Perspective

Engineering Biomass Conversion Processes: A Systems Perspective

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DOI 10.1002/aic.13978

Keywords: biorefineries, biofuels, reactor design, process design, optimization, kinetic modeling, reaction mechanism analysis, supply chain optimization

Introduction

Biomass (e.g., agricultural residues, energy crops, and woody forest residues) is the only renewable source of carbon and a potential resource to substitute fossil hydrocarbons in the production of fuels and chemicals. Reports such as the billion-ton study[1] show that the US alone can sustainably generate enough lignocellulosic waste biomass (ca. one billion tons) to replace a significant portion of hydrocarbon-based products (for example, up to 30% of current gasoline demand). Furthermore, 15% of petroleum consumption in the United States goes toward manufacturing 90% of the one million tons of chemicals produced annually.[2] Biomass conversion to fuels and chemicals can, therefore, play a key role in mitigating the heavy dependence on fossil carbon in the chemical and petrochemical industries.

Recognizing this, legislation and policies have been formulated worldwide to mandate and incentivize biomass conversion to fuels. For example, renewable fuel standards (RFS2)[3]—the US federal mandates on volumes for blending biofuel into transportation fuel—require the production of over 36 billion gallons of biofuels, including over 16 billion gallons of cellulosic and other advanced biofuels by 2022. Incentives[4] such as the biomass crop assistance program (BCAP) provide financial assistance to farmers and operators to grow and deliver biomass for advanced biofuel production. Mandates for producing biofuels and incentives for installing high biofuel blend pumps have come into effect in several states.[5] Similar directives and policies toward greater biofuel production have also been formulated in the EU (biofuels directive 2003/30), China,[6] and India.[7]

Several technical challenges exist toward developing a biomass-based fuels and chemical industry. Biomass has a C:O ratio up to 1:1 (for carbohydrates); it is, therefore, significantly different in composition from crude oil. Furthermore, oxygen is present in different functional forms, such as hydroxyl, ether and carbonyl groups, which require different chemical steps for its removal. Several chemical processing steps have been developed to this end. On the biochemical side, metabolic engineering of microorganisms such as *E. coli* and *S. cerevisiae* has enabled converting feedstock such as starch, lignocellulosic sugars, fatty acids, and glycerol[8] to fuels such as alcohols, isoprenoids, fatty acid esters, alkanes, and terpenes through fermentative and nonfermentative pathways.[9–11] Furthermore, platform chemicals have been synthesized, including diols such as 1,2 propane diol, acids such as succinic and lactic acid, dienes such as isoprene, diamines such as putrescine, and pharmaceuticals and nutraceuticals such as polyketides and terpenoids.[12–14] The field of thermochemical conversion of biomass has also witnessed tremendous progress. A variety of chemical processes, spanning gas phase free-radical pyrolysis to homogeneous and heterogeneous acid, metal, and base catalysis have been developed. Catalytic pyrolysis and reforming of lignocellulose, dehydration of fructose to produce 5-hydroxymethylfurfural (HMF), isomerization of sugars, dehydration and hydrogenolysis, diels-alder addition to oxygenates, and hydroxyalkylation are but a few examples of this rich and rapidly growing research activity.[15–22] Approaches aiming at engineering the product spectrum by relating chemistry, catalyst, and process variables with physical properties[23] have also been proposed.

As a result of resource availability, scientific and technological advancements, and favorable policy, the concept of "biorefinery", the biomass-based parallel of the traditional petroleum refinery, has emerged. It is envisaged that a biorefinery will draw a complex feedstock of biomass and convert it, in a series of processing steps, into valuable products. Figure 1 provides a schematic of a complex biorefinery comprising of a range of thermochemical processes that upgrade lignocellulose to fuels (gasoline and diesel) and chemicals (aromatics, lubricants, and some platforms such as ethylene, furfural, and acrylic acid). More than 200 processing facilities[24,25] have already been setup in a short period in the US to produce corn-ethanol, biodiesel, and cellulosic biofuels; as new processes for upgrading biomass are developed, it is expected that the number and complexity of new facilities will rapidly increase in the near future.

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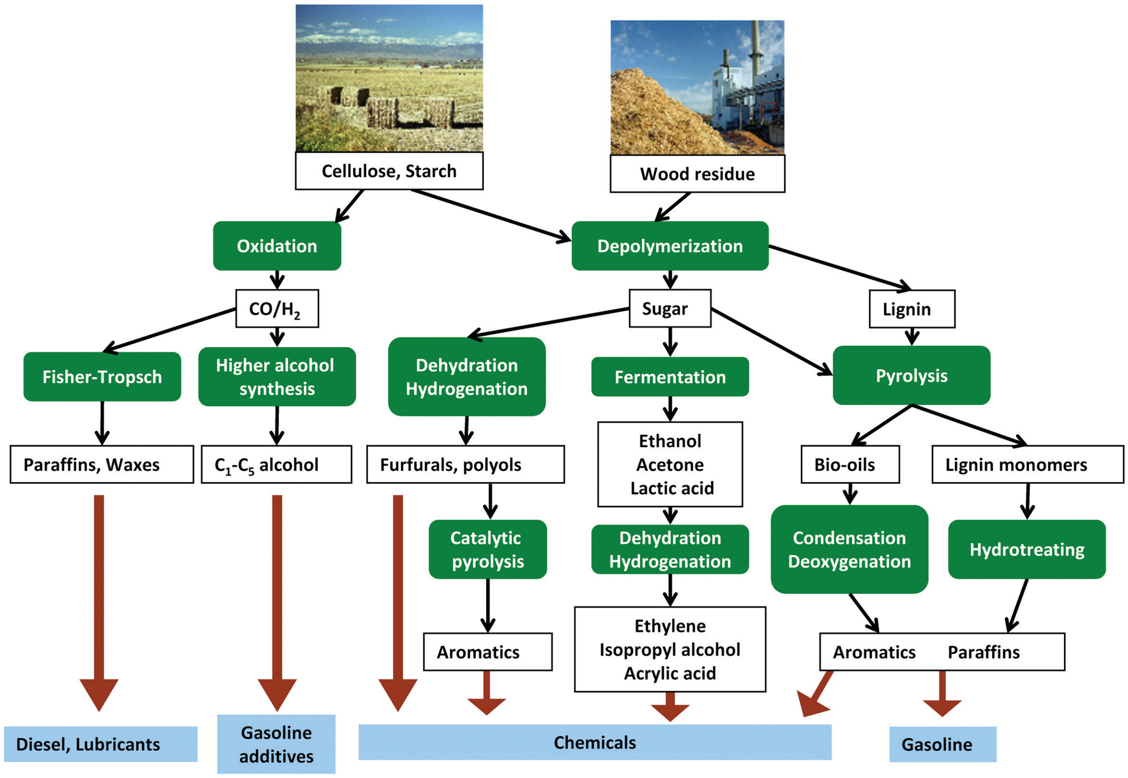

Figure 1. A schematic of a biorefinery.

Systems engineering has been a mainstay in the design, optimization, operation, and control of various aspects of conventional petroleum and chemicals processing.[26] It is also envisioned to play a key role in biorefining. A list of systems engineering and design priority areas in the context of biorefineries, ranging from molecular property calculations, to kinetics estimation, economic optimization, and process design and control was discussed in Regalbuto.[27] The opportunity for redesigning the industrial value chain exploiting the rich molecular structure of biomass was pointed out in Marquardt et al.[28] Such an approach will require simultaneous process and product design involving new chemistries, technologies, and strategies for "tailoring" new molecules.[29] The potential value of applying systems engineering tools in the development of biorefineries and supply chains was discussed in Kokossis and Yang.[30]

Systems challenges in the development of biomass conversion processes and integrated biomass processing plants are indeed numerous. They span multiple levels:

- *Process chemistry*: At this level the goal is to elucidate the spectrum of chemical transformations available for upgrading biomass, and the estimation of the associated kinetics and thermochemistry.
- *Reactor/process design*: The goal here is to identify suitable reactor configurations and operating conditions to selectively produce the desired chemicals and fuels. Subsequently, an integrated design is developed, that achieves production specifications while optimizing for economic/environmental objectives.
- *Enterprise analysis and optimization*: At this level, the focus is on multiple plants typically dependent on the same resources, or a single multiproduct plant. The goal is to determine optimal plant locations, ideal supply and distribution networks, and optimal planning and scheduling strategies, in view of technoeconomic, geographical, and infrastructural constraints.

This Perspective provides an exposition of (1) the outstanding technological and process development questions, and (2) promising future research directions, for designing and implementing economically attractive biomass processing plants. The focus is on downstream processing of biomass-derived intermediates such as sugar and lignin, rather than on upstream conversion of raw biomass. Examples are primarily drawn from thermochemical biomass conversion, but similar considerations will hold in cases involving biochemical conversion. The importance of integrating decision making across different levels is also emphasized through specific examples, along with the need for a suitable software infrastructure.

Process Chemistry

Lignocellulosic and carbohydrate-rich biomass, as mentioned earlier, consists mainly of carbon, oxygen, and hydrogen, with a C:O ratio of 1:1, whereas crude oil and hydrocarbon fuels do not contain any oxygen. This means that new chemical transformations pertaining to reactions of oxygenates for oxygen removal, not considered previously for crude oil processing, become relevant. Also, lignocellulosic biomass comprises a large variety of compounds of different oxygen-containing functional groups and is highly variable in composition. Biomass upgrading to remove oxygen, therefore, involves a host of thermochemical and biochemical routes including gas phase, liquid phase, and catalytic chemistry, as discussed in the Introduction. The plethora of options available for biomass conversion leads to a large spectrum of possible products. For example, C_5 and C_6 sugar monomers can be converted to about a dozen platform chemicals comprising of molecules such as ethanol, levulinic acid, 3-hydroxypropionic acid, sorbitol, 5-hydroxymethylfurfural, lactic acid, and succinic acid. These can further be converted into fuel components and additives such as butanol, methylfuran, and C_{6+} alkanes, and chemicals such as tetrahydrofurans, polyols, polyacids and anhydrides, lactones, esters, olefins, and aromatics. Elucidation of (1) the network of synthetic pathways and products possible for a given biomass feed, and (2) the underlying reaction mechanisms, along with quantitative estimation of thermochemical and kinetic parameters, are major challenges that need to be addressed at the level of process chemistry.

Reaction network generation and analysis

Reaction network generation, often combined with kinetic modeling, has been traditionally used for modeling complex reaction systems in hydrocarbon processing, and more recently for biochemical systems. Several network generators which construct a reaction network on the basis of fundamental elementary steps have been developed to address specific chemistry types; EXGAS[31] (gas phase oxidation chemistry), NETGEN[32] (pyrolysis, Si nanoparticle synthesis, etc.), RMG[33] (gas phase pyrolysis and combustion), RDL[34] and RDL++[35] (catalysis), COMGEN,[36] BioNETGEN,[37] and BNICE[38] are a few examples. In biomass conversion, the wide variety of possible chemical transformations implies that a suitable network generator must be generic in the scope of chemistries it can handle. To this end, such a generator should be able to represent and manipulate chemical concepts of organic chemistry such as atomic configuration, isotopes, bonding types, weak interactions, ligands, Lewis and Brønsted acids and bases, and multiple catalytic sites.

To systematically generate and analyze reaction networks with chemistries pertaining to biomass conversion, the authors and collaborators have developed a computational tool called RING.[39,40] The overall schematic of the tool is given in Figure 2. RING accepts as inputs the initial feedstock reactants and likely reaction rules. It then generates an exhaustive network of reactions and species making extensive use of cheminformatics algorithms. RING also has a broad range of postprocessing network analysis features, which can be used to analyze the topology of the generated reaction network and identify: (a) *pathways* – a sequence of reactions to specific products from initial reactants, (b) *mechanisms* – a set of reactions that constitutes a complete reaction cycle, and (c) *isomer and reaction lumps* – which allows substantial reduction in the size of the generated networks. RING has been used to study gas phase free-radical and electrocyclic chemistry, homogeneous acid and base catalyzed systems, and heterogeneous acid, base, and metal catalysis.[39]

To illustrate RING's analysis capabilities, consider the reaction network corresponding to the system of acid catalyzed conversion of oxygenates.[41] Using a set of acid catalysis elementary steps taken from the literature, including protonation, dehydration, and beta scission as inputs into RING, the complex network associated with the conversion of acetone was generated. Queries in RING for mechanisms to form acetic acid from acetone revealed one mechanism that satisfied the overall experimentally observed stoichiometry. We could further propose experiments to validate, or negate, the plausibility of the mechanism based on the query results from RING. For example, the identified mechanism involved a condensation step (in an aldol reaction), followed by beta scission of a carbon-carbon bond. Therefore, it can be expected that in an experiment run at low conversion, the rate of reaction would be second-order in acetone concentration (due to the initial condensation step). Furthermore, simulations in RING with unlabeled and ^{13}C isotopically labeled acetone as reactants showed that the butene formed by the mechanism would never have exactly two ^{13}C labeled carbons, but can have every other possible isotopomer. This experiment, which is straightforward to conduct, would also be a direct corroboration of the hypothesized mechanism.

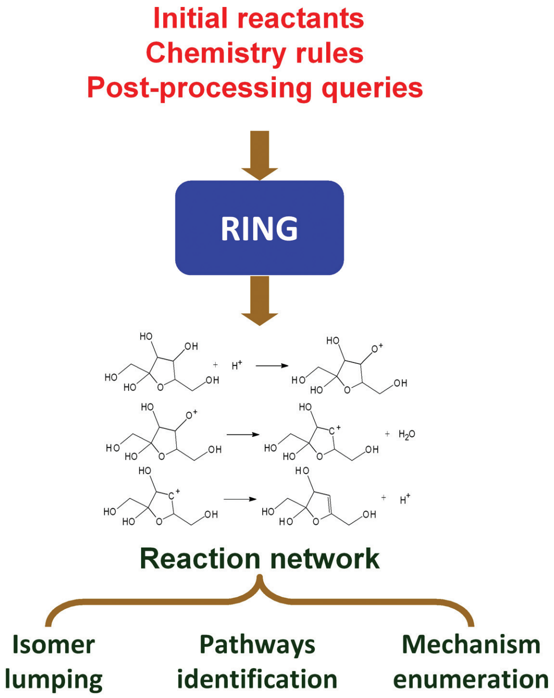

Figure 2. RING: an input-output schematic.

Thermochemistry and kinetics

The preceding discussion highlighted the potential of a topological analysis of a reaction network, coupled with experimentation, to shed light on the underlying reaction mechanisms between reactants and products of interest. The next logical step involves evaluating the thermodynamic feasibility of the generated reaction pathways and determining the kinetic constants for each reaction step. There exists a wide variety of empirical, semiempirical and rigorous methods for tackling these problems.[42] For example, kinetic parameters can be estimated from experimental data; however, the predictability of the resultant model will heavily depend on the quality and the amount of data, and the experimental conditions under which they were generated. Kinetic parameters can also be estimated *a priori* using computational methods (e.g., *ab initio* calculations); given the size of the reaction networks, this is an intractable proposition.

Semiempirical methods for thermochemistry and kinetic modeling, on the other hand, offer a reasonably accurate and scalable alternative, and can be effectively combined with automatic network generators such as RING to allow rapid screening of biomass conversion pathways. Specifically, Benson's[43] group additivity-based methods for computing thermochemical properties cover (a) molecules in gas and condensed phases,[43–46] (b) free radicals,[44,45] (c) metal surface adsorbates,[47] and (d) octanol-water partition coefficients, etc.[48] Furthermore, linear free energy relationships, relating enthalpy/free energy with other molecular properties, have also been proposed to handle solvation phenomena.[49,50]

The accuracy of these methods varies from about 1 kcal/mol for hydrocarbons and small oxygenates in gas phase to about 5 kcal/mol for metal surface adsorbates. In a test collection of more than 50 compounds of size less than 10 heavy (carbon and oxygen) atoms and comprising alkanes, olefins, aromatics, alcohols, ethers, furans, acids, and esters, we determined that the mean absolute error of gas phase enthalpy of formation was about 1.25 kcal/mol.[51] Larger deviations of 2–5 kcal/mol are observed for furan derivatives which can be attributed to the limited representation of such molecules in the dataset used for the parameterization of group values. The discrepancy is expected to be larger for molecules such as (a) fructose and glucose because many possible structural forms are not taken into account in the calculation, and (b) lactic acid or sorbitol because the effect of multiple functional groups is not captured well in the parameterization. These missing gaps can be filled by expanding the original data set to include more oxygenates representative of biomass-derived molecules. The additional data can either be obtained through experimentation or by high-level quantum calculations.[52]

As an example of thermochemical analysis of biomass conversion routes, consider the problem of converting a set of model biomass compounds comprising of C_2 and C_3 oxygenates (acids, alcohols, aldehydes, and ketones) to larger monoalcohols using a collection of heterogeneous acid, base, and metal catalytic reaction steps. These inputs were provided into RING so as to generate an exhaustive network of reactions. Figure 3a shows a set of products representative of the 200 C_4 to C_9 alcohols that can be formed. The entire network is rich in terms of the diversity—size, shape, and characteristics—of synthetically feasible molecules. Figure 3b shows the most atom-efficient synthesis route to synthesize 1-octanol, as obtained from RING. The route involves acetaldehyde as initial reactant which undergoes successive condensation with additional acetaldehyde molecules followed by complete hydrogenation to 1-octanol. Group additivity-based thermochemistry prediction schemes have been recently incorporated into RING to allow for on-the-fly estimation of enthalpy and free energy of species and reactions. Figure 3b also has the standard heat of formation, at 298 K, for major reactant and product species and enthalpy and free energy change of all reactions at 500 K estimated by RING.

Kinetic parameters can also be estimated using semiempirical correlations. Linear free energy relationships and more specifically Brønsted-Evans-Polanyi (BEP) relationships for estimating the activation energy of a reaction step can be valuable in quick estimation of kinetic parameters. Such correlations have traditionally been used for modeling hydrocarbon processing systems,[32,53] and have to be extended to include biomass conversion reactions. Efforts in this direction have already begun, with relationships developed for (a) bond scission reactions on platinum for small molecules,[54,55] and (b) neutral electrocyclic reactions in gas phase pyrolysis of biomass-derived oxygenates.[56] Given that large classes of chemistries appear to follow linear free energy relationships,[57–60] a comprehensive database of such correlations for a variety of chemistries will be of significant value in kinetic modeling. Recently, BEP correlations and scaling relations proposed in Jones et al.[61] were used for quickly estimating kinetics and thermochemistry of ethanol decomposition reactions on a variety of metals.[54] Combination of BEP correlations and group additivity-based estimation of thermochemical properties have also been used to screen out energetically unfavorable reactions in the reaction network pertaining to transition metal catalyzed decomposition of glycerol.[62] These relationships have to be extended to include liquid phase chemistries to allow for modeling several condensed phase chemical systems such as aqueous phase reforming and dehydration of sugars. This, however, is not straightforward because solvent-solute and solvent-solvent interactions also need to be accounted for.

Figure 4 describes a work flow for quantitative analysis of complex reaction systems using RING. Group additivity and linear free energy relationships can be used to estimate the energetics of each reaction in a complex network generated by RING, which could then be used to construct a kinetic model of the system. Such a strategy could be used for rapid comparison of several competing choices of reaction systems and catalysts applicable in biomass conversion.

Reactor and Process Design

Clearly, the practical goal is the design and operation of an "economically optimal" biorefinery, with optimality desired for both the individual processes and the whole. Research in this direction is at its very early stages except for the production of bioethanol from corn, based on what is considered as mature technology. Recent studies have focused on evaluating the cost of producing ethanol from alternative feedstocks,[63] and on increasing the energy efficiency or reducing the water consumption of these processes.[64,65] On the more general concept of biorefinery, several process synthesis studies have also appeared[66,67] aiming to identify optimal biorefinery configurations, albeit with limited data on the techno-economic performance of the individual conversion processes. Indeed, technoeconomic evaluation of process alternatives for the production of bio-based chemicals (other than ethanol) has remained relatively unexplored, despite the vast array of synthetic possibilities and the abundance of studies in the chemistry literature (see Introduction and Process Chemistry sections).

Let us first turn our attention to the engineering questions in reactor and overall process design and optimization, that need to be resolved. Lignocellulose is a solid which has a 50% lower energy density per unit mass compared to fossil fuels, its production is widely distributed and its transportation is costly. These factors suggest that smaller scale (as opposed to the large-scale petroleum refineries) distributed

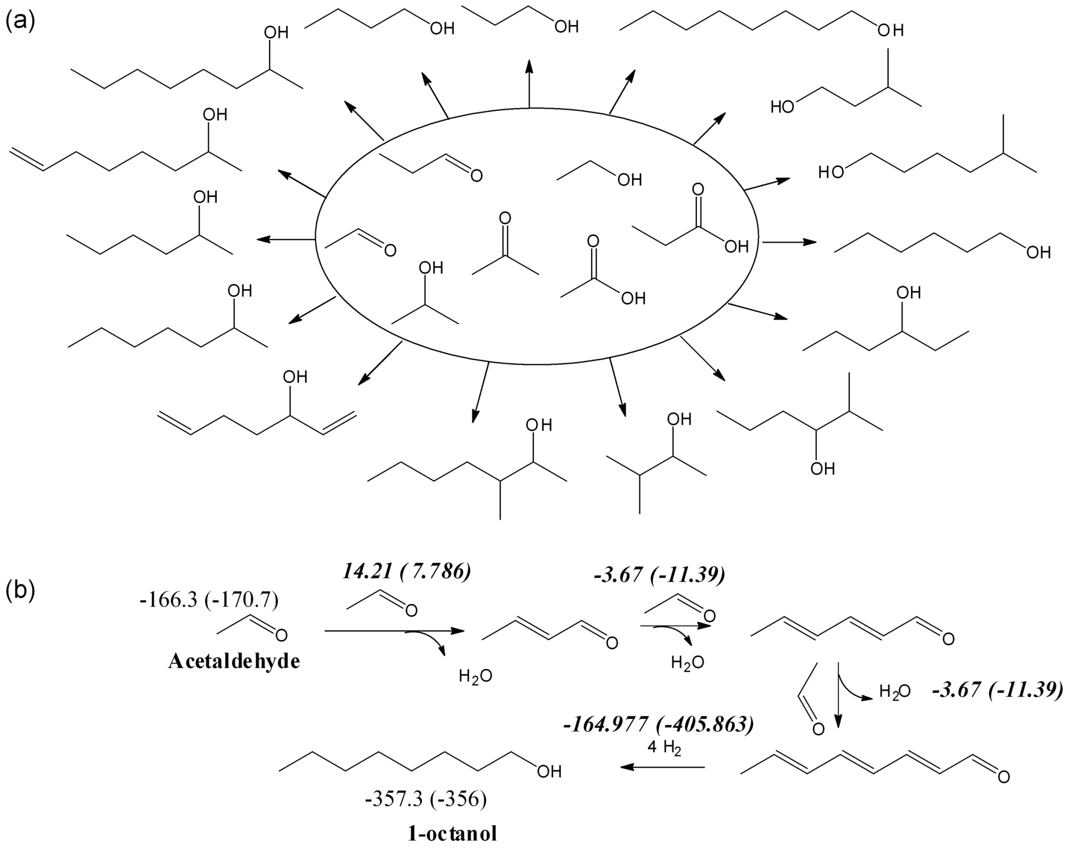

Figure 3. (a) A representative spectrum of alcohols that can be synthesized from small oxygenates, and (b) synthesis route to form 1-octanol.

In bold italics is the free energy change (and enthalpy change) of each reaction at 500 K, while standard enthalpy of formation at 298 K for acetaldehyde, octanol, are also given, calculated using group additivity (and taken from NIST webbook). All values are in kJ/mol.

plants may offer economically more attractive options. Thus, it is essential to develop new, flexible reactor configurations that allow for intermittent operation, can handle variable feeds, avoid conditions such as very high pressures or recycles, and are designed to maximize single pass conversion and product selectivity. An example is a multistage autothermal reactor in which part of the feed is oxidized to produce energy in an exothermic step and the remaining feed is converted into valuable products in an endothermic step.[68] Such coupling of endothermic and exothermic steps, in a single reactor necessitates a reactor model that accurately captures heat transport. Furthermore, several of the chemical processes proposed for biomass conversion involve multiphase reactors, wherein for example, the reaction takes place in one phase and the product of interest is preferentially separated in another phase.[19,69] Equations of state and the estimation of interphase mass-transfer coefficients and partition coefficients become relevant in this case. For reaction systems such as depolymerization of cellulose or pyrolysis of lignin, the feed biomass is solid which reacts in a homogeneous (gaseous or liquid) medium to produce liquid phase products. Reactor models for such systems should also take into account the mechanisms for solid biomass shrinkage and phase change.

Designing biomass conversion reactors rigorously thus requires capturing the chemical transformations, the thermochemistry and kinetics, and the transport properties of biomass-derived compounds accurately. Estimation of other physical properties, such as density, boiling point, vapor pressure, cold flow properties, and fuel characteristics of biomass and its derivatives is also essential. Yet, a database for such properties is currently not available. Many of these bio-based compounds are not included in the databases of existing commercial simulation packages and little information can be found in the NIST Chemistry WebBook.[70] Surprisingly, this is the case for molecules as common as fructose.

In addition, as biomass and petroleum have inherently different chemical compositions, separation and purification operations for biomass-based chemicals differ significantly from those used for oil-derived compounds. For example, biomass feedstocks are nonvolatile and thermally sensitive, limiting the application scope of classical distillation, which dominates separations of oil-based products. Instead, low-temperature separation technologies such as solvent extraction and membrane separation appear as more promising alternatives.

It is, therefore, evident that the production of fuels and chemicals from biomass will entail conceptual synthesis and optimization of novel reaction-separation flow sheets, and development of extensive databases of physical properties, transport, kinetic and thermodynamic parameters, needed to support the design of new processes.

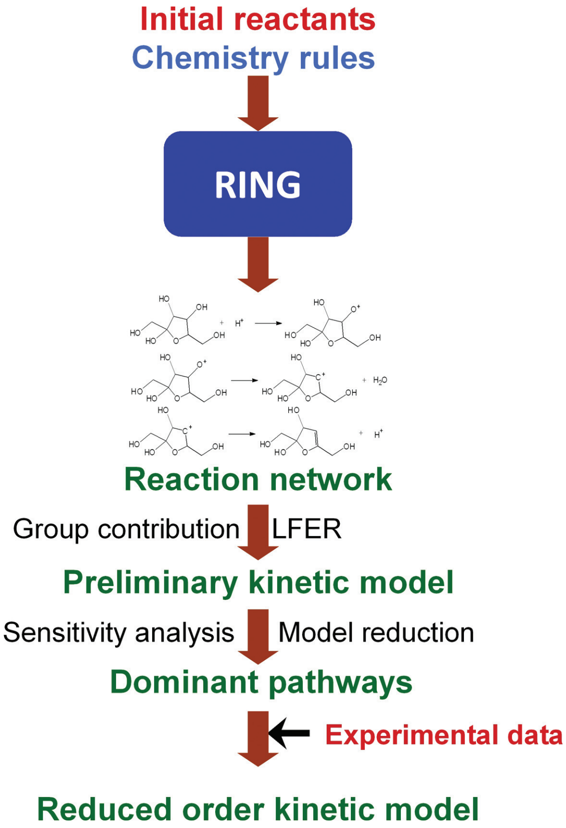

Figure 4. Schematic of kinetic modeling of complex systems with RING.

Technoeconomic analysis of biomass conversion processes

The richness of the possible reaction networks emanating from biomass suggests a large variety of processes as potential candidates in an integrated biorefinery. Each of these processes should be judged in terms of its technical feasibility and economic attractiveness. In this section we will sketch the considerations involved in such a techno-economic analysis by focusing on the production of 5-hydroxymethylfurfural (HMF) from fructose.[71,72] HMF was chosen because it has been recognized as a “key substance between carbohydrate and mineral oil based chemistry”[73] and as having “by far the highest industrial potential for a fructose-based compound”.[74] In particular, HMF can be used to produce 2,5-furandicarboxylic acid (FDCA), a molecule that can be directly used as a replacement for terephthalic acid in the production of analogs of poly(ethylene terephthalate) (PET), and polybutylene terephthalate (PBT), or dimethylfuran (DMF), which is both a fuel and a precursor of p-xylene[21] (see Figure 5a).

HMF is produced by dehydration of fructose in aqueous medium, but rehydrates to produce several byproducts; extraction of HMF from the reaction mixture is the most popular approach for preventing sequential reactions and, thereby, improving HMF yield. The use of an extracting solvent (e.g., methyl isobutyl ketone (MIBK)) and the addition of suitable modifiers to both the organic and the aqueous phases have been proposed to this end.[19]

Based on this approach, we developed two continuous processes for the production of HMF (see Figure 6). The first one considered a biphasic reactor coupled with a liquid-liquid extractor and an evaporator.[71] The second one considered an integrated extractive-reactor, where the reaction of fructose and the separation of HMF take place in the same unit.[72] Detailed kinetics are not available for this reaction. However, a simplified mechanism that neglects the existence of intermediate products and lumps all the byproducts in two classes, i.e., either produced from fructose or HMF (see Figure 5b), and the equations to compute the corresponding kinetic constants, are available in the literature.[75] These were used as the basis to develop a family of kinetic constants that are consistent with the experimental conversion and selectivity reported in Roman-Leshkov et al.[19] (for details see Torres et al.[72]).

The objective was to find the solution that minimized the cost at which HMF has to be sold to balance raw material, energy, and capital costs. The constraints of the optimization problem included mass balances, equilibrium relations, and other operational constraints. The resulting nonlinear constrained optimization problem was solved with the SNOPT solver within the framework of GAMS.

In all cases, the minimum HMF production cost was higher than that of its petroleum derived analogue (p-xylene), with fructose dominating the cost mainly due to a low selectivity toward HMF. Sensitivity analysis with respect to the kinetic constants was used to assess their impact on the process economics. The optimal solutions consistently provided design variable values such that the decomposition of HMF into byproducts was effectively blocked, with all the loss in selectivity, thus, attributed to the parallel reaction that consumes fructose. This fact suggested that research efforts should be directed primarily towards the design of new catalysts and identification of reaction conditions that suppress these parallel reactions (fructose to byproducts), rather than on design modifications to suppress the consecutive reaction (HMF to byproducts).

An additional study on the production of HMF from fructose and its subsequent conversion into 2,5-dimethylfuran (DMF) was performed in Kazi et al.[76] Here, the process was simulated in Aspen Plus and the minimum selling prices (MSPs) of HMF and DMF (now defined as the price at which the net present value (NPV) becomes zero) were found. The results reinforced the idea that bio-based compounds are more expensive than their petroleum derived counterparts mainly due to a high-feedstock price. Techoeconomic analyses for a few other biobased chemicals have also been performed. A summary of these, including costs, method used, chemical pathways and most relevant conclusions can be found in Table 1.

The HMF case study, whose results were summarized earlier, is an illustration of a broader effort that needs to be undertaken in order to examine the economic feasibility of various processing schemes for the production of the top building blocks of the future chemical industry identified by the 2004 report from the Dept. of Energy[82] and its 2012 update.[83] These lists include furans such as furfural, HMF or FDCA; biohydrocarbons such as isoprene; sugar alcohols like glycerol, sorbitol and xylitol and organic acids like levulinic, lactic, or succinic acid. Different approaches for the

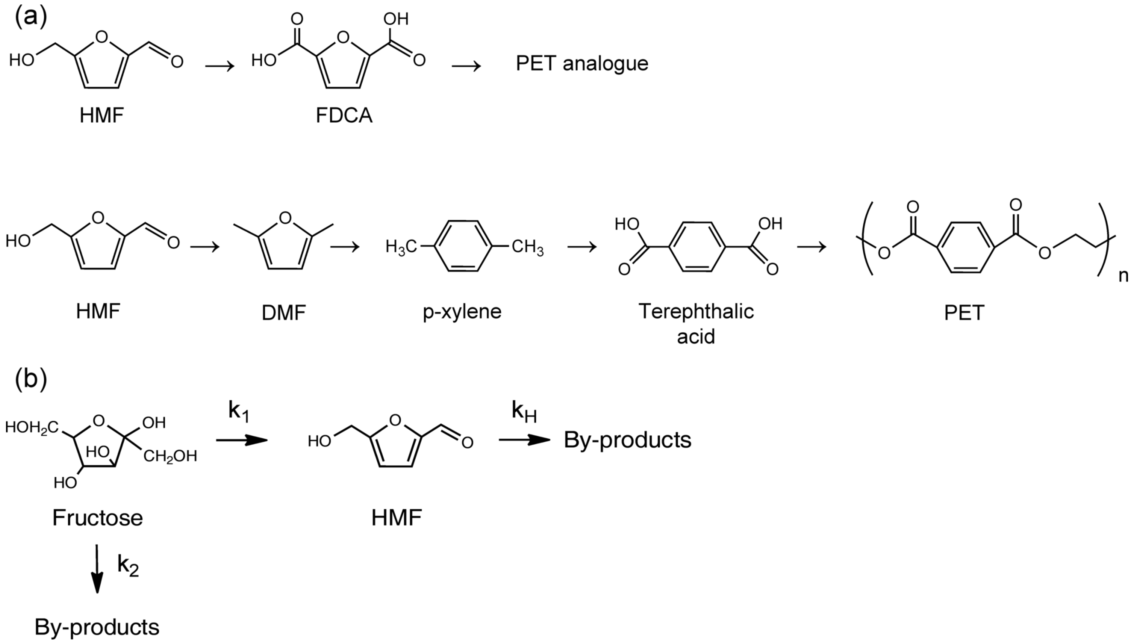

Figure 5. (a) Reaction schematic of FDCA and p-xylene from HMF, and (b) Simplified kinetic model for the conversion of Fructose into HMF[75].

synthesis of these compounds can be found either in the aforementioned reports or in the review article by Corma et al.[16]

Considering the need for a rapid evaluation of these processes and the lack of reliable data to perform detailed technoeconomic studies, a conceptual design approach is a logical first step to evaluate their feasibility.[84,85] Optimization should also be used to determine optimal process flow sheets for a meaningful comparison of process alternatives. This is especially important in the context of biomass conversion, where profitability margins may be especially low due to the potentially high cost of feedstock. The economic potential (EP) which is roughly defined as the difference between revenues and costs,[84,85] is a suitable economic criterion to be maximized if the targeted chemicals are already produced in bulk. If the chemical is either not currently commercially available, or available as a specialty, the minimum price at which the chemical has to be sold so that revenues and costs are balanced (i.e., EP = 0) is a meaningful criterion. More rigorous profitability measures such as the net present value or the investors rate of return (IRR or DCFRR)[86] could also be used, but do not offer a clear advantage over the simpler economic potential at these preliminary stages in which major cost bottlenecks have not been yet identified. Environmental constraints and sustainability measures can subsequently be used to differentiate between economically competitive process options.

Enterprise-Wide Analysis and Optimization

Biomass is a broad term encompassing a diverse set of feedstocks (e.g., crops, grasses, agricultural waste, wood, municipal waste, and landfill gas) that are typically distributed and seasonally available, with considerable uncertainty in composition, quantity and price. Biomass composition can also be affected by harvest and storage methods, and its

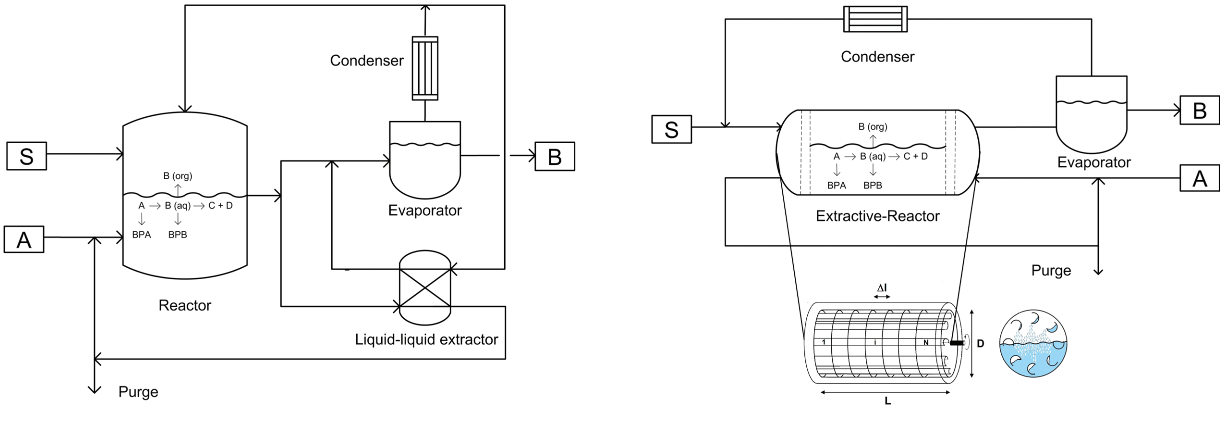

Figure 6. Processes for the production of HMF.

Table 1. Summary on Biomass to Biochemicals Technoeconomic Analyses

Compound	Applications	Path	Estimated Cost	Current cost or oil- derived cost	Feedstock cost	Major factors affecting cost	Ref.
DBK	Industrial solvent	LA → GVL → DBK	7.7-8.5$/kg (MSP)	DBK: 9.07 $/kg; MEK: 0.77 $/kg (industrial large scale solvent)	LA: 3.21 $/kg	LA cost; yield	77
HMF	Renewable chemicals and fuels fuel;	F → HMF → DMF	0.135$/mol (MSP)		F: 13.6$/lb	Fructose cost; yield	76
DMF	Furanic compounds		7.63$/gal (MSP)	gasoline price: 2.91 $/gal			
Alkenes	Liquid hydro-carbon fuel	LB → LA → GVL → butene → alkenes	4.31-7.78 $/GGE (MSP for different feedstocks)	EtOH 5.13 $/GGE (NRL process)	LB various sources (max. cost: corn stover; min cost: loblolly pine)	LB cost; installed equipment cost	78,79
Furfural	Renewable chemicals and fuels	X-olig → X → Furfural	366$/ton 6.72 $/kg (MSP)	1450 $/ton (furfural market price)	Dry xylose: 130 $/ton	Raw material cost and utilities	80
Sugars (glucose, xylose, arabinose, mannose, galactose)		LB → sugars via ionic liquid hydrolysis		40-50 $/kg (commercial product)	Lignocellulosic biomass	Ionic liquid cost	81

Notation: LA = levulinic acid; GVL = γ-valerolactone; MEK = methyl ethyl ketone; DBK = dibutylketone; F = fructose; LB: Lignocellulosic biomass; GGE: gallons of gasoline equivalent; X-olig: xylose oligomers; X: xylose

lower energy density compared to fossil fuels results in costly transportation. Finally, many processes for biomass preprocessing and conversion are in early stages of commercial development, making it difficult to obtain accurate estimates of the current and future state-of-technology. As a result, unique logistical challenges arise at each stage of the biomass to fuels and chemicals supply chain: biomass production, harvesting, storage, preprocessing, transportation, conversion, and market distribution present numerous alternatives which in turn lead to nontrivial supply chain problems, critical to the economic success of the entire industry.

A broad range of interdisciplinary research efforts in agriculture, forestry, and biotechnology, are actively exploring the upstream problems of biomass production and preprocessing. Studies[87–89] have quantified the geographical and temporal distribution of biomass, often using farming projections along with market equilibrium models to capture the connection between land, energy and fuel markets. Biomass feedstock design studies seek to engineer new biomass species or mixtures with desirable characteristics (e.g., low moisture, easier bulk handling or farming, higher sugars content). Examples include design of biomass mixtures (e.g., mixed prairie[90]), woody crops[91] (e.g., hybrid poplar, willow, eucalyptus and southern pine) and energy crops (e.g., switchgrass[92] and miscanthus[93]). It is important to note that the same cannot be done with fossil feedstocks, as their properties are determined by natural processes that occur on a much longer time scale. Biomass preprocessing studies seek to modify the state of biomass in a way that improves downstream handling, storage, transportation and conversion. Preprocessing encompasses a wide array of methods (e.g., baling, size reduction and shredding, densification and pelleting, drying, pyrolysis, gasification, torrefaction, hydrothermal treatment, digestion, pulping, hydrolysis, fiber explosion, and ionic liquid separation).[94] Although often developed for other applications (e.g., pulp and paper, crop engineering, wood logistics, loose material handling, crop storage), this wealth of knowledge is directly useful for the supply chain analysis of biomass-based chemicals and fuels.

The remainder of this section will focus specifically on supply chain analysis and optimization for biofuels, because biofuels have matured to the point where supply chain issues have become important. The current US biofuel industry is dominated by ethanol (mainly produced using starch from corn grain), and biodiesel (mainly produced from soybean oil and waste oils), but cellulosic biofuels (based on nonfood resources such as agricultural waste, grasses and woody crops) are expected to play a large role in the future. The U.S. EPA predicts that 8.7 million gallons of cellulosic biofuels will be produced in 2012,[95] while the RFS mandates require the use of 16 billion gallons of cellulosic biofuel in motor-vehicle fuel by 2022.[96] Expanding the current cellulosic biofuel industry by three-orders of magnitude in a decade to satisfy the RFS mandates will impose significant supply chain challenges, and it is uncertain which processes (and cellulosic biofuels) will be ultimately commercialized. Methods and software tools for modeling and optimizing biofuel supply chain are, therefore, of critical importance in guiding government policy and in the identification of biofuels with the potential to replace petroleum-based transportation fuels. In the following section, we discuss current and ongoing work to develop such tools, and provide a perspective for future developments.

Biofuel supply chain optimization

Biofuel supply chain optimization (SCO) seeks to determine the supply chain configuration that maximizes a desired performance index (e.g., profitability, life cycle emissions, water use and net energy use) by efficiently using biomass resources while satisfying the biofuel market demand. A review of research in this area, as well as in the related field of petroleum and chemical operations research is provided in An et al.[97] A review of the broader area of alternative processes for the production of liquid transportation fuels, including process design and supply chain optimization can be found in Floudas et al.[98] Methods for solving biofuel SCO problems often include the use of geographical information systems,[99] and algorithms for mathematical programming (e.g., linear,[100] nonlinear, integer[101] and multiobjective[102–104]) or metaheuristics (e.g., evolutionary algorithms and agent processes).

Recent research in our group[105,106] has examined the biofuel industry in the 12-state Midwestern US, the region with abundance of available biomass and about 85% of the total capacity for the US corn ethanol industry. A significant amount of data was required for the biofuel SCO studies. Estimates and projections of biomass resource availability from the U.S. Dept. of Energy's 2011 update to the Billion-Ton Study[87,107] were used. This includes road-side price and available quantities of individual feedstocks for each county in the contiguous U.S. This information is the result of a substantial effort involving the U.S. Dept. of Energy, U.S. Dept. of Agriculture (USDA), USDA Forest Service, academic researchers and industry experts to quantify US biomass resources with annual projections through 2030. A multimodal (road and rail) transportation network for the region to determine the cost of transporting biomass and biofuel between counties, existing facilities, new facilities and markets was created by the authors. Seven biomass processing technologies were included in the model: dry-grind corn ethanol,[108] integrated corn and stover process,[108] dilute acid pretreatment of corn stover with cofermentation,[109–112] AFEX pretreatment of perennial grasses with cofermentation,[113] indirect[114,115] or direct[116] gasification with syngas upgrading to mixed alcohols, fast pyrolysis with bio-oil upgrading to naphtha and diesel.[117] Detailed discounted cash flow analysis for each technology that included capital depreciation and taxation was also performed.

An mixed-integer linear programming (MILP) optimization problem was formulated, whose solution would provide the most economical biofuel supply chain configuration for a number of important situations, by determining the optimum location, capacity and technology selection of new facilities, along with biomass sourcing and biofuel distribution to markets. The first case study[106] focused on cellulosic ethanol production when RFS2 is not strictly enforced. The effect of uncertainty was studied through sensitivity and Monte Carlo analysis. Such analyses are necessary for cellulosic biofuels, as many of the underlying conversion processes have not yet been demonstrated commercially. For the nominal case, it was found that there is enough economic incentive for a 4.7 billion gallon per year cellulosic ethanol industry to develop using mainly corn stover. However, based on the uncertainty in prices and technoeconomic factors, it was found that there was a 21.5% chance the industry would not develop. Thus, the Midwest has a potential, if uncertainty can be managed, to provide a large portion of the national RFS2 mandates.

The second case study[105] was focused on the renewable identification number (RIN) system that is intended to ensure compliance with the RFS2 mandates. This system creates a market where obligated parties (e.g., fuel blenders) can trade RINs (numeric codes corresponding to volumes of produced or imported biofuels) to satisfy their RFS2 requirements. RIN markets exist for each of the RFS2 biofuel classifications: renewable fuel (RF), biomass-based diesel (BD), advanced biofuel (AB), and cellulosic biofuel (CB). Once blended, the RIN can be sold to other obligated parties or presented to the EPA. Each gallon of biofuel, thus, has a price equal to the demand price (the price blenders are willing to pay with no RFS2 mandate) plus the value of the RIN. The RF RIN value is currently nearly nothing due to the success of corn ethanol, but the AB RIN value is $0.70/gal.[118] High RIN values like this help to cover the increased costs of commercializing new biofuel technology.

The study was able to capture the effect of the RIN markets by determining minimum biofuel selling prices for the RFS2 biofuel classifications (RF, AB and CB). It was found that the Midwest could produce enough biofuels to meet the national RFS2 mandates in 2015; the technologies can be developed and the biomass is projected to be available. In the optimum supply chain configuration, the installed facilities have positive NPV if the biofuel prices are above $2.39/gal, $2.13/gal, and $1.71/gal for CB, AB, and RF, respectively. Thus, the RIN values are estimated to be worth $0.68/gal for CB and $0.42/gal for AB.

Enterprise-level optimization in the biomass to fuels and chemicals industry requires a comprehensive database of biomass conversion technologies, with well-documented economic and environmental analyses. Such a database should represent the current (and projected) state-of-technology, even if research on design and commercialization of these technologies is ongoing. Fair comparisons between technologies require some level of uniformity in flow sheet detail and economic analysis. Without this uniformity, the SCO results may identify one conversion technology to be more competitive simply because its costs were not properly accounted for (e.g., capital cost was underestimated or missing). This can be a challenge as it is desired to use SCO studies to examine the competition between highly developed technologies (e.g., corn ethanol) and less commercialized technologies (e.g., biomass gasification). It is also a challenge for processes producing novel biomass-based chemicals, for which design and technoeconomic analyses are still at an early stage. Recently, the U.S. National Renewable Energy Laboratory (NREL) released a database of technoeconomic studies, although limited to processes for biofuels and energy generation.[119] Additional studies are required to include life cycle analysis with updated economic and process parameter estimates, and biomass to chemicals processes.

Connecting biomass SCO with the relevant research in the fields of agriculture, forestry, and biotechnology is an ongoing challenge. If done successfully, it can broaden significantly the scope and reach of supply chain decisions. For example, including alternative biomass farming and harvesting methods, or the use of engineered biomass species in the supply chain formulation would allow for additional degrees of freedom on how biomass producers grow and sell biomass (e.g., crop residues can be sold to biorefineries, used as livestock bedding or left on the field to combat erosion and reduce soil nutrient depletion). Future supply chain studies should, therefore, acknowledge and account for these competing production methods and biomass uses.

Finally, government policy decisions are a major consideration at the enterprise level. They may impose requirements on environmental performance, and have a direct effect on supply chain economics through tax incentives, grants and loans. These economic incentives are intended to align profit with the normally conflicting objectives of positive environmental and social impact. Depending on the nature or detail of the supply chain study, it may be important to include local, state or national policy considerations. Results of supply chain optimization can then be used to estimate the effect of the current policy environment, and to help guide future policy decisions.

Integration of Decision-Making across Multiple Levels

The various levels of systems tasks discussed so far are clearly characterized by disparate time and length scales. Nevertheless, as shown in Figure 7, these levels are interdependent. While each level provides a variety of options and estimates of relevant parameters for the analysis at the higher level, the higher level also provides constraints and specifications for the analysis at the lower level. In what follows we discuss several specific opportunities of integrating decision making across multiple levels, along these lines.

Coupling chemistry and reactor/process design

Upgrading biomass to valuable products involves multiple reaction steps. For example, to synthesize fuels from biomass, three broad types of reactions are required: C—C bond formation, C—O bond scission, and saturation of double bonds to make compounds having larger carbon chains with less oxygen and more hydrogen content. The network of synthetic possibilities is vast as discussed in the Process Chemistry section. The different potential thermochemical routes for upgrading biomass can be combined through coupling of: (a) oxygenate reactions based on kinetics (kinetic coupling), (b) several types of active sites either in multifunctional catalysts or multistage reactors and (c) multiple reactors. Such integration can offer high yields and selectivity and in many cases lower capital cost in the form of reduced equipment needs. Several experimental studies have exploited such coupling or multifunctionality of catalysts[120–123]; however, such efforts have yet to be supported by rigorous modeling and design. Detailed kinetic modeling that accounts for all the reaction cycles, along with the appropriate multistage reactor or reactor network model will be a key in developing a framework for the optimal design of such multifunctional/multistage reaction systems. Reactor/process design considerations can then support and guide fundamental chemistry research. A recent work on identifying optimal catalyst parameters that maximize the rate of hydrogen production from the decomposition of ethylene glycol on transition metals and alloys in a CSTR[55] is a step in this direction.

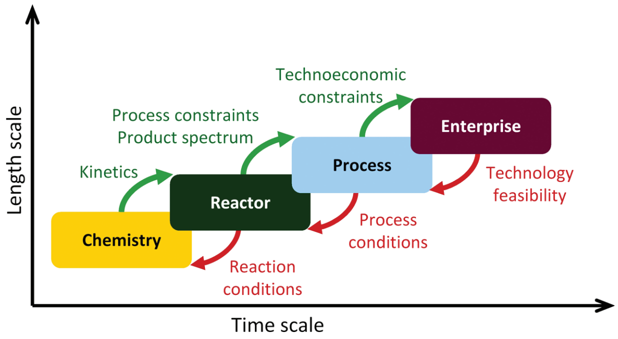

Figure 7. Time and length scales of systems engineering analyses.

The coupling of multiple reaction cascades can also involve homogeneous and heterogeneous chemistry of compounds in the solid, liquid, and vapor phase. Multiple phases are also introduced to exploit solubility differences and aid the preferential separation of the products in one phase, as discussed in the Reactor and Process Design section. In both cases choices made at the chemistry and reactor design level, can have a profound impact on downstream separation steps. A comprehensive approach of chemistry-driven reactor/process design would therefore be highly desirable, and would require integrating computations across the chemistry and process levels.

Coupling chemistry and product selection

There are numerous chemistry options for upgrading biomass to make a variety of chemicals. From a product design perspective, identifying which compounds have desirable properties for target applications becomes a key question. Computer-aided molecular design has been a favored method to identify, using quantitative structure–property relationships (QSPR), the set of potentially valuable compounds. Several mathematically robust and practical methods have been proposed to address the problem of selecting solvents,[124] refrigerants,[125] and designing polymers.[126] These methods sweep the combinatorial space intelligently to construct molecular structures that satisfy property constraints. To use these methods in the context of biomass upgrading requires determining if the identified molecules can actually be synthesized from biomass. This leads to exciting opportunities for integrating chemistry and product/process design. The premise is to enable addressing the questions— *what to make and how?*—simultaneously. The Marquardt group[29,127] has proposed one such method wherein a reaction network is first identified that captures the possible reaction steps that upgrade biomass (or a bioderived platform molecule such as itaconic acid). Molecules with desired properties (e.g., high heat of combustion for a potential fuel compound) are then identified and pathways from initial reactants to these compounds are determined using flux balance analysis. Note that a substantial manual effort is involved in constructing the set of reactions in the aforementioned approach.

A more scalable option is to use the network generation and analysis features of RING in combination with

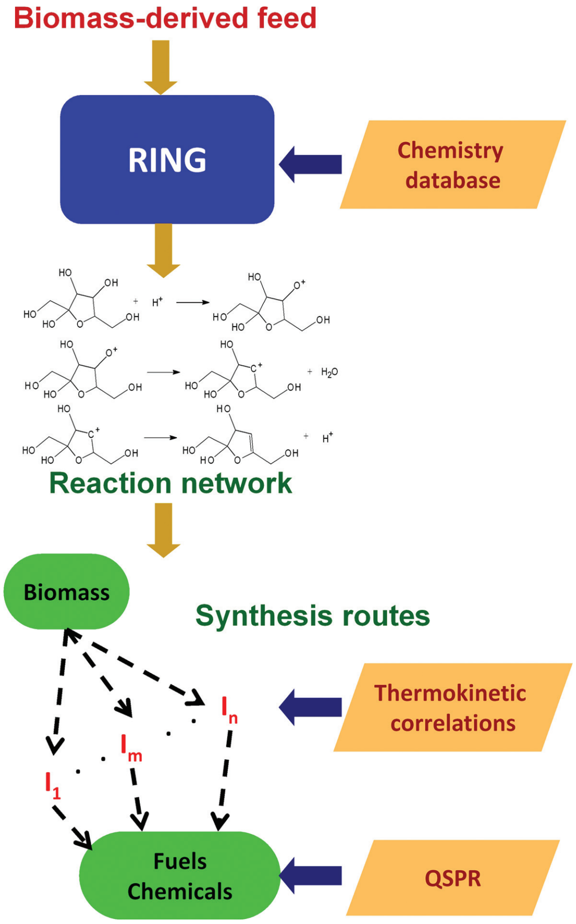

Figure 8. Framework for systematic screening of biomass-derived products and synthesis routes using RING.

semiempirical molecular property estimation to address this problem. Figure 8 depicts the framework we envision for combined product and synthesis route selection. An exhaustive reaction network, on the basis of the known/preferred chemistries, is first generated by RING. The spectrum of generated species can be evaluated for desired properties if QSPRs are available. Once the desired set of compounds has been identified, possible synthesis routes to form these molecules can be queried for in RING. Subsequently, these synthesis routes can be compared on the basis of different thermokinetic parameters such as thermodynamic bottlenecks, energy requirements, and reaction rates. Alternatively, the generated reaction network can be used in an analysis similar to that proposed by Voll and Marquardt[127] whereby optimal fluxes can be estimated. Furthermore, thermochemistry (using group additivity), kinetics (based on LFERs), and physical properties (from QSPRs) can be incorporated into an optimization problem as competing objectives. Such an approach would enable the formulation and solution of optimization problems. This would allow for formulating and solving optimization problems that seek a single product (e.g., a specialty chemical) or a blend (e.g., fuel) that can be synthesized from biomass with high rate/selectivity while satisfying all imposed product specifications.

Coupling process and enterprise design

Coupling of these two levels can help identify the most promising technologies to focus efforts on process improvement and more precise evaluation of associated process costs. Fairly accurate technoeconomic studies are available for commercialized technologies that are already competing for biomass resources. On the other hand, preliminary economic analysis of promising technologies will most likely underestimate their costs. This is especially true for uncommercialized technologies for new chemical markets. Supply chain optimization can then determine which of the promising technologies have geographical niches (i.e., locations where they are the most competitive, even compared to the fully commercialized technologies, for biomass resources and markets). Effort can then be focused on developing more accurate technoeconomic analysis of these technologies at the process level.

An example of such a coupling is local biomass processing. Supply chain concerns about the high cost to transport distributed biomass resources to a central facility have led to a movement to design small-scale units to produce fuels and chemicals that can be used locally (e.g., biomass autothermal reforming[128] with ammonia fertilizer synthesis). Combinations of local and centralized biomass processing have also been proposed (e.g., pyrolysis to bio-oil,[129] and crude fermentation to ethanol[130]). These are cases where enterprise-level concerns lead to completely new process considerations, defying conventional economies of scale that are normally assumed in fuels and chemicals production.

Beyond identifying promising technologies, enterprise-level analysis can also help in developing process performance targets. For example, the enterprise-level analysis is often used to calculate the maximum selling price of a specific fuel or chemical, thus, providing a target for the production costs at the process level analysis. Targets for other process parameters (e.g., yield and life cycle impact) can also be obtained, along with desired product distributions in the case of a multi-product biorefinery, that will balance production of low value high-volume products (e.g., fuels) with that of high value low-volume products to make the biorefinery competitive.

Software Infrastructure

The multiple levels of systems tasks discussed earlier and their integration requires specialized software infrastructure that enables decision-making across the different time and length scales involved. It is practically impossible to build a single software tool that will be able to address all the computational challenges in engineering biomass conversion processes. Furthermore, new tools and methods will continue to be developed to address these challenges, along with the requisite databases. A software architecture that allows integrating such computational tools, adding new features, and implementing custom programs in a flexible and modular manner is, therefore, essential.

Several approaches have been developed for tool integration and multiscale modeling.[131,132] Examples of such integrated computational environments in conventional process engineering applications include EPEE[133] and

CAPE—OPEN.[134,135] Computer scientists have also offered solutions for multiscale modeling, such as multiscale modeling languages (a high-level description language, with graphical and an XML representation[136]).

An alternative approach for an enabling framework is the use of extensible languages.[137] These are approaches to building programming languages in which the language is not seen as monolithic and static, but instead as a flexible and extensible combination of language features that can be swapped in and out as needed by the programmer. RING, our software for network generation and analysis, has been developed using an attribute grammar specification language SILVER[138] and a parser COPPER.[139] These tools allow general-purpose languages to be extended to include domain specific constructs. Extensions into RING for allowing network analysis exploit this extensibility feature. In a similar manner, new additions can be developed independently for tools and functions addressing other levels of computations. Although the use of domain specific languages in process engineering can be traced back to software such as MODEL.LA,[140] the proposed approach offers additional advantages—semantic analysis, domain specific optimizations, and extensibility in terms of including new syntactical and semantic features.

Concluding Remarks

Successful process engineering solutions for designing, deploying, and operating biorefineries will require addressing systems challenges at various levels. These include: elucidation of complex chemical systems for upgrading biomass in terms of mechanisms, kinetics, and thermochemistry; design of novel reactors and reactor networks; synthesis and optimization of novel flow sheets; and supply chain optimization at the enterprise level. Furthermore, the technical challenges and objectives at each level are not independent; each level provides technical feasibility constraints to the level above, and operating conditions to the level below. Thus, several problems arise where multiple levels of computations need to be integrated. The development of an overarching computational software infrastructure is, therefore, highly desirable. While existing tools and methods can be adapted to this end, opportunities abound for pursuing new strategies.

Thus, biomass conversion has created the prospect for a new industry for fuels and chemicals, and has opened up several exciting new vistas in process systems engineering. Challenges span multiple scales, ranging from the molecular level to the regional and national level. They also span diverse fields: from chemistry to economics and computer science. Central in the aforementioned is a systems perspective that enables an integrated approach in discovering new biomass conversion pathways and translating them into concrete engineering processes.

Acknowledgments

P. Daoutidis would like to acknowledge Professors A. Bhan, M. Tsapatsis, and L. D. Schmidt, who, as co-advisors of S. Rangarajan, A. I. Torres, and W. A. Marvin, respectively, have helped shape the research reported and the perspective offered in this article. Financial support from the National Science Foundation (grant CBET-0855863), the Catalysis Center for Energy Innovation (Award No. DESC00001004), an Energy Frontier Research Center funded by the US DOE, the Initiative for Renewable Energy (Large Grant: RL-0004-09) and Doctoral Dissertation Fellowships from the University of Minnesota is gratefully acknowledged.

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