

Techno-economic analysis and life-cycle assessment of cellulosic isobutanol and comparison with cellulosic ethanol and n-butanol

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Abstract: This work presents a detailed analysis of the production design and economics of the cellulosic isobutanol conversion processes and compares cellulosic isobutanol with cellulosic ethanol and n-butanol in the areas of fuel properties and engine compatibility, fermentation technology, product purification process design and energy consumption, overall process economics, and life cycle assessment. Techno-economic analysis is used to understand the current stage of isobutanol process development and the impact of key parameters on the overall process economics in a consistent way (i.e. using the same financial assumptions, plant scale, and cost basis). The calculated minimum isobutanol selling price is \$3.62/gasoline gallon equivalent (\$/GGE) – similar to \$3.66/GGE from the n-butanol process and higher than \$3.26/GGE from the cellulosic ethanol conversion process. At the conversion stage, the n-butanol process emits the most direct CO₂, at 26.42 kg CO₂/GGE. Isobutanol and ethanol plants have relatively similar CO₂ emissions, at 21.91 kg CO₂/GGE and 21.01 kg CO₂/GGE, respectively. The consumptive water use of the biorefineries increases in the following order: ethanol (8.19 gal/GGE) < isobutanol (8.98 gal/GGE) < n-butanol (10.84 gal/GGE). Field-to-wheel life cycle greenhouse gas (GHG) emissions for the ethanol and n-butanol conversion processes are similar at 4.3 and 4.5 kg CO₂-eq/GGE, respectively. The life cycle GHG emissions result for the isobutanol conversion process is 5.0 kg CO₂-eq/GGE, approximately 17% higher than that of ethanol. The life cycle fossil fuel consumption is 39 MJ/GGE for n-butanol, 43 MJ/GGE for ethanol and 51 MJ/GGE for isobutanol. The energy return on investment for each biofuel is also determined and compared: isobutanol (2.2:1) < ethanol (2.7:1) < n-butanol (2.8:1). © 2013 Alliance for Sustainable Energy, LLC. Biofuels, Bioproducts and Biorefining published by John Wiley & Sons Ltd on behalf of Society of Chemical Industry.

Supporting information may be found in the online version of this article.

Keywords: techno-economic analysis; isobutanol; biofuel; lignocellulosic feedstocks; integrated process; life cycle assessment

Introduction

Record-high oil prices, concerns about the environment, and energy security have encouraged the production of chemicals and fuels from domestic renewable resources. The primary biofuel for the gasoline market has historically been ethanol produced from corn. However, a number of drawbacks have been identified with ethanol use: it has a lower energy content compared to gasoline, it is not amenable to pipeline distribution, and the amount that can be blended into gasoline for use in conventional vehicles is limited by environmental regulations and engine compatibility. Higher molecular weight alcohols such as n-butanol and isobutanol have higher energy content and should be more amenable to pipeline distribution. They can be produced from either thermochemical pathways (such as synthesis gas to mixed alcohols) or biochemical pathways (such as fermentation).

Historically n-butanol has been produced by *Clostridia* in acetone-butanol-ethanol (ABE) fermentation processes.¹ *Clostridia* have a broad substrate range capable of completely utilizing glucose, fructose, mannose, sucrose, lactose, starch, and dextrin.² Other sugars including xylose, arabinose, raffinose, and mannitol also are at least partially utilized by these strains. Hexose sugars are metabolized via the Embden-Meyerhof pathway, and pentose sugars are metabolized via the pentose phosphate pathway. *Clostridium beijerinckii* produces solvents in approximately the same ratio as *Clostridium acetobutylicum* does, but isopropanol is produced in place of acetone. These strains are spore-formers and obligate anaerobes with relatively simple growth requirements. Ramey and Yang³ have also been successful in producing higher butanol yields by separating the fermentation into two steps: an acidogenesis phase and a solventogenesis phase, where different organisms are used during each phase.

Isobutanol is produced at very low levels by some native bacteria and yeasts. Recently, Liao and coworkers used an engineered *Escherichia coli*^{4,5} with the introduction of the last two reactions of the Ehrlich pathway to produce isobutanol and reached titer up to 18 g/L. However, isobutanol producing *E. coli* also formed acetate as the major co-product as a result of carbon imbalance of overfeeding, under aerobic conditions. This strategy for the production of isobutanol also has been implemented in *Bacillus subtilis* and *Corynebacterium glutamicum*.⁶ Similarly, a significant level of by-product, such as acetate, is also formed under aerobic conditions. Some success of improvement of the isobutanol tolerance to higher titer was achieved to 21g/L with yield of 76% of theoretical maximum in

99 h.⁷ However, due to the broad mechanisms of toxicity, tolerance to isobutanol is a complex trait and remained challenge for further improving solvent titers with these engineered microorganisms.⁷⁻⁹ An *E. coli* strain improved by complete removal of the pathways' dependence on NADPH can now produce isobutanol anaerobically and at 100% theoretical yield,¹⁰ although the isobutanol concentration is still low in the fermentation broth. Another recent example of anaerobic production of isobutanol using engineered *E. coli* produces isobutanol but with ethanol as a co-product.¹¹

In addition to challenges to fermentation strain development, product purification is a major step and an engineering barrier for the production of biobutanol. Little comparison has been done for purification of biofuels derived from fermentation broth, such as ethanol, isobutanol, and n-butanol. Energy consumption and complexity of the purification process could be an additional technical barrier to large-scale production. The butanol separation techniques include adsorption, liquid-liquid extraction, pervaporation, reverse osmosis, and gas stripping. Due to low concentration of solvents in the fermentation broth, simultaneous fermentation and product removal techniques (such as online gas stripping or vacuum flashing) have been developed extensively and found to be cost effective by improving both separation efficiency and fermentation yields.^{2,12-15} These separation technologies are discussed in the companion paper,¹⁶ along with options that can be combined with simultaneous fermentation for better yield and economics. After the process step of simultaneous fermentation and separation, a product recovery unit is used to purify butanol and by-products to high purities, typically including several distillation columns, extractive columns, or decanters. The butyric acid typically ends up in the butanol product as a trace amount, making this biofuel stream release an unpleasant odor and potentially damaging the fuel properties of butanol, making it unusable as a transportation fuel. Therefore, optimization of the beer column operation is a necessary step for future work. Energy demand for the reboiler is dramatic because it requires vaporizing all of the value-added solvents to promote further separation. This study provides an engineering understanding of the purification process and its impact on overall process cost.

With the rapidly increasing interest in biofuels and the advancement of new biotechnology methods and tools, numerous companies are developing 'biobutanol' production processes. Gevo, Inc. registered isobutanol in the US Environmental Protection Agency's (EPA) Fuel Registration Directory and it is now approved for blending

with gasoline.¹⁷ Gevo broke ground on its first plant on May 31, 2011, in Luverne, Minnesota.^{18,19} Chevron Oronite and Cobalt Technologies' n-butanol was registered with EPA.^{17,20} In 2009, Butamax Advanced Biofuels LLC, a joint venture created by BP and DuPont, was formed to develop biobutanol technology. The company will demonstrate production of bio-butanol at a technology demonstration plant in the UK.²¹

Limited reports have appeared on commercial-scale techno-economic analysis (TEA) of n-butanol production,^{16,22,23} but essentially no one has reported a detailed TEA of isobutanol production from cellulosic materials. The success of the biofuels industry depends not only on economic viability but also on environmental sustainability as assessed by life cycle assessment (LCA). Few LCA studies on the production of biobutanol are available in literature, and the majority focus on corn-based biobutanol rather than on cellulosic biobutanol.^{24,25} As the biofuels industry develops, TEA coupled with LCA will play a key role in process development and targeting of technical, economic, and environmental barriers for these new fuels and feedstocks.

Here we compare production of cellulosic ethanol, n-butanol, and isobutanol in a consistent way (i.e. using the same financial assumptions, plant scale, cost basis, etc.). We compare not only process economics, but also product purification process design and energy consumption, fermentation process technologies, and LCA of various environmental sustainability indicators, including energy return on investment (EROI), GHG emissions, global warming potential (GWP), selected criteria air pollutants (CAPs), consumptive water use, and fossil energy consumption.

Properties of iso- and n-butanol as fuels

Table 1 lists some of the key properties of isobutanol, n-butanol, and ethanol. The properties of conventional gasoline are presented for comparison. Compared to ethanol, n-butanol and isobutanol exhibit nearly 30% higher volumetric energy density, allowing butanol to qualify for 30% more credit under the United States Renewable Fuel Standard law, assuming life cycle GHG emission requirements are met. Butanol's higher energy density also benefits consumers by increasing vehicle driving range to a level very close to that achievable using petroleum-derived gasoline.

Compared to ethanol, these butanol isomers are less soluble in water and hold less water in solution. A small

Table 1. Comparative fuel characteristics.^{26,54}

	N-butanol	Isobutanol	Ethanol	Gasoline
Energy density (MJ/L)	26.9	26.6	21.4	30–33
LHV (MJ/kg)	33.2	33.1	26.8	41–44
Research octane number	96	106	110	88–98
Motor octane number	84	90	90	80–88
Heat of evaporation (MJ/kg)	0.71	0.69	0.92	0.36
Reid vapor pressure (kPa)	2.2	3.3	16	54–103
Boiling point (°C)	117.7	107.9	78	27–225
Solubility at 20°C			miscible	negligible
% wt in water	7.7	8.7		
% wt water in	20.1	20		
Kinematic viscosity @ 20 °C (mm ² /s)	3.6	8.3	1.5	0.37–0.44
Lower flammability limit concentration, vol %	1.4	1.7	3.3	1.4
Upper flammability limit concentration (vol %)	11.3	11.8	19	7.6
Flash point (°C)	37	28	13	–43
Autoignition temperature (°C)	340	415	363	250–300

amount of water is soluble in 10% ethanol-gasoline blends. If water is present above the saturation level of a few tenths of a weight percent, the blend will separate into two phases: an ethanol-water phase and a hydrocarbon-ethanol phase. Even if the ethanol-gasoline blend is a single phase at room temperature, it could separate at colder temperatures. While phase separation is extremely rare in the modern fuel distribution system, should it occur the hydrocarbon-ethanol phase may no longer meet the requirements for use as gasoline. Because butanol is less soluble in water, a butanol-gasoline mixture may be less susceptible to phase separation. This was confirmed by Christensen *et al.*²⁶ who measured the tendency of oxygenate-gasoline blends to absorb water and phase separate at ambient temperature. In their experiment, using a 10:1 gasoline to water volume ratio, nearly 50% of the ethanol was extracted into the water while only about 5%

of n-butanol or isobutanol was extracted. Butanol producers have claimed that this improved tolerance of water will allow butanol-gasoline blends to be transported by pipeline, but this does not appear to have been demonstrated.

Isobutanol has significantly higher research and motor octane numbers than n-butanol does, but both have lower octane numbers than ethanol. In the United States today a large fraction of the gasoline is blended using what is known as a suboctane hydrocarbon blendstock. This material does not meet the minimum octane number requirement until blended with 10% ethanol. Christensen *et al.* showed that in many cases isobutanol (and in all cases n-butanol) will not have adequate octane for the final blend to meet minimum octane number requirements.²⁶ Gasoline vapor pressure is regulated to limit emissions of unburned fuel by evaporation from the fuel tank and engine fuel system. While all three alcohols have much lower vapor pressure than gasoline in neat form, they affect gasoline blend vapor pressure differently. Blending ethanol at levels below about 60 volume percent causes a significant increase in vapor pressure. For 10% blends, this increase is about 7 kPa, as shown in Fig. 1(a). On the other hand, both butanol isomers cause gasoline vapor pressure to go down by about 7 kPa in the 12% to 15% blend range. This is a major advantage of butanol blending that could significantly reduce the cost to produce low vapor pressure gasoline for summer use and allow blending of significantly larger amounts of lower value, high vapor pressure hydrocarbon components in winter months. A related issue is the effect of the alcohols on the gasoline distillation curve. In the United States, ASTM D4814 places limits on the 10%, 50%, and 90% distillation temperatures to ensure acceptable drivability. As shown in Fig. 1(b), blending of ethanol causes a significant depression in the 50% boiling temperature, and reformulation of the hydrocarbon blendstock may be required to meet the standard requirements. The butanol isomers have little or no effect on the 10%, 50%, and 90% distillation temperatures.

None of the alcohols meets the minimum performance requirements specified for automotive spark-ignition engine fuel (ASTM D4814) and thus cannot be used as neat fuels. In the USA, butanol blends with gasoline are considered legal fuels (i.e. substantially similar to gasoline) at up to 2.7 wt% oxygen (about 12.5 vol% butanol) or at up to 3.7 wt% oxygen (about 15.4 vol% butanol) if certain corrosion inhibitor additives are included as required by EPA rulemaking.²⁷ This means that butanol will not affect the long-term durability of emission control systems at these blend levels. Additional environmental requirements are fuel registration and health effects testing. As noted,

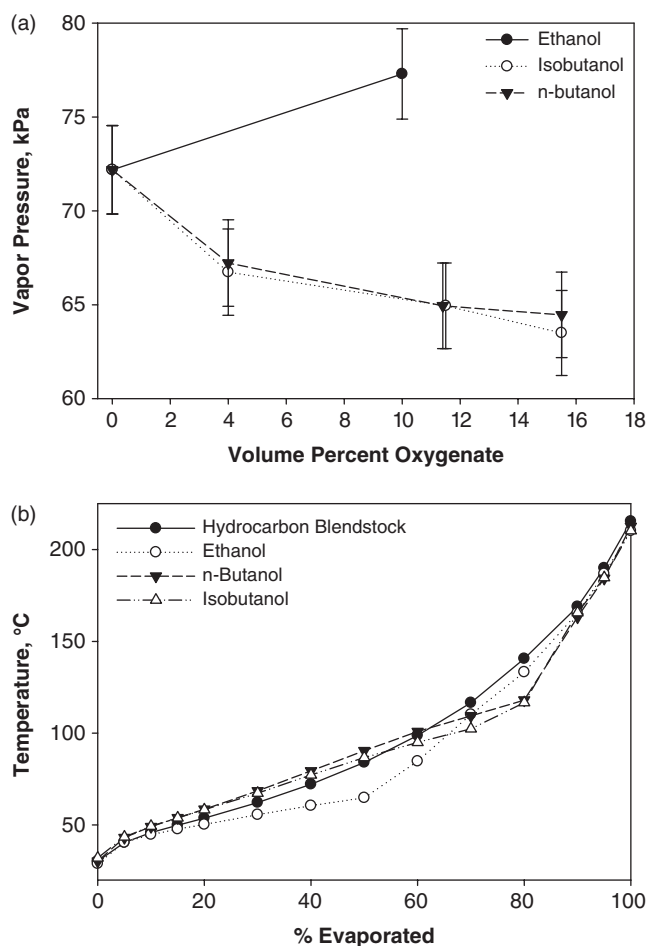


Figure 1. (a) Effect of alcohols on gasoline vapor pressure (dry vapor pressure equivalent, ASTM D5191). Data from Christensen *et al.* (26) (b) Effect of alcohols on gasoline distillation curve; note the significant depression of T50 for ethanol. Data from Christensen *et al.* (26).

Gevo, Inc. has registered isobutanol as a small business and is working to complete Tier 1 and Tier 2 health effects testing requirements.²⁸ Ethanol blends up to 10 vol% (3.7 wt% oxygen) are allowed for all spark-ignition engines and recently, the EPA has allowed 15 vol% ethanol for use in automobiles and light trucks of model year 2001 and newer. The required properties of ethanol for use as a blend component are described in ASTM standard D4806. The ASTM Petroleum Products Committee is currently developing a butanol blendstock standard.

Little if any public data are available on the effect of butanol on modern automobile tailpipe emissions. In a now classic 1982 study, Furey and King tested a 2:1 mixture of methanol and butanols at concentrations of 10% and 18% in four cars – one with an open-loop system and three with closed-loop systems.²⁹ The alcohol mixtures reduced carbon

monoxide at both concentrations in all four cars. NO_x and hydrocarbon (HC) emissions results were mixed, with no consistent trend, and differences in HC emissions between the alcohol blends and pure gasoline were less than 7% in all cases. Emissions testing studies of the most modern Tier 2 vehicles using butanol gasoline blends are very limited. NREL have recently measured emissions from a Tier 2 Bin 5 emission level car and found that for iso- and n-butanol unburned alcohol emissions were only 20% of the level observed for ethanol. However, emissions of butyraldehyde were significantly higher from the n-butanol blends, while emissions of acetone, 2-methyl propanal, and methacrolein were significantly higher from the i-butanol blends (NREL, unpublished results). Additionally, little or no data are available on evaporative emissions effects, which in modern cars could represent up to 50% of all emissions.³⁰ However, recently Kimua *et al.* have shown reduced permeation emissions for isobutanol blends relative to ethanol blends.³¹

One of the major concerns of using alcohol-gasoline blends is combustion enleanment. This is less of an issue for engines equipped with closed-loop fuel control systems because fuel quantity is automatically adjusted to operate near stoichiometric conditions. However, for legacy vehicles, marine, motorcycle, and small non-road engines that use fixed calibration fuel delivery systems (e.g. conventional carburetors) and fixed ignition timing, combustion enleanment with oxygenated fuels could increase exhaust gas and engine component temperatures to levels that could damage the engine. Because butanols have a lower oxygen-to-carbon ratio than ethanol does, they could cause fewer combustion enleanment problems at the same volumetric blending levels.

Material compatibility is another issue that needs to be addressed. Engine components that come in contact with fuel, including fuel lines, fuel tanks, fuel pumps, fuel injectors, carburetors, pressure regulators, valves, o-rings, and gaskets, should be evaluated. The compatibility of these components with ethanol blends is well known, as flex fuel vehicles compatible with up to 85% ethanol have been produced for many years. Although butanols are considered to be less corrosive than ethanol, corrosion was observed in the crankshaft main bearing after n-butanol testing in cold conditions.³² More research needs to be conducted in this area.

Methods

Techno-economic analysis

Process economics analysis includes a conceptual level of process design to develop a detailed process flow diagram

(based on research data); rigorous materials and energy balance calculations (via commercial simulation tools, Aspen Plus); capital and project cost estimation (CAPEX and OPEX, via an in-house model using spreadsheets); a discounted cash flow economic model; and the calculation of a minimum butanol or ethanol selling price.

The process for monomer sugar production from cellulosic biomass is independent of how the sugar is subsequently processed. Therefore, we adopted the cellulose-to-sugar section of the updated NREL biochemical cellulosic ethanol model³³ as a basis for design and modeling of the corn stover-to-isobutanol process. Fermentation and product separations were redesigned to be suitable for butanol production. Literature data and assumptions were used to establish the fermentation yield basis. The conceptual process design, illustrated in Fig. 6 of the companion paper,¹⁶ adapted front-end processing as well as part of the back-end processes of wastewater treatment and combined heat and power from the NREL 2011 design.³³ The design of the conceptual process and operating conditions for major process steps can be found in the NREL 2011 design³³ and in the supplementary materials.

The OPEX calculation for the designed facility was based on material and energy balance calculations using AspenPlus process simulations.³⁴ Raw materials included biomass feedstocks; pre-treatment and neutralization chemicals; nutrients; and wastewater treatment chemicals and polymers. Raw material unit costs were listed in the companion paper.¹⁶ All costs were in 2007 US dollars.

Material and energy balance and flowrate information was used to size equipment and to calculate CAPEX. Capital costs were primarily based on detailed equipment quotations from the NREL 2011 design model for corn stover-derived ethanol. The scaling exponent for the power law was obtained from the NREL 2002 and 2011 design cases^{33,35} for most of the equipment. For equipment not listed in the NREL design cases and for which vendor guidance was not available, the exponent term was assumed 0.6. Standard NREL factors^{33,35} were used to obtain the total project investment from the purchased equipment costs. For conceptual analyses of this type, factored equipment estimates were used to project the total project investment based on the calculation of total capital investment (TCI). A Lang factor (ratio of TCI to the total purchased equipment costs) of 1.8 was used in this study.

Using published engineering methods,³⁶ we generated a discounted cash flow rate-of-return analysis (DCFRROR) using capital and operating cost data. The method for the discounted cash flow calculation in this study assumed 40% equity financing and three years' construction plus

0.25 years start-up. The plant life was assumed to be 30 years. The income tax was 35%. Working capital was 5% of the fixed cost investment. The minimum butanol selling price (MBSP) is the minimum price that the butanol must sell for in order to generate a net present value of zero for 10% internal rate-of-return. The TEA results for cellulosic ethanol were taken from the 2011 NREL design report,³³ not performed in this study.

It should be emphasized that uncertainty exists around conceptual cost estimates such as these, and these values are best used in relative comparison against technological variations or process improvements. Use of absolute values without detailed understanding of the basis behind them could be misleading. We used single-factor sensitivity analysis in the study to capture effects of yields on MBSP to address part of this issue.

Life cycle assessment

The focus of this LCA study was to compare three conversion pathways for converting corn stover to liquid cellulosic biofuels (i.e., isobutanol, n-butanol, and ethanol). SimaPro v.7.3 LCA modeling software³⁷ was used to develop and link unit processes. The Ecoinvent database³⁸ was used for materials and processes that were not developed by the authors. Life cycle inventory data for the conversion processes were based on process modeling outputs from AspenPlus. The LCA modeling approach and assumptions in this study were based on those developed by Hsu *et al.*³⁹ The authors described their methodologies in the paper and they also supplied detailed information describing the construction of the LCA models as well as key parameters for each life cycle stage in the Supporting Information section of the paper.³⁹ Thus, only succinct descriptions of the methodologies are presented here. In addition to using SimaPro to quantify the life cycle GHG emissions and fossil energy demand, AspenPlus was used to estimate direct CO₂ emissions, consumptive water use, and select CAP emissions (NO₂ and SO₂) at the conversion stage. EROI and net energy value (NEV) were also calculated.

The boundary for this LCA study was from field to wheel including embodied energy and material flows. The functional unit for GHG emissions was 1 km traveled by a flex-fuel passenger car (FFV) operated on neat cellulosic biofuels produced in the year 2020. Because the upstream and downstream portions of the conversion processes were identical for the three cellulosic biofuels, the life cycle matrices were also calculated on a gasoline gallon equivalent (GGE) basis. Credits associated with co-products produced at the biorefinery were also quantified.

The corn stover feedstock was assumed to be the co-product of corn grain production. The share of environmental burdens associated with the corn stover production was allocated using the 'product-purpose' approach.⁴⁰ With the product purpose allocation method, all environmental burdens associated with corn grain production were assigned to the corn grain. Any additional burdens required to harvest the stover (e.g. additional nutrient replacement) were assigned to the corn stover. Table 2 shows the key parameters for corn stover production in the SimaPro model. Corn stover was transported from the field to the plant gate via truck for 61 km.

Table 3 lists the key parameters associated with the conversion stage. Neither cellulosic isobutanol nor ethanol process plants were assumed to make any liquid co-product. However, during cellulosic n-butanol production, the biorefinery also produced acetone and ethanol. Ethanol was a liquid fuel and acetone was considered as a chemical solvent and feedstock. Both co-products were treated as an avoided product using the product displacement method.⁴¹ Co-product displacement (also termed *system boundary expansion*) is based on the concept of displacing the existing product with the new product. Cellulosic acetone was considered as a renewable chemical. One kg of acetone produced from the n-butanol process was assumed to displace 1 kg of acetone from petroleum-based production. Similarly, 1 kg of ethanol from the n-butanol process displaced 1 kg of corn ethanol (Table 4). The fossil energy consumption and emissions released during production of petroleum-based acetone and corn grain-derived ethanol were obtained from the Ecoinvent database and are shown in Table 4.

All three biorefineries generated excess electricity. One scenario assumed that the excess electricity could be sold to the grid, providing a co-product credit. Applying the co-product displacement method,⁴¹ the excess electricity co-product displaced an equivalent amount of grid electricity, thus avoiding a significant amount of GHG emissions,

Table 2. Key parameters for corn stover production.

Parameters	Values
Corn stover yield (dry t/ha)	5.38
Dry matter loss during harvesting (%)	5.00
Nitrogen application (kg N/t of stover removed)	9.00
Phosphorus application (kg P ₂ O ₅ /t of stover removed)	0.99
Potassium (kg K ₂ O/t of stover removed)	15.0
N ₂ O conversion rate of N fertilizer (%)	1.33
Harvest moisture (%)	20.0

Table 3. Key parameters for corn stover conversion.

	Ethanol	Isobutanol	N-butanol
Conversion outputs			
Biofuel yield (L/DMT)	330	242	200
Co-product outputs			
Acetone (L/DMT)	–	–	8.09
Ethanol (L/DMT)	–	–	35.8
Electricity export (kWh/MJ)	0.023	0.020	0.025
Conversion inputs (consumption)			
Sulfuric acid (g/MJ)	3.37	3.50	4.29
Ammonia (NH ₃) (g/MJ)	1.79	1.86	2.27
Corn steep liquor (CSL) (g/MJ)	1.97	2.04	2.50
Diammonium phosphate (g/MJ)	0.24	0.25	0.31
Caustic soda (NaOH) (g/MJ)	3.83	3.99	4.88
Lime (CaOH) (g/MJ)	1.52	1.61	1.97
Enzyme loading (g/MJ)	23.5	24.4	30.0
Sugar for enzyme production (g/g enzyme)	0.17	0.17	0.17
NH ₃ for enzyme production (g/g enzyme)	0.01	0.01	0.01
CSL for enzyme production (g/g enzyme)	0.01	0.01	0.01

assuming an average US electricity grid mixture. The GHG credit attributed to the displacement of an average US electricity grid mixture was 0.78 kg CO₂-eq/kWh, as defined by Ecoinvent. However, it is not clear whether power companies would be willing to buy the excess electricity generated from cellulosic biorefinery. Thus, a second scenario assumed that the excess electricity would not be sold to the grid and thus there were no co-product credits for avoided GHG emissions and fossil energy consumption.

The fuel distribution stage included transportation of the product from the biorefinery to the pump. This LCA study was designed to directly compare the conversion of corn

stover into ethanol, isobutanol, and n-butanol for vehicle use. Therefore, only neat biofuels were evaluated, eliminating any gasoline or denaturant blending. Each mode of transportation was assigned different allocations along the various stages between the biorefinery and the refueling station, based on the work by Hsu *et al.*,³⁹ depicted in Fig. 2. Each respective transportation process was incorporated into the SimaPro model.

For the vehicle operation stage, an FFV using neat ethanol, isobutanol, and n-butanol was modeled, with average on-road fuel economy and GHG emissions as projected for 2020 by Argonne National Laboratory's GREET software.⁴² Other life cycle impacts related to the vehicle, such as manufacture, servicing, and end-of-life, were not included. The FFV efficiency in 2020 was 27.2 miles per gasoline gallon equivalent or 2.74 km/MJ. For comparison, the fuel economy and GHG emissions from an average U.S. passenger car consuming conventional gasoline in 2005 were also modeled based on GREET.

EROI was also determined. EROI was calculated as the ratio of energy in the biofuel to the total energy consumed to produce the biofuel.^{43,44} Note that EROI is also termed net energy analysis and should not be confused with NEV. NEV was calculated by summing the lower heating values of the biofuel products (ethanol, isobutanol, or n-butanol) and subtracting the cumulative amount of energy demanded from fossil, nuclear, and renewable sources.^{39,45} For both EROI and NEV, the energy content of avoided products such as electricity and acetone was included by way of the product displacement method.

Results

Base design of cellulosic isobutanol

Process design

The corn stover isobutanol process design includes feedstock handling and storage, product purification, wastewater treatment, lignin combustion, product storage, and

Table 4. GHG emissions and fossil energy consumption for producing petroleum-based acetone and corn grain-derived ethanol as well as US electricity grid as modeled in SimaPro.

	GHG emissions	Fossil energy	Displacement factor
Petroleum-based acetone	2.22 kg CO ₂ -eq/kg	64.8 MJ/kg	1 kg of cellulosic acetone displaces 1 kg of petroleum-based acetone
Ethanol from corn grain	2.05 kg CO ₂ -eq/kg	20.8 MJ/kg	1 kg of cellulosic ethanol displaces 1 kg of corn-based ethanol
Average US electricity mix*	0.78 kg CO ₂ -eq/kWh	9.08/kWh	1 kWh of electricity from biorefinery displaces 1 kWh of US average grid electricity

* Coal (47%), natural gas (17%), Oil (3.3%), nuclear power (20%), biomass (1.1%), wind (0.35%), solar (0.015%), hydroelectric (8.2%), and others (2.5%).

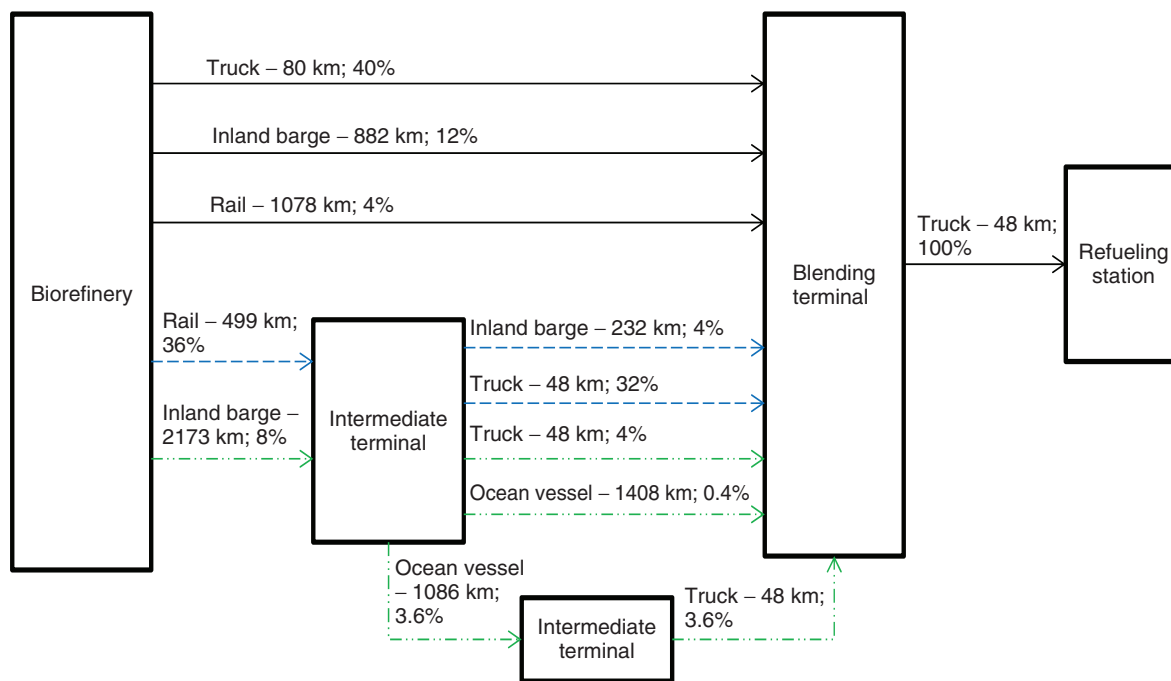


Figure 2. Distance and allocations for fuel product transport from biorefinery to pump based on the work by Hsu et al. (39).

all other required utilities. Detailed process conditions can be found in the supplementary materials. The plant size is 2000 dry metric tons (DMT) per day and it operates 350 days per year. Acid pre-treatment is used, followed by enzymatic hydrolysis (saccharification) of the remaining cellulose (and possibly the remaining hemicelluloses). Pre-treated hydrolyzate is conditioned with ammonia to obtain proper pH for enzymatic hydrolysis. A high concentration of salts in the pre-treated hydrolyzate has been found to dramatically reduce butanol productivity.¹² While the mechanism of this inhibition is unclear, removal of the inhibitors would likely be required to improve product yield. Consequently, in this study, ion exchange columns are added to the pre-treatment process to remove inhibitors (including acetates, salts, and several organic acids).

Enzymatic hydrolysis is initiated in a continuous reactor using a purchased cellulase enzyme. The solids level of enzymatic hydrolysis is assumed to be 20% total solids. The partially hydrolyzed slurry is then batched to a system of parallel anaerobic bioreactors. Hydrolysis is completed in the batch reactor, and then the slurry is cooled to 32 °C and inoculated with organism for fermentation.

Fermentation

Isobutanol could be produced via an anaerobic process using improved *E. coli* strains. Most processing conditions

for fermentation are assumptions for modeling purpose. Continuous vacuum stripping is used for butanol fermentation, shown in Fig. 3. Relatively higher butanol condensate in the vacuum stripper's condenser and the recycling fermentation stream keep the fermentor broth at no more than 2 wt%. Seed strain production is assumed to be the same as that used for *Zymomonas mobilis* production in the cellulosic ethanol design, although oxygen is supplied for cell propagation. The enzymatic hydrolysis residence time is 3.5 days, and fermentation is assumed to last 3 days, assuming most glucose and xylose are fermented to solvent products and microorganism growth. Limited information is available on the production of isobutanol from xylose. Because *E. coli* is known to be capable of utilizing xylose, we assume that isobutanol could be produced from xylose. The sugar to isobutanol conversion yield is assumed to be 85%, with the rest of the sugar being converted to cell mass and other by-products. The resulting fermentation broth (or 'beer') is sent to product recovery. Neither oligomeric sugars nor minor sugars (arabinose, mannose, and galactose) are assumed fermentable, but heating values for all residual sugars are recovered in the boiler section.

Because we assume a 90% xylose yield in dilute acid pre-treatment and a 92% yield of glucan to monomer sugar in enzymatic hydrolysis, the combined sugar yield

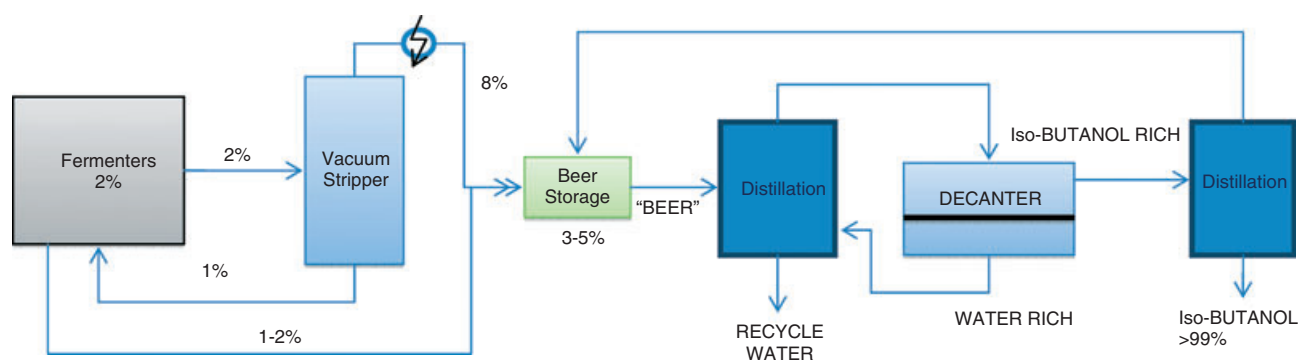


Figure 3. Iso-butanol fermentation with simultaneous stripping and purification process block flow diagram.

to isobutanol is merely 69% of theoretical yield in this process. Similar to the n-butanol model, other sugars are assumed non-fermentable to isobutanol. The beer from both the condensed butanol product from online stripping and the final fermentation broth is fed to the beer storage tank, containing a total of 3.25% isobutanol (or 35 g/L). The bacteria strain is assumed to have a similar inoculum process as that used in the 2011 biochemical design model. Isobutanol fermentation from bacteria is assumed to be anaerobic. Other process conditions are described in the supplementary materials.

Butanol purification process

Vacuum stripping during fermentation can be operated without extra volume in the fermentation tanks for gases. Therefore, we selected this technique for the simultaneous fermentation and butanol removal process in the isobutanol process design. Simulation analysis (dynamic behavior of the process) has revealed that the flash fermentation process could be promising for high productivity of Butanol.^{46,47} Others have found that high product purity could be achieved using a two-vessel partial flash system (with the first vessel acting as a 'distillation column' with two to three plates, and the second acting as a flash vessel) over a two-vessel flash system.^{12,46,47} However, the relatively high yield of butanol has yet to be proven by additional research of this technique. Gas stripping is still the technique that results in the highest product titer in the finished fermentation broth.

Baez *et al.*⁴ showed that by using an engineered micro-organism, sugar can be converted to isobutanol with very few by-products. This finding significantly simplifies the product purification design. The beer from fermentation contains a mixture of isobutanol and water along with other chemicals from pre-treated biomass. A simplified process flow diagram of product purification is shown in

Fig. 3. Only two distillation columns and one decanter are needed. The first column tries to concentrate the overhead product to the ratio of isobutanol and water to provide a liquid-liquid split. The isobutanol-rich stream is sent to the second column to obtain high purity isobutanol as the product – however, this will not be feasible if only a small amount of by-product (such as ethanol or acetone) is present in the beer stream. Low-volatility chemicals will either build up in the recycle streams or become present in the butanol product stream; therefore, they should be removed by additional separation units.

The beer column is used to remove more than 90% of the water, most high boilers (butyric acid, acetic acid, and other organic acids), and solids from the solvents. The remaining water in the beer column overhead product significantly influences the downstream decanter's performance. Optimizing the distillation columns' reflux and reboiler ratio ensures less water in the beer column distillate and minimizes components, such as butyric acid, to the overhead of the column. Energy demand for the reboiler is dramatic because it requires vaporizing all of the value-added solvents to the top of the column.

The solids from distillation and biogas from anaerobic digestion are burned in a fluidized bed combustor to produce high-pressure steam for electricity production and process heat. The majority of the process steam demand is in the pre-treatment reactor and distillation areas. The excess steam produced in the boiler is converted to electricity for use in the plant and for sale to the grid as a co-product.

Process economics

The total cost of the butanol production process includes variable cost (raw material cost, utility cost, and co-product credits); fixed cost (labor, supplies, and overheads); capital depreciation; average income tax; and average return on

Table 5. Operating cost of corn stover isobutanol, 2000 DMT corn stover per day.

Manufacturing costs (cents/gal butanol)	
Feedstock + handling	101.0
Sulfuric acid	3.3
Ammonia	8.9
Glucose (enzyme production)	26.4
Other raw materials	17.7
Waste disposal	3.4
By-product credits	-13.1
Fixed costs	24.0
Capital depreciation	30.2
Average income tax	17.0
Average return on investment	78.4
MBSP	297.1

investment. The economics reflect 2007 US dollars. We used a combination of vendor specifications, existing NREL data-banks, AspenPlus process economics tools, and engineering judgments to estimate equipment cost. Raw material costs are calculated on a per-gallon-isobutanol basis and include biomass feedstock, sulfuric acid for pre-treatment, ammonia for conditioning hydrolyzate, glucose for enzyme production, corn steep liquor, diammonium phosphate, boiler chemicals, and other chemicals.

For a 2000 DMT-per-day plant, the isobutanol yield is 45 million gallons per year, equivalent to 37 million gallons of gasoline. Fixed cost (salaries, maintenance, etc.) is based on the 2011 design model³³ and calculated to per-gallon-butanol basis. Variable cost, fixed cost, capital depreciation, income tax, and return on capital are shown in Table 5. The calculated MBSP is \$2.97/gal, or \$3.62/GGE. Figure 4 illustrates the contribution to the overall cost by process area. Feedstock cost contributes most significantly to the isobutanol production cost.

Sensitivity analysis on sugar yields to butanol

We conducted single-point sensitivity analyses to judge sugar yield's impact on cost. The base case analysis assumes that 85% of glucose and 85% of xylose are converted to isobutanol, with the remaining sugar converted either to microorganism cell mass or to non-value-added products. As of today, this has not been demonstrated, even in the bench scale studies. It is expected that lower sugar yield significantly increases the MBSP. Therefore, we performed a sensitivity analysis using lower sugar

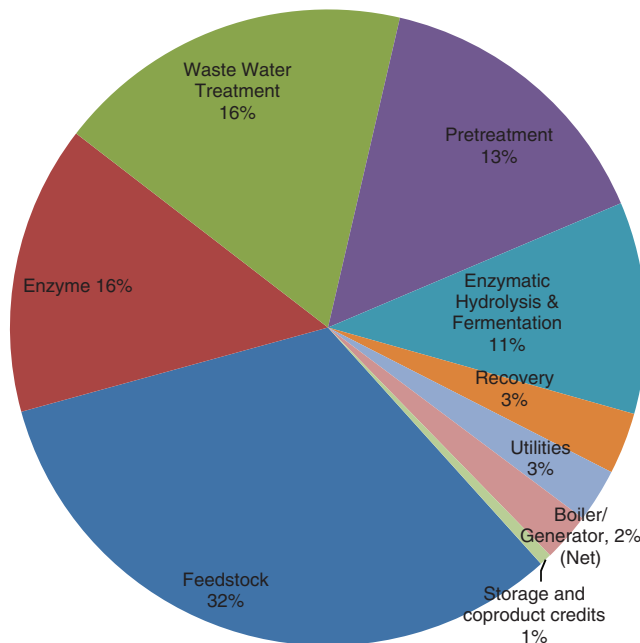


Figure 4. Cost distribution from each process area, based on percentage.

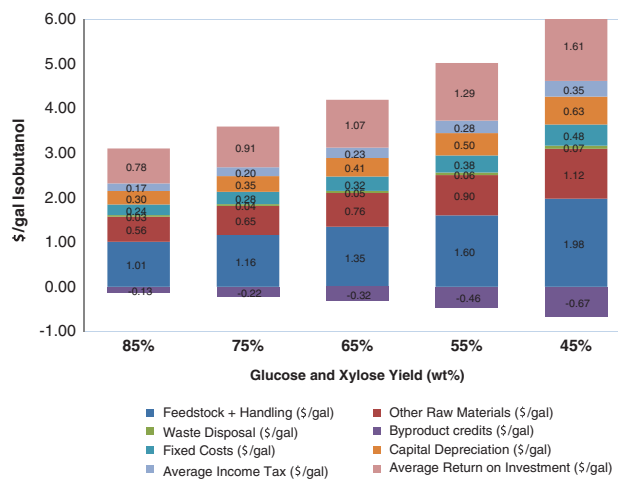


Figure 5. Sensitivity analysis of effect on MBSP of varying glucose and xylose yields to iso-butanol.

yields. The results are illustrated in Fig. 5 for glucose and xylose yields of 45% to 85%. This analysis shows that the MBSP increases from \$2.97/gal to \$5.56/gal when sugar yields decrease from 85% to 45%. On the other hand, if the amount of feedstock delivered is held constant, butanol production drops from 45 to 23 Mgal/year.

When the sugar yield decreases, the feedstock cost portion (on feedstock cost per gallon butanol basis) of the overall production cost increases dramatically, also shown

in Fig. 5. The feedstock contribution almost doubles when glucose and xylose yields to isobutanol decrease from 85% to 45%. All other variables increase with reduced sugar-to-product yield, except for the by-product credit. Lower sugar and isobutanol yields allow more unconverted biomass to be sent to the combustor, which leads to more electricity production for export.

Comparison of cellulosic ethanol, n-butanol, and isobutanol

Here we compare isobutanol, n-butanol, and ethanol from several important aspects in addition to cost, including fermentation process technologies, product purification processes, and emission parameters from the LCA study.

Comparison of fermentation technology

In contrast to cellulosic ethanol fermentation technology, butanol fermentation technology, especially isobutanol fermentation, has not yet been fully demonstrated even in bench studies. Demonstration of isobutanol production by anaerobic fermentation in literature is still limited to glucose utilization and at relative low sugar concentrations. Fermentation of the second most abundant biomass sugar, xylose, by the isobutanol producing strains has not yet been studied. For comparison purposes, we assume a mixed sugar fermentation using saccharified slurry as in the cellulosic ethanol process. In addition, the toxic inhibitors in the hydrolyzates may also affect the fermentation yield. We anticipate that the fermentation technology will likely change when new strains become available in future.

Comparison of product purification process

Purification process design

The process design with isobutanol as a single product from fermentation results in a simpler separation scheme (shown in Fig. 3) compared with the multi-product purification of cellulosic sugar to n-butanol.¹⁶ More than six major operation units are involved to purify n-butanol, acetone, ethanol, and hydrogen (the separation process scheme was shown in the companion paper). For purification of n-butanol, approximately 90% of the water is removed from the dehydration column (first distillation column). Downstream distillation columns further separate and purify acetone, ethanol, and n-butanol from residual water, combined with a decanter and a molecular sieve adsorption unit to purify high-grade ethanol. Typically, the butanol and water azeotrope can be broken by extractive distillation using a solvent, similar to

extractive distillation for breaking an ethanol and water azeotrope. However, this option not only adds significant complexity to this conversion process but also adds cost. Previous research has explored how to take advantage of the vapor-liquid-liquid equilibrium phase behavior between butanol and water.¹⁶ It was found that a decanter could be applied to break the binary azeotrope (minimum boiling azeotrope) between butanol and water, even in the presence of ethanol. This fact is not only true for n-butanol, but also for isobutanol purification. To maximize the liquid-liquid separation in the decanter, temperature serves as the primary control mechanism.

To purify ethanol from the cellulosic conversion process, two distillation columns are used and combined with one molecular sieve adsorption unit to achieve 99.5% ethanol purify. The comparison of unit operations for purifying ethanol, isobutanol, and n-butanol is shown in Table 6.

Purification process energy consumption

Energy consumption to achieve target product purity (set as 99.5% for both butanol and ethanol) for fuel application is analyzed and illustrated in Fig. 6 using a per-gallon-product basis. The much higher energy consumption to purify n-butanol is mainly due to the necessity to purify the value-added by-products (shown in Table 7). If

Table 6. Numbers of unit operations of ethanol, isobutanol, and n-butanol purification from fermentation broth.

	Ethanol	Isobutanol	N-butanol
Distillation column	2	2	4
Molecular sieve adsorption unit	1	–	1
Decanter	–	1	1

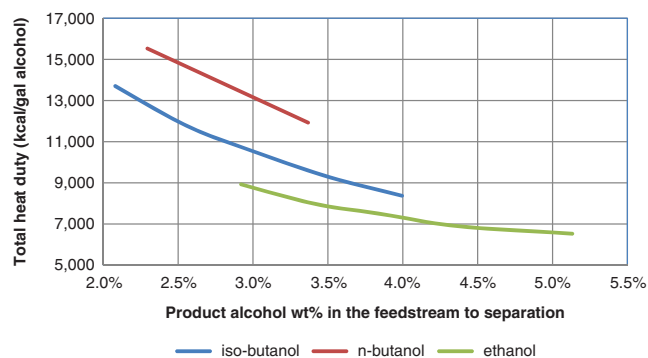


Figure 6. Energy consumption for cellulosic ethanol, isobutanol, and n-butanol.

Table 7. Process production economics comparison.

	Ethanol	Isobutanol	N-butanol
	95% glucose and 85% xylose yields	85% glucose and xylose yields	ABE molar ratio 0.5:9:0.5, 85% glucose and xylose yields
Butanol production (MMgal/yr)	–	45	37
Acetone production (MMgal/yr)	–	–	2
Ethanol production (MMgal/yr)	61	–	7
Fuel production equivalent to gasoline, exclude acetone (MMgal/yr)	40	37	35
% of theoretical yield	76%	69%	59%
TCI (\$M)	423	428	433
Minimum ethanol or butanol selling price (\$/gal)	\$2.15	\$2.97	\$3.04
Energy equivalent to gasoline (%)	65.8%	81.9%	82.8%
Gasoline equivalent MFSP (\$/gal)	\$3.27	\$3.62	\$3.66

isobutanol and ethanol concentrations in the feed streams are the same, the energy consumption (per gallon of fuel basis) for the ethanol case is slightly lower than it is for isobutanol. However, with simultaneous product recovery in isobutanol fermentation, the isobutanol concentration could be much higher than for the batch fermentation used in this study. Potentially this could make the energy consumption for cellulosic isobutanol production lower than that required for cellulosic ethanol.

Comparison of overall process economics

The process economics results for fuel production, total project investment, and minimum fuel selling price are shown in Table 7. For the purpose of consistency, the feedstock rate is assumed to be 2000 metric dry tons per day. For the cellulosic n-butanol model, we selected a near-ideal case for the comparison. That is, the product molar ratio is assumed as 0.5:9:0.5 for acetone to n-butanol to ethanol, respectively. Both xylose and glucose yields are assumed to be 85%, which is consistent with the assumptions for the isobutanol base case. The cellulosic ethanol cost analysis is taken from the 2011 NREL design report,³³ a targeted case, in which glucose yield to ethanol is 95% and xylose yield to ethanol is 85%.

Using the same amount of feedstock, annual production of ethanol is the highest, at 61 Mgal, compared with 45 Mgal for isobutanol and 37 Mgal for n-butanol. However, if these three cases are compared using the GGE basis, fuel production (shown in Table 7) is close for all three cases, simply due to similar assumptions of sugar yields. The minimum fuel selling prices (for ethanol and butanol), calculated using discounted cash flow analysis, are compared using the gasoline equivalent. The cost of

Table 8. Capital cost comparison of cellulosic ethanol, n-butanol, and isobutanol.

Capital costs	Cellulosic conversion (million)		
	Ethanol	Isobutanol	N-butanol
Pre-treatment	\$30	\$30	\$30
Neutralization/conditioning	\$3	\$7	\$7
Saccharification & fermentation	\$31	\$32	\$32
On-site enzyme production	\$18	\$18	\$18
Distillation and solids recovery	\$22	\$19	\$22
Wastewater treatment	\$49	\$51	\$51
Storage	\$5	\$3	\$4
Boiler/turbogenerator	\$66	\$67	\$67
Utilities	\$7	\$8	\$7
Total installed equipment cost	\$232	\$235	\$238

ethanol is slightly lower than the costs for isobutanol and n-butanol.

Table 8 compares the capital costs by area for the three cellulosic biofuel cases. It shows that costs associated with areas of recovery, wastewater treatment, and combustor are higher for butanol production than for ethanol production due to lower fuel yield and a more complex co-product portfolio. Vacuum gas stripping adds roughly \$6 million (out of \$19 million of isobutanol capital and out of \$22 million of n-butanol purification capital, as shown in Table 8) to the fermentation cost for both butanol cases, compared to the fermentation cost for ethanol. The capital costs required for distillation and solid recovery are similar, with isobutanol's required capital in this area slightly lower than that for

ethanol and n-butanol. Although there are two more distillation columns in the purification of n-butanol by-products (acetone and ethanol), the size of the molecular sieve adsorption unit is much smaller than what is in the cellulosic ethanol process – this is due to the much lower ethanol production in the cellulosic n-butanol conversion process. The total installed equipment costs for all three cases are quite similar (\$232 million to \$238 million), with the cellulosic ethanol conversion process having the lowest capital cost.

MBSP from the isobutanol process is lower than that from n-butanol process, assuming the same feedstock flow rate, sugar yield, and simultaneous fermentation and vacuum product removal. This is mainly due to the higher production yield of isobutanol compared to n-butanol, but also partially due to the simpler product recovery area contributing to lower capital costs as well as less energy consumption in that area.

Comparison of LCA parameters

Direct biorefinery emissions and consumptive water use

The direct emissions (CO₂, NO₂, SO₂) and consumptive water use (i.e. make-up water) from the cellulosic butanol and ethanol production processes are shown in Table 9. The CO₂ emission is inversely proportional to the product yield. Higher biofuel yields provide less unconverted biomass available for the combustor. The n-butanol process releases the most CO₂, at 26.42 kg CO₂/GGE. Isobutanol and ethanol plants have relatively similar CO₂ emissions, emitting 21.91 kg CO₂/GGE and 21.01 kg CO₂/GGE, respectively. CO₂ is generated during cellulase (or enzyme) production and fermentation but largely comes from the combustion process. Note that all three processes produce only biogenic CO₂ (origin from biomass) – there are no direct fossil CO₂ emissions from these conversion plants because they are energy self-sufficient and do not require any make-up fossil fuel.

Table 9 also shows that n-butanol plants emit more criteria air pollutants (NO₂ and SO₂) than isobutanol and

ethanol plants do. NO₂ is essentially thermal NO₂, which is formed through high temperature oxidation of the diatomic nitrogen found in combustion air. SO₂ emissions from the biochemical process directly depend on the amount of sulfuric acid introduced to the pre-treatment reactor. The acid loading for the plants is 18 milligrams per gram (mg/g) dry biomass. Direct plant SO₂ emissions can potentially be reduced with improvement in pre-treatment technology that uses less sulfuric acid. The current levels of SO₂ emissions reported in Table 9 are the controlled emissions (i.e. after the flue gas desulfurization step that converts 92% of SO₂ from the flue gas of the combustor into calcium sulfate with lime (calcium hydroxide)).

The consumptive water use of the biorefineries (shown in Table 9) increases in the following order: ethanol (8.19 gal/GGE) < isobutanol (8.98 gal/GGE) < n-butanol (10.84 gal/GGE). More than 90% of net water loss for the biochemical process is from the cooling tower (mostly evaporative loss), in which approximately 52% is for the condensing turbine. For comparison, Wu *et al.*⁴⁸ reported that, on average, gasoline refining consumes approximately 1.5 gallons of water per gallon of gasoline refined.

Life cycle assessment

Figure 7 presents the field-to-wheels projected GHG emissions for an FFV propelled 1 km using neat ethanol (E100), isobutanol, or n-butanol produced from corn stover. The stacked bar depicts the contribution from each life cycle stage. Stages that contribute the most are feedstock production and harvesting, corn stover conversion, and feedstock preprocessing. Co-product credits are associated with the conversion stage. The electricity co-product credits for the ethanol and isobutanol cases are 0.050 kg CO₂-eq/km and 0.045 kg CO₂-eq/km, respectively. For the n-butanol case, in addition to the co-product displacement credit of excess electricity (0.055 kg CO₂-eq/km), there are also co-product displacement credits from acetone (0.007 kg CO₂-eq/km) and ethanol (kg CO₂-eq/km). The field-to-wheels GHG emissions for the three cellulosic biofuels considered increased in the following order: ethanol (0.10 kg CO₂-eq/km) < n-butanol (0.11 kg CO₂-eq/km) < isobutanol (0.12 kg CO₂-eq/km). The same GHG emissions profile holds for the scenario when GHG emissions associated with the excess electricity cannot be avoided. In that case, the field-to-wheels GHG emissions become 0.15 kg CO₂-eq/km (a 32% increase) for ethanol, 0.16 kg CO₂-eq/km (a 34% increase) for n-butanol, and 0.17 kg CO₂-eq/km (a 27% increase) for isobutanol. The life cycle GHG emissions of the 2005 baseline average gasoline are 0.32 kg

Table 9. Comparison of direct process GHG (CO₂) emissions, CAP (NO₂ and SO₂) emissions, and consumptive water use.

	Ethanol	Isobutanol	N-butanol
CO ₂ , biogenic (kg/GGE)	21.01	21.91	26.42
SO ₂ (g/GGE)	11.31	12.52	15.02
NO ₂ (g/GGE)	13.47	23.33	28.04
Water (gal/GGE)	8.19	8.98	10.84

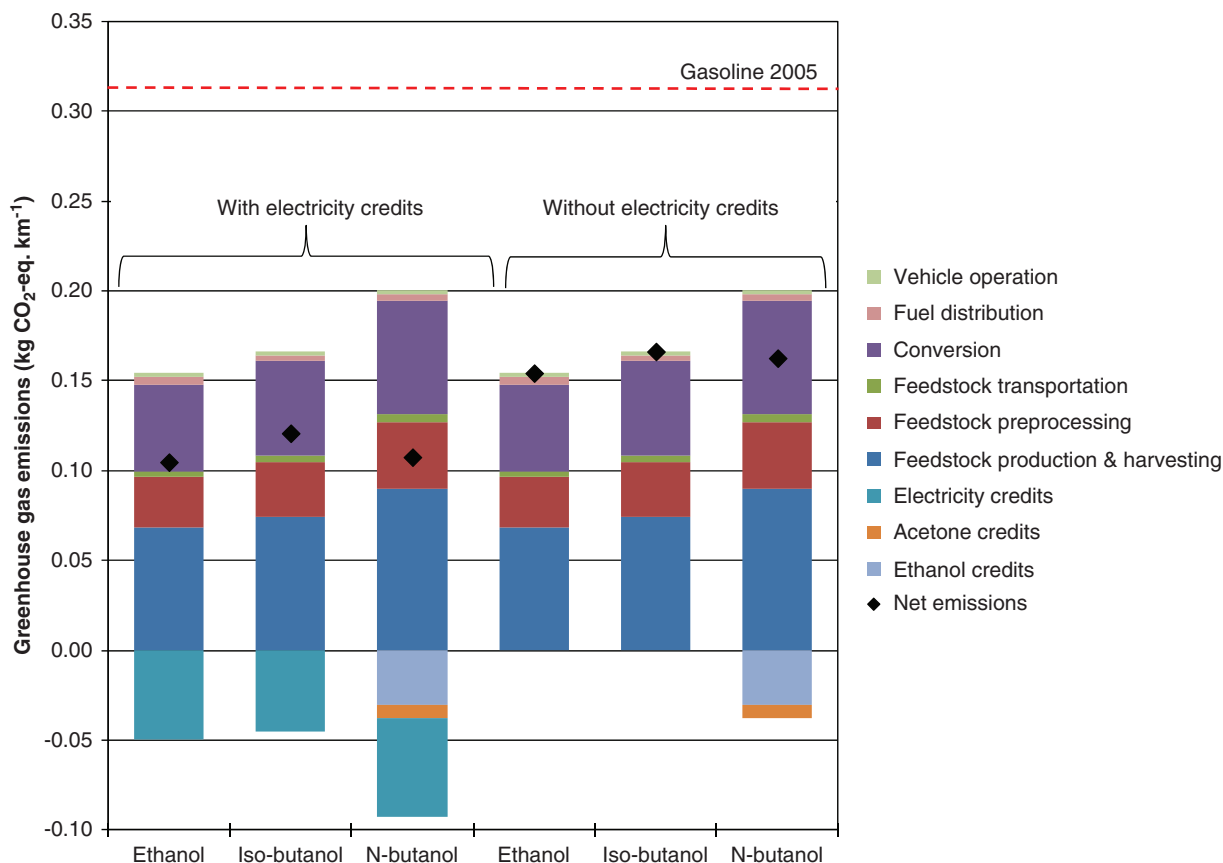


Figure 7. Field-to-wheels projected GHG emissions for an FFV propelled 1 km using neat ethanol (E100), iso-butanol, or n-butanol produced from corn stover. The stacked bar depicts the contribution from each life cycle stage. Co-product credits are associated with the conversion stage. The dashed line represents 1 km traveled by a U.S. passenger car using conventional gasoline in 2005.

CO₂-eq/km, significantly higher than all cases evaluated here.

On the gasoline gallon equivalent basis (GGE), the ethanol and n-butanol conversion processes have about the same GHG emissions, 4.3 kg CO₂-eq/GGE and 4.5 kg CO₂-eq/GGE, respectively (Table 10). GHG emissions for the isobutanol conversion process are higher at 5.0 kg CO₂-eq/GGE. Additionally, the n-butanol process has the lowest fossil fuel consumption (39.2 MJ/GGE), followed by the ethanol process (43.12 MJ/GGE). The isobutanol process has the highest fossil fuel consumption at 51.24 MJ/GGE. The high co-product credits for the n-butanol conversion process compensate for the high fossil energy demand from the other areas. Without the electricity displacement credits, both GHG emissions and fossil energy input for all three biofuels are significantly higher. It is noteworthy that the direct biorefinery CO₂ emissions at the conversion stage (shown in Table 10) are biogenic CO₂ (i.e., CO₂ absorbed from the atmosphere

and incorporated as biomass). With its biomass origin, biogenic CO₂ does not contribute to the increase of GHG emissions in the atmosphere⁴⁹ and is not considered in the Intergovernmental Panel on Climate Change (IPCC) global warming methodology.⁵⁰ Biogenic CO₂ typically is not counted as a contributor to global warming in IPCC global warming methodology because it is assumed that the emitted CO₂ is removed from the atmosphere during the same time horizon of the GWP estimate. Hence, the GHG emissions contributed by the direct plant emission for the evaluated processes are solely from the associated underlying processes (e.g. inputs/outputs to and from the facility to support process operation).

We also assessed the conversion processes based on EROI and NEV. As shown in Table 10, the NEVs for the current evaluated cellulosic biofuels are all positive: 90 MJ/GGE for n-butanol, 87 MJ/GGE for ethanol, and 76 MJ/GGE for isobutanol. Positive NEV is one of the criteria for an alternative transportation fuel to be a substitute for

Table 10. Life cycle metrics comparison.

Metrics	Units	With electricity displacement credits			Without electricity displacement credits		
		Ethanol	Isobutanol	N-butanol	Ethanol	Isobutanol	N-butanol
GHG emissions	kg CO ₂ -eq/GGE	4.3	5.0	4.5	6.5	7.0	6.9
Fossil energy input	MJ/GGE	43	51	39	69	75	67
Energy return on investment (EROI)	MJ/MJ	2.7:1	2.2:1	2.8:1	1.5:1	1.4:1	1.5:1
Net energy value (NEV)	MJ/GGE	87	76	90	51	43	68

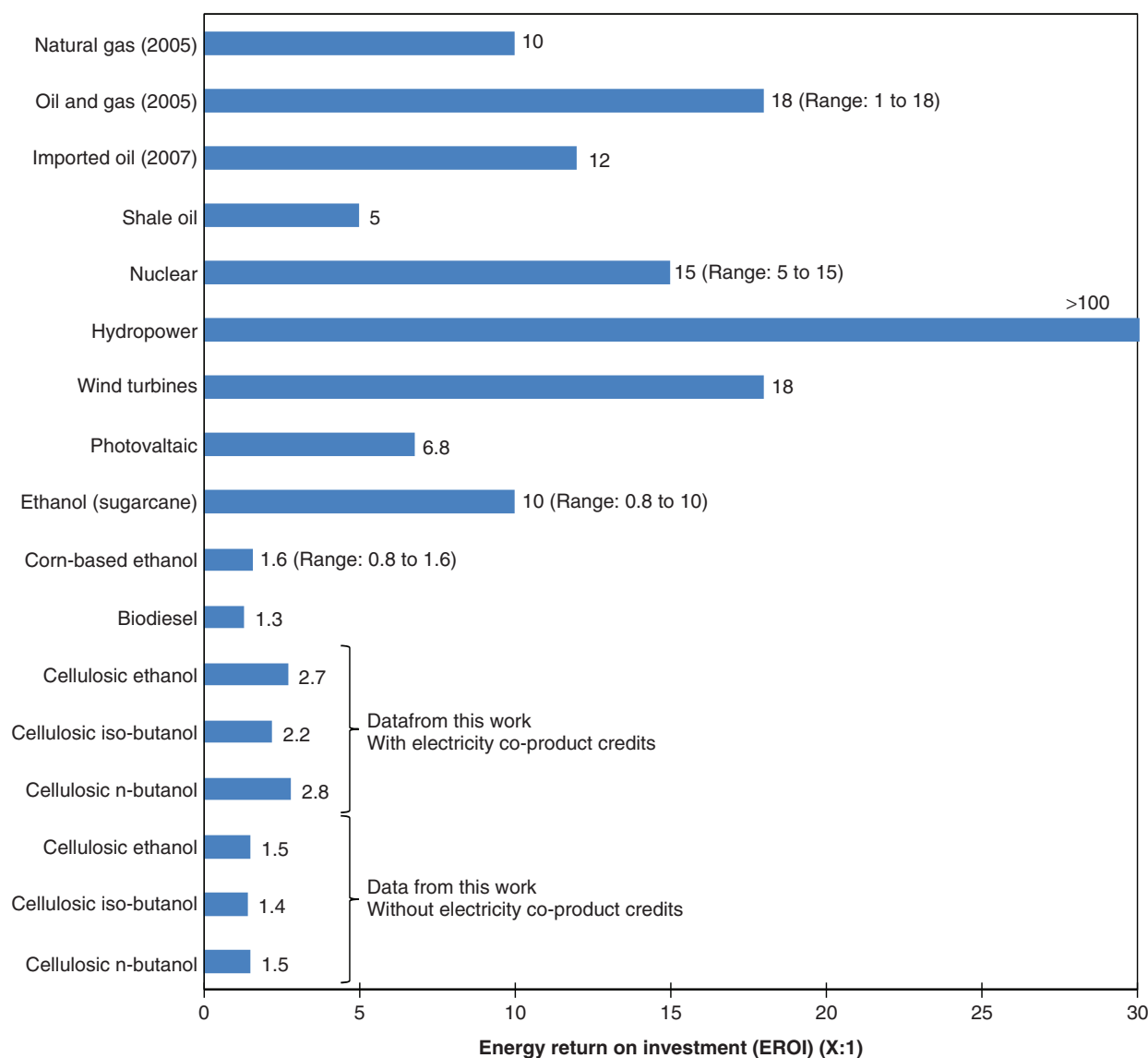


Figure 8. Energy return on investment (EROI) of various energy sources for the United States. Literature data for the figure are obtained from Table 2 from Murphy *et al.* (53).

conventional gasoline. NEVs are lower without the co-product electricity credits.⁵¹ For comparison, Farrell *et al.* found that the NEV for the corn-based ethanol production

process was about 5 MJ/L (29 MJ/GGE).⁴⁵ Ethanol derived from switchgrass has been shown to have higher NEV, on average 21.5 MJ/L (124 MJ/GGE).⁵² An NEV of 6.53 MJ/L

(30 MJ/GGE) for corn-based butanol from the ABE fermentation process has been reported.²⁴

EROI is the ratio of how much energy is gained in the form of biofuel from a biofuel production process compared to how much of the energy is required to produce the biofuel. Table 10 shows that EROI values for the three cellulosic biofuels are 2.8:1 for n-butanol, 2.7:1 for ethanol, and 2.2:1 for isobutanol. A comparison of EROI values obtained in this work with literature values for other energy sources⁵³ is shown in Fig. 8. EROI values for the biofuels from this study appear to be slightly higher than those reported for corn-based ethanol and biodiesel. In comparison, fuels produced from fossil energy show an overall EROI of greater than 5:1. Hall *et al.*⁴³ attempted to determine the minimum EROI for an energy production process that could potentially be sustainable. The minimum EROI of about 3:1 was determined for both oil and corn-based ethanol at the mine-mouth or farm-gate. They also claimed that any biofuel with an EROI of less than 3:1 would require the input of fossil fuels and that most biofuels have EROI below 3:1. However, any discussion and comparison of EROI for liquid biofuels should be viewed as preliminary due to two key facts: (i) the cellulosic biofuel production technologies are still in their nascent stage, and (ii) there is not yet a universal standard protocol for quantifying the energy costs associated with biofuel production for an EROI calculation. EROI values for cellulosic biofuels are likely to improve in the future as a result of continued conversion technology development and advancements in cellulosic feedstock production and logistics.

Conclusions

Results from the detailed techno-economic analysis conducted for corn stover to isobutanol conversion technology show that if xylose and glucose yield to isobutanol in fermentation could reach 85%, the MBSP will be \$2.97/gal or \$3.63/GGE. The sensitivity analysis applied to sugar yields shows that the MBSP increases from \$2.97/gal to \$5.56/gal (not gasoline equivalent) if sugar yield decreases from 85% to 45%. There is no significant difference when comparing the MBSPs of n-butanol and isobutanol. Both butanol costs are slightly higher than that of cellulosic ethanol when compared by minimum fuel selling prices on the gasoline equivalent basis. The processing technique using simultaneous vacuum stripping and fermentation results in similar total capital investment for both n-butanol and isobutanol. When compared with ethanol process, the estimated energy consumption to purify butanol is

slightly higher than it is for purifying ethanol. This is due to a larger amount of recycles (i.e. two recycle loops for isobutanol versus four recycle loops for n-butanol) to the beer column, demanding more energy for the column operation. Energy consumption per gallon of n-butanol is almost 40% higher than it is for ethanol, and 30% higher than it is for isobutanol, because additional energy is used to purify the by-products, acetone and ethanol. Isobutanol shows promise to be a viable gasoline blending component. It has a higher energy density and similar anti-knock characteristics when compared with ethanol. Isobutanol is also less soluble in water, suggesting that fewer problems will occur in transportation and storage.

Compared to ethanol production, isobutanol and n-butanol production processes exhibit higher direct CO₂ (all biogenic), SO₂, and NO₂ emissions, as well as higher consumptive water use, at the conversion stage. However, our life cycle assessment results show that the life cycle metrics for all three cellulosic biofuels are not widely different. The ethanol case exhibits the lowest net GHG emissions (0.10 kg CO₂-eq/km or 4.3 kg CO₂-eq/GGE), and n-butanol via ABE fermentation requires the least fossil energy consumption (39 MJ/GGE). The combination of lower fossil energy input and high co-product displacement credits (not just from electricity, but also from acetone and ethanol) compensates for the lower n-butanol yield and results in higher EROI (2.8:1) and NEV (90 MJ/GGE). On the other hand, isobutanol exhibits modestly higher GHG emissions (0.12 kg CO₂-eq/km or 5.0 kg CO₂-eq/GGE) and fossil energy consumption (51 MJ/GGE) as well as lower EROI (2.2:1) and NEV (76 MJ/GGE). Co-product credits play an important role in the calculation of the life cycle metrics. Excluding co-product displacement credits from electricity exhibits a significant (>25%) negative impact on each metrics category. LCA results also suggest that although n-butanol and isobutanol production routes have different yields at the biorefinery conversion stage, their environmental performances are largely comparable in terms of GHG emission burdens.

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