethylene molecule contains no oxygen. Converting sugar into PE is, for this reason, not very efficient: all the oxygen atoms in the sugar need to be removed, which is typically done by eliminating CO_2 from the glucose molecule. This essentially means that when you are removing the six O-atoms in sugar to make PE you also remove three C-atoms and hence, only three C-atoms are left to make PE from. Using CO_2 in a biorefinery concept to make new molecules, can improve the efficient use of biomass though.

In PLA the oxygen is kept retained as part of the molecular chain, hence the efficiency of PLA is higher than PE (See also Figure 3).

Another reason why ethylene scores relatively low in this BUE-comparison, is the fact that the conversion rates themselves for this drop-in chemical are low. This observation can be explained thermodynamically; whereas glucose is energetically relatively low and therefore stable, creating a more reactive, e.g. more energy-containing, C-double bond for ethylene is entropically unfavourable. Therefore, either more energy, additional reactants, or more cost-intensive catalysts have to be used to make sure that the chemical balance is reached quicker. Consequently, 100% conversion is difficult to achieve and further reduces the stoichiometric yield for the ethylene production (31.1%).

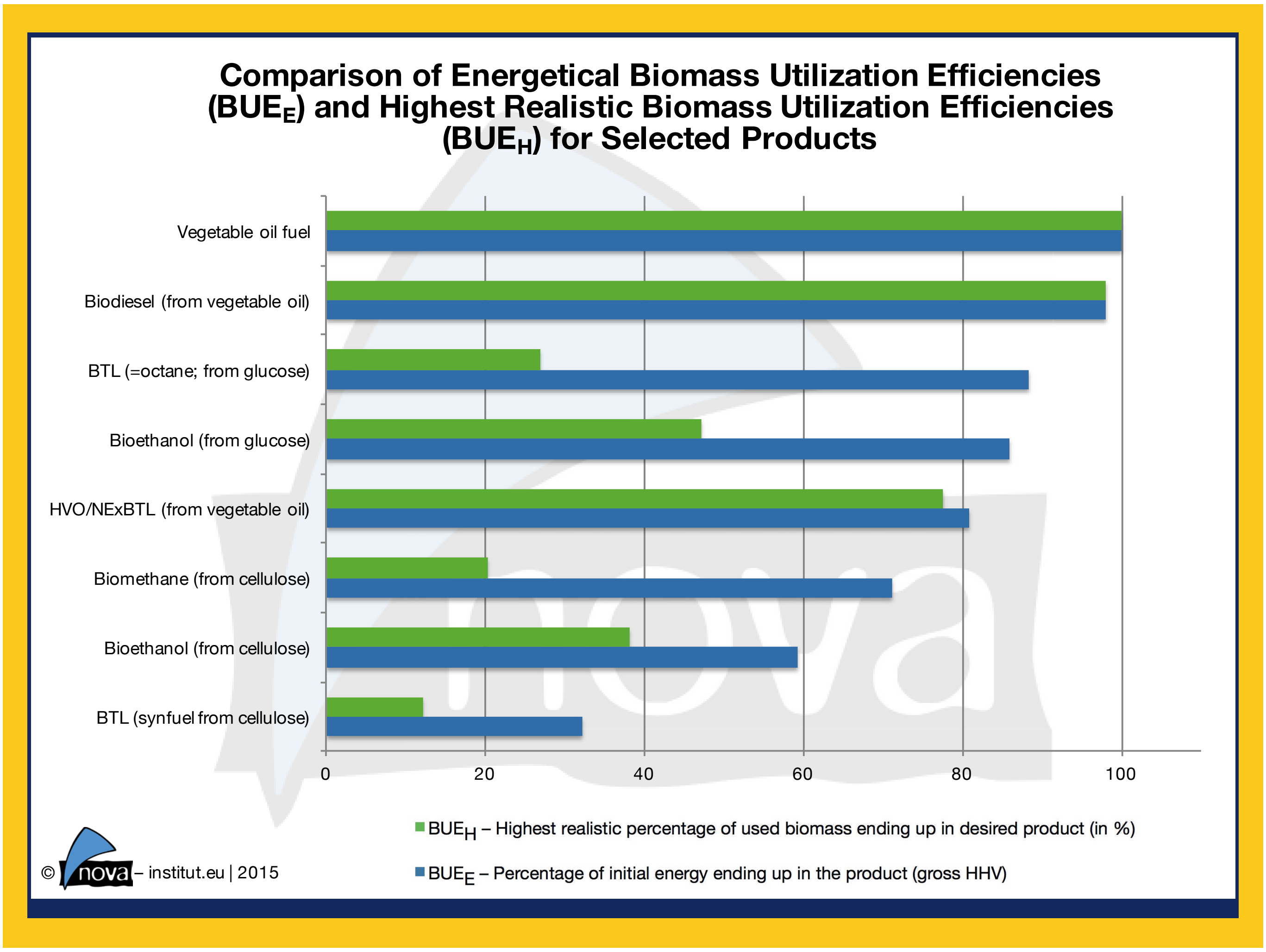

Figure 4: Comparison of Energetic BUE$_E$ with Highest Realistic BUE$_H$ for selected compounds

1.7 Implications of BUE$_E$

The energetic biomass utilization efficiency (BUE$_E$) is defined as the HHV (higher heating value) of the product divided by the HHV of the reactant. Figure 4 shows the higher energy density of vegetable oil-derived fuels, biodiesel and vegetable oil fuel, which reach a BUE$_E$ of 100% (vegetable oil fuel) and 98.7% (biodiesel). The produced energy carrier consists almost exclusively of carbon and hydrogen, whereas the carbohydrate reactants contain 53% oxygen, which reduces the energy density. In contrast, when carbohydrates are used for bio-based materials, this oxygen can be used more effectively.

When using oils for fuels, the BUE$_E$ is also favourable because of the low amount of oxygen in the oils themselves (Figure 3). Nonetheless, considering alkyl glucosides, both energetic and material uses seem feasible because they reach comparable BUE$_S$ and BUE$_E$ respectively (Goebbels 2010).

It is interesting to see that oxygenated molecules (e.g. PLA) score highly with regards to non-energetic BUEs when they are used for the creation of materials. This is because the oxygen present in the original biomass is fully utilized in the final material produced.

However, the presence of oxygen in the final material reduces the energy density, for instance petrol has a high energy-content in comparison to biomass (Frenzel et al. 2012). To reach these high energy content levels, by for example producing ethylene from glucose, every oxygen atom has to be removed. To make this reaction possible, the energy levels have to be increased by either adding heat energy or suitable reactants (containing more chemical energy).

Figure 4 clearly shows that typical biofuels – except those based on vegetable oil – show a much better energetic BUE than a non-energetic BUE. So they are suitable as fuel but not as a starting point for chemicals and plastics, where more efficient solutions are available.

2 Methodology

Several experimental and theoretical approaches to determine the yields of bio-based products were developed (Labatut et al. 2011 and references therein). This paper defines, introduces and applies a new term, the "Biomass Utilization Efficiency (BUE)"; a new and relatively simple approach to evaluate and compare different bio-based chemicals, materials and fuels based on the input-biomass, the used conversion process and the end product. A BUE analysis answers the following questions: How efficient is the biomass utilized? What share of the biomass is ending up in the final product?

2.1 Definitions

The central terms and definitions used in this methodology are:

BUE

Biomass Utilization Efficiency (BUE) is defined as the percentage of the initial biomass ending up in the final product based on the molar mass of the reactant (= biomass) and target product.

BUE_S

The stoichiometric or theoretical BUE_S describes the percentage of biomass feedstock ending up in the final product only based on the chemical reaction itself.

Starting from the stoichiometry of the main chemical reactions, the BUE_S can be calculated based on the mass of the reactants and resulting products. Dividing the mass of the product by the mass of the reactants, gives the theoretical percentage of biomass weight ending up in the product.

BUE_L and BUE_H

The BUE_L is the lowest yield and the BUE_H is the highest yield currently published. For determining the BUE-low and BUE-high, realistic yields for the described synthetic route are based on a literature survey of the latest yields reached in scientific publications (up until April 2015) as well as personal communication with industry experts.

Multiplying this theoretical mass yield (= BUE_S) with the actual conversion rates (obtained from literature review) results in a realistic BUE_L or BUE_H for the biomass-process-products combinations studied in this report. When feasible, the valorisation of other resulting products from biomass was also taken into account (for example when PA11 is produced from ricinoleic acid, heptanal can also be sold). For the sake of simplicity, the possible cascade use of e.g. the leftover fermentation broth and CO_2 created during the main reactions were not further analysed in our approach.

An even more detailed analysis is possible starting from the C, H and O content of the biomass and resulting products and calculating the yield on an elementary level. By this, it becomes easier to see which portion of the biomass gets lost.

Even though molar mass was used, the mass is only expressed in grams or tons respectively, for brevity's sake. All calculations are based on biomass dry weight and weight percentage and the energy it takes to e.g. produce the hydrogen, needed in some of our mentioned reactions, was not further taken into account.

BUE_E

The same methodology was applied to calculate the BUE_E, using now the gross higher heating value (HHV; also referred to as gross calorific value, GCV). This includes the amount of heat produced by complete combustion of the biomass or product and the energy needed to react the biomass to the desired product.

The following chapters will show the limits of our methodology, as well as, compare the BUE to several other established green chemistry metrics and relevant European standards.

2.2 Comparison to green chemistry metrics

The principles of green chemistry demand waste minimisation and energy efficiency in the production of chemicals and the use of renewable feedstocks where possible (Anastas and Warner 1998). In order to assess the efficiency of chemical reactions, mass metrics have been developed to calculate the proportion of reactants incorporated into the product or the amount of waste created. Three prominent examples are presented in the following table (Table 3). Note that E-factor is different to atom economy and reaction mass efficiency because the mass of the product is used as the denominator of the equation. E-factor also considers auxiliary components, not just the reactants. Atom economy (AE) is a theoretical assessment and does not consider the process yield whereas reaction mass efficiency (RME) does.

Table 3: Selected green chemistry metrics.

Metric	Calculation	Reference
E-factor	$\frac{Waste\ /kg}{Mass\ of\ product\ /kg}$	Sheldon 2007
Atom economy	$\frac{Molecular\ mass\ of\ product\ /g \cdot mol}{Molecular\ mass\ of\ reactants\ /g \cdot mol}$	McElroy 2015
Reaction mass efficiency	$\frac{Mass\ of\ product\ /kg}{Mass\ of\ reactants\ /kg}$	McElroy 2015

The biomass utilization efficiency (BUE) only considers the material of biomass origin in the calculation, therefore it could be seen as a partial metric, but still with an obvious link to the existing green chemistry metrics. Instead, it is better to consider BUE as a different type of metric with a focus on feedstock valorisation, instead of the process waste. It is useful to establish and compare the relationships between BUE and other metrics to test its validity and worth given the presence of several alternative calculations that are available for much the same purpose.

If the mass (M /g) and relative molecular mass (RMM /g•mol-1) of a substance or feedstock are regarded as the summation of biomass and non-biomass components, the following equations are formed:

$$RMM = RMM^{biomass} + RMM^{other}$$

$$M = M^{biomass} + M^{other}$$

The equation describing atom economy can be expanded to demonstrate its similarity to BUE_S, with the identical sections presented in green text:

BUE_S

BUE$_\text{S}$:

$$
\begin{aligned}
\mathbf{BUE_S} &= Amount\ of\ biomass\ incorporated\ into\ product\ (stoichiometric\ limit)\\
&= \frac{RMM_P^{biomass}\cdot ideal\ moles_P}{\sum\left(RMM_R^{biomass}\cdot ideal\ moles_R\right)}\\
&\equiv \frac{Bio\ based\ content_P\ \cdot RMM_P\ \cdot ideal\ moles_P}{\sum\left(RMM_R^{biomass}\cdot ideal\ moles_R\right)}
\end{aligned}
$$

Atom economy (AE)

Atom economy (**AE**):

$$
\begin{aligned}
\mathbf{AE} &= \frac{Molecular\ mass\ of\ product\ \frac{}{g}\cdot mol^{-1}}{Molecular\ mass\ of\ reactants\ \frac{}{g}\cdot mol^{-1}} = \frac{RMM_P\ \cdot ideal\ moles_P}{\sum\left(RMM_R\ \cdot ideal\ moles_R\right)}\\
&= \frac{\left(RMM_P^{biomass}+RMM_P^{other}\right)\cdot ideal\ moles_P}{\sum\left(\left\{RMM_R^{biomass}+RMM_R^{other}\right\}\cdot ideal\ moles_R\right)}\\
&= \frac{RMM_P^{biomass}\cdot ideal\ moles_P}{\sum\left(RMM_R^{biomass}\cdot ideal\ moles_R\ + RMM_R^{other}\cdot ideal\ moles_R\right)}\\
&+ \frac{RMM_P^{other}\ \cdot ideal\ moles_P}{\sum\left(RMM_R\ \cdot ideal\ moles_R\right)}
\end{aligned}
$$

In much the same way the yield adjusted BUE, either BUE_H or BUE_L, can be compared to reaction mass efficiency in an analogous fashion:

$\text{BUE}_\text{H/L}$

BUE$_\text{H/L}$:

$$
\begin{aligned}
\mathbf{BUE_{H/L}} &= Actual\ amount\ of\ biomass\ incorporated\ into\ product\\
&= \frac{RMM_P^{biomass}\cdot ideal\ moles_P}{\sum\left(RMM_R^{biomass}\cdot ideal\ moles_R\right)}\cdot Yield_P
\end{aligned}
$$

Reaction mass efficiency (RME):

Reaction mass efficiency (**RME**):

$$
\begin{aligned}
\mathbf{RME} &= \frac{Mass\ of\ isolated\ product\ /kg}{\sum Mass\ of\ reactants\ /kg} = \frac{M_P}{\sum M_R} = \frac{RMM_P\ \cdot ideal\ moles_P}{\sum\left(RMM_R\ \cdot ideal\ moles_R\right)}\cdot Yield_P\\
&= \frac{M_P^{biomass}+M_P^{other}}{\sum\left(M_R^{biomass}+M_R^{other}\right)} = \frac{\left(RMM_P^{biomass}+RMM_P^{other}\right)\cdot ideal\ moles_P}{\sum\left(\left\{RMM_R^{biomass}+RMM_R^{other}\right\}\cdot ideal\ moles_R\right)}\cdot Yield_P\\
&= \left\{\frac{RMM_P^{biomass}\cdot ideal\ moles_P}{\sum\left(RMM_R^{biomass}\cdot ideal\ moles_R\ + RMM_R^{other}\cdot ideal\ moles_R\right)}\right.\\
&\left. + \frac{RMM_P^{other}\cdot ideal\ moles_P}{\sum\left(RMM_R\ \cdot ideal\ moles_R\right)}\right\}\cdot Yield_P
\end{aligned}
$$

In bio-refinery processes where biomass is the only, or at least the primary feedstock, the relationship between BUE and the equivalent green chemistry metric is quite proportional. However, deviations occur when biomass is combined with other substantial feedstocks. Figure 5 shows the relationship between BUE_S and atom economy (AE), and also $\text{BUE}_\text{H/L}$ and reaction mass efficiency (RME) for the examples presented in this report. The equivalence line showing proportionality between the pairs of metrics is closely adhered to. Data points above the trendline are present when functionalisation of biomass occurs, resulting in losses of material not considered biomass. An example is during the functional group interconversions required to convert castor oil into the polyamide PA11. Datapoints below the trend line in Figure 5 are caused by inefficient use of biomass, followed by subsequent reactions with non-biomass substances. An example would be aerobic fermentation of sugars to ethanol (with loss of carbon dioxide), followed by conversion to ethylene glycol.

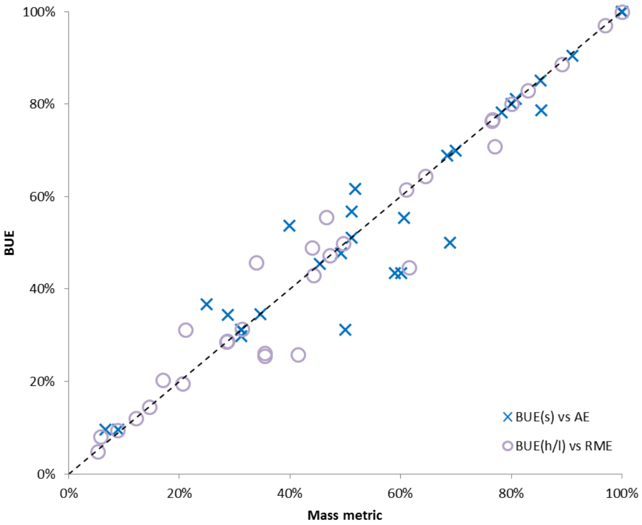

Figure 5: The comparison between BUE and related green chemistry mass metrics.

In Figure 5 the BUE values have been calculated using the actual quantities of biomass that have been incorporated into each product, as described by the chemical equations featured in this paper. This sometimes leads to results with lower biomass utilisation than expected. Another method of accounting for the incorporation of biomass in products is possible using the newly developed European standard for total bio-based content (prEN 16785-2). Here, any atoms covalently bonded to a bio-based carbon atom are also considered as bio-based. (The proportion of bio-based carbon atoms can be validated analytically using radiocarbon methods such as that described in CEN/TS 16640.) In the example of an oxidation, there is a difference in the resulting BUE depending on whether the introduced oxygen is regarded as bio-based or not. The effect of changing the calculation is demonstrated in Figure 6. Using prEN 16785-2 could be considered as more generous in accounting for the biomass in a product, but at the same time possibly misleading. This highlights the difference between emphasising the use of a feedstock, as BUE intends to do, and present European standardisation where the focus is on the final article.

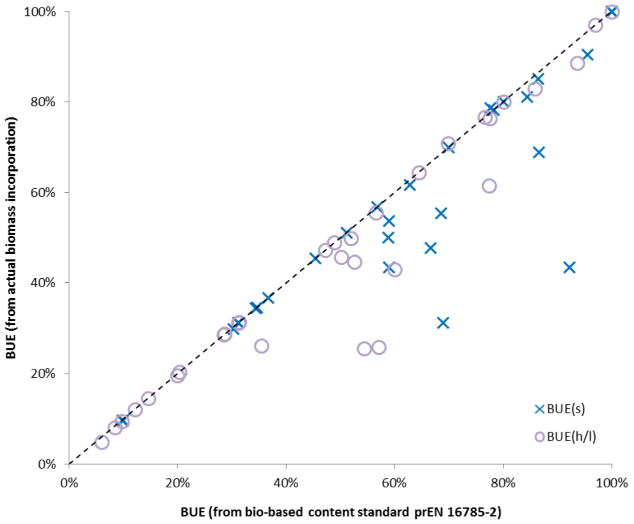

Figure 6: The influence of the calculation of bio-based content on the final BUE.

Remarkably, Frenzel and colleagues (2014) reached similar results to ours, in terms of the ranking of PLA and PE, by analyzing the exergy of various synthetic routes. They used the following definition for exergy: "(chemical) Exergy is that part of energy that can be completely converted into work in a reversible process in exchange with the environment" (Frenzel et al. 2013). It is a measure of the effects caused by the chemical composition of a molecule (e.g. the C:H:O ratios calculated above) and the effects of molecular structure (e.g. the very reactive C=C double bond of ethylene with high exergy Frenzel et al. 2014). Firstly, they showed that molecules with high oxygen content have low exergy. Secondly, to minimize losses in exergy, substantial changes in the chemical structure should be avoided. Thirdly, when low-oxygen containing products are desired, biomass that also contains low levels of oxygen should be used (e.g. vegetable oils) to fulfil the principle of maintaining comparable levels of exergy for the reactant and the end product (Frenzel et al. 2013, 2014). For instance, total exergy loss is the lowest for the petrochemical PE synthesis, even though chemical exergy is lost by the exothermal polymerisation. However, this heat can be used to cover the heat of the other reactions and therefore reduces the utility costs. In contrast, the low-exergy glucose has to be converted into high-exergy PE by the creation of low-exergy by-products. As in our mass calculations, these by-products are lost for PE and subsequently cause a high need for the raw material glucose.

2.3 Limitations of the BUE and similar methodologies

The developed BUE analysis, as well as similar approaches, has the following methodological limitations:

1. BUE does not take into account whether a process is endothermic or exothermic. This aspect can have a high impact on the ecological and economical sustainability of a process because of additional process energy, which might be needed for the chemical reaction and downstream processing. The latter can outweigh the benefits of the bio-based conversion process, e.g. in the case of an azeotrope as encountered for acetic acid.
2. Market attractiveness mainly relates to price and functionality. It therefore can be less relevant how a chemical ranks in the BUE analysis, if the chemical provides a desired functionality at an attractive price point (Veith 2015).
3. Regarding ecological considerations, it is also important to consider the functional performance of a product, which is often intrinsically linked with higher longevity. Higher functionality may correlate with more complex conversion steps that may translate to a higher production footprint. However, even though some products have a higher footprint in their production, this can be more than compensated by better functionality (e.g. longevity) and consequently footprint savings in the use-phase of the product. Functional and life cycle performance of the chemical should therefore always also be considered to obtain a holistic picture (Veith 2015).
4. The calculated results are based on what is publically available today in the literature (last update April 2015) and conversations with industry experts. The real efficiencies might be higher but are not published by industry due to confidentiality reasons.
5. In industrial plants, reactions are often not run to completion, with high selectivity to the desired product preferential to conversion of the reactants. Therefore, not 100% of the substrate is used directly, especially if there is a chemical equilibrium between reactant and product, which means that some product will react back. Industrial systems can remove the product and continue to react the starting materials, but this is diffuicult to quantify through the BUE analysis described here.
6. Furthermore, actual efficiencies are normally a compromise between processing cost (CAPEX and OPEX) and throughput (processing time). "An example: In enzymatic hydrolysis of cellulosic biomass, it is possible to reach very high yields, close to 100%. It just takes a very long time (which will demand large tanks in full scale production) and consumes lots of expensive enzymes. In a full-scale production, one needs to go for a compromise between yield and cost (CAPEX and OPEX). Normally the optimum is in the range of 80–90% yield." (Rødsrud 2015).
7. The BUE method does not take into account the energy use and environmental impacts related to bio-feedstock supply (for example, the supply of vegetable oil supply can be accompanied by larger environmental impacts than starch).
8. In some cases a full environmental assessment can differ from the BUE results, for example, cellulose fibres from wood are regarded as a good replacement of cotton, environmentally speaking. It saves fertilizers, energy and minimizes soil distortion and water consumption. However, cotton is also bio-based and by applying our methodology, 100% of the biomass is used. In the case of cellulose fibres only 40–50% of the wood is preserved in the cellulose fibres. In this particular case, the BUE calculation would rank cotton better than cellulose fibres (Alwarsdotter 2015).
9. It should also be considered that the stoichiometric BUE may differ by a factor of three to four or even more from the real BUE value (BUE_H; see examples in section 3). It is hence not advisable to use BUE_S as a proxy for BUE_H or BUE_L.

In the following chapters the BUE approach will be applied to more than 30 examples such as bio-based fuels, chemical building blocks and polymers.

3 Using biomass for fuels

3.1 Biomethane

Biogas (defined here as CH_4) is created by anaerobic (without oxygen) microbial processes in special refineries using various feedstocks (carbohydrates, fats, proteins). To derive the stoichiometry of the chemical equation we used a simplified version of the Buswell-Formula (Buswell and Mueller, 1952). Furthermore, we assumed that the produced NH_3 and H_2S fractions of the fermentations are negligible:

$C_aH_bO_cN_dS_e + (a - b/4 - c/2 + 3d/4 + e/2) \text{ x } H_2O \rightarrow (a/2 - b/8 + c/4 + 3d/b + e/4) \text{ x } CO_2 + (a/2 + b/8 - c/4 - 3d/b - e/4) \text{ x } CH_4 + d \text{ x } NH_3 + e \text{ x } H_2S$

We only consider plant-derived biomass with the estimated formula: $C_{38}H_{60}O_{26}$ (Antranikian 2006; Goebbels 2010). The Buswell formula (mentioned above) is therefore adapted to become:

(1) $C_{38}H_{60}O_{26} + 10\, H_2O \rightarrow 18\, CO_2 + 20\, CH_4$
(2) *biomass + water → carbon dioxide + biomethane*
(3) *932 g + 10 x18 g → 18 x 44 g + 20 x 16 g*

BUE

The numbers given in equation 3 are calculated from the atomic mass and the stoichiometry of the equation (932 g is 38 x 12 + 60 x 1 + 26 x 16). Therefore, in theory, 932 g biomass yields 320 g biomethane or 34.8% methane. Consequently, 2.91 tons of biomass are needed to produce 1 ton of methane.

Starting from lignocellulosic material such as straw, a conversion rate of 59% to biomethane can be reached without pretreatment (Schumacher et al. 2014). Taking this into account, the realistic BUE drops to 20.3% biomethane from lignocellulosic material. Therefore, 4.93 tons of straw are needed to obtain 1 ton of biomethane.

Calculating the elementary yield, starting biomass has 38 carbon atoms yielding 20 carbons converted into methane, or a 52.63% C-yield. All hydrogen from the biomass is transformed into methane and all oxygen goes in CO_2. This process theoretically loses almost half of the initial carbon and all of the oxygen. Using realistic conversion rates, the carbon yield drops further to 37.17% (52.63 x 59%).

BUE$_E$

Wheat straw has an HHV (higher heating value) of 14.3 kJ/g. Burning 4.93 tons of wheat straw (quantity needed for 1 ton of biomethane, see above) generates 70.4 kJ. Methane itself has an HHV of 50 kJ/g. Consequently, 71% (= 50 / 70.4) of the initial energy contained in wheat straw realistically ends up as energy in methane. When using theoretical data, the energy yield increases to 120% ((2.91 x 14.3)/(1 x 50)).

Table 4: Comparison of BUE of biomethane production.

Percentage of C, H, O of total mass of biomass (upper row)	C	H	O	BUE$_S$	BUE$_H$ (lower value is BUE$_L$)
Biomass ($C_{38}H_{60}O_{26}$ = 932 g)	48.9	6.4	44.6		
Percentage of biomass-derived C, H, O in end product (lower row)					
Methane (20 x CH_4 = 20 x16 g)	52.6	100.0	0.0	34.8	20.3

3.2 Bioethanol

Various processes, feedstocks and microorganisms, which can also vary in their utilization of C5/C6-sugars, are available to produce bioethanol. Ethanol can be produced anaerobically using e.g. glucose at high yields of 92.3% (Stryer 1975; Hama et al. 2014). Dividing the molecular weight of two moles of ethanol (2 x 46 g/mol) by the 180 g/mol coming from the glucose results in a BUE$_S$ of 51.1%. Meaning that 51.1% of biomass (here considered to be glucose) is converted to bioethanol. 84.9 g ethanol can be produced from glucose or 2.12 tons of glucose are needed to create 1 ton of ethanol. With the yield of the two reactions mentioned above, this BUE$_S$ is reduced to 47.2%.

Assuming an HHV of 15.6 kJ/g for glucose, directly burning the 2.12 g glucose needed for ethanol production results in 34.6 kJ energy (Morais et al. 2014). In contrast 1 g ethanol creates 29.7 kJ. Division of those energy values gives an BUE$_E$ ending up in ethanol of 85.8%.

(1) $1\ C_6H_{12}O_6 \rightarrow 2\ C_2H_5OH + 2\ CO_2$
1 glucose → 2 ethanol + 2 carbon dioxide
180 g/mol → 2 x 46 g/mol + 2 x 44 g/mol

(2) $(C_6H_{10}O_5)_n + n\ H_2O \rightarrow nC_6H_{12}O_6 \rightarrow 2n\ C_2H_5OH + 2n\ CO_2$
cellulose + n water → n glucose → 2n ethanol + 2n carbon dioxide
cellulose + n water → n x 180 g → 2n x 46 g + 2n x 44 g

In the following example, pre-treated wheat straw was used to produce 0.29 g ethanol per g straw at a conversion rate of 86% (Saha et al. 2014). To describe it differently, with lignocellulosic material as feedstock, 33.7% of this biomass end up as ethanol. Considering the 86% yield cited for this fermentation the BUE is then reduced to 29%. In other words, 6.75 tons of wheat straw equal 1 ton of ethanol. In these calculations the possible valorisation of products other than glucose (e.g. lignin and hemicellulose), was disregarded.

Interestingly, when considering an HHV of wheat straw of 13.4 kJ/g, directly burning the 6.75 g needed for 1 g ethanol production would result in 90.4 kJ energy. In contrast, burning 1 g of ethanol generates only 29.7 kJ of energy (Kreuger et al. 2011; Hansen et al. 2014.). This means that only 32.9% (= BUE$_E$) of the energy content of the reactant can realistically be used in ethanol.

Considering anhydroglucose units, the building block of cellulose, as a starting point, also results in two ethanol molecules. Dividing the 96 g of the ethanol molecular weight by the weight of an anhydroglucose unit (162 g) gives a BUE$_S$ of 56.8%. In reality, a conversion rate of 61–67% of cellulose to glucose can be reached, thereby reducing the realistic bioethanol yield to 34.6–38.1% (Kamm et al. 2007; Yamada 2013; Pulidindi 2014). In other words, 2.7 tons cellulose are needed to make 1 ton of ethanol.

Applying this rationale by using the gross HHV, 2.7 g of cellulose equal 2.7 g x 18.6 kJ/g = 50.22 kJ (Demirbas, 2009). Dividing this value by 1 g x 29.7 kJ/g equals 59.2%. This means that 59.2% of the initial energy ends up in the final product.

Table 5: Comparison of BUE of bioethanol production from glucose.

Percentage of C, H, O of total mass of biomass (upper row)	C	H	O	BUE$_S$	BUE$_H$ (lower value is BUE$_L$)
Glucose ($C_6H_{12}O_6$ = 180 g/mol)	40.0	6.7	53.3		
Percentage of biomass-derived C, H, O in end product (lower row)					
Bioethanol (2 x C_2H_6O = 92 g/mol)	66.7	100.0	33.3	51.1	47.2

Table 6: Comparison of BUE of bioethanol production from cellulose.

Percentage of C, H, O of total mass of biomass (upper row)	C	H	O	BUE$_S$	BUE$_H$ (lower value is BUE$_L$)
Cellulose ($C_6H_{10}O_5$ = 162 g/mol)	40.0	6.7	53.3		
Percentage of biomass-derived C, H, O in end product (lower row)					
Bioethanol (2 x C_2H_6O = 92 g/mol)	66.7	100.0	40.0	56.8	34.6 – 38.1

3.3 BTL (Biomass to liquid)

The first step of the BTL-procedure is pyrolytic gasification of biomass. Here, every carbon of glucose is converted into CO and CO_2. The carbon monoxide further reacts to –(CH_2)- synfuel building blocks (Noureldin et al. 2014). Carbon is however lost in the subsequent reactions; based on the equations summarized below, 180 g glucose can theoretically yield 56 g carbohydrate monomers (= 31.1% BUE$_S$). In reality, when for instance, octane is the desired product, another H_2 for the end groups of the carbohydrate chain is needed (i.e. for the reduction of the aldehyde). This hydrogen is created in equation

3 from the reaction of CO and water. The carbon in carbon monoxide is originally derived from glucose as represented in equation 1. This essentially means that the production of octane needs an additional one sixth of monosaccharide (1/6 x 180 g = 30 g) to account for the H_2 needed for the end of the molecular chain (Goebbels 2010). Consequently, 390 g monosaccharide (2 x 180 + 30) yields 114 g of octane (C_8H_{18}). In other words, 3.42 tons of glucose result in 1 ton of octane. Apart from the polymerisation, the realistic yield of 91.7% of the process also has to be taken into account (Bezergianni et al., 2014). Henceforth, one is left with 104.5 g octane and a realistic BUE of 26.8%.

With an HHV of 15.6 kJ/g for glucose, the required 3.42 g for production of 1 g octane, would create 53.3 kJ energy if the glucose were to be burned directly, whereas 1 g octane has an HHV of 47 kJ. In other words, 88.2% of the initial energy content is carried over to the octane product.

$(1)\ 1\ C_6H_{12}O_6 \rightarrow 6\ C + 6\ H_2O$
$(2)\ 6\ C + 6\ CO_2 \rightarrow 12\ CO$ *(Boudouard reaction)*
$(3)\ 8\ CO + 8\ H_2O \rightarrow 8H_2 + 8CO_2$
$(4)\ 4\ CO + 8\ H_2 \rightarrow \text{-(}CH_2\text{)-} + 4\ H_2O$
$\mathbf{(5)\ C_6H_{12}O_6 \rightarrow 4\ \text{-(}CH_2\text{)-} + 2\ H_2O + 2\ CO_2}$

Table 7: Comparison of BUE of BTL production.

Percentage of C, H, O of total mass of biomass (upper row)	C	H	O	BUE$_S$	BUE$_H$ (lower value is BUE$_L$)
Glucose ($C_6H_{12}O_6$ = 180 g/mol)	40.0	6.7	53.3		
Percentage of biomass-derived C, H, O in end product (lower row)					
Octane (C_8H_{18} = 114 g/mol)	66.7	75.0	0.0	**31.1**	**26.8**

When wood is used in the BTL-process, the usable carbohydrates, cellulose and hemicellulose vary from 60–70 % depending on factors such as type of wood and process used to isolate the carbohydrates (Goebbels 2010; Nikbakht et al. 2014 and references therein). Consequently, 4.89–5.7 tons of wood equal 1 ton of octane. This means lignocellulosic biomass is transformed by 20.4–17.5% to octane.

When the heating values of BTL-derived octane (47 kJ/g) are compared to wood (19 kJ/g), it is remarkable that directly burning the 4.89–5.7 g of wood, needed to create 1 g BTL, results in 92–108 kJ energy. Burning 1 g of BTL, on the other hand, only yields 47 kJ energy.

Cellulose as basis for synfuel productions is based on the following chemical reaction with a realistic yield of 35% (Noureldin 2014): $C_6H_{10}O_5 \rightarrow 4\ CH_2 + H_2O + 2\ CO_2$

Applying the realistic yield to the stoichiometric value gives a BUE of 12.1% for synfuel production. To put it differently, 8.26 tons of cellulose are needed to create 1 ton synfuel with an HHV of 49.5 kJ/g (Linstrom et al. 2014). When cellulose would be directly utilized for energy, 153.6 kJ would be generated (8.26 g x 18.6 kJ/G; Demirbas 2009). Division of 1 g x 49.5 kJ by 153.6 kJ yields 32.2% energy ending up in the product (Linstrom et al. 2014).

Table 8: Comparison of BUE of BTL process starting from cellulose.

Percentage of C, H, O of total mass of biomass (upper row) and	C	H	O	BUE$_S$	BUE$_H$ (lower value is BUE$_L$)
Cellulose ($C_6H_{10}O_5$ = 162 g/mol)	40.0	6.7	53.3		
Percentage of biomass-derived C, H, O in end product (lower row)					
Synfuel (4 x CH_2 = 56 g/mol)	66.7	80.0	0.0	**34.6**	**12.1**

Table 9: Comparison of higher heating values for wood and BTL.

	kJ/g	g	kJ total
Wood	19.0	5.2	98.0
BTL	47.0	1.0	47.0

3.4 Biodiesel

A wide array of oils is available (from plants or animals, mainly produced from palm oil, soybean oil and rapeseed oil) as a source for triglycerides in the transesterification reaction which creates biodiesel ($C_{15\text{-}25}H_{28\text{-}48}O_2$) and glycerol ($C_3H_8O_3$). It is a renewable substitute for petrodiesel with a comparable HHV of 37.1–41 kJ/g (for biodiesel) and 43 kJ/g (for petrodiesel). Moreover, biodiesel is essentially free of sulphur and aromatics and emits less exhaust fumes when burned. Additionally, the glycerol, produced in the transesterification, is a reaction product that is valuable in its own right (Demirbas 2009; FNR 2014). Apart from the triglycerides, either methanol or ethanol is used as the second reactant. On the one hand, ethanol can be produced from renewable resources, on the other hand, methanol is, amongst other things, cheaper. In the graph below, the different consecutive reactions and the overall stoichiometry are detailed. For our calculations we assumed the use of methanol (CH_3OH = 32 g) and an average chain length for R of $C_{18}H_{35}$. Subsequently, the triglyceride has a molecular weight of 926 g ($C_{60}H_{110}O_6$) and the resulting ester/biodiesel 392 g ($C_{20}H_{38}O_2$). Depending on the reaction conditions the yield can vary from reactions catalysed enzymatically (72%) to alkali-catalyzed transesterfications, which use, for example, alkaline metal alkoxides (CH_3ONa) (98%) (Demirbas 2009; Goebbels 2010; Peng et al. 2012).

$(1)\ C_{60}H_{110}O_6 + 3\ CH_4O \rightarrow 3\ C_{20}H_{38}O_2 + C_3H_8O_3$
(2) triglyceride + 3 methanol → glycerol + 3 fatty acid alkyl ester (biodiesel)
(3) 926 g + 3 x 32 g → 3 x 310 g + 92 g

Table 10: Comparison of BUE of biodiesel production.

Percentage of C, H, O of total mass of biomass (upper row)	C	H	O	BUE$_S$	BUE$_H$ (lower value is BUE$_L$)
Triglyceride ($C_{60}H_{110}O_6$ = 926 g/mol)	64.9	10.3	24.7		
Percentage of biomass-derived C, H, O in end product (lower row)					
Biodiesel (3 x $C_{20}H_{38}O_2$ = 3 x 392 g/mol)	95.0	92.3	50.0	**100.0**	**72.7 – 98.0**
Glycerol ($C_3H_8O_3$ = 92 g/mol)	5.0	7.7	50.0	**9.9**	**72.7 – 98.0**

When comparing the HHV of rapeseed oil (37.6 kJ/J) and the resultant biodiesel (37.1 kJ/J), theoretically 98.7% of the initial energy of the used reactant ends up in the biodiesel products (FNR 2014). Assuming that 72.7–98% of biomass is converted into biodiesel, 1.37–1.02 g triglycerides are needed for the production of 1 g biodiesel. Using the HHV of rapeseed oil mentioned above, 38.3–51.5 kJ energy is contained in the amount of triglycerides needed for 1 g biodiesel. The energy content of the latter is 37.1 kJ.

3.5 Vegetable oil fuel

Plant oils can be added directly to normal diesel fuel or engines can be modified to completely run on plant oils. In theory, 100% of this biomass can be used as gasoline (Goebbels 2010).

3.6 Hydrotreated vegetable oils respectively NExBTL

NExBTL is Neste Oil's trade name for paraffinic renewable diesel, which comes from hydrotreated (hydrogenated) vegetable oil (HVO). HVO works as a drop-in fuel and can therefore replace conventional diesel by 100% while demonstrating lower emissions. In addition, compared to biodiesel, consisting of fatty acid methyl esters, it has a higher shelf life (Nylund et al. 2011). The hydrotreatment step is used to remove the oxygen from the triglycerides and by adjusting the isomerization conditions the cold flow characteristics of the resultant mixture of n- and isoparaffins can also be adapted. Rapeseed oil has a relative average molar mass of 867.5 g/mol ($C_{56}H_{99}O_6$) due to the high percentage of oleic acid (Bynes et al. 2014). To apply this average molecular weight to table 11, we assumed R = $C_{20}H_{40}$ and R' = C_7H_{14}. The resulting, relevant paraffins (2 x ($C_{20}H_{40}$-CH_2-CH_3) = 618 g and C_7H_{14}-CH_3= 113 g) add up to 731 g. Dividing the products with the molecular weight of rapeseed oil (864 g) shows that this procedure can produce 84.5% (= BUE_S) paraffins from biomass. To put it differently, 1.18 tons of biomass (here: rapeseed oil) are needed for 1 ton of combined paraffins. Realistically, it has been shown that 77.6% can be reached, which means that 1.29 tons of biomass are required for the production of 1 g paraffins (Bezergianni et al. 2014). Apart from that, the propane, which is also created in the reaction (see below), is a valuable product.

Using an HHV of paraffin of 46 kJ/g and for HVO equalling to 44.1 kJ/g, shows that directly using the needed 1.28 g HVO for energetic purposes yields 56.9 kJ. Dividing the paraffin energy of 44.1 kJ/g by the calculated 56.9 kJ for HVO results in 77.5% of HVO reactant ending up in the paraffin product (Linstrom and Mallard 2001; FNR 2014).

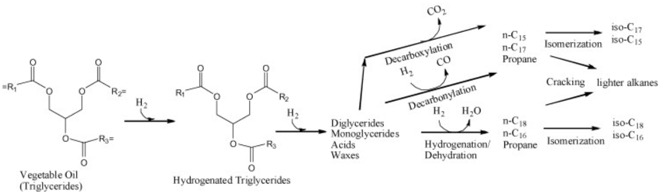

Figure 7: Hydrotreatment of fatty acids (Source: Gandarias et al. 2013).

Table 11: Comparison of BUE of NExBTL production.

Percentage of C, H, O of total mass of biomass (upper row)	**C**	**H**	**O**	**BUE_S**	**BUE_H (lower value is BUE_L)**
HVO (mainly oleic acid: $C_{56}H_{99}O_6$ = 867 g/mol)	77.5	11.4	11.1		
Percentage of biomass-derived C, H, O in end product (lower row)					
Combined paraffins ($2^*(C_{20}H_{40}$-CH_2-$CH_3)$ = 618 g/mol and C_7H_{14}-CH_3 = 113 g/mol)	91.1	100.0	0.0	**84.6**	**77.6**

4 Material use of biomass for chemical building blocks

4.1 Acetic Acid

Acetic acid is an important building block for PVA (poly vinyl acetate) by reacting with ethylene to form the vinyl acetate monomer (Harmsen et al. 2014). There are different ways of acetic acid production by acidogenic fermentation. For example, 100 g of corn stover biomass can be fermented to 21.84 g acetic acid. Moreover, depending on the microorganism used, either C5 or C6 sugars can be utilized in the fermentation (Zhao et al. 2014). When glucose is directly fermented to acetic acid with an expected yield of 80%, 144 g are formed from 180 g glucose. In other words, 1.25 tons of glucose needs to be fermented to produce 1 ton of acetic acid. A recent publication indicates that acetic acid production from glucose fermentation can even reach yields of around 90% (Yan et al. 2014).

a) Direct production process:

$C_6H_{12}O_6 \rightarrow 3\ CH_3COOH$

glucose → 3 acetic acid

180 g → 3 x 60 g

Table 12: Comparison of BUE of direct acetic acid production.

Percentage of C, H, O of total mass of biomass (upper row)	**C**	**H**	**O**	**BUE_S**	**BUE_H (lower value is BUE_L)**
Glucose ($C_6H_{12}O_6$ = 180 g/mol)	40.0	67.0	53.3		
Percentage of biomass-derived C, H, O in end product (lower row)					
Acetic acid (3 x CH_3COOH = 3 x 60 g/mol)	100.0	100.0	100.0	**100.0**	**80.0 – 90.0**

Another possibility is to firstly produce ethanol from glucose and then oxidize it further to acetic acid. At a Wacker Chemie pilot plant, this approach is used with an acetic acid yield of 90% (De Guzman 2010; Goebbels 2010). Applying this method, 120 g acetic acid can be produced from 180 g glucose. Taking the 90% yield into consideration the acetic acid amount is reduced to 108 g, or 1.67 tons of glucose are needed for the production of 1 ton of acetic acid. Even though this approach reduces the acetic acid output in comparison to direct glucose fermentation by 25%, the plant operation is more versatile. For instance, the solvent methyl ethyl ketone and the building block 1,4-butanediol can also be created on site. Apart from having other uses the mentioned chemicals can further be reacted in the same plant to acetic acid again (De Guzman 2010).

b) Acetic acid production via ethanol intermediate:

(1) $C_6H_{12}O_6 \rightarrow 2\ C_2H_5OH + 2\ CO_2$
glucose → 2 ethanol + 2 carbon dioxide
180 g → 2 x 46 g + 2 x 44 g
(2) $2\ C_2H_5OH + 2\ O_2 \rightarrow 2\ CH_3COOH + 2\ H_2O$
2 ethanol + 2 oxygen → 2 acetic acid + 2 water
2 x 46 g + 2 x 16 g → 2 x 60 g + 2 x 18 g
Overall: $\boldsymbol{C_6H_{12}O_6 \rightarrow 2\ CH_3COOH + H_2O + 2\ CO_2}$

Table 13: Comparison of BUE of acetic acid production (with ethanol as intermediate).

Percentage of C, H, O of total mass of biomass (upper row)	**C**	**H**	**O**	**BUE_S**	**BUE_H (lower value is BUE_L)**
Glucose ($C_6H_{12}O_6$ = 180 g/mol)	40.0	6.7	53.3		
Percentage of biomass-derived C, H, O in end product (lower row)					
Acetic acid (3*CH_3COOH = 3 x 60 g/mol)	100.0	100.0	100.0	**66.7**	**60.0**

4.2 Lactic Acid (LA)

The building block lactic acid can be produced by glucose fermentation. It is a building block for polymers such as polylactic acid (PLA), which can replace fossil-based chemicals such as polystyrene. Moreover, catalytic dehydration of lactic acid can be employed to make the adhesive/paint ingredient polyacrylic acid (PAA). At the moment, starch/sugar-rich biomass (e.g. corn, sugar cane) is used and research is underway to use lignocellulose as a non-food, alternative feedstock (Harmsen et al. 2014). Depending on the microorganism used, which normally produces lactic acid to support its own metabolism, yields of 85–97% were shown experimentally (Endres 2013; Wang et al. 2014).

(1) $C_6H_{12}O_6 \rightarrow 2\ C_3H_6O_3$
(2) glucose → 2 lactic acid
(3) 180 g → 2 x 90 g

Table 14: Comparison of BUE of lactic acid production.

Percentage of C, H, O of total mass of biomass (upper row)	**C**	**H**	**O**	**BUE_S**	**BUE_H (lower value is BUE_L)**
Glucose ($C_6H_{12}O_6$ = 180 g/mol)	40.0	6.7	53.3		
Percentage of biomass-derived C, H, O in end product (lower row)					
Lactic acid (2 x $C_3H_6O_3$ = 2 x 90 g/mol)	100.0	100.0	100.0	**100.0**	**85.0 – 97.0**

4.3 Succinic acid (SA)

SA is an intermediate of the citric acid cycle and an end product in anaerobic metabolism (Kurzrock and Weuster-Botz 2010; Goebbels 2010; Pinazo et al. 2015). Theoretically, 201.8 g SA is formed from 180 g glucose. The extra weight originates from 37.84 g carbon dioxide required for the reaction. To keep the numbers comparable, the maximum BUE_S that can be reached was set at 100% regardless. Consequently, 148.73 g (180 g/(180 + (0.86 x 44 g) x 180 g) of glucose is participating in the formation of 201.8 g SA. With a yield of 90%, this gives a realistic value of 181.62 g of SA (Endres 2013).

(1) $C_6H_{12}O_6 + 0.86\ CO_2 \rightarrow 1.71\ C_4H_6O_4 + 1.74\ H_2O$
(2) Glucose + 0.86 x carbon dioxide → 1.71 x succinic acid + 1.74 x water
(3) 180 kg + 0.86 x 44 kg → 1.71 x 118 kg + 1.74 x 18 kg

Table 15: Comparison of BUE of succinic acid synthesis.

Percentage of C, H, O of total mass of biomass (upper row)	**C**	**H**	**O**	**BUE_S**	**BUE_H (lower value is BUE_L)**
Glucose ($C_6H_{12}O_6$ = 180 g/mol)	40.0	6.7	53.3		
Percentage of biomass-derived C, H, O in end product (lower row)					
Succinic acid (1.71 x $C_4H_6O_4$ = 201.8 g)	100.0	100.0	100.0	**100.0**	**80.6 – 90.0**

4.4 1,3-propanediol (PDO)

PDO can either be made by fermenting glycerol directly or by using glucose as a feedstock (Bieblet al. 1998; Muska and Alles 2005). DuPont uses the latter as a building block for PTT-fibres (Polytrimethylene terephthalate) (Kurian 2005). Yields of 60% were reported for the glucose-to-PDO fermentation (Nakamura and Whited 2003; Saxena et al. 2009; Endres 2013). In theory, 84.4% (= BUE_S) of glucose is converted to PDO (1.18 tons glucose = 1 ton PDO). Taking the yield into account, 180 g glucose fermentation results in only 91.2 g of PDO, thereby reducing the BUE to 50.7% (with 1.97 tons glucose needed for one ton of PDO).

(1) $C_6H_{12}O_6 \rightarrow 2\ C_3H_6O_3 + 2H_2 \rightarrow 2\ C_3H_8O_3 \rightarrow 2\ C_3H_8O_2 + H_2O$
(2) glucose → 2 dihydroxyacetone + 2 hydrogen → 2 glycerol → 2 PDO + water
(3) 180 g → 2 x 90 g + 2 x 2 g → 2 x 90 g → 2 x 76 g + 18 g

Table 16: Comparison of BUE of PDO production.

Percentage of C, H, O of total mass of biomass (upper row)	**C**	**H**	**O**	**BUE_S**	**BUE_H (lower value is BUE_L)**
Glucose ($C_6H_{12}O_6$ = 180 g/mol)	40.0	6.7	53.3		
Percentage of biomass-derived C, H, O in end product (lower row)					
1,3-Propandiol (2 x $C_3H_8O_3$ = 2 x 76.1 g)	100.0	100.0	100.0	**84.4**	**40.2 – 50.7**

4.5 1,4-Butanediol (BDO)

BDO is another important building block because it can replace ethylene glycol by polycondensation of the corresponding diacids and diols to get the thermoplastic polybutylene terephthalate (PBT). It is possible to polymerize BDO with succinic acid to polybutylene succinate (PBS: Harmsen et al. 2014). E. coli can be used to ferment sugar to form SA as an intermediate and to finally yield BDO (Goebbels 2010; Yim et al. 2011). Currently, yields of microbial BDO-synthesis are 90%, so from 180 g BDO only 162 g is generated (Endres 2013; Hasebeck et al. 2013).

(1) $C_6H_{12}O_6 + 0.86\ CO_2 \rightarrow 1.71\ C_4H_6O_4 + 1.74\ H_2O$
Glucose + 0.86 x carbon dioxide → 1.71 x succinic acid + 1.74 x water
180 g + 0.86 x 44 g → 1.71 x 118 g + 1.74 x 18 g
(2) $2\ C_4H_6O_4 + 4\ H_2 \rightarrow 2\ C_4H_{10}O_2 + 4\ O_2$
2 succinic acid + 4 hydrogen → 2 butanediol + 4 oxygen
2 x 118 g + 4 x 2 g → 2 x 90 g + 4 x 16 g

Table 17: Comparison of BUE of BDO production.

Percentage of C, H, O of total mass of biomass (upper row)	**C**	**H**	**O**	**BUE$_S$**	**BUE$_H$ (lower value is BUE$_L$)**
Glucose ($C_6H_{12}O_6$ = 180 g/mol)	40.0	6.7	53.3		
Percentage of biomass-derived C, H, O in end product (lower row)					
1,4-butanediol (2 x $C_4H_{10}O_2$ = 2 x 90 g/mol)	100.0	100.0	66.7	**100.0**	**76.9 – 90.0**

4.6 5-Hydroxymethylfurfural (HMF)

HMF is a versatile intermediate in polymer synthesis for instance, and offers various synthetic possibilities due to its rich chemistry. In one example, it can be used to make furandicarboxylic acid (FDCA), which in turn can be further processed into a replacement for PET in bottles (see further down in the paper), polyamides, polyurethanes, thermosets and plasticizers (Rosatella et al. 2011). Sugars (fructose and glucose) are dehydrated to hydroxymethylfurfural (HMF) at the expense of three water molecules. Theoretically, this adds up to 70% (= BUE$_S$) of the glucose being converted into HMF (126 g/mol of product per 180 g/mol of feedstock). Consequently, 1.43 tons of glucose is needed for production of 1 ton of HMF. Depending on reaction conditions and use of catalyst, this reaction has a conversion ranging roughly from 86% to 92% when using ionic liquids (Koopman et al. 2010; Luterbacher et al. 2014, van Putten 2015). Applying those values to the stoichiometric BUE of 70% results in a realistic range of 60.9% (= BUE$_L$) to 64.4% (= BUE$_H$). Those percentages translate to 1.55–1.64 tons glucose being reacted to 1 ton HMF in a real world setting.

(1) $C_6H_{12}O_6 \rightarrow C_6H_6O_3 + 3\ H_20$
(2) glucose → HMF + 3 water
(3) 180 g → 126 g + 3 x 18 g

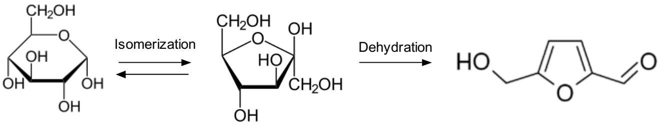

Figure 8: Synthesis routes from glucose/fructose to form HMF (adapted from Rosatella et al. 2011).

Table 18: Comparison of BUE of HMF production.

Percentage of C, H, O of total mass of biomass (upper row)	**C**	**H**	**O**	**BUE$_S$**	**BUE$_H$ (lower value is BUE$_L$)**
Glucose ($C_6H_{12}O_6$ = 180 g/mol)	40.0	6.7	53.3		
Percentage of biomass-derived C, H, O in end product (lower row)					
5-Hydroxymethylfurfural ($C_6H_6O_3$ = 126 g/mol)	100.0	50.0	50.0	**70.0**	**60.9 – 64.4**

4.7 Ethylene

The monomer ethylene can be made by fermentation of glucose to create ethanol which is in turn dehydrated catalytically. DSM and POET are also at pilot plant stage for fermenting lignocellulosic material (Harmsen et al. 2014). Due to the two step process and the detour via ethanol a BUE$_S$ of only 31.1% (56 g/mol / 180 g/mol) can be achieved when ethylene is produced using fermentation. Taking into account the highest possible (according to our literature survey) yield at the moment of 92.3% for the glucose to ethanol fermentation and 99.7% for conversion of ethanol to ethylene, we end up with a realistic BUE of 28.6% (Fan et al 2012; Hama et al. 2014). Discounting yields, the production of 1 ton of ethanol requires 1.96 tons of glucose. Subsequently, 1.64 tons of ethanol are used for the production of 1 ton of ethylene. To summarize, 3.44 tons of glucose are needed for 1 ton of ethylene. Taking the yields into consideration for both steps, 3.5 tons of glucose are needed for 1 ton of ethylene.

(1) $C_6H_{12}O_6 \rightarrow 2\ C_2H_5OH + 2\ CO_2$
glucose → 2 ethanol + 2 carbon dioxide
180 g → 92 g + 88 g
(2) $2\ CH_3CH_2OH \rightarrow 2\ C_2H_4 + 4\ H_2O$
2 ethanol → 2 ethylene + 4 x water
92 g → 56 g + 4 x 18 g

On the laboratory scale there are still efforts underway to produce ethylene directly via fermentation. These studies use metabolic engineering and the fact that ethylene is, for example, also a plant hormone and therefore part of the natural metabolism of several species. For instance, introducing the EFE molecule (ethylene-forming enzyme) from Pseudomonas syringae into *S. Cerevisiae* to produce ethylene in lab-scale chemostats has been demonstrated, but the yields and cultivations conditions still have to be significantly optimized. At the moment, the highest observed yields were 8 moles ethylene to 10 moles glucose (8 x 28 g/mol / 10 x 180 g/mol), which translates to 12.4% glucose being directly converted into ethylene (Eckert et al. 2014 and references therein).

Table 19: Comparison of BUE of ethylene production.

Percentage of C, H, O of total mass of biomass (in %)	**C**	**H**	**O**	**BUE$_S$**	**BUE$_H$**
Glucose ($C_6H_{12}O_6$ = 180 g/mol)	40.0	6.7	53.3		
Biomass-derived C, H, O in end product (in %)					
Ethylene (2 x C_2H_4 = 56 g/mol)	66.7	66.7	0.0	**31.1**	**28.6**

4.8 Mono-ethylene glycol (MEG)

Ethylene glycol is an important building block for polymers such as PEF and PET. It can also be used by itself for example to deice airplanes or as a heat transfer agent (Rebsdat and Mayer 2005). There are several ways to synthesize MEG from biomass, for instance, it can be made from ethylene, via the precursors glucose and ethanol.

As mentioned earlier, 3.5 tons of glucose are needed to produce 1 ton ethylene. This can be processed further via ethylene oxide to get ethylene glycol (Rebsdat and Mayer 2005). If this conversion is at 100%, one can assume that 1.64 tons of glucose also yields 1 ton ethylene glycol. In reality, 2.2 tons of ethylene equal 1 ton of ethylene glycol. It has recently been shown that cellulose can be converted into MEG with a yield ranging between 61% and 83%. The low yield can be explained due to various occurring side reactions such as hydrogenation, isomerisation, hydrogenolysis and dehydration which form sorbitol, erythritol, glycerol and 1,2-propanediol respectively. Glucose is converted by a retro-aldol reaction to glycol aldehyde and this is further hydrogenated to ethylene glycol (van de Vyver et al. 2011; Ooms et al. 2014).

1) Synthesis via ethylene:

$C_2H_4 \rightarrow C_2H_4O + H_2O \rightarrow C_2H_6O_2$

ethylene → ethylene oxide + water → ethylene glycol

28 g → 44 g + 18 g → 62.1 g

2) Direct synthesis (using cellulose-derived glucose):

$C_6H_{12}O_6 + 3\ H_2 \rightarrow 3\ C_2H_6O_2$

glucose + 3 x hydrogen → MEG

180 g + 3 x 2 g → 3 x 62,1 g

Table 20: Comparison of BUE of MEG production.

Percentage of C, H, O of total mass of biomass (in %)	C	H	O	BUE$_S$	BUE$_H$ (lower value is BUE$_L$)
Glucose ($C_6H_{12}O_6$ = 180 g/mol)	40.0	6.7	53.3		
Biomass-derived C, H, O in end product (in %)					
MEG *via* Ethylene (3 x $C_2H_6O_2$ = 3 x 62.1 g/mol)	100.0	100.0	100.0	**31.1**	**28.6**
MEG (direct synthesis)				**100.0**	**61.0 – 81.0**

4.9 Isoprene

This building block is used by a variety of organisms to construct isoprenoids. In the chemical industry, isoprene, at the moments of petrochemical origin, is used as a starting material to make synthetic rubber, pesticides and medicines (Lv et al. 2013). Moreover, together with bio-based acrylic acid, it can be further reacted to give terephthalic acid, which is one of the monomers used in PET synthesis (Miller et al. 2014). Various feedstocks can be used to form bio-based isoprene, for instance, glycerol, CO_2 or glucose with various microorganisms (Lv et al. 2013; Bentley et al 2014; Miller et al. 2014; Zurbriggen et al. 2014). Even though the photo-autotrophic production of isoprene from CO_2 has only a stoichiometric BUE of 30.9% and a realistic BUE of 27.2%, the fact that it captures 5 carbon dioxide molecules ($5CO_2 + 4\ H_2O \rightarrow C_5H_8 + 7\ O_2$) distinguishes it from the other production routes (Bentley et al. 2014). Producing isoprene with glucose as the feedstock has a stoichiometric BUE of 45.4%. Taking this together with a realistic but low yield for the reaction between 30.2–32%, means that instead of the 2.2 tons of biomass needed for the production of isoprene, 6.9–7.3 tons biomass are actually required (Lv et al. 2013; Liu et al. 2014; Zurbriggen et al. 2014).

$5\ C_6H_{12}O_6 \rightarrow 6\ C_5H_8 + 6\ H_2O + 12\ O_2$

5 x glucose → 6x isoprene + 6 x water + 12 x oxygen

5 x 180 g → 68.1 g + 6 x 18 g + 12 x 32 g

Table 21: Comparison of BUE of isoprene production.

Percentage of C, H, O of total mass of biomass (in %)	C	H	O	BUE$_S$	BUE$_H$ (lower value is BUE$_L$)
Glucose ($C_6H_{12}O_6$ = 180 g/mol)	40.0	6.7	53.3		
Biomass-derived C, H, O in end product (in %)					
Isoprene (C_5H_8 = 6 x 68.1 g/mol)	83.3	66.7	0.0	**45.4**	**13.7 – 14.5**

4.10 Acrylic Acid

This building block can be used to form poly-acrylic acid which is an important constituent in adhesives and coatings. Moreover, it can form various copolymers (e.g. latex/acryl paints, Harmsen et al. 2014). Acrylic acid can be produced from glycerol, which occurs in significant amounts as a side stream of the biodiesel production and can therefore be valorized by the creation of another value-added chemical. In a one-pot system, it was shown that acrylic acid can be produced with yields around 40% (Witsuthammakul and Sooknoi 2012; Harmsen et al., 2014). The theoretically needed 1.28 tons glycerol to make 1 ton acrylic acid, relates to 3.21 tons feedstock when assuming a realistic yield of 40% for the conversion to acrylic acid. This boils down to a realistic BUE of 31.2%

$C_3H_8O_3 + 0.5\ O_2 \rightarrow C_3H_4O_2 + 2\ H_2O$

glycerol + 0.5 x oxygen → acrylic acid + 2 x water

92.1 g → 72.1 g + 2 x 18 g

Table 22: Comparison of BUE of acrylic acid production.

Percentage of C, H, O of total mass of biomass (in %)	C	H	O	BUE$_S$	BUE$_H$ (lower value is BUE$_L$)
Glycerol ($C_3H_8O_3$ = 92.1 g/mol)	39.1	8.7	52.1		
Biomass-derived C, H, O in end product (in %)					
Acrylic Acid ($C_3H_4O_2$ = 72.1 g/mol)	100.0	50.0	66.7	**78.3**	**31.3**

4.11 2,5-furandicarboxylic acid (FDCA)

FDCA is structurally very similar to terephthalic acid, one of the monomers used to create PET, and can therefore create the furan (5C—ring instead of 6C-ring of PET) homologue PEF (see PEF-chapter later in this paper, Sousa et al., 2013). The oxidation of HMF to FDCA can be performed with a 97% yield (Koopman et al. 2010; van Aken 2011; van Putten et al. 2013; Luterbacher et al. 2014) and so the stoichiometric BUE of 86.67% is reduced to 84.1%. Furthermore, HMF has a BUE$_L$ of 60.9% and a BUE$_H$ of 64.4% which also has to be accounted for in our calculations. Therefore, 51.2–54.1% glucose ends up in FDCA when acknowledging the realistic BUEs in the 2 main synthesis steps from glucose via the HMF intermediate to FDCA. To put it differently, 1.85–1.95 tons of glucose can be converted to 1 ton FDCA.

$C_6H_6O_3 + 1.5\ O_2 \rightarrow C_6H_4O_5 + H_2O$

HMF + 1.5 oxygen → FDCA + water

126 g + 1.5 x 32 g → 156.1 g + 18 g

Table 23: Comparison of BUE of FDCA production.

Percentage of C, H, O of total mass of biomass (in %)	C	H	O	BUE$_S$	BUE$_H$ (lower value is BUE$_L$)
Glucose ($C_6H_{12}O_6$ = 180 g/mol)	40.0	6.7	53.3		
Biomass-derived C, H, O in end product (in %)					
FDCA ($C_6H_4O_5$ = 156.1 g/mol)	100.0	33.3	83.3	**86.7**	**51.2 – 54.1**

4.12 Para-xylene (pX)

Para-xylene is used as a building block for polyester and the most important of the PET-precursors, terephthalic acid, can be made by oxidizing p-xylene (Harmsen et al. 2014; Sheldon et al. 2014). As mentioned earlier, HMF can be produced with realistic yields varying from 60.9 to 64.4%. HMF reacts further to 2,5-dimethylfuran (DMF) in reality with yields up to 93.4% (Zu et al. 2014). The reaction of DMF with ethylene to form pX has been published at 100% (Davis and Pacheco 2014). Taking all those yields together with the yield for bio-based ethylene production (28.6%) results in a BUE of 9.6% for para-xylene production via the above-mentioned synthetic routes from glucose. In other words, 10.4 tons of biomass are needed to produce 1 ton pX.

$C_6H_8O + C_2H_4 \rightarrow C_8H_{10} + H_2O$

DMF + ethylene → pX + water

96.1 g + 28 g → 106.2 g + 2 x 32 g

Table 24: Comparison of BUE of pX production.

Percentage of C, H, O of total mass of biomass (in %)	C	H	O	BUE$_S$	BUE$_H$ (lower value is BUE$_L$)
Glucose ($C_6H_{12}O_6$ = 180 g/mol)	40.0	6.7	53.3		
Biomass-derived C, H, O in end product (in %)					
pX (C_8H_{10} = 106.2 g/mol)	100.0	50.0	0.0	**59.0**	**9.6 – 10.2**

4.13 Terephthalic Acid (TPA)

TPA is one of the monomers used to make, among other compounds, the following polymers: Poly(trimethylene terephthalate) (PTT), which is mainly used in textile fibres; PBT (= poly(butylene terephthalate)), a technical polymer for speciality applications; PET (polyethylene terephthalate), used in packaging such as bottles (Harmsen et al. 2014). It can be produced from p-xylene with yields as high as 98% or by cycloaddition of bio-based acrylic acid and isoprene. Taking into account the BUE$_{Hs}$ of both molecules and the 68% yield of the last reaction reduces the BUE$_H$ for TPA significantly (Miller et al 2014). Consequently, one needs at least 10 tons glucose to make TPA (via the p-xylene route).

$C_5H_8 + C_3H_4O_2 + O_2 \rightarrow C_8H_6O_4 + 3\ H_2$

isoprene + acrylic acid + oxygen → TPA + 3 x hydrogen

68.1 g + 72.1 g + 32 g → 166.1 g + 3 x 2 g

Table 25: Comparison of BUE of TPA production.

Percentage of C, H, O of total mass of biomass (in %)	C	H	O	BUE$_S$	BUE$_H$ (lower value is BUE$_L$)
Glucose ($C_6H_{12}O_6$ = 180 g/mol)	40.0	6.7	53.3		
Biomass-derived C, H, O in end product (in %)					
TPA with isoprene + acrylic acid intermediates ($C_8H_6O_4$ = 166.1 g/mol)	100.0	50.0	66.7	**92.2**	**2.9 – 3.1**
TPA *via p*-xylene oxidation					**9.4 – 10.0**

5 Material use of biomass for biopolymers

5.1 Polyethylene (PE)

Ethylene can be polymerized to polyethylene by using the same equipment as for petrochemical PE (Goebbels 2010). The ethylene monomer can be polymerized with 100% efficiency to PE (Endres 2013). Therefore the same calculations and C/H/O ratios apply as calculated in the chapter on ethylene (please refer to Table 19).

5.2 Poly(butylene) succinate (PBS)

PBS can be made by using various polymerisation techniques from BDO and SA. It is a polyester with comparable mechanical properties to polypropylene (PP) and is biodegradable. Moreover, it exhibits thermoplastic processibility and can be blended with other polymers such as PLA to alter its properties (Adamopoulou 2012; Harmsen et al. 2014). In theory, the two building blocks SA and BDO can be produced with 100% yields from glucose. This means that the molar mass of the PBS functional unit ($(C_8H_{12}O_4)_n$ 172 g/mol) can be divided by the molar mass of glucose (180 g/mol) resulting in a BUE$_S$ of 95.5%. Realistically, SA is made from biomass with yields varying between 80.6% and 90% and BDO shows yields of 76.9–90%. Using direct polyesterification under microwave irradiation those building blocks can be polymerized to PBS with 81.3% efficiency (Adamopoulou 2012). When taking all the yields for the different steps into account one comes up with a BUE$_L$ of 50.4 and a BUE$_H$ of 63.0%. In other words, to realistically make 1 ton of SA and BDO each one would need 2.22 and 2.54 tons of glucose respectively. Taking the 81.3% efficiency of the polymerization reaction (which needs 1.09 tons of SA and BDO each to make 1 ton of PBS) into account, in total 2.41–2.73 tons glucose will be needed for the production of 1 ton PBS.

(1) $n\ C_6H_{12}O_6 \rightarrow C_4H_6O_6 + C_4H_{10}O_2 \rightarrow (C_8H_{12}O_4)_n + 2H_2O + O_2$

(2) n glucose → SA + BDO → PBS + 2 x water + oxygen

(3) n x 180 g → 118.9 g + 90.1 g → 172 g + 2 x 18 g + 32 g

Table 26: Comparison of BUE of PBS production.

Percentage of C, H, O of total mass of biomass (upper row)	C	H	O	BUE_S	BUE_H (lower value is BUE_L)
Glucose ($C_6H_{12}O_6$ = 180 g/mol)	40.0	6.7	53.3		
Percentage of biomass-derived C, H, O in end product (lower row)					
Poly(butylene) succinic acid (($C_8H_{12}O_4)_n$ = 172 g/mol)	100.0	100.0	66.7	**95.5**	**50.4 – 63.0**

5.3 Polylactic acid (PLA)

PLA is an aliphatic, thermoplastic polyester with a wide range of applications (e.g. food service ware, woven and non-woven fibers, 3D-printing) and can be processed with the standard equipment of the petrochemical industry (Garlotta 2001; Harmsen et al. 2014). It is mainly produced by formation of the lactide dimer and subsequent ring opening polymerization. These processes have different yields depending on the technology used. For instance, lactide exists as D-/L-/meso-isomers and unreacted lactide, which can inhibit the reaction. By using primary amines supported on resins, this unreacted lactide could be removed, without affecting the polymerization to PLA, with a yield of 98.7% (Alba et al. 2015). In theory, 80% of the glucose-biomass ends up in PLA (144 g/mol / 180 g/mol). This means that 1.25 tons glucose would be needed to produce 1 ton of PLA. In reality, the yield to produce LA (85–97%, mentioned in the "LA chapter") and the conversion rate of the polymerization reaction to yield PLA (98.7%) also have to be taken into account. Therefore, PLA production has a BUE_L 67.1% and a BUE_L of 76.6%. This is equal to 1.3–1.49 tons glucose being needed for 1 ton PLA.

(1) $n\ C_6H_{12}O_6 \rightarrow 2n\ C_3H_6O_3 \rightarrow C_6H_8O_4 + n\ H_2O \rightarrow 2\ (C_3H_4O_2)_n$
(2) n glucose → 2n lactic acid → lactide + n water → 2 polylactic acid
(3) n x 180 g → 2n x 90 g → 144 g + n x 18 g → 144 g

Table 27: Comparison of BUE of polylactic acid production.

Percentage of C, H, O of total mass of biomass (upper row)	C	H	O	BUE_S	BUE_H (lower value is BUE_L)
Glucose ($C_6H_{12}O_6$ = 180 g/mol)	40.0	6.7	53.3		
Percentage of biomass-derived C, H, O in end product (lower row)					
Polylactic acid (2 x ($C_3H_4O_2)_n$) = 144 g/mol)	100.0	66.7	66.7	**80.0**	**67.1 – 76.6**

5.4 Polyhydroxybutyrate (PHB) as an example of Polyhydroxyalkanoates (PHA)

PHA can be created by fermentation using a multitude of different substrates (e.g. glucose, maltose, sucrose; Honsa 1992; Gumel 2013). These hydroxyl fatty acid-derived polyesters have very diverse properties; due to their chemical properties, the PHAs with short chains (scl-PHA) are thermoplastic and the ones with a medium chain length (mcl-PHAl) are elastomeric (Belgacem and Gandini 2008) PHB belongs to the scl-PHAs. Using the synthetic route detailed below, 180 g of glucose are converted into 86 g of PHB-monomer ($C_4H_6O_2$). This is equal to 2.09 tons of glucose being needed for 1 ton of PHB. Riedel and colleagues (2013) were able to reach a total recovery of 84% PHB in Ralstonia eutropha, thereby reducing the theoretical 180 g glucose to 72.24 g for 86 g of PHB. These numbers are equal to a BUE_S of 47.8% and a realistic BUE of 40.1%.

(1) $C_6H_{12}O_6 + 2\ CoA + 1.5\ O_2 \rightarrow 2\ C_2H_3O\text{-}CoA + 2\ CO_2 + 3\ H_2O$
(2) $2\ C_2H_3O\text{-}CoA \rightarrow \text{-}(C_4H_6O_2)\text{-} + 2\ CoA$
(3) $C_6H_{12}O_6 + 1.5\ O_2 \rightarrow \text{-}(C_4H_6O_2)\text{-} + 2\ CO_2 + 3\ H_2O$

Table 28: Comparison of BUE of PHB production.

Percentage of C, H, O of total mass of biomass (upper row)	C	H	O	BUE_S	BUE_H (lower value is BUE_L)
Glucose ($C_6H_{12}O_6$ = 180 g/mol)	40.0	6.7	53.3		
Percentage of biomass-derived C, H, O in end product (lower row)					
Polyhydroxybutane ($C_4H_6O_2$ = 86 g/mol)	66.7	0.0	33.3	**47.8**	**40.1**

5.5 Polyamides

This major class of engineering plastics are known in layman's terms as nylons. They are abbreviated to PAx.y, where the first number denotes the number of carbon atoms in the diamine monomer and the second describes the number of carbons in the diacid. PA11 is manufactured by Arkema from castor oil and is fully bio-based. The seed of the plant Ricinus communis contains 45% castor oil, which in turn has a fatty acid composition of 85% ricinoleic acid (Harmsen et al. 2014). Assuming that the conversion steps starting from ricinoleic acid are 100% efficient, 61.4% (BUE = 6 x 183 g / 6 x 298 g) of the used ricinoleic acid mass is are theoretically retained in the polyamide. If one takes into consideration that only 45% of the plant seeds are castor oil and from this oil only 85% consist of ricinoleic acid, this means that 23.5% of the ricinus plant biomass ends up as PA11. In other words, 8.5 tons of plant are needed for the manufacture of 1 ton PA11. Even though this looks discouraging at first sight, 2 by-products of the PA11 synthesis (heptanal and glycerol) have a market of their own meaning that the biomass is used to a greater extent. For example, starting from ricinoleic acid and assuming a 100% conversion rate for all the reactions, the PA11-synthesis also yields 38.6% of the by-product heptanal. Consequently heptanal, which is used in fragrances (e.g. jasmine scent in washing powder) and can act as a lubricant due to its low freezing point, can be sold separately. In addition, bio-based heptanal is 100% linear compared to heptanals synthesized using classical petrochemical methods (Metzger and Bonscheuer 2006; Borg et al. 2009). Furthermore, undecenoic acid, can be used as a surfactant, has bacteriostatic properties and provides fungal restistance. Consequently, it is used to treat athletes foot and in diapers (Bort et al. 2009). For the table below, ricinoleic acid (RA) was defined as "biomass". Seeing as that castor oil only contains 85% of RA a realistic yield of 52.2% was calculated.

Interestingly, ricinoleic acid can also be used to make PA5.10, PA4.10, PA6.10 and PA10.10 using sebacic acid as an intermediate instead of undecane acid as it is shown below for PA11 synthesis (Endres 2013).

(1) 2 Castor oil + 6 $H_2O \rightarrow 6\ C_{18}H_{34}O_3 + 6\ CH_4O \rightarrow 2\ C_3H_8O_3 + 6\ C_{19}H_{36}O_3 \rightarrow 6\ C_{12}H_{24}O_2 + 6\ C_7H_{14}O \rightarrow 6\ C_{11}H_{22}O_2 \rightarrow 6\ C_{11}H_{21}BrO_2 \rightarrow 6\ C_{11}H_{23}NO_2 \rightarrow 3\ [\text{-NH-}(CH_2)_{10}\text{-CO}]_n + 3\ H_2O$

(2) 2 Castor oil →6 ricinoleic acid + 6 methanol → 2 glycerol + 6 methyl ricinoleate → 6 methyl 11-undecanoate + heptanal →6 11-undecenoic acid → 6 11-bromoundecanoic acid → 6 11-aminoundecanoic acid → 3 polyamide-11 + 3 water

(3) 2 x 932 g + (6 x 18 g) → 6 x 298 g + 32 g → 2 x 92 g + 6 x 312 g → 6 x 200 g + 6 x 114 g → 6 x 186 g → 6 x 265 g → 6 x 201 g → 6 x 183 g + 6 x 18 g

Table 29: Comparison of BUE of PA11 production.

Percentage of C, H, O of total mass of biomass	**C**	**H**	**O**	**BUE$_S$**	**BUE$_H$ (lower value is BUE$_L$)**
Ricinoleic acid (6 x $C_{18}H_{34}O_3$ = 6 x 298 g/mol)	72.5	11.4	16.1		
Percentage of biomass-derived C, H, O in end product					
PA11 (6 x NH-$C_{10}H_{10}$-CO = 6 x 183 g/mol)	55.6	32.4	33.3	61.4	49.5 – 52.5
Heptanal (6 x $C_7H_{14}O$ = 6 x 114 g/mol)	38.9	41.2	33.3	38.3	30.7 – 32.5
Glycerol (2 x $C_3H_8O_3$ = 2 x 92 g/mol)	5.6	7.8	33.3	10.3	8.8
Total biomass in valorizable products	100.0	81.4	100.0	**100.0**	**89.0 – 93.8**

5.6 Poly(ethylene furandicarboxylate) (PEF)

PEF is a new bio-based material, which could replace PET for products like bottles. Compared to PET, PEF has a higher thermal stability but at the same time a lower melting point so it can therefore be processed at lower temperatures (Harmsen at al. 2014). Instead of terephthalic acid as a monomer, PEF uses 2,5-furandicarboxylic acid (2,5-FDCA) and furthermore, the other monomer ethylene glycol could also be replaced by BDO to create the polymer poly(butylene furandicarboxylate) (PBF; Harmsen et al. 2014). To get FDCA, sugars are dehydrated to HMF (see chapter with detailed calculations for this building block further up in this paper).

To sum up our calculations for the two PEF monomers EG and FDCA, EG has a stoichiometric BUE of 100% which translates into a BUE$_L$ of 61% and a BUE$_H$ of 81%. For FDCA, a BUE$_S$ of 86.7% from glucose was calculated together with real world yields of 51.2–54.1% which also take into account the first synthetic step (glucose to HMF).

Based on the equation below one can further proceed with calculating how much glucose is needed to make 1 ton of PEF; theoretically, 780 kg FDCA are required (5 x 156 g/mol). Applying the highest yield of 54.1% results in 1441.8 kg glucose needed for the reaction from FDCA to PEF. For 310 kg EG (5 x 62 g/mol / 0.81), 382.7 kg glucose are required. Adding those glucose amounts together, 1824.5 tons of glucose equal 1000 tons PEF, or, in other words, 54.8% glucose ends up in PEF.

$C_6H_4O_5 + C_2H_6O_2 \rightarrow C_8H_8O_6 + H_2O$
1 FDCA + 1 ethylene glycol → 1 PEF + 1 water
156 g + 62 g → 200 g + 18 g

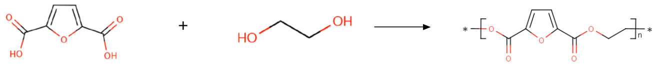

Figure 9: Schematic of PEF synthesis from ethylene glycol and FDCA (adapted from Saliger 2013).

Table 30: Comparison of BUE of PEF production.

Percentage of C, H, O of total mass of biomass (upper row)	**C**	**H**	**O**	**BUE$_S$**	**BUE$_H$ (lower value is BUE$_L$)**
Glucose (2 x $C_6H_{12}O_6$ = 2 x 180 g/mol)	40.0	6.7	53.3		
Percentage of biomass-derived C, H, O in end product (lower row)					
Poly(ethylene furandicarboxylate) ($C_8H_8O_6$ = 200 g/mol)	66.7	33.3	50.0	**55.6**	**54.8**

5.7 Polyethylene terephthalate (PET)

This large volume polymer (annual global production of ca. 50 million tons), is best known for its use in bottles and fibres (Sheldon 2014). To make 1 ton of PET, approximately 5.2 times TPA and MEG, according to the chemical equation shown below, will be required. TPA can realistically be produced from bio-based p-xylene with BUE$_H$ of 10.2% (see above). This means that instead of 863.2 kg (5.2 x 166 g/mol) TPA being needed for 1 ton of PET, 8462.7 kg glucose is needed. MEG has a BUE$_H$ of 81% and therefore 398 kg (5.2 x 62.1 g/mol / 0.81) glucose is needed to make the required amount of MEG in the PET production process. Consequently, 8.8 tons of glucose is needed to make 1 ton of PET. To put it differently, only a small fraction of glucose ends up in PET with a realistic BUE of 11.4%.

$n\ C_8H_6O_4 + n\ C_2H_6O_2 \rightarrow (C_{10}H_8O_4)_n + 2n\ H_20$
n x 166 g + n x 62.1 g →n x 192 g + 2n x 18 g
n x TPA + n x MEG → PET + 2n x water

Table 31: Comparison of BUE of PET production.

Percentage of C, H, O of total mass of biomass (upper row)	**C**	**H**	**O**	**BUE$_S$**	**BUE$_H$ (lower value is BUE$_L$)**
Glucose (2x$C_6H_{12}O_6$ = 2 x 180 g/mol)	40.0	6.7	53.3		
Percentage of biomass-derived C, H, O in end product (lower row)					
PET ($(C_{10}H_8O_4)_n$ = 192 g/mol)	83.3	33.3	33.3	**53.3**	**11.4**

5.8 Polymers from cellulose and starch

Cellulose and starch are polymers from glucose. Starch has storage functions whereas cellulose provides structure to the plant and is very stable, chemically speaking. Starch on the other hand can be easily broken down into its glucose molecules. This is due to the fact that starch has α-1,4- and α-1,6- glycosidic bonds. In contrast, the linear homopolymer cellulose has β-1,4- bonds between its glucose monomers. The heteropolymer hemicellulose is using β-1,4- and β-1,6-bonds and is made up by different sugars (C5, C6) and substituents such as acetyl groups/esterified phenolic acids (Antranikian 2006; Buruiana et al. 2014). Consequently, only some specialist bacteria and fungi can completely break down the bonds in cellulose (Goebbels 2010).

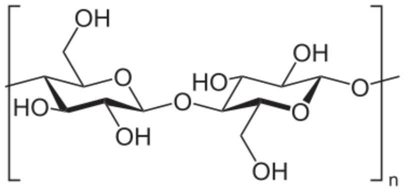

Figure 10: Cellulose monomer.

5.8.1 Regenerated cellulose

The major source for cellulose today is wood. After pulping and bleaching, celluloses with different purity are obtained. While lignin and extracts are largely removed from these pulps, different amounts of hemicelluloses are still present depending on the final application. Paper pulps benefit from a larger content of hemicelluloses but pulps utilized for fibre spinning or cellulose derivatives require a higher purity, which is often given by the content of pure cellulose (alpha-cellulose). In addition to a high purity, the molar mass (also degree of polymerization, DP) often require adjustments, e.g. controlled DP reduction. Fibres (e.g. Rayon, Modal, Lyocell) and films (cellophane, sponges) are made from these purified celluloses. 100% of cellulose is claimed to be usable for material. Realistically, it has to be taken into account that pulp is comprised of only 88% alpha-cellulose (Dadi et al. 2006; Endres and Siebert-Raths 2009; Goebbels 2010; Graupner et al. 2014).

5.8.2 Cellulose Derivatives

Cellulose derivatives are formed from purified, dissolved pulp with almost no hemicellulose content. Two main groups can be distinguished, cellulose ethers and cellulose esters (Goebbels 2010).

a) Cellulose ethers

Using an ether bond, stable functional groups (e.g. hydroxypropyl, hydroxyethyl) can be added to the cellulose molecule. The corresponding cellulose ethers are used as additives to tune viscosities in a variety of formulations (Endres and Siebert-Raths 2009; Goebbels 2010).

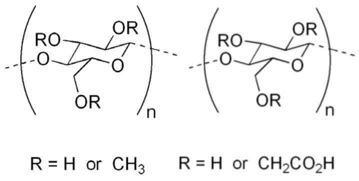

Figure 11: Methylcellulose (left) and carboxymethylcellulose (right) as example of cellulose ethers.

b) Cellulose esters

Other functional groups (especially acetic/propionic/butanoic acids), are linked to cellulose through an ester bond. They can be used for a variety of applications, for example, thermoplastic foams and composite materials (Endres and Siebert-Raths 2009; Goebbels 2010; Quintana et al. 2012; Wang et al. 2014).

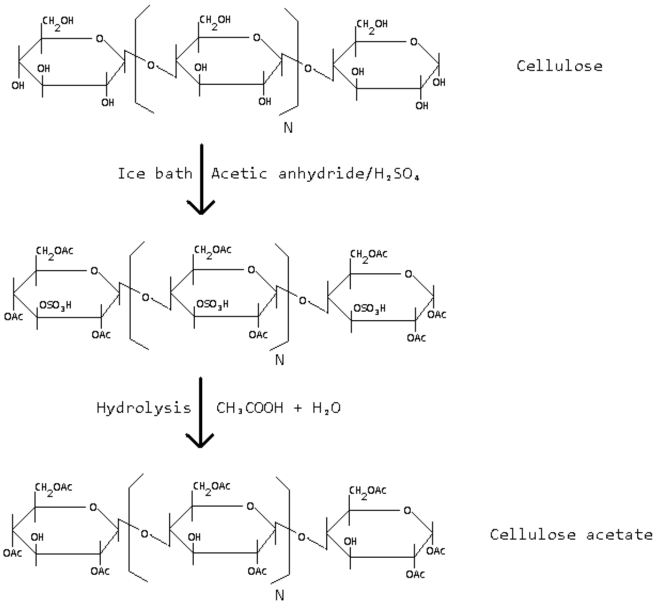

Figure 12: Cellulose acetate preparation.

5.9 Polymers from starch

Carbohydrates have the general chemical formula Cx(H_2O)y; for monosaccharides x is equal to y and in disaccharides y = x-1. For polysaccharides, where polymerisation degree is DPn and the molar mass is 162 g/mol, the following formula applies (the reducing end of the polymer chain is normally neglected)

$DPn = n\ x162\ g$

(1) Hydrolysis: n(anhydroglucose) + n(water) → n(glucose)

$162\ g + 18\ g \rightarrow 180\ g$

Using the relation of the polymer to the hydrolyzed mass 180n: Therefore, in case of complete hydrolysis (n>1000) the relation of polymer to hydrolyzed mass approaches 100%.

A starch-based biopolymer stores 15.2 g water per 12 g carbon, which, for energetic uses, is detrimental. In contrast, when starch-derived polymers are used as a basis for materials, they can be utilized for product formation (Goebbels 2010). For the manufacture of thermoplastic starch with 70% starch content, 30% plasticizer is used, hence, 100% of the originally used starch ends up in the real product (Endres 2013).

5.10 Tensides/Surfactants: Alkyl glucosides

These molecules are characterized by having a polar hydrophilic part and a non-polar lipophilic part. Consequently, they can promote the formation of emulsions by combining an oily and a water-based phase. In anionic, glucose-based tensides, the hydrophilic part of the molecule is formed by a carbohydrate (Goebbels 2010).

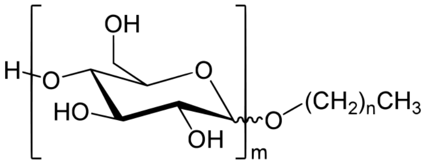

Figure 13: Structural formula of an alkyl glucoside.

To get alkyl glucosides, glucose has to react at the reducing end with a hydrophobic long chain alcohol (chain length ranging between 8–16 carbons). Both glucose and starch can be reactants. To get the fatty alcohol, oils or fats are broken down and their fatty acid methyl esters are reduced. In this reaction a mixture of alkylpolyglucosides are created (alkyl-mono/di/tri-oligoglycosides). To distinguish the different molecules, the length of the alkyl chain (depending on the alcohol chain length) and the degree of polymerisation (defined by the ratio of fatty alcohol to glucose used in the reaction) are applied as criteria (von Rybinski and Hill 1998). 100% (= BUE_S) glucose is utilized in this application (realistic yield when using fatty alcohols in excess: 90–96%; Goebbels 2010; Zhou et al. 2011). The fatty alcohol (providing the hydrophobic alkyl chain) from palm oil can be used for the production of dodecylpolyglucoside. Another useful side-product from this reaction is glycerine.

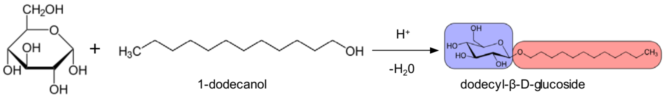

Figure 14: Synthesis route of alkyl glucoside.

5.11 Lubricating and hydraulics oils

Vegetable oils can also be used as lubricants, for example in hydraulics applications (Goebbels 2010). Realistically, yields of only around 80% have been reached despite the theoretical possibility of 100% conversion (= BUE_S) (Miao et al. 2014).

6 Application of our method to a hypothetical biorefinery

There are various biorefinery concepts and some are already installed and in operation based on wood, straw, bagasse and other agricultural waste streams as feedstocks. In this exercise, various components of biomass are assumed to be combined with a variety of technologies (integration of combined heat and power technology (CHP) to use heat created by exothermic reactions in endothermic processes) to create different products (multiple chemicals and fuels) and increase the percentage of biomass which eventually ends up in the various products. In this hypothetical biorefinery, with corn stover as biomass resource, we will try to establish a theoretical and realistic maximum BUE for the combination of process routes contained in the biorefinery setup. Therefore, we also included selected pretreaments, e.g. an organosolv process, without using acid as solvent, but neglected preprocessing steps such as drying and grinding of the corn stover. We are aware that biomass and especially additional energy is lost in these steps but decided that this would increase the complexity of the approach unnecessarily.

Table 32: Lignocellulosic composition of different 2nd generation feedstocks (adapted from: Ragauskas et al. 2014).

Plant Resource	% Hemicellulose	% Cellulose	% Lignin
Pine	23	48	28
Eucalyptus	24–26	39–46	29–32
Poplar	16–22	42–48	21–27
Corn Stover	31	37	18
Miscanthus	24–33	45–52	9–13
Switch Grass	26–33	32–37	17–18

6.1 Lignin Stream

Assuming that; 100 g corn stover is comprised of 31 g hemicellulose, 37 g cellulose and 18 g lignin; only 50–90% of lignin can be recovered from the organosolv fractionation of the 3 major corn stover components; this leaves 9 g or 9% of lignin to make a product, e.g. vanillin (Zakseski et al. 2010; Huijgen et al. 2014; Ragauskas et al. 2014). It has been shown that making BDO and adipic acid from lignin is also profitable and reduces greenhouse gas emissions (Davis et al. 2013). It has further been demonstrated that muconic acid can be made from lignin with a 75% yield, but for the sake of clarity we will focus on vanillin as the value-added chemical in this model lignocellulose biorefinery (Davis et al. 2013; Vardon et al. 2015). We will use the following approximation of the lignin monomer-formula for our calculations: $(C_{31}H_{34}O_{11})_n$ (Li et al. 2014). Using the chemical reaction below, 70.8% of lignin-biomass can be converted into vanillin (644 g/mol / 465 g/mol). Considering the low yield of 7.6–23% in this reaction, only a BUE_L of 5.38 and a BUE_H of 16.23% of lignin is converted into vanillin (Araujo et al. 2010; Araujo et al. 2014). To put these values into the perspective of the biorefinery, depending on the efficiency of the organosolv pretreatment, 9.0–16.2 g of lignin remain of the originally used 100 g corn stover. Applying real world yields, the minimal vanillin mass from 9 g lignin is 0.48 g and in the best case scenario using 16.2 g of lignin and a realistic yield of 16.23% is 2.63 g vanillin. If one was to only produce vanillin from corn stover, 208.3 tons of corn stover would be needed to produce 1 ton of vanillin (worst-case scenario). Assuming maximum yields and efficiency, this value is reduced to 38.02 tons of corn stover for 1 ton vanillin.

$$(1)\ (C_{31}H_{34}O_{11})_n + 8.5\ O_2 \rightarrow 3\ C_8H_8O_3 + 5\ H_2O + 7\ CO_2$$

lignin + 8.5 x oxygen → 3 x vanillin + 5 x water + 7 x carbon dioxide

$$582\ g + 272\ g \rightarrow 456\ g + 90\ g + 308\ g$$

Table 33: Comparison of BUE of vanillin production from lignin.

Percentage of C, H, O of total mass of biomass	C	H	O	BUE_S	BUE_H (lower value is BUE_L)
Lignin ($(C_{31}H_{34}O_{11})_n$ = 582 g/mol)	63.9	5.8	30.2	**70.8**	**5.4 – 16.2**
Percentage of lignin-derived C, H, O in end product					
Vanillin (3 x $C_8H_8O_3$ = 3 x 152 g/mol)	77.4	70.6	81.8		

6.2 Hemicellulose Stream

The main hemicelluloses found in corn stover after organosolv pretreatment are glucan (83.26%) and xylan (14.56%) (Buruiana et al. 2014). The pretreatment itself causes a total hemicellulose loss of 3–5%, meaning that only 29.4–30.1 g are left of the 31 g hemicelluloses contained in corn stover dry biomass (Kabir et al. 2015). It might be possible to sell glucan directly because, it has been suggested that, due to its effects on food texture, it can be used as an emulsifier and food additive. Moreover, it also lowers total blood cholesterol levels and blood lipid profile (Yoshida et al. 2014).

Regarding xylan, it can easily be further reacted via xylose as an intermediate to furfural using an acid catalyst. Furfural is an important building block for further chemical synthesis e.g. furfuryl alchohol and eventually products such as nylon-6. Furfural in itself has, amongst other things, fungicidal and solvent properties (Zeitsch 2000). It has to be taken into account that xylose itself can already be valorized because it is extensively used in the sugar industry. For example, by hydrogenation of xylose, the artificial sweetener xylitol can be produced (Mesa et al. 2014; Mittal et al. 2015).

In theory, 64% of xylose ends up in the furfural product in this reaction. Discounting all realistic yields for the reactions and pretreatment, this would mean that of the original 4.51 g xylene from the 100 g postulated corn stover drymass, 2.89 g can react to furfural. If only using corn stover only to make furfural, one would need 34.6 tons corn stover to produce 1 ton furfural.

The xylan removal after the organosolv process can be executed at 90–100% efficiency and the reaction of xylan to xylose has been published to be performed between 88.6 – 98.6% (Liu and Wyman 2005; Mittal et al. 2015). If one takes into account all the afore-mentioned, yield reducing elements, the original 60.4% is reduced to a range between 45.75% (0.95 x 0.886 x 0.9 x 0.604) and 57.77% (0.97 x 0.986 x 1 x 0.604). Subsequently, from the 4.51 g xylan theoretically contained in corn stover, only 2.06–2.61 g furfural can be made. To put it differently, between 38.31 and 48.54 tons corn stover is required for the production of only 1 ton of furfural.

$(2)\ C_5H_{10}O_5 \rightarrow C_5H_4O_2 + 3\ H_2O$
xylose → furfural + 3 x water
150.1 g → 96.1 g + 54 g

Table 34: Comparison of BUE of furfural production from xylose.

Percentage of C, H, O of total mass of biomass	**C**	**H**	**O**	**BUE$_S$**	**BUE$_H$ (lower value is BUE$_L$)**
Xylose ($C_5H_{10}O_5$ = 150.1 g/mol)	40.0	6.6	53.3		
Percentage of biomass-derived C, H, O in end product					
Furfural ($C_5H_4O_2$ = 96.1 g/mol)	100.0	40.0	40.0	**60.4**	**45.7 – 57.8**

6.3 Cellulose Stream

Kabir and colleagues (2015) indicated that the presently used cellulases can convert 90% of cellulose into glucose. The organosolv treatment reduces the total amount of cellulose contained in corn stover from 37 g (when assuming 100g corn stover originally being used for these exemplatory calculations) by 3% to 35.89 g (Buruiana et al. 2014; Ragauskas et al. 2014). Theoretically, 100% of the cellulose is converted into lactic acid based on stoichiometry alone. Applying the above-mentioned yields, 85–97% of lactic acid is produced from the fermentation (Endres 2013; Harmsen et al. 2014; Wang et al. 2014). These different steps sum up to a BUE of 74.2–84.7% (0.9 x 0.97 x 0.85 or 0.97) and therefore, of the 37 g cellulose originally contained in 100 g corn stover, 27.45–31.1 g of lactic acid can be produced realistically. Consequently, production of 1 ton lactic acid requires 3.64 – 3.21 tons of corn stover.

$(3)\ (C_6H_{10}O_5)_n + n\ H_2O \rightarrow n\ x\ C_6H_{12}O_6 \rightarrow 2\ C_3H_6O_3$
cellulose + n x water → glucose → 2 lactic acid
162 g + n x 18 g → 180 g → 2 x 90 g

Table 35: Comparison of BUE of LA production from cellulose

Percentage of C, H, O of total mass of biomass	**C**	**H**	**O**	**BUE$_S$**	**BUE$_H$ (lower value is BUE$_L$)**
Cellulose ($(C_6H_{10}O_5)_n$ = 162 g/mol)	44.4	6.2	49.4		
Percentage of biomass-derived C, H, O in end product					
Lactic Acid (2 x $C_3H_6O_3$ = 2 x 90g/mol)	100.0	100.0	100.0	**100.0**	**74.2 – 84.7**

To sum up, the total theoretical BUE$_S$ of the biorefinery converting lignin, xylose and cellulose, from corn stover, to the given products is 68.42%. In reality, when the efficiencies of the pre-treatment and the reactions are taken into account the realistic BUE of the biorefinery is reduced to 42.13–51.87%. These percentages can rise with the selection of more efficient products from the lignin fraction and by also using the glucan fraction – this variety is not taken into account with this theoretical biorefinery.

7 List of abbreviations

AA	Acetic Acid
AE	Atom economy
BDO	1,4-Butanediol
BTL	Biomass to liquid
BUE	Biomass utilization efficiency
DMF	2,5-dimethylfuran
EG	Ethylene glycol
FDCA	2,5-furandicarboxylic acid
GCV	Gross calorific value
HMF	5-hydroxymethylfurfural
HHV	Higher heating value
LA	Lactic acid
MEG	Mono-ethylene glycol
PA	Polyamide
PAA	Poly(acrylic) acid
PBS	Poly(butylene) succinate
PE	Polyethylene
PEF	Poly(ethylene furandicarboxylate)
PET	Polyethylene terephthalate
PDO	1,3-Propanediol
PHA	Polyhydroxyalkanoate
P(3)HB	Polyhydroxybutyrate
PLA	Poly(lactic) acid
PP	Polypropylene
PTT	Poly(trimethylene) terephthalate
pX	para-xylene
RME	Reaction mass efficiency
RMM	Relative molecular mass
SA	Succinic acid
TPA	Terephthalic acid

8 References

Adamopoulou, E. (2012): Poly(butylene succinate): A Promising Biopolymer. PhD Dissertation, University of Athens.

Anastas, P. T.; Warner, J. C.: Green Chemistry: Theory and Practice, Oxford University Press: New York, 1998, p.30. By permission of Oxford University Press.

Antranikian, G. (2006): Angewandte Mikrobiologie. Springer-Verlag Berlin Heidelberg.

Alba, A., du Boullay, O. T., Martin-Vaca, B., & Bourissou, D. (2015): Direct ring-opening of lactide with amines: application to the organo-catalyzed preparation of amide end-capped PLA and to the removal of residual lactide from PLA samples. Polymer Chemistry 6, 989–997.

Alwarsdotter, Y. 2015: SEKAB, personal communication via email.

Araújo, J. D., Grande, C. A., & Rodrigues, A. E. (2010): Vanillin production from lignin oxidation in a batch reactor. Chemical Engineering Research and Design, 88(8), 1024–1032.

Araújo, J. D. P. (2014): Production of vanillin from lignin present in the Kraft black liquor of the pulp and paper industry. Advances in Plant Biology 4, pp 277–289.

Bezergianni, S., Dimitriadis, A., & Chrysikou, L. P. (2014): Quality and sustainability comparison of one-vs. two-step catalytic hydroprocessing of waste cooking oil. Fuel, 118, 300–307.

Borg, P., Lê, G., Lebrun, S., & Pées, B. (2009): Example of industrial valorisation of derivative products of Castor oil. Oléagineux, Corps Gras, Lipides, 16(4), 211–214.

Buruiana, C. T., Vizireanu, C., Garrote, G., & Parajó, J. C. (2014): Bioethanol production from hydrothermally pretreated and delignified corn stover by fed-batch simultaneous saccharification and fermentation. Energy & Fuels, 28(2), 1158–1165.

Buswell, A. M., and H. F. Mueller, H.F. (1952): Mechanism of methane fermentation. Industrial & Engineering Chemistry 44.3: 550–552.

Bynes, Adrian N., Ingvar Eide, and Kåre B. Jørgensen (2014): Optimization of acid catalyzed transesterification of jatropha and rapeseed oil with 1-butanol. Fuel 137: 94–99.

Dadi, A. P., Varanasi, S., & Schall, C. A. (2006): Enhancement of cellulose saccharification kinetics using an ionic liquid pretreatment step. Biotechnology and Bioengineering, 95(5), 904–910.

Davis, M. E., & Pacheco, J. (2014): U.S. Patent No. 20,140,364,631. Washington, DC: U.S. Patent and Trademark Office.

Davis, R., Tao, L., Tan, E. C. D., Biddy, M. J., Beckham, G. T., Scarlata, C. & Schoen, P. (2013): Process design and economics for the conversion of lignocellulosic biomass to hydrocarbons: Dilute-acid and enzymatic Deconstruction of biomass to sugars and biological conversion of Sugars to Hydrocarbons (No. NREL/TP-5100-60223). National Renewable Energy Laboratory (NREL), Golden, CO.

De Guzman, D. (2010): Wacker licenses bio-acetic acid process. Available from: http://www.icis.com/blogs/green-chemicals/2010/04/wacker-licenses- bio-acetic-aci.html. (Accessed on 25/11/2014).

de Jong, E., Higson, A., Walsh, P., & Wellisch, M. (2012): Bio-based Chemicals Value Added Products from Biorefineries. IEA Bioenergy, Task42 Biorefinery.

Demirbas, A. (2009): Progress and recent trends in biodiesel fuels. Energy conversion and management 50.: 14–34.

Diels, L. (2015): Vito, personal communication via email.

Eckert, C., Xu, W., Xiong, W., Lynch, S., Ungerer, J., Tao, L. & Yu, J. (2014): Ethylene-forming enzyme and bioethylene production. Biotechnol Biofuels, 7(1), 33.

EN 16575: European Standard EN 16575 “Bio-based products – Vocabulary”, August 2014.

Endres, H. J., & Siebert-Raths, A. (2009): Technische Biopolymere. Rahmenbedingungen, Marktsituation, Herstellung, Aufbau und Eigenschaften, Hrsg.: Hanser Fachbuch, 152.

Endres, H. J. (2013): Biopolymers – facts and statistics. http://ifbb.wp.hs-hannover.de/downloads/index.php?site=Statistics&nav=3-0-0-0-0 accessed on 12/12/2014.

European technical specification CEN/TS 16640, Bio-based products: Determination of the bio-based carbon content of products using the radiocarbon method, 2014.

European draft standard prEN 16785-2, Bio-based products – Bio-based content – Part 2: Determination of the bio-based content using the material balance method, 2015.

Fan, D., Dai, D. J., & Wu, H. S. (2012): Ethylene formation by catalytic dehydration of ethanol with industrial considerations. Materials, 6(1), 101–115.

FNR (2014): Basisdaten Bioenergie Deutschland 2014. http://mediathek.fnr.de/media/downloadable/files/samples/b/a/basisdaten_9x16_2014_web_v02.pdf accessed on 18/12/14.

Frenzel and Pfennig (2012): Biomasse als Rohstoff für die Chemie. http://www.chemieundmore.de/ archive/125,402281/Biotechnologie/Biomasse-als-Rohstoff-fuer-die-Chemie.html accessed on 18/12/14.

Frenzel, P., Fayyaz, S., Hillerbrand, R., & Pfennig, A. (2013): Biomass as Feedstock in the Chemical Industry–An Examination from an Exergetic Point of View. Chemical Engineering & Technology, 36(2), 233–240.

Frenzel, P., Hillerbrand, R., & Pfennig, A. (2014): Exergetical Evaluation of Biobased Synthesis Pathways. Polymers, 6(2), 327–345.

Gandarias, Iñaki, and Pedro Luis Arias (2013): Hydrotreating catalytic processes for oxygen removal in the upgrading of bio-oils and bio-chemicals. Ed. Z. Fang. INTECH Open Access Publisher, 2013. Garlotta, D. (2001). A literature review of poly (lactic acid). Journal of Polymers and the Environment, 9(2), 63–84.

Goebbels, F. (2010): Biochemischer Vergleich der stofflichen und energetischen Nutzung von nachwachsenden Rohstoffen. From: Studie zur Entwicklung von Förderinstrumenten für die stoffliche Nutzung von nachwachsenden Rohstoffen in Deutschland. FKZ: 22003908.

Graupner, N., Fischer, H., Ziegmann, G., & Müssig, J. (2014): Improvement and analysis of fibre/matrix adhesion of regenerated cellulose fibre reinforced PP-, MAPP-and PLA-composites by the use of< i> Eukalyptus globulus</i> lignin. Composites Part B: Engineering.

Gumel, A. M., M. S. M. Annuar & Y. Chisti (2013): Recent Advances in the Production, Recovery and Applications of Polyhydroxyalkanoates. Journal of Polymers and the Environment, 21 (2), pp. 580–605.

Hama, S., Nakano, K., Onodera, K., Nakamura, M., Noda, H., & Kondo, A. (2014): Saccharification behavior of cellulose acetate during enzymatic processing for microbial ethanol production. Bioresource technology, 157:1–5.

Hansen, M. A. T., Jørgensen, H., Laursen, K. H., Schjørring, J. K., & Felby, C. (2013): Structural and chemical analysis of process residue from biochemical conversion of wheat straw (< i> Triticum aestivum</ i> L.) to ethanol. Biomass and Bioenergy, 56, 572–581.

Harmsen, P.F.H., Hackmann, M.M. and H.L. (2014): Green building blocks for bio-based plastics. Biofuels, Bioproducts and Biorefining 8.3: 306–324.

Haselbeck, R., Trawick, J. D., Niu, W., & Burgard, A. P. (2013): U.S. Patent No. 8,377,667. Washington, DC: U.S. Patent and Trademark Office.

Honsa, S. L. (1992): U.S. Patent No. 5,174,927. Washington, DC: U.S. Patent and Trademark Office.

Huijgen, W. J. J., Linden, R., Reith, J. H., & Uil, H. D. (2014): Development of a Lignocellulose Biorefinery Concept based on Organosolv Pretreatment. Policy Studies, 2013, 2012.

Kabir, M. M., Rajendran, K., Taherzadeh, M. J., & Horváth, I. S. (2015): Experimental and economical evaluation of bioconversion of forest residues to biogas using organosolv pretreatment. Bioresource technology, 178, 201–208.

Kamm, B., Gruber, P. R., & Kamm, M. (2007): Biorefineries–industrial processes and products. Ullmann’s Encyclopedia of Industrial Chemistry.

Koopman, F., Wierckx, N., de Winde, J. H., & Ruijssenaars, H. J. (2010): Efficient whole-cell biotransformation of 5-(hydroxymethyl) furfural into FDCA, 2, 5-furandicarboxylic acid. Bioresource technology, 101(16), 6291–6296.

Kreuger, E., Sipos, B., Zacchi, G., Svensson, S. E., & Björnsson, L. (2011): Bioconversion of industrial hemp to ethanol and methane: the benefits of steam pretreatment and co-production. Bioresource technology, 102(3), 3457–3465.

Kurzrock, T., & Weuster-Botz, D. (2010): Recovery of succinic acid from fermentation broth. Biotechnology letters, 32(3), 331–339.

Labatut, R.A., Angenent, L.T. and. Scott, N.R. (2011): Biochemical methane potential and biodegradability of complex organic substrates. Bioresource technology 102.3: 2255–2264.

Li, J. (2014): A multicale approachh to parameterization of burning models for polymeric materials. Doctoral dissertation, University of Maryland.

Linstrom, P. J., & Mallard, W. G. (2001): The NIST Chemistry WebBook: A chemical data resource on the internet. Journal of Chemical & Engineering Data, 46(5), 1059–1063.

Liu, C., & Wyman, C. E. (2005): Partial flow of compressed-hot water through corn stover to enhance hemicellulose sugar recovery and enzymatic digestibility of cellulose. Bioresource Technology, 96(18), 1978–1985.

Liu, C. L., Fan, L. H., Liu, L., & Tan, T. W. (2014): Combinational biosynthesis of isoprene by engineering the MEP pathway in Escherichia coli. Process Biochemistry, 49(12), 2078–2085.

Luterbacher, J. S., Rand, J. M., Alonso, D. M., Han, J., Youngquist, J. T., Maravelias, C. T. & Dumesic, J. A. (2014): Nonenzymatic sugar production from biomass using biomass-derived γ-valerolactone. Science, 343(6168), 277–280.

Lv, X., Xu, H., & Yu, H. (2013): Significantly enhanced production of isoprene by ordered coexpression of genes dxs, dxr, and idi in Escherichia coli. Applied microbiology and biotechnology, 97(6), 2357–2365.

Marques-Marinho, F. D., & Vianna-Soares, C. D. (2013): Cellulose and Its Derivatives Use in the Pharmaceutical Compounding Practice. http://dx.doi.org/10.5772/56637.

McElroy, C. R., Constantinou, A., Jones, L. C., Summerton, L., & Clark, J. H. (2015): Towards a holistic approach to metrics for the 21st century pharmaceutical industry. Green Chemistry, 17(5), 3111–3121.

Mesa, L., Morales, M., González, E., Cara, C., Romero, I., Castro, E., & Mussatto, S. I. (2014): Restructuring the processes for furfural and xylose production from sugarcane bagasse in a biorefinery concept for ethanol production. Chemical Engineering and Processing: Process Intensification, 85, 196–202.

Metzger, J. O., & Bornscheuer, U. (2006): Lipids as renewable resources: current state of chemical and biotechnological conversion and diversification. Applied Microbiology and Biotechnology, 71(1), 13–22.

Miao, S., Wang, P., Su, Z., & Zhang, S. (2014): Vegetable-oil-based polymers as future polymeric biomaterials. Acta biomaterialia, 10(4), 1692–1704.

Miller, K. K., Zhang, P., Nishizawa-Brennen, Y., & Frost, J. W. (2014): Synthesis of Biobased Terephthalic Acid from Cycloaddition of Isoprene with Acrylic Acid. ACS Sustainable Chemistry & Engineering, 2(8), 2053–2056.

Mittal, A., Vinzant, T. B., Brunecky, R., Black, S. K., Pilath, H. M., Himmel, M. E., & Johnson, D. K. (2015): Investigation of the role of lignin in biphasic xylan hydrolysis during dilute acid and organosolv pretreatment of corn stover. Green Chemistry.

Morais, A. R., Dworakowska, S., Reis, A., Gouveia, L., Matos, C. T., Bogdał, D., & Bogel-Łukasik, R. (2014): Chemical and biological-based isoprene production: Green metrics. Catalysis Today, 239, 38–43.

Muska, C.F. and Alles C. (2005-05-11): Biobased 1,3-Propanediol A New Platform Chemical For The 21st Century. BREW Symposium.

Nakamura, C. E., & Whited, G. M. (2003): Metabolic engineering for the microbial production of 1, 3-propanediol. Current opinion in biotechnology, 14(5), 454–459.

Nikbakht, Ali M., Hadi Javidi, and Hamed Rahmati (2014): Design and Fabrication of a Reactor for Producing Bio-Char from Agricultural Wood Residues. International Conference on Food, Agriculture and Biology (FAB-2014) June 11–12.

Noureldin, Mohamed, M.B. (2014): Benchmarking, insights, and potential for improvement of Fischer–Tropsch-based biomass-to-liquid technology. Clean Technologies and Environmental Policy 16.1: 37–44.

Nylund, N. O., Erkkila, K., Ahtiainen, M., Murtonen, T., Saikkonen, P., Amberla, A., & Aatola, H. (2011): Optimized usage of NExBTL renewable diesel fuel. OPTIBIO. Espoo.

Ooms, R., Dusselier, M., Geboers, J. A., de Beeck, B. O., Verhaeven, R., Gobechiya, E. & Sels, B. F. (2014): Conversion of sugars to ethylene glycol with nickel tungsten carbide in a fed-batch reactor: high productivity and reaction network elucidation. Green Chemistry, 16(2), 695–707.

Peng, B. (2012): Transformation of triglycerides and fatty acids into biofuels with sulfur-free catalysts (Doctoral dissertation, Universität München).

Pinazo, J. M., Domine, M. E., Parvulescu, V., & Petru, F. (2015): Sustainability metrics for succinic acid production: A comparison between biomass-based and petrochemical routes. Catalysis Today, 239, 17–24.

Pulidindi, I. N., Kimchi, B. B., & Gedanken, A. (2014): Can cellulose be a sustainable feedstock for bioethanol production?. Renewable Energy, 71, 77–80.

Putten, R. J. V. (2015): Experimental and modelling studies on the synthesis of 5-hydroxymethylfurfural from sugars (Doctoral dissertation, University of Groningen).

Quintana, R., Persenaire, O., Bonnaud, L., & Dubois, P. (2012): Recent advances in (reactive) melt processing of cellulose acetate and related biodegradable bio-compositions. Polymer Chemistry, 3(3), 591–595.

Ragauskas, A. J., Beckham, G. T., Biddy, M. J., Chandra, R., Chen, F., Davis, M. F. & Wyman, C. E. (2014): Lignin valorization: improving lignin processing in the biorefinery. Science, 344(6185), 1246843.

Rebsdat, S. and Mayer, D. (2005): Ethylene Glycol. Ullmann's Encyclopedia of Industrial Chemistry, Weinheim: Wiley-VCH,

Riedel, S. L., Brigham, C. J., Budde, C. F., Bader, J., Rha, C., Stahl, U., & Sinskey, A. J. (2013): Recovery of poly (3-hydroxybutyrate-co-3-hydroxyhexanoate) from Ralstonia eutropha cultures with non-halogenated solvents. Biotechnology and bioengineering, 110(2), 461–470.

Rødsrud, G. 2015: Borregard, personal communication via email.

Rosatella, A. A., Simeonov, S. P., Frade, R. F., & Afonso, C. A. (2011): 5 Hydroxymethylfurfural (HMF) as a building block platform: Biological properties, synthesis and synthetic applications. Green Chem., 13(4), 754–793. http://pubs.rsc.org/en/content/articlelanding/2011/gc/c0gc00401d (last accessed: 2015-05-27).

Saha, B. C., Nichols, N. N., Qureshi, N., Kennedy, G. J., Iten, L. B., & Cotta, M. A. (2014): Pilot scale conversion of wheat straw to ethanol via simultaneous saccharification and fermentation. Bioresource Technology.

Saliger, R. (2013): Herstellung von Hydroxymethylfurfural aus Kohlenhydraten (Doctoral dissertation).

Saxena, R. K., Anand, P., Saran, S., & Isar, J. (2009): Microbial production of 1, 3-propanediol: recent developments and emerging opportunities. Biotechnology advances, 27(6), 895–913.

Schumacher, B., Wedwitschka, H., Hofmann, J., Denysenko, V., Lorenz, H., & Liebetrau, J. (2014): Disintegration in the biogas sector–Technologies and effects. Bioresource technology.

Schmitz, N., Henke, J. and Klepper, G. (2009): Biokraftstoffe – Eine vergleichende Analyse [Biofuels – A comparative analysis]. Gulzow, Germany: Fachagentur Nachwachsende Rohstoffe.

Sheldon, R. A. (2007): The E factor: fifteen years on. Green Chemistry, 9(12), 1273–1283.

Sheldon, R. A. (2014): Green and sustainable manufacture of chemicals from biomass: state of the art. Green Chemistry, 16(3), 950–963.

Sousa, A. F., Matos, M., Freire, C. S., Silvestre, A. J., & Coelho, J. F. (2013): New copolyesters derived from terephthalic and 2, 5-furandicarboxylic acids: A step forward in the development of biobased polyesters. Polymer, 54(2), 513–519.

Stryer, Lubert (1975): Biochemistry. W. H. Freeman and Company.

van Aken, T. (2011): Avantium presentation at CT Forum Amsterdam. (events.cleantech.com/amsterdam/sites/default/files/CTForum Amsterdam_Avantium.pdf; Accessed on 25/11/2014).

Van de Vyver, S., Geboers, J., Jacobs, P. A., & Sels, B. F. (2011): Recent advances in the catalytic conversion of cellulose. ChemCatChem, 3(1), 82–94.

van Putten, R. J., van der Waal, J. C., de Jong, E., Rasrendra, C. B., Heeres, H. J., & de Vries, J. G. (2013): Hydroxymethylfurfural, a versatile platform chemical made from renewable resources. Chemical reviews, 113(3), 1499–1597.

Vardon, D. R., Franden, M. A., Johnson, C. W., Karp, E. M., Guarnieri, M. T., Linger, J. G. & Beckham, G. T. (2015): Adipic acid production from lignin. Energy & Environmental Science.

Veith, S. 2015: DuPont, personal communication via email.

von Rybinski, W., & Hill, K. (1998): Alkyl polyglycosides—properties and applications of a new class of surfactants. Angewandte Chemie International Edition, 37(10), 1328–1345.

Wang, C., Li, Q., Wang, D., & Xing, J. (2014): Improving the lactic acid production of< i> Actinobacillus succinogenes</i> by using a novel fermentation and separation integration system. Process Biochemistry.

Wang, J., Lu, X., Ng, P. F., Lee, K. I., Fei, B., Xin, J. H., & Wu, J. Y. (2014): Polyethylenimine coated bacterial cellulose nanofiber membrane and application as adsorbent and catalyst. Journal of Colloid and Interface Science.

Witsuthammakul, A., & Sooknoi, T. (2012): Direct conversion of glycerol to acrylic acid via integrated dehydration–oxidation bed system. Applied Catalysis A: General, 413, 109–116.

Yamada, R., Nakatani, Y., Ogino, C., & Kondo, A. (2013): Efficient direct ethanol production from cellulose by cellulase-and cellodextrin transporter-co-expressing Saccharomyces cerevisiae. AMB Express, 3(1), 1–7.

Yan, B. H., Selvam, A., Xu, S. Y., & Wong, J. W. (2014): A novel way to utilize hydrogen and carbon dioxide in acidogenic reactor through homoacetogenesis Bioresource technology, 159, 249–257.

Yim, H., Haselbeck, R., Niu, W., Pujol-Baxley, C., Burgard, A., Boldt, J. & Van Dien, S. (2011): Metabolic engineering of Escherichia coli for direct production of 1, 4-butanediol. Nature chemical biology, 7(7), 445–452.

Yoshida, T., Honda, Y., Tsujimoto, T., Uyama, H., & Azuma, J. I. (2014): Selective isolation of β-glucan from corn pericarp hemicelluloses by affinity chromatography on cellulose column. Carbohydrate polymers, 111, 538–542.

Zakzeski, J., Bruijnincx, P. C., Jongerius, A. L., & Weckhuysen, B. M. (2010): The catalytic valorization of lignin for the production of renewable chemicals. Chemical reviews, 110(6), 3552–3599.

Zeitsch, K. J. (2000): The chemistry and technology of furfural and its many by-products (Vol. 13). Elsevier.

Zhao, X., Wang, L., Lu, X., & Zhang, S. (2014): Pretreatment of corn stover with diluted acetic acid for enhancement of acidogenic fermentation. Bioresource technology, 158, 12–18.

Zhou, D. P., Huang, Y. R., & Ge, Z. (2011): Synthesis of alkyl polyglucoside by NaHSO_4• H_2O under microwave irradiation. Detergent & Cosmetics, 12, 007.

Zu, Y., Yang, P., Wang, J., Liu, X., Ren, J., Lu, G., & Wang, Y. (2014): Efficient production of the liquid fuel 2, 5-dimethylfuran from 5-hydroxymethylfurfural over Ru/Co 3 O 4 catalyst. Applied Catalysis B: Environmental, 146, 244–248.

Zurbriggen, A., Kirst, H., & Melis, A. (2012): Isoprene production via the mevalonic acid pathway in Escherichia coli (bacteria). BioEnergy Research, 5(4), 814–828.

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- nova paper #5: New Methodology for Techno-Economic Evaluations of Innovative Industrial Processes by nova-Institute (nTEE) 2014-11.
- nova paper #6: Options for Designing a New Political Framework of the European Bio-based Economy. 2015-05.
- nova paper #7: Global bioeconomy in the conflict between biomass supply and demand. 2015-10.
- nova paper #8: Definition, Calculation and Comparison of the "Biomass Utilization Efficiency (BUE)" of Various Bio-based Chemicals, Polymers and Fuels. 2015-11.