Perspective

The Biorenewables Opportunity - Toward Next Generation Process and Product Systems

Wolfgang Marquardt, Andreas Harwardt, Manuel Hechinger, Korbinian Kraemer, Joern Viell, and Anna Voll
AVT - Process Systems Engineering, RWTH Aachen University, 52056 Aachen, Germany

DOI 10.1002/aic.12380

Keywords: bioeconomy science, biomass, bio-based chemicals, biofuels, product design, process synthesis, process systems engineering

Introduction

Technological and scientific progress has undoubtedly been pushed by the exploitation of fossil carbon. These natural resources have been generated over millions of years. Biomass has been produced by photosynthesis capturing carbon dioxide (CO_2) from the atmosphere. The stalling plants and organisms have been converted in subsequent geochemical processes into coal, petroleum and natural gas stored in geological formations. Today, this pocket of sunlight feeds our society in terms of fuels, chemicals and materials, so far only constrained by available technologies to extract carbon from its reservoir. Given the seemingly unlimited availability of fossil carbon, the industrial value chains have been geared toward petroleum and natural gas as raw materials for the production of carbon-based products in the past.

The exploitation of fossil carbon proceeds faster than its regeneration in the natural carbon cycle. The accelerating carbon depletion not only reflects the growing world population, but also the globally improving living standard. Some studies predict the complete depletion of accessible fossil carbon well before the end of this century.[1] Others are more optimistic and do not believe that "peak oil" will be reached anytime soon.[2] While any such prediction is highly uncertain and therefore debatable, climate experts widely agree that anthropogenic carbon conversion contributes significantly to the increase of the CO_2 concentration in the atmosphere and, as a consequence, of the average surface temperature on our planet.[3] These trends can only be stopped if the cumulative anthropogenic emissions of CO_2 can be bounded to a trillion tons of carbon[4]— ultimately requiring equilibrating CO_2 fixation and release, which does not seem to be possible without a switch from fossil to biorenewable carbon resources.

Although biomass has always been used as a source of energy and as a raw material, it constitutes only a small fraction of the current total carbon use. Current biomass use is restricted to low-volume products and to the large-scale production of bioethanol. The transition from the current fossil-based to a future bio-based carbon economy is expected to evolve continuously in the coming decades, gradually impacting all process industries. Easily accessible regenerative feedstock like plant oils, sugar or starch will be transformed first into common molecular products. A continuous changeover to more complex biorenewable feedstock's like agricultural residues, industrial wastes, green plants, wood, or algae will occur. Ultimately, the petrochemical product tree will be replaced by a bio-based alternative.

This raw materials shift should not be considered a threat, but rather a unique opportunity to redesign the industrial value chain from biorenewable raw materials to new products. A full exploitation of biorenewables requires the direct use of their rich molecular structure to the extent possible. The complete degradation of biomass into C_1 building blocks by gasification or methanation would clearly miss a unique opportunity. Rather than reusing existing value chains — the most economical scenario at first glance — the raw materials shift should not only address new technologies for molecular transformation and up- and downstream processing, but also aim at a new range of molecular products to consequently exploit the nature of the feedstock.

This Perspective aims at elucidating the opportunities and challenges resulting from the inevitable raw materials switch from a process systems perspective. We first dwell into the nature of biorenewables to set the stage for a new chemical engineering paradigm. The remainder of the article will focus on interacting systems problems in biorenewables processing, including plant production, biomass pretreatment, novel reaction pathways, sustainable processes and novel product systems.

Nature of Biorenewables

Biorenewables can obviously only replace fossil carbon feedstock, if the annual production of biomass can satisfy the future global carbon demand — an issue which has been a

---

Correspondence concerning this article should be addressed to W. Marquardt at wolfgang.marquardt@avt.rwth-aachen.de.

subject of controversy. In the so-called “billion ton study” Perlack et al.[5] report that 1.3 billion dry tons of lignocellulosic biomass is expected to be producible in the US alone without a severe change of land-use. This amount could replace about 50% of the US annual petroleum demand. A more recent study[6] has put more emphasis on sustainability and came up with a more modest estimate of 550 million dry tons per year. The capacity could be increased, if existing crop land were used more efficiently, and if plants with higher specific yield became available. Langeveld et al.[7] argue that biorenewables can be produced sustainably in sufficient quantity without competing with food production, if the biomass were used completely in integrated industrial value chains linking the production of food, cattle feed, transportation fuels and other bio-based products. None of these studies accounts for a likely reduction of the transportation fuel demand due to a gradual shift toward solar-powered electro-mobility. Thus, there are good reasons to expect that the global agricultural production capacity will be sufficient to sustainably satisfy the future carbon demand for the production of bio-based materials including liquid transportation fuels.

Biomass constitutes of an enormous variety of plant species with varying morphology and chemical composition. Regardless of the phenotype, any plant comprises *lipids, starch, cellulose, hemicelluloses, lignin, proteins* and *minerals* in varying amounts (see Figure 1). *Lipids* are hydrophilic molecules with a relatively simple structure. They occur in plant seeds and in some kinds of algae in large amounts. Fatty acids, for example, are unbranched, saturated or unsaturated carboxylic acids with up to 24 carbon atoms; they have been used as industrial feedstock for a long time. *Starch* is a polymer built from glucose monomers. In the case of amylose, linear chains are arranged in a dense helical structure, while amylopectin consists of branched chains. Starch accumulates in particular in fruits, seeds, rhizomes and tubers. Like amylose, *cellulose* is a linear glucose polymer mainly found in plant cell walls. The alternating direction of the ether bonds results in chains which can be linked by hydrogen bonds to form crystalline fibrils. *Hemicelluloses* consist of macromolecules similar to cellulose. The shorter chains consist of pentoses and hexoses; they form the glue between cellulose and lignin by means of covalent and hydrogen bonds. *Lignin* is an aromatic polymer most commonly occurring in wood. It does not show a well-defined chemical structure, but is rather a random polymer formed from three prevailing aromatic monomers, namely p-hydroxyphenyl, guaiacyl, and syringyl phenylpropanoid, largely linked by ether bonds. *Proteins* and *minerals* occur in small and varying amounts in any plant species.

In contrast to fossil carbon, biomass is not just a mixture of chemical components. Wood, for example, shows a complex ultrastructure (Figure 1) evolved by nature to conduct water, to store biochemical energy and to provide mechanical stability.[8] The wood stem consists mainly of longitudinal dead cells with different structural features. The seasonal growth rate and the circumferential formation result in cells differing in diameter and wall thickness. The cell wall consists of several layers with specific chemical composition and morphology. While the primary wall consists of lignin and small amounts of cellulose, the secondary wall is formed by cellulose fibrils differently oriented in the sublayers. The paracrystalline microfibrils are bundled into fibrils which are embedded in a stabilizing amorphous matrix of lipids, proteins, hemicelluloses and lignin. The resulting rigid assembly forms a natural anisotropic composite material, which is designed to withstand mechanical, biological and chemical stress.

The constitution of plant biomass comprises an enormous variety of polymeric substances with multifunctional molecular structures forming morphologies of rich diversity. While the hydrogen to carbon ratio is lower in biomass compared to oil, the oxygen to carbon ratio is higher in biomass than in fossil carbon due to plentiful hydroxyl groups. The pronounced difference in elemental composition, molecular structure and morphology and the variety of plant phenotypes present in biorenewable feedstock has to be accounted for in tailored future industrial value chains.

Toward Biorenewables-based Chemical Engineering

Today, more than 90% of the fossil carbon is used only for its energy content. This pattern should not be followed in the future, because of the low efficiency of converting solar energy into biomass. Agrawal and Singh[9] convincingly argue the case for converting solar radiation directly into electrical energy by photovoltaics, and for restricting the use of biomass to the production of carbon-based molecular products. The sustainable use of bio-based carbon suggests integrated manufacturing in biorefineries[10] to selectively transform the variety of molecular structures into a range of products including liquid transportation fuels, chemicals, polymers, pharmaceuticals, pulp and paper, food or cattle feed.[11] Polygeneration of such material products together with steam and electricity is yet another important objective,[12] but the increasing availability of solar, wind or geothermal power in industrial processing might render such partial conversion of biomass to energy even less attractive.

The development of integrated biorefineries requires a true quantum leap in chemical engineering.[11] Rather than following current industrial practice,[13] where macromolecules present in the biomass are broken into C_1 building blocks first, which are next reassembled into the desired functional molecules, the synthesis power of nature should be used to the maximum possible extent. For this purpose, the rich molecular structure in the biomass has to be accessed without significant degradation. The highly functionalized polymers have to be selectively depolymerized first. Next, the resulting molecular structures need to be isolated and catalytically refunctionalized into target molecules. Such an advanced strategy offers the chance to establish conversion processes with higher carbon efficiency and lower entropic losses compared to conventional thermochemical processes. Although conceptually attractive, its implementation requires the tailoring of the industrial value chains to the nature of the bio-based raw materials.

Preserving the natural molecular structures in the raw materials requires a shift from gas-phase reactions at high temperatures, prevalent in petroleum-based chemical engineering, to liquid-phase reactions at lower temperatures. Likewise, low-temperature separation technologies should be favored over classical distillation if possible. Higher viscosities of the process media and the management of large amounts of water are inevitable side-effects offering their own challenges.

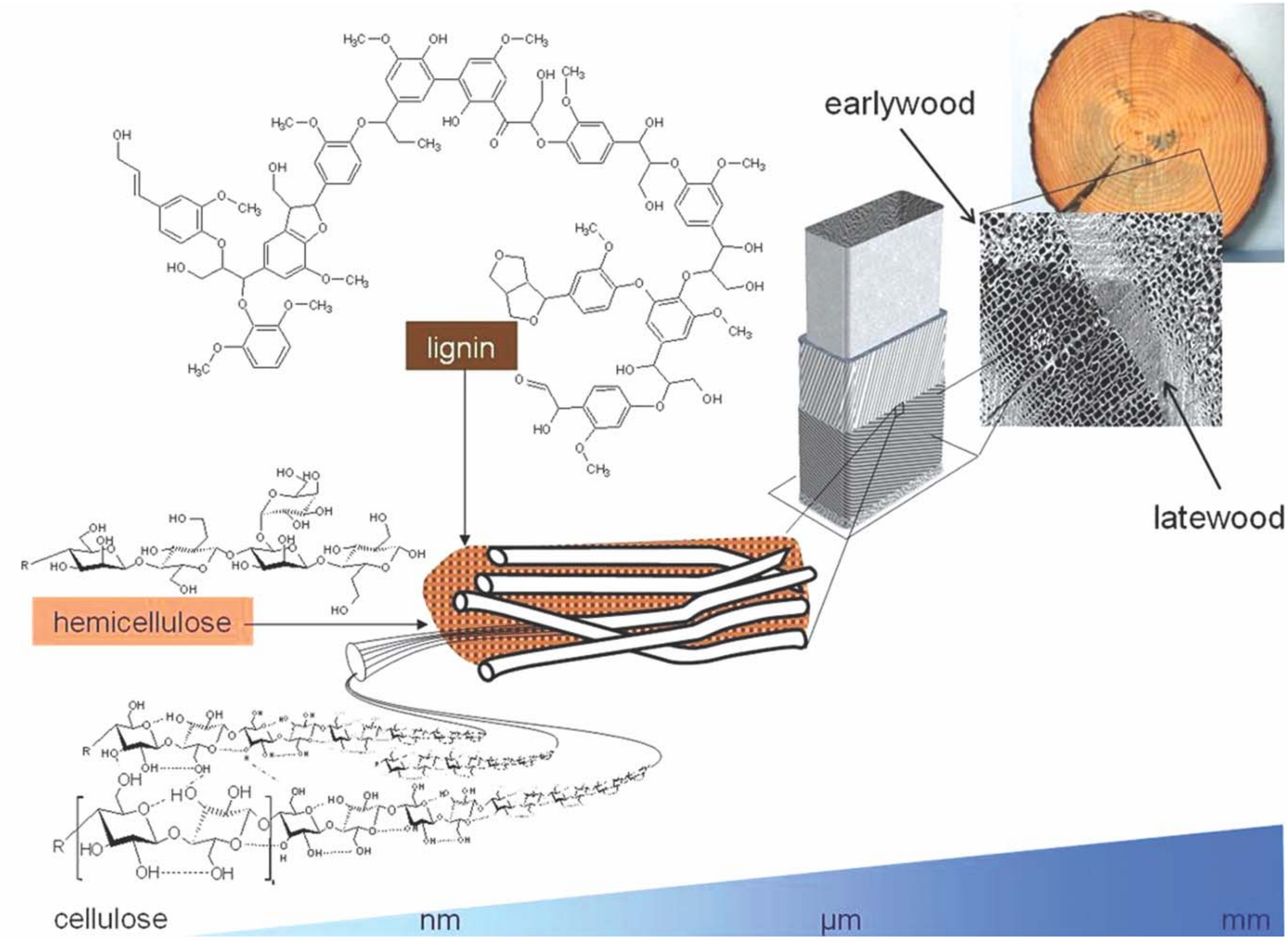

Figure 1. Chemical composition of wood and its structural features on different length scales.

The elemental composition of biorenewables suggests the transition from established to new molecular products which still provide the same functional properties expected by the consumer. If the current product tree was preserved, the surplus oxygen in the raw material would have to be removed either as CO_2 or H_2O. While the former reduces carbon efficiency and contributes to the climate problem directly, the latter requires large amounts of hydrogen which have to be produced sustainably, for example, by costly solar-powered water splitting. Obviously, future product trees should accommodate the native oxygen content of biomass to the extent possible to reduce the need for deoxygenation.

These considerations imply the need for a radical shift from petroleum-based to biorenewables-based chemical engineering aiming at new value chains with a new range of oxygenated products, novel production routes and integrated biorefineries built from intensified unit operations which operate at moderate conditions. Obviously, this transition offers the chance to reinvent the process industries with global and long-term impact.

The intricate dependencies between the supply of biomass by agricultural cultivation, the pretreatment of the biomass, its molecular transformation and processing into target molecules and the structure-property relations of the end product ask for a holistic approach. The methods and tools of process systems engineering offer the right means to achieve integrated solutions close to the global optimum rather than falling into the trap of studying irrelevant problems or presenting solutions with negative side effects. Figure 2 shows a rough sketch of the major interacting systems problems along the value chain from plant production to bio-based products. The nature of these problems will be briefly sketched in the remainder of this article.

Sustainable Production of Tailored Feedstock

While the chemical composition of fossil carbon feedstock has been determined by natural geochemical processes and thus has to be taken as a given, the situation is completely different for bio-based feedstock, which itself is an outlet of agricultural production. Therefore, there is an opportunity to control the feedstock quality — the molecular composition and morphological structure of the biomass — within ecological constraints to properly match the subsequent valorization process. Clearly, biomass production has to efficiently use the limited cultivable land area, preserve the natural CO_2 sequestration potential of soil, and avoid irreversible soil exhaustion.[14] Hence, it comprises a first important systems problem

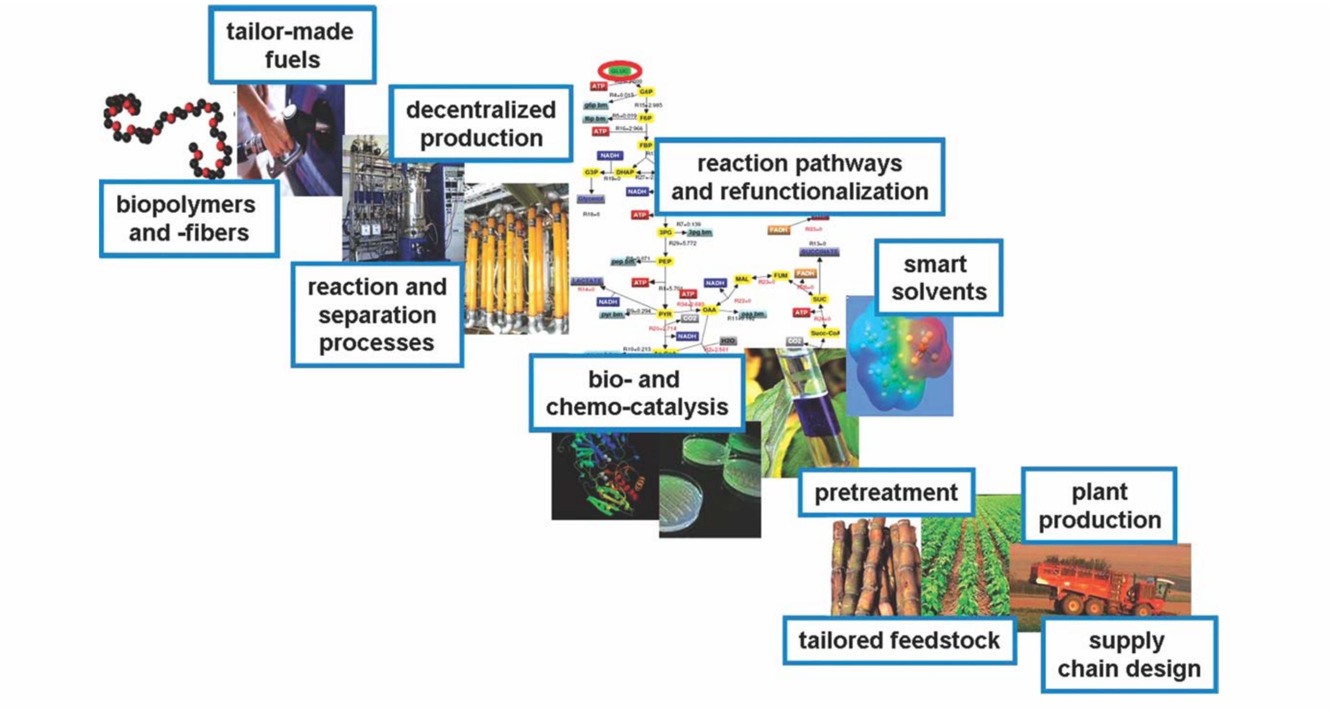

Figure 2. Set of interacting systems problems: from biorenewables production to novel oxygenated molecular products.

linking chemical engineering with the earth, plant and agricultural sciences.

An intensification of biomass production can proceed in different directions. The selection and breeding of plant species offer a first opportunity. Natural ecosystems consist of a variety of species, each with a specific productivity occupying an individual niche.[15] This variety together with the competition and differentiation between the species of a plant community results in a robust flora. In contrast, current agricultural cultivation relies on monocultures with well-known problems like a high sensitivity to pest and the risk of soil exhaustion. Recent studies show that diversity contributes to higher yield and improves sustainability. For example, Hille et al.[16] report higher yield if C4-plants are cultivated together with nitrogen fixing legumes, while Tilman et al.[17] show more than double bioenergy yield with low-input and high-diversity grass cultures with better CO_2 sequestration and less agrochemicals use. The feedstock from such mixed cultures is clearly more complex than from monocultures and requires more sophisticated processing technologies.

The yield per unit of used land can also be improved by a reduction of the regeneration time of plant growth. For example, expression of pine glutamine synthetase in poplar[18] results in an increase of 141% in tree height in 3 years[19] without altering the chemical composition and ultra-structure of the wood, thus, suggesting negligible ecological impact. Breeding can also target at tailoring the chemical composition or morphology of a plant species. For example, low minerals content may favor plant comminution during mechanical pretreatment, while a tailored biopolymer composition of cell walls could simplify biochemical pretreatment and impact the ratio of the platform chemicals produced.

Another opportunity refers to the production process itself which can be optimized by an adjustment of the production conditions using established process control techniques. For example, fertilizer and other agrochemicals consumption, irrigation and ambient CO_2 concentration can be used as manipulated variables to drive the productivity to an optimum. The immense variation in chemical composition during the plant lifetime suggests optimal harvesting conditions. The periodic character of plant production can be exploited using ideas from run-to-run control.[20] Given the huge amounts of water used in agricultural processes, particular emphasis has to be put on the water management, which is a systems problem on its own.

Biomass Pretreatment

While a unifying pretreatment of fossil carbon feedstock is accomplished by simple separation and cracking, the heterogeneity of largely solid biorenewables and the objective of gaining access to the natural molecular structures asks for sophisticated pretreatment processes. Accordingly, pretreatment has to match both the raw material and the subsequent molecular transformations. Efficient pretreatment significantly impacts the economics of biomass valorization, because it can contribute 20–40% of the overall production costs.[21] Established thermochemical pretreatment can process different kinds of biomass simultaneously. However, it not only requires capital-intensive large-scale plants, but also annihilates nature's synthesis power. Alternatively, the pretreatment process should target well-defined substrates with a set of desired pretreatment products similar to current practice in pulp and paper or corn mills. Future pretreatment processes need to address the selective production of multiple products from possibly even different kinds of biomass.

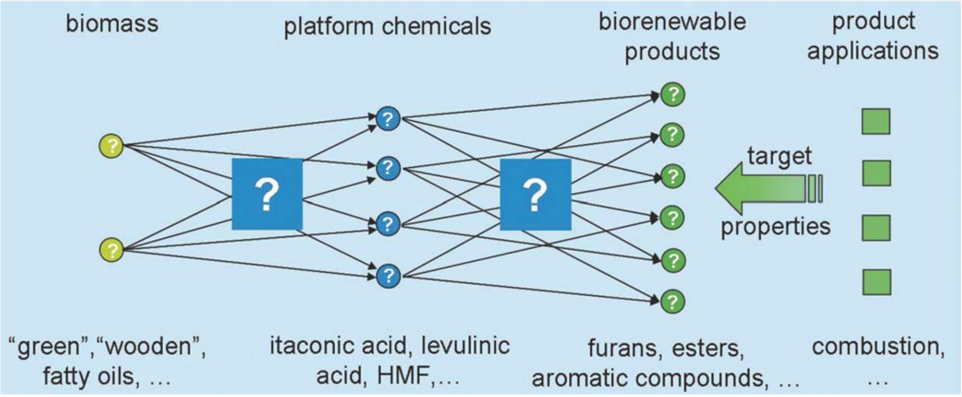

Figure 3. The integrated synthesis problem: raw material selection and design, reaction pathway synthesis, process and product design.

Considering the predominant carbohydrate fraction of cellulose and hemicelluloses in biomass, hydrolysis is a first logical step to functionalize the resulting sugar monomers. Direct enzymatic hydrolysis of lignocelluloses results in low time-space yield, because of the restricted accessibility of the paracrystalline regions and the lignin-carbohydrate complex.[22] Of course, strong acids are able to hydrolyze also crystalline cellulose, but come with a lot of waste and a broad range of degradation products.[10] To exploit the favorable economics of the enzymatic hydrolysis of carbohydrates,[23] the lignin-carbohydrate complex should be broken first, ideally combined with removing crystalline cellulose, to accelerate selective hydrolysis.[24]

At present no efficient biocatalytic approaches are known to break the chemical structure of lignin. Different kinds of chemical treatment are currently used to relieve the lignocellulosic structure such as Kraft pulping. However, these treatments often suffer from sulfonation of lignin, difficulties in recycling the active chemical agents, and the focus on maximizing fiber yield instead of isolating the major biomass constituents. A promising alternative is the Organosolv process.[25] The ether bonds of lignin are cleaved by nucleophilic attack in water/alcohol mixtures at moderate conditions. Hemicelluloses are depolymerized to sugars in aqueous solution. The delignified cellulose is insoluble and can be easily isolated. Removal of the organic solvent induces precipitation of lignin. Hence, Organosolv pulping leads to cellulose, lignin and hemicelluloses fractions and largely preserves the native molecular structure. A novel promising concept, still in the exploratory phase, relies on pretreatment of lignocelluloses in ionic liquids (IL).[26] The striking feature is the capability of certain IL to dissolve crystalline cellulose at moderate temperatures. The dissolved cellulose can be selectively depolymerized to oligomers largely avoiding further degradation by an acid heterogeneous catalyst.[27] Since the properties of IL can be tuned over a wide range, they may be tailored either toward selective cleaving of lignin or effective depolymerization of carbohydrates.

So far, even established pretreatment processes are not well-understood and systematic process design is lacking.[23] The characterization of the feedstock and an investigation of the physicochemical fundamentals on the molecular and morphological levels are expected to lay the foundation for a model-based tailoring of pretreatment to the specific type of raw material, and to integrate it with controlled depolymerization and subsequent conversion to intermediate platform chemicals.

Novel Routes from Intermediates to Products

The raw materials shift will also require a quantum leap in catalysis. Since the native molecular structure is supposed to be preserved, the focus of catalysis research will have to shift from building functional structures out of simple building blocks to the re-functionalization of complex molecular structures. Highly selective chemocatalysts for dehydration, cyclization, ring opening, hydrogen transfer and C-O bond manipulation must be explored. Enzymatic or whole-cell biocatalysts are often high-performance alternatives resulting in high selectivity and yield.[24] Hybrid catalysts, combining enzymes with chemocatalysts in a complex molecular or nanoparticulate structure, constitute even more sophisticated options. Finally, the combination of bio- and chemocatalytic conversions along the reaction pathways offers new and largely unexplored opportunities.[28]

Consequently, novel production pathways linking different kinds of bio-based feedstock to intermediate platform chemicals and novel innovative products with specified properties must be explored as sketched in Figure 3. The variety of plant species and the flexibility in tailoring the feedstock to the desired valorization, the alternative intermediates, the opportunities in bio- and chemocatalysis, and finally the novel products with higher oxygen content result in a large superstructure of production routes. These alternatives must be systematically evaluated and screened for promising candidates to identify those with favorable overall properties including carbon efficiency, hydrogen demand, energy consumption, or production cost. Ideally, such an evaluation should precede research in catalysis and production processes to identify promising options.

While lifecycle analysis is well-established for evaluating existing production routes, methods for an assessment of the potential of reaction pathways in an early research phase are largely lacking. Rather than just using elemental balances,[29] ideas from metabolic flux analysis[30] can be transferred to the analysis of reaction networks in the context of biorenewables processing. This reaction network flux analysis (RNFA) first compiles all known and possible reaction steps toward desired products in a reaction network based on the open literature, on experts' knowledge or on prediction algorithms ultimately based on quantum chemical computations. An optimization problem is formulated to maximize yield, and to possibly account for additional objectives which satisfies the underdetermined linear mole balances of the network nodes. All possible reaction pathways connecting the starting and the target chemicals can be detected by mixed-integer programming.[31] The identified alternatives can then be classified according to different criteria. This stoichiometry-centric approach can be extended to consider other aspects including yield, separation factors, or even a rough estimate of production cost to link RNFA to process synthesis. Promising reaction pathways can be detected, bottlenecks can be identified and tasks for catalysis research can be formulated. RFNA offers a promising screening methodology for a better integration of bio- and chemocatalysis on the one hand, and of catalysis and process design on the other. A proof of concept has been reported recently.[32] Two pathways in a reaction network linking furfural and itaconic acid to the fuel candidates 2- and 3-methyltetrahydrofuran (MTHF) via 49 intermediates by 66 reactions have been shown to equally maximize yield, but strongly differ in the number of reactions and in hydrogen usage. Even such simple classification criteria can foster the subsequent research process regarding suitable substrates, hydrogen supply or separation process requirements and can help to benchmark new against existing processing routes.

Sustainable Manufacturing by Systematic Process Synthesis

The transition from petroleum-based to biorenewables-based chemical engineering will pose novel process and supply chain synthesis problems to accommodate the nature of the raw materials and novel pathways to new molecular products.

The volumetric energy density of biomass is a factor of roughly 20 lower than that of oil, thus rendering biomass transportation over long distances economically unattractive. The feedstock may be restricted to high energy density materials like wood, biomass may be densified as pellets,[33] or it may be upgraded to slurries or platform chemicals before transportation.[34] Not only the low-energy density of biomass, but also the seasonal supply and its diversity suggest a radical change in production technology. Rather than relying on world-scale plants requiring immense capital investment, the valorization chains will shift to a decentralized production of platform chemicals in small-scale low-cost plants, which can even be built by small and medium sized enterprises in developing countries. These plants are operated close to the biomass production sites not only to reduce transportation cost, but also to offer the possibilities to recycle water, minerals and biological waste back into the agricultural production.[7] Flexible multisubstrate, multiproduct plants are envisioned, which are tailored to the plant species on site and allow for agile operation to handle seasonal dynamics. Modularization and miniaturization of plant equipment are as important as the simplification and automation of plant operation to satisfy the needs of decentralized operation in an agricultural environment.

Systematic process and supply chain synthesis will see a renaissance to meet the objective of high efficiency despite the significantly more complex production pathways. While process and supply chain synthesis are still considered largely in isolation, many more interactions are conceivable in biorenewables processing (see Figure 2). Process synthesis has to be tightly integrated with (bio-)chemical research to assess the economic potential of some reaction pathway in an early stage. The advantages of such an interdisciplinary effort have been demonstrated recently in a case study aiming at a novel chemistry and production process for 2-MTHF from the substrate levulinic acid by a combination of hydrogenation and dehydration.[34] The homogeneously catalyzed reaction achieves a high yield of 95%. The reactor effluent is separated at low-energy demand in two heteroazeotropic distillation columns coupled by a liquid-liquid phase split to recover 2-MTHF and water at high purities. Flow sheet design has been based on rough experimental reaction kinetics, quantum chemical property estimation and an incremental process synthesis framework.[36]

Often, biorenewables process synthesis has to address the removal and the recycling of water which has to be processed in large quantities. For example, most fermentation processes suffer from low product concentrations in aqueous solution resulting in nontrivial separation tasks. As an illustration, the broth in biobutanol fermentation contains less than 10 g/L butanol accompanied by a roughly equal amount of acetone and ethanol. Only hybrid separation processes can reduce energy consumption well beyond the specific energy content of the product.[37] Systematic process synthesis linking computer-aided molecular design, thermodynamically sound short-cut methods and rigorous mixed-integer nonlinear optimization resulted in a heat-integrated hybrid extraction-distillation process with the lowest specific energy demand reported in literature.[38]

Inverting the Value Chain by Product Design

The molecular structure of novel bio-based, oxygenated products is determined by the functional requirements of an application (see Figure 3). Consequently, biorenewables not only offer a unique opportunity to select an appropriate molecular structure matching the desired functional product properties, but to tailor the complete industrial value chain to achieve the desired function at lowest lifecycle cost. Consequently, the value chain has to be inverted to (1) identify a molecular structure providing the desired function, (2) find a suitable reaction pathway linking a platform chemical to the product, (3) select an appropriate feedstock, and finally (4) design the most economic process integrated into its associated supply chain. This extended version of the process-product design problem,[39,40] has not been yet addressed in its entirety.

The concept is briefly illustrated in the context of 3rd generation biofuels. Rather than relying on known biofuel molecules, the fuel, its production process and the combustion engine are subject to joint optimization to achieve the best performance along the whole value chain from raw materials to wheel.

In a first step, a new bio-based fuel component has to be identified matching the requirements of modern low-temperature combustion engines by model-based product design. This design relies on mathematical models to predict thermodynamic and combustion kinetic properties of not yet existing fuel candidates from molecular structure. While group contribution methods have been shown to work well for a wide range of thermodynamic properties, there is a lack of experience regarding their applicability to reaction kinetics. Hechinger and Marquardt.[41] show that quantitative structure-property relations are preferable over group contribution methods for the prediction of the laminar burning velocity, a measure of flame propagation in spark ignited engines. This kind of result provides the opportunity to formulate the inverse problem, namely to identify a yet unavailable molecular structure matching not only desired thermodynamic, but also combustion kinetic properties of third generation biofuels.

Such a fuel design strategy can be combined in a second step with an algorithmic search for suitable production routes. For example, RNFA has been linked with fuel design[42] to demonstrate the advantages of integrating the selection of novel biofuel components with the performance evaluation of the production route to systematically assess the trade-off between combustion properties and production effort.

Conclusions

This article intends to raise awareness of the tremendous opportunities for process systems engineering in the context of the inevitable switch from fossil to biorenewable carbon resources. Truly sustainable solutions require a much wider perspective than presently taken. The prevailing focus on the energy content of biomass and on the replacement of petroleum-based liquid transportation fuels by biofuels should be shifted toward the exploitation of the rich molecular structure of biorenewables synthesized by nature. The polygeneration of novel oxygenated products, heat and electricity in highly integrated biorefineries could gradually replace the current infrastructure in the process industries. Multiscale modeling and the model-based synthesis of the complete value chain are viewed as core methodological paradigms. Although process systems engineers do not have the expertise to equally contribute to all relevant aspects, they are well-trained to take a leading role in addressing the multi-faceted and cross-disciplinary decision-making problems in collaboration with plant and earth scientists, chemists, biologists, (bio-)chemical engineers, as well as application experts.

Acknowledgments

This work was performed as part of the Cluster of Excellence "Tailor-Made Fuels from Biomass", funded by the Excellence Initiative of the German federal and state governments to promote science and research at German universities. The authors would like to acknowledge fruitful discussions with their cluster colleagues, in particular with J. Buechs, J. Klankermayer, W. Leitner, N. Peters, S. Pischinger, A. Pfennig, and A. Spiess.

Literature Cited

1. Fayazz S, Frenzel P, Köster M, Kollmeier B, McIntyre J, Meier K, Müller M, Schmidt J, Schmidt P, Somoza I, Weber N, Weinert T, Ayesterán J, Kopriwa N, Pfennig A. Wie können wir zukünftig ausreichend Energie nachhaltig bereitstellen? *CLB Chemie Labor Biotechnik*. 2009;60:1–2.
2. Gorelick SM. Oil Panic and the Global Crisis. Chichester, UK: Wiley-Blackwell; 2010.
3. Parry M, Canziani O, Palutikof J, van der Linden P, Hanson C, eds. Climate Change 2007 - Impacts, Adaptation and Vulnerability. Cambridge University Press; 2007.
4. Allen MR, Frame DJ, Huntingford C, Jones CD, Lowe JA, Meinshausen M, Meinshausen N. Warming caused by cumulative carbon emissions towards the trillionth tonne. *Nature* 2009;458:1163–1166.
5. Perlack RD, Wright LL, Turhollow A, Graham RL, Stokes B, Erbach DC. Biomass as Feedstock for a Bioenergy and Bioproducts Industry: The Technical Feasibility of a Billion-ton Annual Supply; 2005. US Dept. of Energy and US. Dept. of Agriculture, Forest Service. ORNL/TM-2005/66.
6. Natonal Research Council. Liquid Transportation Fuels from Coal and Biomass: Technological Status, Costs, and Environmental Impacts. National Academies Press; 2009.
7. Langeveld H, Meeusen M, Sanders H, eds. The Biobased Economy: Biofuels, Materials and Chemicals in the Post-oil Era. Earthscan; 2010.
8. Fengel D, Wegener G. Wood: Chemistry, Ultrastructure, Reactions. Berlin: de Gruyter; 1989.
9. Agrawal R, Singh NR. Solar energy to biofuels. *Annu Rev Chem Biomol Eng*. 2010;1:343–364.
10. Kamm B, Gruber PR, Kamm M, eds. Biorefineries - Industrial Processes and Products. Weinheim: Wiley-VCH; 2005:1–2.
11. Hatti-Kaul R. Biorefineries- a path to sustainability? *Crop Sci*. 2010;50:S152–S156.
12. Gassner M, Maréchal F. Thermo-economic process model for thermochemical production of Synthetic Natural Gas (SNG) from lignocellulosic biomass. *Biomass Bioenergy*. 2009;33:1587–1604.
13. Lange JP. Lignocellulose conversion: an introduction to chemistry, process and economics. *Biofuels Bioprod Biorefin*. 2008;1:39–48.
14. Forgione J, Hill J, Tilman D, Polasky S, Hawthorne P. Land clearing and the biofuel carbon debt. *Science*. 2008;319:1235–1237.
15. Whittaker RH. Dominance and diversity in land plant communities. *Science*. 1965;147:250–260.
16. Hille J, Lambers R, Harpole WS, Tilman D, Knops J, Reich PB. Mechanisms responsible for the positive diversity-productivity relationship in Minnesota grasslands. *Ecology Letts*. 2004;7:661–668.
17. Tilman D, Hill J, Lehman, C. Carbon-negative biofuels from low-input high-diversity grassland biomass. *Science*. 2006;314:1598–1600.
18. Gallardo F, Fu J, Cantón FR, García-Gutíerrez A, Cánovas FM, Kirby EG. Expression of a conifer glutamine synthetase gene in transgenic poplar. *Planta*. 1999;210:19–26.
19. Jing ZP, Gallardo F, Belén PM, Sampalo R, Romero J, Torres de Navarra A, Cánovas FM. Improved growth in a field trial of transgenic hybrid poplar overexpressing glutamine synthetase. *New Phytologist*. 2004;164:137–145.

20. Wang Y, Gao F, Doyle FJ III. Survey on iterative learning control, repetitive control, and run-to-run control. *J Process Contr*. 2009;19:1589–1600.
21. Yang B, Wyman CE. Pretreatment: the key to unlocking low-cost cellulosic ethanol. *Biofuels Bioprod Bioref*. 2008;2:26–40.
22. Zhang Y, Lynd, L. Toward an aggregated understanding of enzymatic hydrolysis of cellulose: noncomplexed cellulase systems. *Biotechnol Bioeng*. 2004;88:797–824.
23. Lynd L, Wyman C, Gerngross T. Biocommodity engineering. *Biotechnol Progr*. 1999;15:777–793.
24. Stephanopoulos G. Challenges in engineering microbes for biofuels production, *Science*. 2007;315:801–804.
25. Michels J, Wagemann K. The German lignocellulose feedstock biorefinery project. *Biofuels Bioprod Biorefin*. 2010;4:263–267.
26. Kilpeläinen I, Xie H, King A, Grainstrom M, Heikkinen S, Argyropoulos D. Dissolution of wood in ionic liquids. *J Agric Food Chem*. 2007;55:9142–9148.
27. Rinaldi R, Schüth F. Design of solid catalysts for the conversion of biomass. *Energy Environ Sci*. 2009;2:610–626.
28. Vennestrøm PNR, Christensen CH, Pedersen S, Grunwaldt JD, Woodley J. Next-generation catalysis for renewables: combining enzymatic with inorganic heterogeneous catalysis for bulk chemical production. *ChemCatChem*. 2010;2:249–258.
29. Cherubini F, Strømman AH. Production of biofuels and biochemicals from lignocellulosic biomass: estimation of maximum theoretical yields and efficiencies using matrix algebra. *Energy Fuels*. 2010;24:2657–2666.
30. Schilling C, Schuster S, Palsson B, Heinrich R. Basic concepts and scientific applications in the post-genomic era. *Biotechnol Progr*. 1999;5:296–303.
31. Mavrovouniotis M, Bonvin D. Towards design of reaction pathways. *AIChE Symp Series*. 1995;304:41–51.
32. Besler A, Harwardt A, Marquardt W. Reaction networks - A rapid screening method. In: Jezowski J, Thullie J, eds. Proceedings of Escape 19. Elsevier; 2009:243–248.
33. Sokhansanj S, Mani S, Turhollow A, Kumar A, Bransby D, Lynd L, Laser M. Large-scale production, harvest and logistics of switchgrass (Panicum virgatum L.) - current technology and envisioning a mature technology. *Biofuels Bioprod Biorefin*. 2009;3:124–141.
34. Henrich E, Dahmen N, Dinjus E. Cost estimate for biosynfuel production via biosyncrude gasification *Biofuels Bioprod Biorefin. 3* 2009;3:28–41.
35. Geilen FMA, Engendahl B, Harwardt A, Marquardt W, Klankerrmayer J, Leitner W. Selective and flexible transformation of biomass-derived platform chemicals by a multifunctional catalytic system. *Angew Chem*. 2010, in press. DOI 10.1002/anie201002060.
36. Marquardt W, Kossack S, Kraemer K. A framework for the systematic design of hybrid separation processes. *Chin J Chem Eng*. 2008;16:333–342.
37. Qureshi N, Hughes S, Maddox IS, Cotta MA. Energy-efficient recovery of butanol from model solutions and fermentation broth by adsorption. *Bioprocess Biosyst Eng*. 2005;27:215–222.
38. Kraemer K, Harwardt A, Bronneberg R, Marquardt W. Separation of butanol from acetone-butanol-ethanol fermentation by a hybrid distillation-extraction process combining extraction and distillation. In: Pierucci S, Buzzi Ferraris G, Eds. Proceedings of Escape 20. Elsevier; 2010:7–12.
39. Gani R. Chemical product design. *Comput Chem Eng*. 2004;28:2441–2457.
40. Bardow A, Steur K, Gross J. Continuous-molecular targeting for integrated solvent and process design. *Ind Eng Chem Res*. 2010;49:2834–2840.
41. Hechinger M, Marquardt W. Targeted QSPR for the prediction of the laminar burning velocity of biofuels. *Comput Chem Eng*. 2010;34:1507–1514.
42. Voll A, Hechinger M, Marquardt W. Towards integrated product and process design for biofuels, In: Pierucci S, Buzzi Ferraris G, eds. Proceedings of Escape 20. Elsevier; 2010:709–714.