



Process systems engineering studies for the synthesis of catalytic biomass-to-fuels strategies

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ABSTRACT

The goal of this paper is to show how chemical process synthesis and analysis studies can be coupled with experimental heterogeneous catalysis studies to identify promising research directions for the development of strategies for the production of renewable fuels. We study five catalytic biomass-to-fuels strategies that rely on production of platform chemicals, such as levulinic acid and fermentable sugars. We first integrate catalytic conversion subsystems with separation subsystems to generate complete conversion strategies, and we then develop the corresponding process simulation models based on experimental results. Our analyses suggest that catalytic biomass-to-fuel conversion strategies could become economically competitive alternatives to current biofuel production approaches as a result of iterative experimental and computational efforts.

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1. Introduction

Driven by energy challenges facing the world today, fundamental research has focused on development of technologies that offer sustainable and affordable alternatives to meet growing global energy demand while addressing environmental and social issues (Farrell et al., 2006; Hill et al., 2006; Dale, 2008). Lignocellulosic biomass offers a promising alternative to satisfy future energy demand because it is a widely abundant and a potentially carbon neutral source for producing a wide range of fuels and fuel additives (Chhedha et al., 2007; Demirbas, 2007; Alonso et al., 2012; Wettstein et al., 2012). Lignocellulosic biomass primarily consists of three polymeric components: cellulose (C₆-sugars), hemicellulose (mainly C₅-sugars) and lignin. In the last few decades, a wide range of conversion technologies have been developed for the effective utilization of each biomass fraction (Huber et al., 2006; Bozell and Petersen, 2010; Naik et al., 2010; Bond et al., 2014).

The major challenge in the conversion of biomass to liquid fuels is the effective extraction of the sugars in biomass (Mosier et al., 2005). To address this challenge, a common approach is to fractionate biomass into its components using pretreatment, including dilute acid (Humbird et al., 2011), lime (Eggeman and Elander, 2005), hot water (Tao et al., 2011), ionic liquid (Klein-Marcuschamer et al., 2011; Sen et al., 2012b, 2012c), alkaline hydrogen peroxide (Banerjee et al., 2011) and ammonia fiber expansion (Sendich et al., 2008; Bals et al., 2011). Following the pretreatment, lignin is typically used for heat and power generation via combustion (Holladay et al., 2007), while the hemicellulose and cellulose fractions can be converted to various fuels and fuel additives typically via three major routes: biochemical, thermochemical and catalytic (Anex et al., 2010). The biochemical conversion strategies, primarily based on enzymatic hydrolysis and microbial fermentation (Gnansounou and Dauriat, 2010), offer high overall biomass-to-fuel yields (50–55 mol%), but require high enzyme costs, 15–20% of the total production cost (Conde-Mejia et al., 2013). Thermochemical conversion technologies, such as pyrolysis and gasification, operate at high temperatures (pyrolysis: 573–973 K, gasification: >1100 K), thereby resulting in high energy requirements (Lange, 2007). Catalytic conversion strategies can offer advantages such as less expensive processing with high selectivity and carbon yield at milder processing conditions (Alonso et al., 2010).

Although the technologies outlined above have been demonstrated at laboratory scale, process synthesis and technoeconomic

Abbreviations: PSE, process systems engineering; LA, levulinic acid; FA, formic acid; SA, sulfuric acid; GVL, γ -valerolactone; BL, sec-butyl levulinate; BF, sec-butyl formate; BA, butyl acetate; GGE, gallon of gasoline equivalent; SBP, 2-sec-butyl phenol; NREL, National Renewable Energy Laboratory; HEN, heat exchanger network; MSP, minimum selling price; EOS, equation of state; MT, metric tons.

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evaluation are critical steps for translating these technologies into economically attractive processes (Aden and Foust, 2009; Grossmann and Guillén-Gosálbez, 2010; Pokoo-Aikins et al., 2010; Floudas et al., 2012; Stuart and El-Halwagi, 2012; Daoutidis et al., 2013; Yuan et al., 2013). Several researchers have developed methods for the development of various biorefinery configurations based on specific conversion technologies (Sammons Jr et al., 2008; Klein-Marcuschamer et al., 2010; Kokossis and Yang, 2010; Martín and Grossmann, 2011; Pham and El-Halwagi, 2012; You et al., 2012; Baliban et al., 2013; Gebreslassie et al., 2013; Kelloway and Daoutidis, 2013; Kim et al., 2013; Gong and You, 2014). In addition, several studies have focused on the techno-economic analysis of biochemical (Cardona and Sánchez, 2007; Kazi et al., 2010) and thermochemical (Mohan et al., 2006; Swanson et al., 2010; Wright et al., 2010) strategies. However, there are not many systems-level studies for catalytic biomass-to-fuels conversion technologies.

Accordingly, in this paper we present a series of studies for the synthesis and analysis of five catalytic biomass-to-fuels conversion strategies that rely on production of platform chemicals such as levulinic acid (Alonso et al., 2011; Braden et al., 2011; Gürbüz et al., 2011; Alonso et al., 2013) and fermentable sugars (Luterbacher et al., 2014). In addition to evaluating the economic potential of these strategies, we also aim to show how systems-level studies can be used in parallel with heterogeneous catalysis studies to identify the major technological bottlenecks and cost drivers, thereby pointing the way to new research directions and guide experimental research. Toward this aim, we outline our joint efforts over a period of five years (2010–2014). While many of the analyses in this paper have appeared separately in the literature, our goal here is to illustrate how the synthesis and analysis of integrated processes can lead to basic science developments which in turn were used for updated analyses, ultimately leading to iterative improvements. We hope that this exposition will illustrate the synergies between process systems engineering and heterogeneous catalysis and inspire similar research efforts.

The paper is structured as follows: in Sections 2 and 3, we describe the chemistry of the systems we study, and present five biomass-to-fuels strategies synthesized based on distinct catalytic technologies. Our chemical process design studies are summarized in Section 4. Section 5 discusses energy efficiency calculations, a topic often overlooked despite its paramount importance (since our goal is to replace fossil fuels). The results of the techno-economic evaluation are presented in Section 6. Finally, in Section 7 we discuss a series of alternatives as well as the impact of uncertainty in a subset of parameters.

2. Cellulose conversion strategies

We first explore different options for the conversion of the cellulose fraction of biomass into liquid hydrocarbon fuels (butene oligomers) via production of levulinic acid (LA) and formic acid (FA) intermediates from the sulfuric acid (SA) catalyzed deconstruction of cellulose (Fig. 1). The biomass is first pretreated using dilute acid to remove the hemicellulose fraction, then filtered. The hemicellulose is converted to solubilized xylose and subsequently used to produce heat and generate electricity, while the insoluble cellulose is further converted to hydrocarbons. Following cellulose deconstruction, the main challenge is to extract biomass-derived intermediates (such as LA, FA and γ -valerolactone (GVL)) that are at low concentrations from the SA-containing aqueous phase. Separation of SA from the intermediates is also critical to prevent its negative effects in downstream catalytic conversion processes. To this end, we developed strategies that effectively recover biomass-derived intermediates while recycling almost 100% of the SA back to the cellulose deconstruction step.

2.1. Chemistry

Levulinic acid (LA) has been identified as a versatile platform molecule for production of liquid hydrocarbon fuels, fuel additives, as well as a variety of chemicals (Bozell and Petersen, 2010). Using an aqueous SA solution (0.5 M) as a catalyst, the cellulose fraction of biomass can be deconstructed to LA and FA in a batch reactor at 473 K and 16 bar with a high yield (55 mol%), while the remaining cellulose is degraded to form humins (Serrano-Ruiz et al., 2010). Following cellulose deconstruction, the LA can be converted to GVL with near quantitative yields over a bimetallic catalyst (RuRe(3:4)/C (Braden et al., 2011) or RuSn(1:4)/C (Alonso et al., 2011) using internal hydrogen released from FA decomposition, at 493 K and 36 bar. The GVL production from LA partially reduces the oxygen content and increases the energy density while keeping sufficient functionality to produce the final fuel compounds. Braden and co-workers (Braden et al., 2011) showed that the presence of Re in the catalyst is crucial to maintain catalytic stability for GVL production in the presence of SA. Alternatively, a less expensive catalyst (RuSn(1:4)/C) can be used if the biomass-derived intermediates are extracted from the SA-containing aqueous solution prior to GVL production (Alonso et al., 2011). To eliminate the use of external solvents, Dumesic and co-workers (Gürbüz et al., 2011) suggested that LA and FA can be converted to their esters using butene, a product of the process, in a reactive extraction unit where the esters spontaneously separate from the SA containing aqueous solution by forming their own organic phase, while any remaining LA and FA are also extracted in the ester phase. In the reactive extraction unit, 60 mol% of the LA can be converted to *sec*-butyl levulinate (BL) and 49 mol% of the FA can be converted to *sec*-butyl formate (BF) at 353 K and 35 bar. Then, the BL and unconverted LA can be reduced to GVL with near quantitative yields over a dual-catalyst bed system (10 wt% Pd/C and 5 wt% Ru/C) at 443 K and 35 bar (Gürbüz et al., 2011). In the last step, GVL can be converted to a mixture of larger alkene oligomers (liquid hydrocarbon fuels) using a dual reactor conversion approach. First, the ring opening of GVL produces an isomeric mixture of unsaturated pentenoic acids, which are decarboxylated over silica alumina ($\text{SiO}_2/\text{Al}_2\text{O}_3$) forming a mixture of butene isomers and CO_2 . Finally, butene isomers can be oligomerized into larger molecular weight alkene species using a solid acid catalyst (Amberlyst-70) with near quantitative yields, leading to mixtures of gasoline and jet fuel range alkenes (Bond et al., 2010). As shown in Fig. 1, the “potential” cellulose-to-butene yield is found to be ~54 mol%. Here, “potential yield” is meant to be the maximum achievable overall yield if there would be no loss in separation subsystems.

2.2. Process synthesis

As mentioned earlier, the main challenge for the SA-catalyzed conversion of cellulose is the separation of biomass-derived intermediates from the SA-containing aqueous solution. To overcome this challenge, we synthesized three strategies that effectively extract intermediates from the aqueous solution and convert them into liquid hydrocarbon fuels. The details of the design and analysis of these strategies are presented in Sections 4–6, while the major assumptions are given in Table S2 in the supplementary content.

2.2.1. Strategy A

Strategy A is based on the catalytic system that uses RuRe/C catalyst for reduction of LA to GVL using the internal hydrogen produced from FA decomposition in the presence of SA (Braden et al., 2011) and it is shown in Fig. 2. To separate GVL from the SA solution, which was the major challenge in this strategy, we developed a multi-stage extraction process that can separate 98% of the GVL from the aqueous solution using butyl acetate (BA) as a

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