

# Beyond Petrochemicals: The Renewable Chemicals Industry\*\*

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biomass · H/C ratio · industrial chemistry ·  
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The use of renewable resources has attracted significant attention in recent years for many different reasons.<sup>[1,2]</sup> Renewable resources include electricity made from kinetic energy stored in wind, potential energy stored in water, thermal energy stored as heat underground and as solar influx in the form of electromagnetic radiation, and energy stored in chemical bonds in the case of biomass. Although renewable resources have been used for various purposes for centuries, there is currently a significant focus on expanding and optimizing this use in the form of new technologies fit for the 21st century.

The use of biomass as a resource has developed rapidly in recent years, and it will become an important contributor to our available resources in the future. Biomass sets itself aside from the other renewable resources, since the energy it contains is stored as chemical bonds. This characteristic allows biomass to be used for several purposes apart from electricity and heat generation, such as the production of liquid fuels and chemicals. Indeed, biomass is the only renewable source of useful carbon atoms. Although biomass is annually renewable, it is still a scarce and limited resource, especially when produced in a sustainable manner, and it is important to use it in the most efficient way. This Essay argues for the production of select chemicals, thereby effectively replacing petroleum, as an efficient use and illustrates some of the current efforts that are made in the chemical industry towards adoption of biomass as a feedstock.

## Availability of Biomass Resources

In recent years, a large number of processes for producing fuels and chemicals from biomass have been demonstrated.<sup>[3–7]</sup> When the potential of these processes is discussed, it is often done in the context of the current world situation. This approach gives an unclear picture of the actual merit of the process, as large-scale industrial production using biomass will drastically alter the premises. To consider the true potential of a process and its ability to substitute or compete with a fossil-based analogue, absolute numbers of the demand and the amount of potential feedstock must be considered. In the U.S., the total demand for crude oil is approximately one billion, i.e.  $10^9$  metric tons per year ( $\text{ty}^{-1}$ ).<sup>[8]</sup> In comparison, the amount of biomass used for electricity generation and the production of biofuels and other nonfood bioproducts constitutes about 190 million tons.<sup>[9]</sup> As a consequence, biomass production must be increased drastically to replace all products derived from petroleum with biomass. The total sustainable biomass potential is estimated by the U.S. Department of Energy to be at least 1.2 billion tons per year in the U.S.,<sup>[\*]</sup> a target reachable within 50 years.<sup>[9]</sup> This rough comparison illustrates how present demand for oil and future availability of biomass can become comparable on a weight basis, as shown in Figure 1, and although the quantities reported are based on U.S. statistics, and are thus not necessarily representative of other countries, the conclusions can be extrapolated to the rest of the industrialized world.

The comparison on a weight basis is, however, somewhat misleading, as biomass has a lower energy and carbon density than crude oil; on a weight basis, oil contains approximately twice the amount of carbon atoms and chemically stored energy as biomass. Therefore, the proposed sevenfold increase of the U.S. biomass production will not constitute a large enough resource to completely replace the current demand for oil. Thus, as the use of biomass in industry increases, it will at some point become a scarce resource, and its utilization should for this reason be considered wisely. Current economic feasibility studies of processes using biomass as feedstock, which use a zero or even negative

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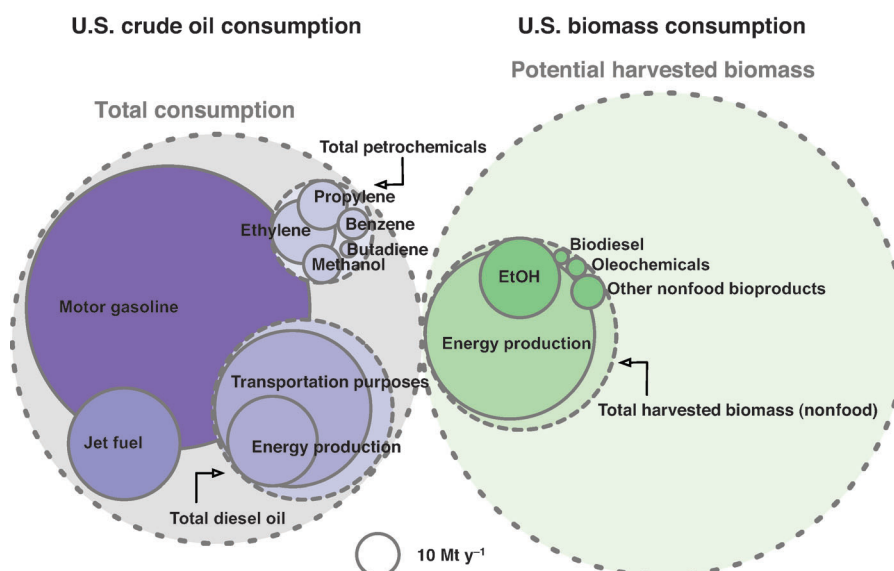
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[\*] The total 1.2 billion tons calculated and described by the U.S. Department of Energy can potentially be harvested sustainably each year, with only minor changes to current forestry and agricultural practices and without compromising edible crops.



**Figure 1.** Total U.S. oil consumption compared to potential and currently harvested nonfood biomass divided into its main uses. The area of each circle is proportional to the consumed amount.

feedstock price, are therefore unrealistic if these processes are to be carried out on a scale that is comparable to that of current petrochemical processes. Thus, for long-term planning, the mature market must be considered instead of the current market. This is of course by no means a simple task. Large-scale use of biomass as feedstock will drastically alter the market, and much of the biomass that is currently considered a waste product will eventually become a valuable feedstock as demand increases, since the quantities available are not sufficient to completely saturate the market. Thus, there will be no biomass waste in the future, only biomass resources.

For the reasons mentioned above it is necessary to consider the best use of biomass resources. As also shown in Figure 1, the amount of oil presently used in the chemical industry to produce fossil platform chemicals, that is, methanol, ethylene, propylene, butadiene, benzene, toluene, and the xylenes,<sup>[10]</sup> is comparable in volume to the total amount of biomass harvested for nonfood purposes. The potential biomass supply should therefore be sufficient to replace oil in this application, and a complete transition from petroleum to biomass feedstocks seems entirely feasible for the production of chemicals, although it implies significant technological

and economic challenges. Currently, however, most of the available biomass is used directly for electricity production, and only a small fraction is upgraded to higher-value products, largely covered by ethanol. In fact, only a few biomass-based processes are currently able to compete with petrochemical processes on commercial terms.

### Biomass Utilization

To further discuss how biomass is best utilized, we will use the effective H/C ratio, which is the ratio between hydrogen and carbon atoms in the molecule adjusted for heteroatoms. For a molecule containing only carbon, hydrogen, and oxygen, the ratio is calculated by the simple formula in Equation (1).

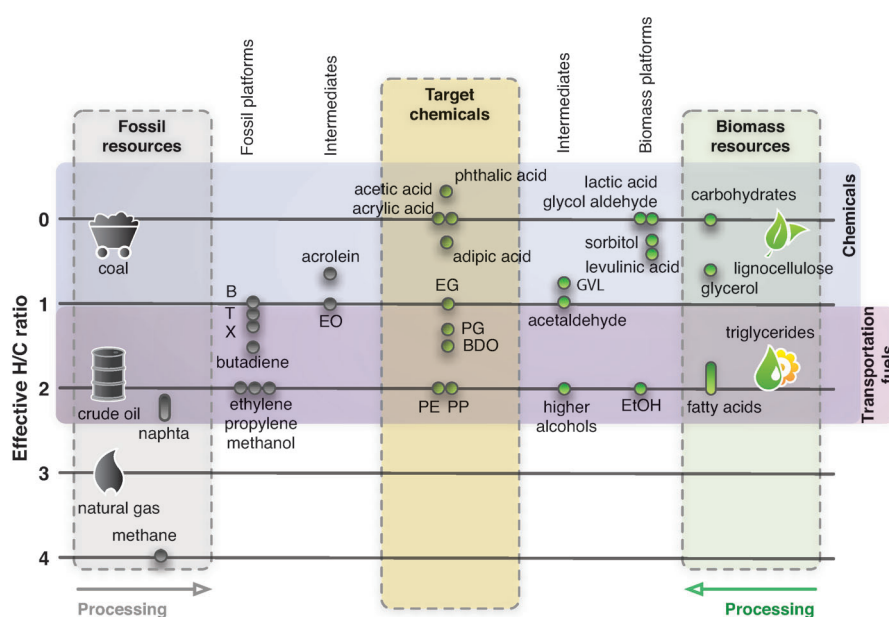
$$\text{H/C ratio} = \frac{n(\text{H}) - 2n(\text{O})}{n(\text{C})} \quad (1)$$

The formula provides a quantitative number for the overall degree of oxidation in a given molecule. In this way, carbohydrates can be regarded as “hydrated coal”. Figure 2 shows the most common fossil and biomass-based resources, as well as a number of platform, intermediate, and target chemicals. Horizontally they are arranged according to their degree of processing, with the target chemicals at the center. Vertically, the molecules are arranged according to their effective H/C ratio. Chemical reactions resulting in a horizontal shift in Figure 2 include isomerization reactions, (de)hydrations, and condensation or fragmentation reactions, while redox reactions imply a vertical shift.

Transportation fuels have an effective H/C ratio in the range of 1 to 2.3 (purple box), which is close to the ratio of crude oil. This ratio implies a high energy density, and it is thus ideal for liquid fuel purposes. Commodity chemicals, on



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**Figure 2.** Effective H/C ratio map of current and future bulk chemicals as well as feedstocks with a qualitative indication of the degree of processing. B = benzene, BDO = 1,4-butanediol, EG = ethylene glycol, EO = ethylene oxide, GVL =  $\gamma$ -valerolactone, PE = polyethylene, PG = propylene glycol, PP = polypropylene, T = toluene, X = xylenes.

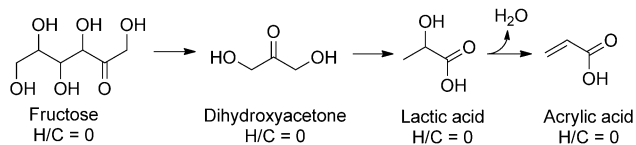
the other hand, span a much wider H/C ratio (blue box), which is more comparable to that of biomass. A wide gap in the effective H/C ratio between a resource and a target chemical implies that a lengthy process is needed for its conversion. Sugars, for example, have a similar effective H/C ratio to many functionalized high-value chemicals and should therefore be a more ideal feedstock than fossil resources in some cases. By utilizing biomass as feedstock for the production of chemicals instead of fuels, the necessity for deoxygenation, which is one of the biggest challenges when making fuels from biomass, is partially or completely avoided. Oxygen-rich chemicals such as ethylene glycol, acetic acid, and acrylic acid are examples of chemicals that could be obtained more efficiently from biomass than is possible from fossil resources. Since oxidation reactions typically involve product loss owing to overoxidation, it would be desirable if these reactions could be avoided, or at least their use minimized, when producing chemicals; an objective which seems simpler to achieve when starting from lignocellulosic biomass. Olefins, on the other hand, have an H/C ratio far from that of biomass, which implies that biomass is a poor starting point. It seems that the vast amounts of olefins produced by the chemical industry today will not be easy to directly replace by biomass-based olefins, and the ideal solution is to develop alternative materials with an effective H/C ratio in the range of 0 to 1, thereby indirectly replacing olefins.

These considerations mainly apply to the carbohydrate fraction of lignocellulosic biomass. Since lignin does not possess a well-defined structure, performing selective chemistry on this resource is particularly challenging. Currently, the best approach for converting lignin appears to involve gasification to yield synthesis gas. This approach presents a route either through methanol to olefins or hydrocarbons via

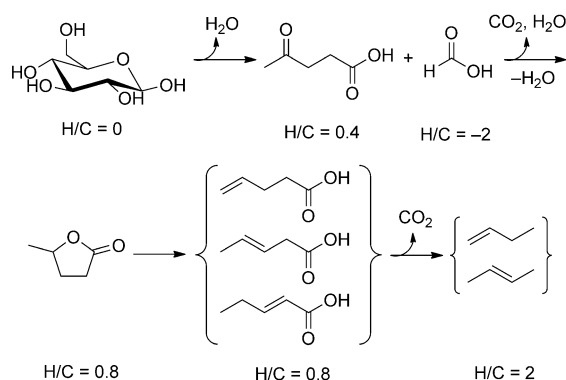
the methanol-to-hydrocarbons (MTH) process or directly to hydrocarbons in the transportation fuel regime through Fischer–Tropsch synthesis.

The considerations above assume that processes exist that can convert biomass to desired products, which is not the situation in all cases. The fossil platform chemicals are produced in chemical reactions that utilize the inherent chemistry of naphtha, that is, its ability to undergo fragmentation reactions at high temperatures leading to olefins and cyclodehydrogenation reactions leading to aromatics. To efficiently convert biomass to fuels or chemicals, it is similarly necessary to exploit the chemical pathways that sugars are likely to undergo and identify catalysts and conditions that promote these. In biological systems, retroaldol condensation reactions are central for the conversion of hexoses (glycolysis), and nature has optimized this pathway with a series of enzymes, leading to the efficient production of compounds such as ethanol and lactic acid from biomass. It is also possible to use inorganic catalysts to promote this type of chemistry. An example is the conversion of fructose to lactic acid using Lewis acidic zeolites.<sup>[11]</sup> Here, the hexose first fragments to form two triose sugars, which are isomerized into lactic acid (Scheme 1). The lactic acid can be used directly,<sup>[12,13]</sup> or it can be dehydrated to produce acrylic acid, which is currently produced from propylene. This situation would represent an ideal use of biomass, since the effective H/C ratio of sugar and acrylic acid are both 0, thus negating the need for redox reactions.

Another pathway that sugars are likely to undergo is cyclodehydration leading to furan-type products such as furfural and 5-hydroxymethylfurfural (5-HMF).<sup>[14]</sup> These chemicals have little use in themselves, but they can be further converted into more useful compounds such as levulinic acid and  $\gamma$ -valerolactone (GVL, Scheme 2). GVL



**Scheme 1.** Retroaldol and isomerization reactions of fructose to yield lactic acid, which can further be dehydrated into acrylic acid with no change in the H/C ratio in any of the steps.

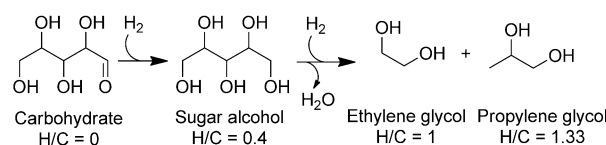


**Scheme 2.** Example of how disproportionation and release of highly oxidized species can act as a “hydrogen” donor for the remaining molecule. Presented is the conversion of glucose into levulinic and formic acid and further into GVL using formic acid as hydrogen donor and releasing  $\text{CO}_2$  in the process. The GVL is afterwards converted to butenes, again by the release of  $\text{CO}_2$ .

could be an interesting platform chemical for the production of polymers<sup>[15,16]</sup> as well as a central intermediate if the desired end products are hydrocarbons.<sup>[17]</sup> By removing oxygen in the form of fully oxidized species, such as carbon dioxide, which have no heating value, little energy is lost and the energy content of the product per carbon atom is effectively increased.<sup>[18]</sup> Further upgrade of GVL to butene can be achieved by the release of a second carbon dioxide molecule.<sup>[19–22]</sup> These combined reactions constitute a very elegant pathway from hexoses with an effective H/C ratio of 0 to hydrocarbons with a ratio of 2. The price for upgrading the biomass is paid by the co-production of carbon dioxide. This reaction pathway is well-suited for fuel production, since a significant energy densification has taken place.

In a scenario where there is a renewable electricity surplus or large fluctuations in the electricity production, yet other options may become attractive. In this case, storing the surplus energy as chemical energy in organic molecules, such as hydrocarbons, provides an ideal solution. This will require large amounts of hydrogen, which is currently produced almost exclusively by steam reforming of fossil natural gas, but which could also be supplied by electrolysis. For instance, sorbitol can be hydrodeoxygenated to yield alkanes in the  $\text{C}_1$ – $\text{C}_6$  range using a bifunctional hydrogenation/acid catalyst.<sup>[23]</sup> In addition to allowing for relatively simple storage of energy in molecules, this approach has the further advantage that the products are compatible with the existing petrochemical infrastructure. Another approach is the hydrogenolysis of biomass feedstocks to yield propylene and ethylene glycols, as

shown in Scheme 3. This conversion can be performed by combining basic and noble-metal catalysts. In this manner high-value chemicals, traditionally produced from crude oil, can be selectively prepared from carbohydrates.<sup>[24–26]</sup>



**Scheme 3.** Hydrogenolysis of biomass-derived sugars to yield diols.

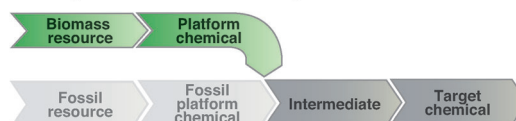
Additionally, concentrated carbon dioxide could be seen as a resource rather than a by-product, and the carbon dioxide formed in the upgrade of hexoses to hydrocarbons or during ethanol fermentation can be used to produce methanol. In this way the surplus energy can be used to increase the pool of useful carbon atoms for chemicals and fuel purposes.

### Different Value Chains in the Conversion of Biomass

It is useful to discuss value chains of chemicals to get a simple overview of the necessary conversion and purification steps in the production of target chemicals from renewable resources.<sup>[2]</sup> When addressing the issue of how biomass can be converted into useful chemical products, we propose that two overall strategies can be undertaken. Figure 3 summarizes these two strategies through renewable chemical value chains and their fossil counterparts. The strategies differ in their compatibility with the existing fossil value chain and therefore also in the extent to which existing processing technology and infrastructure can be adapted (see also box). Both value chains start with a biomass resource, which is converted to a higher-value product by means of either a conversion or a purification step.

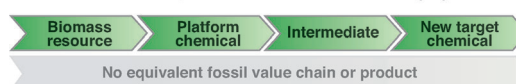
#### Drop-in strategy

• existing value chain • utilizes existing infrastructure • mature market



#### Emerging strategy

• new value chain • requires new infrastructure • emerging market



**Figure 3.** Two overall different value chains in the utilization of biomass depending on the compatibility with existing infrastructure and fossil value chain.

The “drop-in” strategy is characterized by the conversion of a biomass resource into a platform from which existing



intermediates can be obtained. Typically the challenges are to develop a competitive process targeted towards a predetermined end product and initially to compete with fossil equivalents. An example of this strategy is the conversion of sugar cane or corn (biomass resources) by fermentation into ethanol (platform chemical) and then by dehydration into ethylene, which can serve as an intermediate for polymerization, oxidation, halogenation, alkylation, or other reactions to produce target chemicals or products. In this approach the scene is already set; the product can enter a mature market, and furthermore a large part of the necessary infrastructure and technology already exists to capitalize upon the value-added chemical product. Note that the point of entry from the renewable value chain does not necessarily lie before the existing fossil intermediate. They may also converge later in the value chain. This is the case with target chemicals such as propylene glycol made from glycerol, for which the market may not yet be fully matured and which as such represent borderline cases.

The “emerging” strategy given in Figure 3 represents a completely new value chain with an emerging product in the end. This situation imposes several challenges as compared to the former, albeit also advantages. Typically the final product does not have to compete directly with existing products, and the inherent functionality present in the parent compound or biomass feedstock can be exploited to a much larger extent. The product may emerge as a consequence of utilization of the functionality of the feedstock or of the most suitable and cost-effective conversion route for the feedstock, rather than the resource needing to be converted into an already-existing product. In this case, new markets may have to be developed; the entire technology to produce the added-value chemical should be developed or, at best, extensive modification of existing technology is required. This approach therefore requires extensive initial investments and long-term commitment compared to the former “drop-in” strategy. At present, possible examples could include 2,5-furandicarboxylic acid or levulinic acid ketals, which are both products of hexose dehydration reactions. Both of these are, however, still at an early development stage.

#### Ethylene (“Drop-In” Strategy)

Ethylene is currently the organic chemical with the highest worldwide annual production (ca. 110 Mt y<sup>-1</sup>). Almost 80% is used in the production of polymers, primarily polyethylene (PE), and 12% is used for ethylene oxide and glycol.<sup>[32]</sup> The production is primarily based on cracking of naphtha,<sup>[32]</sup> which induces only a small change in H/C ratio (< 0.33), however, it can also be produced from fermentation of carbohydrates into ethanol and subsequent dehydration, a process with large changes in H/C ratios from the starting material to the ethylene platform ( $\Delta(\text{H/C}) = 2.0$ ) and with further fluctuations if the ethylene is converted to ethylene glycol or oxide, for example ( $\Sigma(\Delta(\text{H/C})) \geq 3.0$ ). The first move in this field came from the Brazilian company Braskem, who in 2010 launched a 200 000 t y<sup>-1</sup> production of ethylene (0.17% of total world demand), with further processing into PE.<sup>[33]</sup> No modifications to downstream processing of ethyl-

ene are necessary, as existing infrastructure already exists, which is also what makes it a drop-in approach. Furthermore, the technology for fermentation of sugars into ethanol is well-known. These factors represent large advantages, as relatively small capital investments are required and all steps are well known, including the dehydration step from ethanol into ethylene. However, it is also apparent that only a small fraction of the ethylene produced from petroleum can be replaced in this way owing to the sheer amount of ethylene produced.

#### Hexose Dehydration Products (“Emerging” Strategy)

The dehydration product of hexose sugars, 5-HMF, can be oxidized to furan-2,5-dicarboxylic acid, a possible alternative to terephthalic acid for polymer production,<sup>[13,34]</sup> or hydrogenated to 2,5-dimethylfuran, an octane booster with excellent blending properties.<sup>[33]</sup> Although a significant amount of research has gone into optimizing the process, no industrial or pilot-scale process has yet been demonstrated. A significant problem in the process is the rehydration of HMF to levulinic acid and formic acid, a reaction which is also catalyzed by acids. An alternative approach is to instead use levulinic acid as the platform chemical, thus avoiding the problem of stabilizing the intermediate. Recently, a large amount of research has gone into this approach.<sup>[15,16,35,36]</sup> Currently, the U.S. company Segetis has started up a process in which ketals are produced from the levulinic acid platform with a production of 136 t y<sup>-1</sup> of levulinic acid ketals, with plans for a second plant.<sup>[37,38]</sup> Although no large-scale market currently exists for these ketals, they can possibly find use as non-petroleum-based plasticizers and solvents and as polyols for polymer production. Specifically, Segetis is working together with PolyOne to develop the use of these ketals as plasticizers. The need for extensive process development and construction of infrastructure defines this as an emerging strategy. As such, significant investments are necessary; however, the facile nature of the hexose dehydration reaction makes this an interesting route.

#### Propylene Glycol (A Strategy In Between)

Propylene glycol (PG) has a medium-size existing market (currently ca. 1.4 Mt y<sup>-1</sup>),<sup>[39]</sup> but an even larger potential market can be envisioned (> 2 Mt y<sup>-1</sup>) because it, among other uses, is suitable for deicing purposes. Compared to a currently produced deicer, ethylene glycol (EG), which is produced by conventional petrochemical methods and with a large existing production (> 6 Mt y<sup>-1</sup>),<sup>[40]</sup> PG is nontoxic and thus has a large advantage over its petrochemical analogue. PG can be produced from glycerol that today should be regarded as a renewable resource or perhaps even a renewable platform.<sup>[41]</sup> When the changes in H/C ratio are considered in the production of the two glycols, they are somewhat similar. For EG production, crude oil or naphtha is converted into ethylene and further into EG by oxyfunctionalization, with an overall  $\Delta(\text{H/C})$  of about 1.0. Starting from glycerol, the oxyfunctionality is, to a small extent, removed when it is converted into PG, leading to  $\Delta(\text{H/C}) = 0.67$ . Several companies have announced their production of PG from glycerol, including Archer Daniels Midland (ADM),

Cargill/Ashland, and Senegy. ADM has furthermore developed a process where sorbitol, derived from corn, can also be used as a feedstock and thus introduced several renewable value chains ending with PG, allowing for a large flexibility in the feedstock. As the renewable value chain enters an existing value chain at a late stage, this way to PG can be placed in the borderline between the drop-in and emerging strategies and is a good example of how things are not always clear-cut.

### Current Trends in Industry

Currently we observe the production and development of chemicals from biomass in industry to be motivated by at least three overall factors. In some cases, the knowledge and technology is already present to process one type of biomass resource, demanding only small capital investments, whereby the low-value nature of certain biomass feedstocks may be exploited. The results may also be products with no petrochemical equivalents, such as lactic acid or furfural, that can already compete on completely commercial terms. Especially microbial production of  $C_2$ – $C_6$  acids is a fast-evolving approach mainly driven by large developments in biotechnology and metabolic engineering.<sup>[27]</sup> A second factor is the answer to a general demand for renewable or “green” products from the consumer, exemplified by the PlantBottle from the Coca-Cola company. Such initiatives furthermore give a sustainable image to all agents involved in the value chain—something everybody can benefit from. Thirdly, on the political side, subsidies and funding is provided to reduce the dependence on fossil resources and to decrease the environmental impact. This is most visible for the conversion of biomass to transportation fuels, owing to their large consumption, as exemplified by the U.S. ethanol industry.

As an analogue to the petrochemical refinery, the concept of a biorefinery has emerged to integrate production of fuels, power, and chemicals for maximum efficiency; a subject that has attracted much scientific interest during the last ten years. Although only about 5–10 % of the crude oil is converted into chemicals, these generate roughly 50 % of the profit in current petrochemical refineries.<sup>[28]</sup> Since this ratio will most likely not change drastically in future biorefineries, it indicates the large economic potential in producing chemicals from biomass. In general, the price of transportation fuels is determined by the feedstock price as an effect of more than 100 years of optimization in oil refineries, making them extremely efficient. The conversion of biomass has yet to undergo any significant optimization, and the price of fuels from biomass is still governed by the cost of processing, making it difficult to become competitive with fossil counterparts. On the other hand, the processing costs when chemicals are produced from oil account for a much larger portion of the total costs, which should make it easier for the renewable value chain to become competitive and thus be implemented in large scale.

The annual production of oleochemicals (chemicals produced from fats and vegetable oils) is in the range of 10–15 Mt  $y^{-1}$ .<sup>[29,30]</sup> Although this volume is by no means as large as the petrochemical industry, it illustrates that large-scale production of chemicals is possible when biomass is used as a

feedstock. It is interesting to note that some of the major oleochemical producers are joint ventures between traditional chemical producers and plantation operators. This situation further illustrates that the conversion of biomass requires a number of diverse competences; from the production and extraction of feed, thus ensuring a good raw material quality, to the more conventional chemical conversion of platform chemicals into target chemicals. Few corporations currently possess all of these competencies in-house, especially where lignocellulosic feedstocks are concerned. Therefore it is common to see strategic alliances formed between companies to ensure that all steps in the value chain are covered.

Table 1 lists a number of potential and current bulk chemicals that can be produced from biomass, together with some of the major players and alliances involved in the development and production from biomass resources. For each chemical, the market type is also indicated: either an existing market (typically of the petrochemical equivalent) or an emerging market, wherefrom the overall strategy and value chain (as discussed earlier) can be deduced. Large corporations active in the field of renewable chemicals have primarily chosen to focus on existing and large markets, such as ethylene, propylene, acrylic acid, and epichlorohydrin with little uncertainty of demand. As described earlier, these chemicals have to compete with the existing petrochemical products, which will require a high degree of optimization of the processing steps. Conversely, the development of products for emerging markets for example,  $C_4$  diacids, 5-HMF, and levulinic acid derivatives are governed by smaller budgets, and typically academia spin-offs are involved owing to the higher risks attributed to uncertainty and long-term commitment.

### A Renewable Chemical Industry

As mentioned above, the vast majority of biomass used in industry today is burned to generate electricity. This use seems injudicious, as on-grid energy production is the sector where fossil resources can most easily be replaced by alternative sources such as wind, geothermal, or nuclear. Thus, upgrading of the biomass to higher-value products to replace crude oil seems a more sensible approach. As seen in Figure 1, the majority of crude oil is converted into transportation fuels, and it would therefore initially seem as though the replacement of this fraction would be the most crucial. There are, however, a number of problems with this approach, as outlined above: the amount of available biomass, the significantly different characteristics of transportation fuels and biomass, and lastly, the fact that transportation fuels are relatively low-value products. Instead, energy for transportation needs could be mediated through batteries or fuel cells, with the energy for these being produced by the above-mentioned on-grid energy sources. Fuel production from biomass should be limited to applications where electrical power is not a feasible alternative, for example, for aviation and marine applications. This approach will, however, require an extensive modification of the current transportation

**Table 1:** Overview of chemicals that are currently produced, or could be produced, from biomass together with their respective market type, size of the market, and potential biomass feedstock. Major players involved are also given.

Chemical	Market type	Market size (Mty <sup>-1</sup> ) <sup>[a]</sup>	Major player(s)	Feedstock
acetic acid	existing	9.0	–	ethanol
acrylic acid	existing	4.2	Arkema, Cargill/Novozymes	glycerol or glucose
C <sub>4</sub> diacids	emerging	(0.1–0.5)	BASF/Purac/CSM, Myriant	glucose
epichlorohydrin	existing	1.0	Solvay, DOW	glycerol
ethanol	existing	60	Cosan, Abengoa Bioenergy, ADM	glucose
ethylene	existing	110	Braskem, DOW/Crystalsev, Borealis	ethanol
ethylene glycol	existing	20	India Glycols, Dacheng Industrial	glucose or xylitol
glycerol	existing	1.5	ADM, P&G, Cargill	vegetable oil
5-hydroxymethylfurfural	emerging	–	–	glucose/fructose
3-hydroxypropionic acid	emerging	(≥0.5)	Novozymes/Cargill	glucose
isoprene	existing/emerging	0.1 (0.1–0.5)	Danisco/Goodyear	glucose
lactic acid	existing/emerging	0.3 (0.3–0.5)	Cargill, Purac/Arkema, ADM, Galactia	glucose
levulinic acid	emerging	(≥0.5)	Segetis, Maine Bioproducts, Le Calorie	glucose
oleochemicals	existing	10–15	Emery, Croda, BASF, Vantage Oleochemicals	vegetable oil/fat
1,3-propanediol	emerging	(0.1–0.5)	Dupont/Tate & Lyle	glucose
propylene	existing	80	Braskem/Novozymes	glucose
propylene glycol	existing/emerging	1.4 (≥2.0)	ADM, Cargill/Ashland, Senenergy, Dacheng Industrial	glycerol or sorbitol
polyhydroxyalkanoate	emerging	(0.1–0.5)	Metabolix/ADM	glucose

[a] Market size of an existing market is given as its current size including production from fossil resources; for emerging markets the expected market size is reported in parenthesis.

infrastructure, a transition which will require decades to accomplish.

If biomass is instead used as a feedstock for the chemical industry, many of the problems associated with fuel production are avoided. The currently available biomass should be sufficient to replace fossil resources for the production of chemicals, and the characteristics of biomass and many bulk chemicals are similar. Furthermore, by sensible choice of target chemicals, the value addition could be significantly higher. Since the cost of developing the necessary processes can be significant, and because the initial process will inevitably be relatively inefficient, it makes sense to focus on high-value products, allowing for faster widespread adoption. The challenges in this case will be the development of efficient processes for the collection, handling, and pretreatment of biomass and for the selective conversion of biomass feedstocks; these are processes that in general only exist for the edible parts of biomass today. Since these challenges are present irrespective of the final use of the biomass resources as chemicals or fuels, the current research into second-generation biofuels will also benefit the future renewable chemical industry. This relationship is further emphasized by the fact that many of the compounds currently

produced by the biofuels industry, either as the main product or as byproducts, could be interesting platform chemicals for the chemical industry: Ethanol could be used as a starting point for producing acetic acid, ethylene, or ethylene glycol, while glycerol can be dehydrated to acrolein, which can be further converted into acrylic acid.<sup>[2,31]</sup> Thus in the short term, the production of transportation fuels is a good way of establishing the infrastructure needed for large-scale industrial utilization of biomass while alternative uses of biomass are being developed and at the same time the consumption of fossil resources in the transportation sector is reduced.

The production of transportation fuels from biomass, however, relies on the premise that biomass is a resource available in excess amounts, a premise which will likely not hold in the future. Thus careful consideration is needed when determining how to utilize the available resources to the fullest, both in terms of maximizing profits and in terms of minimizing the consumption of fossil resources. For this decision the cumulative change in the effective H/C ratio of the overall process, from feedstock to target chemical, is a

simple measure of the efficiency of a given reaction path; excessive fluctuations should be avoided to minimize energy and mass losses. Instead of attempting to forcefully convert the feedstock into platforms that were chosen because they were convenient to produce from fossil resources, the inherent functionality of the new feedstock should be utilized to the fullest extent possible by clever design of the reaction pathway and through catalytic control. When new value chains starting from biomass are developed, high-value chemicals should be targeted initially to ensure that the process is economically feasible despite the relatively high processing costs, which must be expected. As these value chains mature, they can be branched out to encompass an increasingly larger fraction of the chemical industry. The shift from a fossil-based chemical industry to one based on biomass still poses many challenges, but the possibilities are also great: to develop a more sustainable chemical industry utilizing a more versatile feedstock supply and producing products with superior properties.

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