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Advanced Biofuels of the Future: Atom-Economical or Energy-Economical?

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Introduction

The transportation sector accounts for 50% of global fossil fuels consumption, leading to more than 70%, 40%, and 19% of the emitted CO, NO_X, and CO_2, respectively.[1] To curb these negative environmental impacts, the Renewable Fuel Standard (RFS) was established in 2006 demanding that transportation fuels in the United States contain an increasing volume of renewable fuels, starting from 4 billion gallons in 2006 and ascending to 36 billion gallons in 2022.[2] In 2016, cornstarch ethanol production was capped at a maximum of a 15 billion gallon contribution toward the 2022 statute, while advanced biofuels fell below the statutory target of 7.25 billion gallons in 2016, by a large margin.[3] While a further increase in bioethanol production is possible, such an increase is not compelling because the permissible 10% ethanol content in gasoline (E10) was fulfilled in 2017, and a higher ethanol content is not fully supported by the current transportation infrastructure (Blend Wall). Higher ethanol concentration requires an approval or waiver from the Clean Air Act and must meet certain specifications, such as Reid vapor pressure, before implementation.[3] Therefore, alternative types of fuels should be produced at industrial scales to meet the RFS targets. While this need is recognized, current research policies[4] identify atom-economical pathways as the most promising; and, furthermore, the fact that annual RFS requirements[2] are in terms of volume, favoring the development of strategies that lead to oxygenated fuels. Accordingly, this study aims to identify other critical factors that could become equally important in the assessment of new conversion technologies and alternative biofuels.

To this end, we consider two representative strategies: (1) a biochemical conversion to ethanol (BCE), based on the National Renewable Energy Laboratory,[5,6] with a higher technology readiness level (TRL) and (2) a catalytic conversion to alkenes (CCA), based on γ-valerolactone (GVL) biomass deconstruction and catalytic upgrading,[7,8] with a lower TRL. Specifically, we compare and contrast the impact of three different factors: (1) carbon yield, (2) heat and power requirements to run the biorefinery, and (3) fuel quality.

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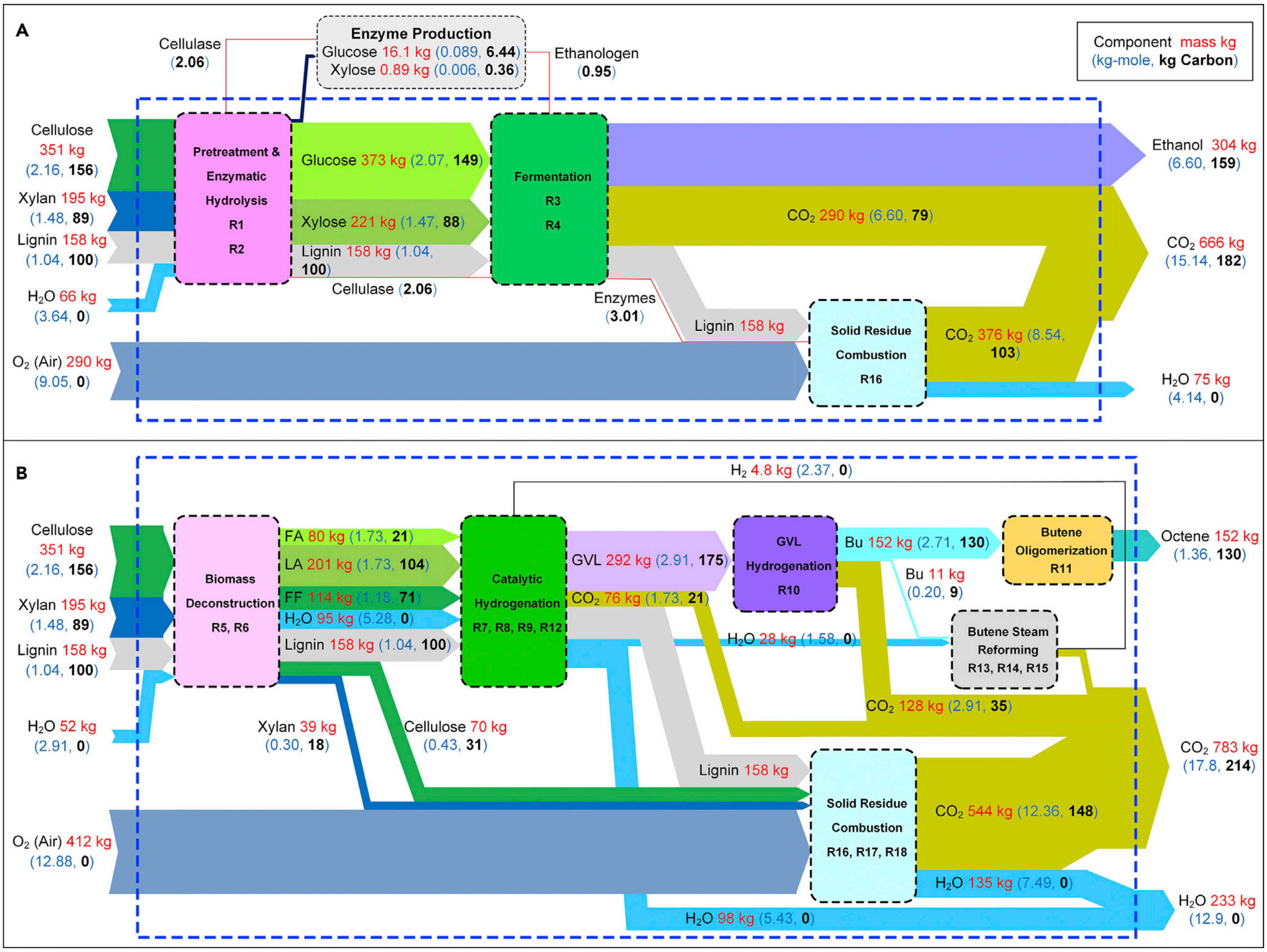

Figure 1. Material and Carbon Balance Results

(A and B) Material, molar, and carbon balance of the (A) biological conversion to ethanol (BCE) and (B) catalytic conversion to alkenes (CCA) strategies for conversion of one ton of dry corn stover.

Results and Discussion

Analyses are performed for conversion of one ton (1 Mg) dry corn stover (DCS), which contains about 35.0% cellulose, 19.5% xylan, and 15.8% lignin.[5] Detailed information about conversion assumptions and modeling approach for BCE and CCA strategies are provided in the Methods section. Ethanol and diesel fuel produced by the BCE and CCA, respectively, along with excess electricity are assumed to be consumed in an internal E100, diesel engine, and electric motor with a fuel/electricity-to-mechanical energy conversion efficiency of 20%, 30%, and 60%, respectively.[9,10]

Atom Balance and Carbon Efficiency

Figure 1 shows the results of mass, atom, and carbon balance for the two strategies. Carbon losses in the biochemical strategy are caused by CO_2 formation during sugar fermentation (R3 and R4). The main sources of carbon loss in the catalytic strategy include the formation of humins during biomass deconstruction, ring opening of GVL to form butene (R10), formic acid formation (R5) during biomass deconstruction, and steam reforming of butene (R13–R15) for hydrogen production. About 7% of the butene produced in the CCA strategy must be steam reformed to produce 4.8 kg of hydrogen for the catalytic hydrogenation. Results show that the BCE and CCA strategies conserve about 159 and 130 kg, respectively, of the carbon in the produced fuel out of 156 + 89 kg carbon that enters the process as cellulose and xylan, respectively. This is equal to a 65% and 53% biomass-to-fuel carbon efficiency for the BCE and CCA, respectively, which makes the former a more atom-economical strategy. The amount of ethanol produced in the BCE strategy is 304 kg, which is twice as much as the 152 kg of octene (Oc) produced in the CCA strategy, mainly because of the oxygen content of ethanol.

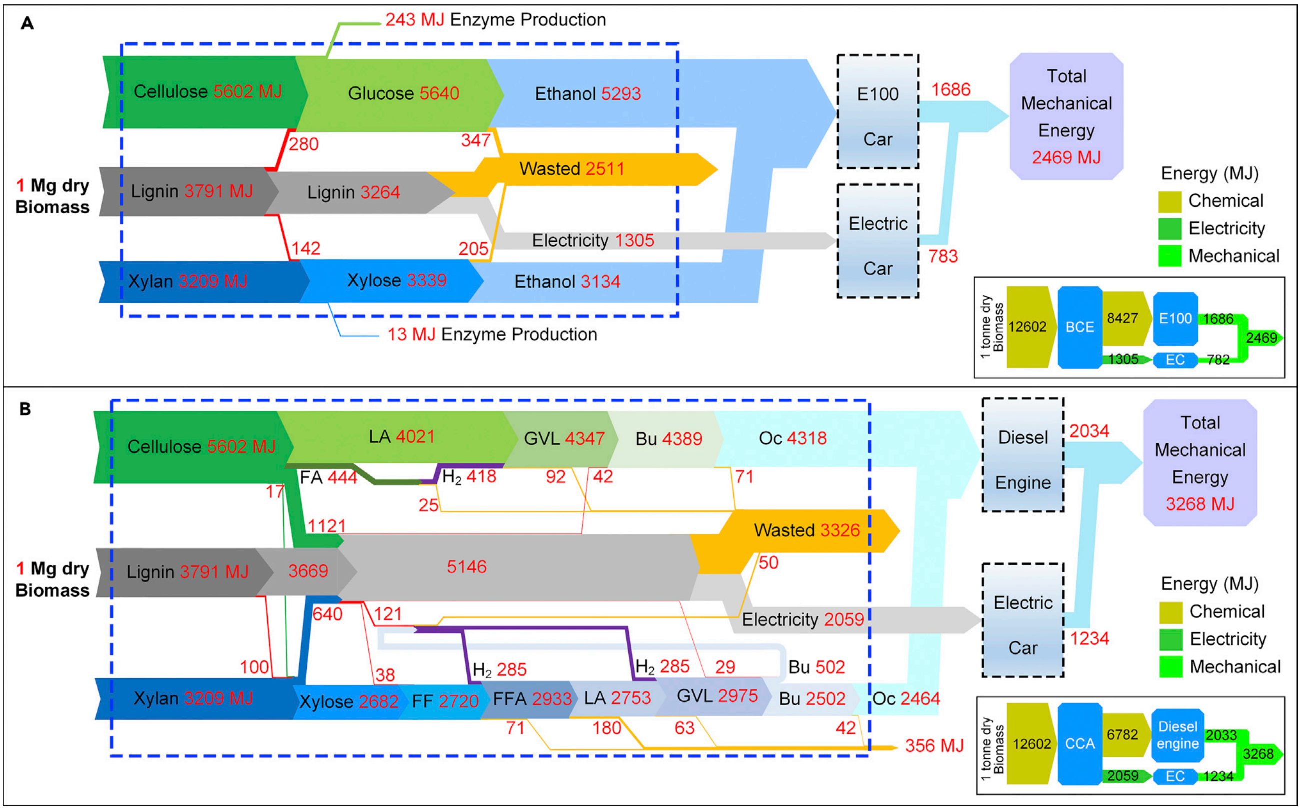

Figure 2. Energy Balance Results

(A and B) Energy balance of the (A) BCE and (B) CCA strategies for conversion of one ton dry corn stover.

Energy Balance

The results from the energy analysis are presented in Figure 2. The energy content of the fuel produced by the BCE strategy is about 8,427 MJ from a total of 8,811 MJ available in the cellulose and xylan contained in one ton of DCS. In the CCA strategy, about 10% of the energy content of cellulose is lost to formic acid formation (R5). However, about 94% of that energy is recovered as hydrogen through formic acid decomposition (R12), which provides about 42% of total hydrogen demand in the CCA. The energy content of the produced Oc is 6,782 MJ. Thus, the BCE strategy leads to about 24% more energy production, in the form of liquid fuels, than the CCA strategy. However, the larger amount of solid residues in the CCA strategy yields 2,059 MJ of electricity, which is significantly higher (58%) than the 1,305 MJ of electricity generated in the BCE strategy.

Interestingly, the mechanical energy obtained from Oc (diesel fuel) combustion is 2,034 MJ, which is about 21% more than the 1,686 MJ of mechanical energy generated from ethanol combustion. Hence, despite being more atom-economical, the BCE strategy is 17% less energy efficient, highlighting the critical role of fuel quality and engine efficiency. Furthermore, the results indicate that, if the infrastructure for widespread adoption of electric cars were available, then the advantage of the CCA strategy, in terms of total mechanical energy (from both liquid fuel and electricity) would be even bigger. Specifically, the CCA strategy would lead to 3,268 MJ of mechanical energy (1,234 MJ from electricity) compared with 2,469 MJ for the BCE strategy (783 MJ from electricity).

Importantly, we note that if results from detailed technoeconomic analysis (TEA) (see Data and Software Availability section) were used,[5,7] then BCE and CCA strategies would yield 7,142 and 5,983 MJ of ethanol and diesel, respectively, which would result in 1,427 and 1,795 MJ of mechanical energy, respectively, thereby leading to the same insights. Finally, at current state of technology, the BCE and CCA strategies have an energy return on investment of 47.1% and 37.7%, respectively, defined as energy in products (lower heating value of biofuel and electricity) over the energy in the biomass.

Methods

Modeling Basis and Assumptions

The energy assessment is performed using lower heating value of components and heat of reactions, calculated from enthalpy of formation data extracted from the component database of an Aspen Plus process simulator. Conversion data are based on the literature. To

Table 1. Reactions in the Biological Conversion to Ethanol and Catalytic Conversion to Alkenes Strategies

Strategy	Reactions	$\Delta H_{(Reaction)}$ (kJ)	Conversions Reported (%)	Conversions Considered (%)
Bioethanol Strategy[5,6]				
Acid thermal hydrolysis				
R1	xylan + H_2O → xylose	96.7	75–90	100
Enzymatic hydrolysis				
R2	cellulose + H_2O → glucose	129.1	80–90	100
Fermentation				
R3	glucose → 2 ethanol + 2 CO_2	−167.8	92–95	100
R4	xylose → 5/3 ethanol +5/3 CO_2	−139.8	85	100
Overall reactions				
	cellulose + H_2O → 2 ethanol +2 CO_2		74–86	95.8[a]
	Xylan + H_2O → 5/3 ethanol +5/3 CO_2		64–77	99.6[a]
Catalytic Strategy[7,8]				
Biomass deconstruction				
R5	cellulose → LA + FA	−9.2	61–75	80
R6	xylan → FF + 2 H_2O	127.7	56–73	80
Catalytic hydrogenation and upgrading				
R7	FF + H_2 → FFA	−60.8	90–99	100
R8	FFA + H_2O → LA	−153.3	60–80	100
R9	LA + H_2 → GVL + H_2O	−52.8	>95	100
R10	GVL → Bu + CO_2	24.0	70–99	100
R11	Bu → 1/2 Oc	−40.5	82–99	100
Formic acid decomposition				
R12	FA → CO_2 + H_2	−14.9	100	100
Overall reactions				
	cellulose → 1/2 Oc + H_2O + 2CO_2		33–74	80
	xylan + 2H_2 → 1/2 Oc + 2H_2O + CO_2		16–57	80
Butene steam reforming				
R13	Bu + 2 H_2O → 3 CH_4 + CO_2	−132.8	100	100
R14	CH_4 + H_2O → CO + 3 H_2	205.7	80	100
R15	CO + H_2O → CO_2 + H_2	−41.2	98	100
Combustion				
R16	lignin +8.5 O_2 →8 CO_2 + 4 H_2O	−3,659.7	99	100
R17	cellulose +6 O_2 → 6 CO_2 + 5 H_2O	−2,592.0	99	100
R18	xylan +5 O_2 → 5 CO_2 + 4 H_2O	−2,171.0	99	100

Components: cellulose $C_6H_{10}O_5$, xylan $C_5H_8O_4$, lignin $C_8H_8O_3$, glucose $C_6H_{12}O_6$, xylose $C_5H_{10}O_5$, LA $C_5H_8O_3$, FA CH_2O_2, GVL $C_5H_8O_2$, FF $C_5H_4O_2$, FFA $C_5H_6O_2$, Bu C_4H_8, Oc C_8H_{16}.

[a]Considering sugar loss for enzyme production.

simplify the presentation, optimistic conversions are considered (see Table 1), but the energy requirements for product recovery and purification are not considered. However, we note that the main insights and findings of this study would be identical if the analyses were based upon detailed simulation and TEA results (see Data and Software Availability section). The heat required for endothermic reactions is provided by burning lignin at 80% chemical-to-heat conversion efficiency.[9] After fulfilling heating requirements, the remaining lignin and unreacted solids are burned for steam and consequently power generation at an overall 40% fuel-to-electricity energy conversion efficiency.[9]

Bioethanol Strategy

The BCE strategy employs acid thermal hydrolysis (ATH), as pretreatment, which converts xylan into xylose sugars by adding dilute sulfuric acid (catalyst) and high pressure steam for the hydrolysis reaction (R1). The hydrolysate is cooled, diluted, and neutralized via ammonia addition. Following ATH, cellulose is enzymatically hydrolyzed by cellulases to glucose sugars for a 10 mg protein/g cellulose loading.[6] This equals to 42 kg glucose/ton of cellulose for an enzyme production yield of 0.24 kg/kg of glucose.[5] About 4% of the sugars are consumed in seed trains to produce ethanologen, a co-fermenting bacteria, which converts glucose (R3) and xylose (R4) to ethanol in fermenters. Fermentation products are concentrated using two distillation columns, and dehydrated to 99.5% ethanol by molecular sieves adsorption. Solid fermentation residues are recovered and sent to a combustor to produce heat for steam and power production.

Catalytic Strategy

The catalytic strategy employs GVL and small amounts of sulfuric acid to fractionate biomass into cellulose, hemicellulose, and lignin. Cellulose is converted to glucose, 5-hydromethoxyfurfural, and an equimolar mixture of levulinic acid (LA) and formic acid (FA) (R5). Hemicellulose is converted to xylose and then to furfural (FF) (R6), while the remaining cellulose and xylan form humins. Biomass deconstruction is the limiting step with a 61%

cellulose-to-LA (R5) and 56% xylan-to-FF (R6) conversions.[7] Solid residues, including humins and lignin, are separated and used to produce heat and power. In the first catalytic upgrading stage, FF is hydrogenated to furfuryl alcohol (FFA) (R7), and then FFA is catalytically hydrolyzed to produce LA (R8). Consequently, LA is catalytically hydrogenated to produce GVL (R9) using hydrogen from formic acid decomposition (R12) and steam reforming of a small fraction of butene oligomers produced downstream.[11] The reforming reactors include a prereformer to convert butene to methane (R13), a primary reformer (R14), and a shift reactor (R15) (see Table 1). The produced GVL is partly recycled to the biomass deconstruction reactor and the rest is catalytically converted to a mixture of butene oligomers using two consecutive gas-phase tubular reactors.[8] In the first reactor, butene isomers are produced by decarboxylation of unsaturated pentanoic acid isomers generated from GVL ring opening (R10). In the second reactor, butene mixtures are oligomerized over a solid acid catalyst to produce longer chain alkene hydrocarbons (R11). The operating conditions, residence time, and catalyst could be controlled to yield diesel range fuels, which, in this analysis, are represented by Oc.

Data and Software Availability

Additional results and analyses, based on detailed simulations of processes based on the BCE and CCA strategies, can be found at: http://maravelias.che.wisc.edu/wp-uploads/2018/08/Supplementary-data-Joule-Future-Energy.pdf.

Conclusion

The analysis reported herein showed that, contrary to conventional wisdom, seeking atom-economical biomass-to-fuels strategies may not necessarily be the optimal objective toward the development of the next-generation biofuels. Specifically, it was shown that a more energy-efficient strategy leading to higher quality biofuel can be better than a strategy that is more atom-economical. In general, it was shown that there are three major drivers affecting the overall efficiency of a biofuel strategy: (1) carbon yield, (2) process energy requirements, which indirectly determine excess electricity production, and (3) biofuel type and quality, which determine the engine efficiency and thus fossil fuel displacement. The three aforementioned drivers should be considered simultaneously toward the selection of alternative biofuels and development of new biofuel strategies.

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AUTHOR CONTRIBUTIONS

Conceptualization, P.F. and C.T.M.; Methodology, P.F. and C.T.M.; Software, P.F.; Formal Analysis, P.F.; Investigation, P.F. and C.T.M.; Visualization, P.F.; Writing – Original Draft, P.F. and C.T.M.; Writing – Review & Editing, P.F. and C.T.M.; Supervision, C.T.M.; Project Administration, C.T.M.; Funding Acquisition, C.T.M.

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