PROCESS ENGINEERING OF BIOREFINERIES:
RECENT RESULTS AND NEW RESEARCH VISTAS

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Abstract

Biomass conversion is a renewable alternative to produce fuels and chemicals. Development and optimization of biorefineries involves process engineering challenges at various scales, ranging from the chemistry of the conversion processes, to reactor and process design and optimization, and to enterprise-level economic and supply chain analysis. In this article we discuss recent results in each of these levels, specifically, (a) complex thermochemical reaction network analysis using an in-house software, (b) process design and optimization for continuous production of chemicals (5-hydroxymethylfurfural) from biomass, and (c) supply chain optimization for biomass sourcing and facilities location in the mid-western US. Set in this context, we further discuss new research vistas at each level, and opportunities for advantages of integration of research tasks across multiple levels.

Keywords

Biorefineries, reactor and process design, reaction mechanism analysis, supply chain optimization.

Introduction

Biomass conversion is a prospective “green” alternative to produce fuels and chemicals. Biorefineries, akin to petroleum refineries, will convert a complex biomass feedstock in a series of chemical and physical processing steps to obtain the desired products. Although considerable emphasis has been given so far to the “upstream” conversion of biomass to intermediate platforms (sugars or syngas), progress in “downstream” conversion to chemicals and intermediates is still lagging.

Process Engineering is a mainstay in design, optimization, operation, and control of petroleum refineries. Therefore, it is also envisioned to play a key role in biorefining. Marquardt et al. (2010), for example, propose an integrated approach involving simultaneous product and process design to exploit the “rich molecular structure of biorenewables”, instead of proceeding via gasification to C1 and subsequent synthesis. This, they argue, would involve, new chemistries (low-temperature liquid-phase), technologies (low-temperature separation technologies), as well as “tailoring” new products. In another recent review, Kokossis et al. (2010) emphasize the potential value of applying systems engineering tools, such as synthesis, optimization, and modeling in the development of biorefinery processes and supply chains in both first and second generation refining. Process synthesis from a broad spectrum of feedstocks, products, and chemistries, integration of multiple processes, retrofitting the petroleum refineries, and design of supply chains featuring a decentralized network of facilities all require systems engineering solutions. Biorefining, thus, opens up new avenues in process engineering; however, several challenges, and hence, opportunities emerge.

Process engineering, conventionally, encompasses computational tasks spanning multiple time and length scales:

(a) Process chemistry - At this level, we are interested in elucidation of the chemical transformations taking place at the molecular level, and calculation of thermodynamic and kinetic parameters, typically based on atomistic or molecular simulations,
products from initial reactants, and isomer and reaction lumps. Network generation and analysis is governed by user-input rules; hence, the term rule-based. Being quick, exhaustive, versatile and flexible, RING is applicable in mechanistic analysis of complex reaction systems to get a qualitative insight into the dominant chemical transformations occurring in the system. Such an analysis, in conjunction with experimental and computational data, can help understand the system in consideration. We have applied RING to study several complex systems; we discuss one such example below for illustration.

![Figure 1: Pathways to HMF from Fructose. Shown in red is the literature-proposed pathway](image)

Fructose dehydration to 5-hydroxymethylfurfural (HMF) has received tremendous interest recently because HMF is a valuable chemical (see next section). To explore the mechanisms of fructose dehydration, we input into RING typical homogeneously catalyzed elementary steps for oxygenates–protonation (and its reverse step, deprotonation) of C=C and -OH groups, dehydration, hydride shifts, allylic rearrangement, and deprotonation to form C=O groups. We do not include steps such as cracking because under the conditions of operation, cracking is not observed. The generated network contains ~1500 reactions. Shortest pathways to HMF from furanose form of fructose were identified and are shown in Figure 1. The pathway in red was proposed by Antal et al. (1990) on the basis of experimental observations which are also satisfied by the two other pathways shown in the figure (details in Rangarajan et al., 2011). This suggests that further experimental/computational studies are required to determine the correct pathway. This example suggests the utility of RING as a tool to aid and direct experimental and computational research.

Proceeding further from a “qualitative network analysis” to a more “quantitative” analysis requires the incorporation of thermochemistry and kinetics. Subsequently, reactor-level models can be built to provide optimal reactor designs that satisfy the requirements discussed in the previous section. Predicting thermochemistry ab initio for molecules such as fructose is computationally expensive making it almost impossible to evaluate thermodynamics for an entire reaction network.
Group contributions for gas phase chemistry for small-to-medium hydrocarbons and some oxygenates are available in the literature for quick thermochemistry calculation; however, the availability and accuracy of groups to encompass the whole spectrum of biomass-derived molecules is yet to be completely addressed. Kinetic parameters of reactions of these oxygen-containing compounds also need to be estimated from experimental data and/or computational analysis. In this context, application of linear free-energy and scaling relationships for quick estimation of kinetics over a broad range of catalytic materials for certain chemistries, such as by Ferrin et al. (2009) can be very valuable. Although not accurate, these estimates can provide a means for quick screening of mechanisms. Such an analysis would be particularly valuable when applied together with the network generation and analysis feature of RING, because the network can be generated and analyzed on the basis of the kinetics in a rule-based manner.

Biomass conversion, as discussed earlier, can involve multiple chemical steps in different reactors; reactor-level designs should look at all these reactors in an integrated manner because these reactors interact with each other. The choice of the series of chemical transformations to upgrade biomass then can be made on the basis of reactor-level models of these reactor cascades. Thus, a network of interacting reactors that function as cascades involving multifunctional catalytic chemistries needs to be optimized rather than just a single reactor. Uncertainty in biomass production and distributed resources imply that distributed, yet well-connected, networks of small-scale biorefineries may be required; reactors, therefore, need to be able to handle multiple feedstocks and operate intermittently, operating at low temperatures, pressures, and high conversion.

**Process design of biomass conversion**

Process design and optimization of biorefineries for biofuels production has been the focus of several studies. For example, the National Research Council report (NRC, 2000) presents a study on the economics of producing ethanol from wood chips and Karuppiah et al. (2008) optimized the energy efficiency of a corn based bioethanol plant. On the other hand, design and optimization of biomass-to-chemicals processes remain relatively unexplored. Currently, 90% of the chemicals annually produced in the United States (NRC, 2000) are obtained from fossil sources, and it is well established that the incorporation of processes to produce these low-volume high-value chemicals will be essential to ensure the economic feasibility of the future biorefinery. Therefore, the evaluation of the possible alternatives to produce them is a key step in the development of biorefineries.

Recent work from our group (Torres et al., 2010) addressed this problem by focusing on the production of HMF. This choice is based on the fact that HMF has been recognized as a “key substance between carbohydrate and mineral oil based chemistry” (Schiweck et al., 1991) and as having “by far the highest industrial potential for a fructose based compound” (Perosa et al., 2007). In particular, HMF is the precursor of 2,5-furandicarboxylic acid (FDCA) a molecule that can be directly used as a replacement for terephthalic acid in the production of analogs of polyethylene terephthalate (PET) and polybutylene terephthalate (PBT).

HMF, produced by dehydration of fructose in aqueous medium, 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 (more details in Torres et al., 2010). Based on this approach, we developed two continuous processes for the production of HMF. The first one (Torres et al., 2010) considered a biphasic reactor coupled with a liquid-liquid extractor and an evaporator. The second one was an alternative in which we claimed that HMF recovery can be improved if reaction of fructose and separation of HMF take place in a single unit, the extractive-reactor one (Torres et al., 2011).

In both cases, 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 result was a nonlinear program whose solution was found using the GAMS interface with the solver SNOPT. The solution of the optimization problem for different extracting solvents, fructose prices, and kinetic scenarios showed that the minimum HMF cost is higher than that of its oil-derived analogue, with fructose dominating the cost. These results suggested that approaches different than solvent extraction in combination with lower fructose prices and more selective kinetics should be considered in order to further reduce the cost of HMF.

Similar studies were performed by Anex and coworkers (Patel et al., 2010 and Kazi et al., 2011). These contributions respectively address the production of HMF from fructose and its subsequent conversion into 2,5-dimethylfuran (DMF) and the production of dibutyl ketene (DBK, an important industrial solvent) from levulinic acid. Both processes were simulated using Aspen Plus and the minimum selling price (now defined as the price at which the net present value (NPV) becomes zero) were found. The results reported in these studies reinforced the idea that bio-based compounds are more expensive than their petroleum derived counterparts mainly due to a high feedstock price.

Similar approaches need to be applied to evaluate the feasibility of processes for the production of other important bio-based chemicals. As a starting point,
processes to efficiently produce those identified by DOE as the top twelve of the future chemical industry, need to be identified. Several alternatives for the synthesis of these chemicals from biomass can be found in the literature (see e.g. Corma et al., 2007). Different process flowsheets for their production can be proposed by translating these laboratory scale reaction-separation methods into large scale continuous processes.

One of the major challenges when evaluating these processes is the lack of reliable data or correlations, spanning a wide set of conditions, on physical, thermochemical, and transport properties of these bio-based compounds. In addition, data regarding chemical transformations is usually given by reporting the conversion and selectivity at which certain product can be obtained from certain feedstock. Elucidation of the chemical pathways is a very active research area, but the use of simplified kinetics (in which intermediates are neglected and by-products are lumped into single terms) or “black box” models, is still very common.

From the process design point of view, due to the fact that biomass and oil have inherently different chemical compositions, upgrading biomass involves a host of unit operations that were not considered previously for crude oil processing, and have now become relevant. As an example, biomass is non volatile and thermally sensitive, making distillation, which dominates separations of oil-based products, unsuitable. Instead, lower temperature alternatives such as solvent extraction and membrane separation need to be explored. Biomass such as lignocellulose is cheaper than other hydrocarbon sources; however, upgrading this feedstock may involve several deoxygenation and carbon-carbon bond formation steps, thereby leading to a higher overall processing cost. Process design focusing on integrating these new separation methods with new chemistries and reactors is, therefore, essential. In addition, as most bio-based products are the intermediates of consecutive reactions, processes in which reaction and separation are integrated in a single unit should be considered in order to obtain them in high yields. The development of reliable and comprehensive models for these operations is an open task.

Finally, profit maximization and selling price minimization have been the most commonly used bases to evaluate and compare different production routes. However, many of the processes to produce bio-chemicals involve the use of organic solvents or energy intensive separations. Therefore, their viability will not only depend on economic considerations but also on their sustainability and energy efficiency. Several environmental and energy impact indicators have been proposed to evaluate chemical processes (see e.g. the WAR algorithm in Cabezas et al., 1999). These indicators can be either used as a tool to rank optimal economic candidates or introduced as a second objective function in order to pursue a more ambitious multi-objective optimization approach. Introduction of these indices at the process design level is major factor that needs to be addressed.

Enterprise-level analysis

Large-scale biorefinery operation poses significant challenges for biomass and biofuel logistics. It is a computational challenge to determine how to efficiently utilize biomass resources at the enterprise level. Biomass resources, including grains, crop residues, wood, municipal waste and landfill gas, have non-uniform compositions, are geographically distributed and seasonally available. Furthermore, in the face of uncertain biofuel markets it is paramount that each enterprise make smart supply chain decisions to mitigate risk, maximize profits and reduce environmental impact. Ideally, enterprises would cooperatively install biorefineries in a region to efficiently utilize biomass and distribute biofuels. In addition, information on optimal refinery locations, overall sustainability of refining technology, and life cycle analysis is valuable to the government for imposing regulations as well as providing incentives. For example, the current US biofuel blending mandates enforced by the EPA require classifying renewable fuel based on life cycle emission using the Argonne GREET model of biofuel supply chain activities (US EPA, 2010). Optimization of the biomass-to-biofuel supply chain can then be thought of as an idealization of the true industry development, and is thus useful to local and national government to predict the effect of biofuel policy.

In a recent study (Marvin et al., 2011), we addressed the problem of determining the optimal supply chain to convert agricultural residues (barley, corn, oats and wheat) to ethanol for a region comprised of biomass producers and candidate biorefinery locations in a 9-state region in the Midwestern U.S. Agricultural residues are abundant in the Midwest (Perlack et al., 2005), making it an important region for any lignocellulosic biomass study. The objective function was to maximize the net present value (NPV) of the entire supply chain with decision variables including biorefinery construction and capacity, and biomass harvest and logistics. NPV was calculated assuming a plant lifetime of 20 years and discount rate of 10%. NPV is an important economic objective because it directly addresses the rate of return for profit seeking enterprises. County-level biomass producers were considered with annual harvest bounded by the estimated residue availability in each of the 779 counties of the region. Unit biomass transportation cost was a function of Google Maps highway transportation distances to candidate biorefinery sites. Candidate biorefinery sites were chosen based on population and adequate highway infrastructure. One biorefinery technology that converts agricultural residues into ethanol via fermentation (Humbird and Aden, 2009) was considered with multiple capacities available. Ethanol was sold on site with no logistical costs.
Mass balance constraints govern the logistical and biorefinery construction (binary) variables. The optimization problem was then written as a mixed integer linear program (MILP) and solved using IBM ILOG CPLEX. The optimal supply chain for the region is shown in Figure 2 for the base case economic and technological parameters. It was optimum to construct biorefineries in 65 of the 69 candidate biorefinery sites for a total regional capacity of 4.7 billion gallons of ethanol annually. NPV was $7.07 billion with an internal rate of return of 12.1%.

A sensitivity analysis on the optimum revealed that the biofuel supply chain is sensitive to economic and technological parameter changes. This was done by computing a new optimal supply chain after each parameter in the model was changed. For example, an ethanol sale price decrease of 5% had a negligible effect on the supply chain and a 10% decrease resulted in smaller installed biorefineries, but no biorefineries were installed above a 15% ethanol price decrease. Ethanol price stabilization through government policy would then be quite useful for this single biorefinery technology supply chain. In reality, the enterprises would have multiple competing technologies and could change operating conditions to give some flexibility to their supply chain as prices vary.

The inclusion of multiple competing technologies and additional biomass feedstocks into this optimization framework will better approximate the diversity seen in the biofuel industry, as well as provide valuable information to the process design level. It is envisioned then that this enterprise-level analysis can determine minimum “black box” process parameters targets (e.g. product slate, flexibility and yield) which must be met for a biorefinery to be competitive. Furthermore, the enterprise-level analysis provides a best-case scenario for biorefinery technology profitability and environmental impact. These could be valuable insights in the case of lignocellulosic biorefinery technologies, where there is huge uncertainty in operating costs and emissions at commercial scale. Other recent optimization studies have started to account for multiple biorefinery technologies (Schmidt et al., 2010, You et al., 2011, and Giarola et al., 2011) and transportation options to determine situations where they become competitive.

Discussion, conclusions, and future work

Successful design, development, and operation of biorefineries necessitates addressing key process engineering challenges involved at various levels: elucidation of the complex chemical processes involving a variety of chemistries, quantitative thermo-kinetic and reactor-level models, novel reactor designs using these models, process design and optimization of key biomass-derived chemicals based on economics and sustainability, and enterprise-level analysis and optimization.

In addition to challenges and opportunities at each level, biomass conversion offers significant potential for integrating multiple levels. The multiple thermochemical steps in biorefining can be coupled through kinetic and reaction coupling of oxygenates multifunctional catalysis, multi-catalytic-bed reactors, and multiple interconnected reactors (Simonetti and Dumesic, 2009). Analysis of reactor-level models in such cases cannot preclude process chemistry. The coupling of these multiple reaction cascades involves homogeneous and heterogeneous chemistry of compounds in the solid, liquid, and vapor phase, and involves chemistry of hydrophilic oxygen-containing and hydrophobic hydrocarbon molecules in multiple reaction units. The design of such reactors and reactor networks is non-trivial and profoundly affects the downstream separation processes. Process design done in conjunction with rigorous reactor-level models will be able to address these issues better. The nature, source, quantity of biomass and the local demand and supply of fuels and chemicals, optimizing locations of plants, their capacities and product slate will determine what chemistry and processes have to be adopted, and how they are to be operated and controlled. Integration of process design with enterprise-scale analysis and optimization enables the consideration of factors such as macroeconomics, policy, and infrastructure in determining the appropriate technology for process development.

Such integration requires adequate computational software support. Such support does exist for traditional refineries (e.g. software tools such as ASPEN PLUS and gPROMS). One option here is to augment the existing tools with the databases and design/optimization/control protocols as they are developed for biorefinery processes. An alternative approach is to build from scratch a new overarching framework that seamlessly allows for integration of several tools that can interact with each other and also with custom-built programs. A possible approach to building such an infrastructure is by using...
extensible languages (Van Wyk and Heimdahl, 2005). The framework, in such a case, would be a general-purpose language (like Java or C++) extended with domain-specific syntax and semantics covering the four levels of process engineering.

Biomass conversion, thus, opens up several exciting new vistas in process engineering. Challenges span a wide spectrum involving multiple length scales (from reaction kinetics to supply chains), areas and fields (from chemistry to economics and computer science), with potential for an integrated approach to address multiple problems concurrently.

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