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Bio-butanol vs. Bio-Ethanol: A technical and economic assessment for corn and switchgrass fermented by yeast or *Clostridium acetobutylicum*

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Abstract

Fermentation-derived butanol is a possible alternative to ethanol as a fungible biomass-based liquid transportation fuel. We compare the fermentation-based production of n-butanol vs. ethanol from corn or switchgrass through the liquid fuel yield in terms of the lower heating value (LHV). Industrial scale data on fermentation to n-butanol (ABE fermentation) or ethanol (yeast) establishes a baseline at this time, and puts recent advances in fermentation to butanol in perspective. A dynamic simulation demonstrates the technical, economic and policy implications.

The energy yield of n-butanol is about half that of ethanol from corn or switchgrass using current ABE technology. This is a serious disadvantage for n-butanol since feedstock costs are a significant portion of the fuel price. Low yield increases n-butanol's life-cycle greenhouse gas emission for the same amount of LHV compared to ethanol. A given fermenter volume can produce only about one quarter of the LHV as n-butanol per unit time compared to ethanol. This increases capital costs. The sometimes touted advantage of n-butanol being more compatible with existing pipelines is, according to our techno-economic simulations insufficient to alter the conclusion because of the capital costs to connect plants via pipeline.

Keywords: ethanol, butanol, ABE fermentation, economics, biofuel, corn, switchgrass, yeast, *Clostridium*

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Introduction

The issues and merits of biomass-based liquid transportation fuels such as ethanol are under intense discussion in the public [1,2], and in the engineering and scientific communities [3,4]. Nevertheless, the U.S. capacity for fermentation based ethanol mostly from corn stood recently at over 45.4 $hm^3\ y^{-1}$ [5] (current and under construction) exceeding the projections of the United States Department of Agriculture [6]. The U.S. Energy Independence and Security Act (EISA) of 2007 mandates 136.3 hm^3 biofuels y^{-1} for the U.S. market by 2022 of which corn-based ethanol is capped at 56.8 $hm^3\ y^{-1}$.

Fermentation-derived butanol has attracted renewed interest as a fuel and recent reviews are available [7,8] in addition to classical papers [9,10]. Announcements by a consortium of companies to produce fuel n-butanol by fermentation on the industrial scale have increased the interest [11]. Efforts by other private companies (for example Gevo Inc., CO, or Cobalt Biofuels, CA) to produce butanol have given us a reason to investigate the fundamentals of this biofuel.

Fermentation of biomass to ethanol using the yeast *Saccharomyces cerevisiae* is an ancient technology. Biomass fermentation producing n-butanol using microorganisms of the genus *Clostridium* (termed Acetone Butanol Ethanol or ABE fermentation) based on the seminal work by Weizmann [12] has been performed on the industrial scale (multi-tonne per day per facility) in the U.S. early in the 20th century, in Russia [13] until the late 1980's, in South Africa until the early 1980's, and is currently performed industrially in China with production goals up to 1 million tonnes of ABE solvents per year [14].

It appears that a comparison of the biofuels ethanol and butanol may be useful to see what motivation or de-motivation exists to ferment biomass to butanol (and some ethanol) instead of only ethanol for use as a transportation fuel. A quantitative techno-economic comparison is executed, starting with a classical chemical engineering elemental (carbon) balance for both processes, and using the lower heating value (LHV) of the liquid fuel products per unit mass of feedstock as the criterion of comparison. An economic analysis is then shown for corn ethanol vs. corn n-butanol, followed by an engineering estimate for industrial ethanol+n-butanol production from a cellulosic feedstock compared to ethanol production using an advanced yeast.

Background

The lower heating value as the basis of liquid bio-fuel production comparison

The lower heating value (LHV) of the ethanol (yeast fermentation) or ethanol + n-butanol (ABE fermentation) will be used to compare the conversion of a given mass of feedstock to the target bio-fuel. The LHV is taken as the heat of combustion at 25°C and atmospheric pressure reduced by the enthalpy of evaporation of the water formed during combustion since water leaves an internal combustion engine as vapor. Table 1 shows some pertinent and reference values [15, 16, 17].

The LHV is used here as a reasonable yardstick since both bio-butanol and bio-ethanol would likely be used in similar internal combustion engines. Energy content per volume of fuel (higher for n-butanol than ethanol), distance driven per volume of fuel etc. are often used in discussing biofuels. The LHV from a given amount of feedstock is a more neutral way of comparinf biofuels for similar engines. As an aside, a comparison of bio-ethanol to bio-diesel would be more complex since Diesel engines deliver more mechanical work per unit LHV since they are thermodynamically more efficient than Otto-type engines.

The choice of LHV vs. the sometimes employed HHV (higher heating value) does not change the overall conclusions of the considerations below since the difference is relatively small.

The carbon mass balance as a tool to compare bio-ethanol with bio-butanol

Figure 1 shows an overview of the fermentation based processing to ethanol or n-butanol+ethanol. The requirement for sterility for ABE fermentation will be discussed below.

Carbon is obviously the element of greatest interest when evaluating liquid biofuel production since the ultimate goal is to convert carbon residing in biomass to a liquid hydrocarbon that can be used in an internal combustion engine. The carbon *in starch* is used as the input mass flow for corn since only starch is fermented. Figure 2 demonstrates that about two thirds of the carbon in the incoming starch is converted to ethanol in the state-of-the-art yeast-based process. The remaining carbon is found as CO_2 gas leaving the fermenters, in biomass produced, and as a small amount of unfermented starch.

A carbon mass balance is a simple and rapid check on the consistency of reported or claimed experimental results and serves as a first level tool for comparing processes. The energy balance

is the next step in a meaningful comparison of biofuel production processes since it will reveal the amount of energy needed to produce a unit of energy as target fuel LHV and thereby also paves the way for a subsequent exergy or "quality of energy" analysis. We execute only the carbon mass balance here since the yield of fuel LHV per mass of feedstock is crucial especially when similar processes all based on fermentation and faced with similar downstream issues (separation of dilute alcoholic product from aqueous fermentation broth) are compared.

Yield assumptions

A central issue for any process comparison is the yield here defined as mass of fuel per mass of biomass processed or similarly the LHV of biofuel per mass of biomass processed.

A recent survey of the U.S. fuel ethanol industry by Argonne National Laboratory for the Renewable Fuels Association [18] reported a yield of 0.33 liters denatured ethanol per kg corn which is equivalent to about 0.30 kg pure ethanol per kg corn assuming the yield above is taken as ethanol at 20°C.

The yield of n-butanol per mass of corn is of paramount importance since feedstock costs are often a crucial fraction of the overall production cost of bio-based liquid fuels. Early reports for industrial ABE fermentation of corn by *C. acetobutylicum* are available [19] at a scale of 100 tonnes of solvent produced per day at two plants. About 3 kg of starch were reportedly converted to 1 kg of mixed solvents (33wt% solvents relative to the mass of starch from corn) with a weight ratio of n-butanol/acetone/ethanol of 6/3/1 and at a final concentration of 2.5 wt% of combined solvents in the fermentation broth. This corresponds to about 0.11 kg n-butanol per kg of corn using the composition in Table 2. Current full scale industrial ABE yields and solvent compositions are available from China [14]. A 6.2/3.0/0.8 mass ratio of n-butanol to acetone to ethanol is reported to yield 2.8 kg of solvents per kg of starch. The early data above was used in the analysis shown here.

Thirty four (34) wt% combined solvents yield on glucose is reported by others [20]. Another review [9] reports a 6/3/1 mass ratio of n-butanol/acetone/ethanol from ABE fermentation. Recent work using modified *Clostridium* spp. [21] reports a yield of up to 45 wt% of solvents at the laboratory scale. This work has been used to evaluate n-butanol production positively compared to yeast-based ethanol [22]. While this yield may seem encouraging compared to the above 33 wt% of solvents on starch, it must be said that a yield on a pure and easily metabolized

substrate in a carefully constructed and often costly fermentation medium in the laboratory will likely be difficult to reproduce in an industrial-scale fermentation on a natural substrate such as mash from dry-milled corn.

A sophisticated two-stage fermentation process for bio-butanol production with an extrapolated yield claim of 0.30 kg n-butanol per kg corn has been reported based on laboratory experiments [23]. A simple carbon balance may shed light on this claim. The composition of corn (Table 2) results in 543 mol of carbon available in form of starch per 25.4 kg of corn compared to 9.5 liters of n-butanol (20°C) containing about 414 mol of carbon. Therefore, a rather surprising 76% conversion of starch carbon to n-butanol carbon is claimed, which far exceeds the state-of-the-art performance of yeast-based bio-ethanol. Substantial CO_2 formation, however, can very likely not be avoided, as well as some carbon loss to form biomass, and some loss of starch that is not completely fermented. The claim of 0.30 kg n-butanol per kg corn may contain additional assumptions. The proposed novel two-stage fermentation using immobilized microorganisms also appears not to have been demonstrated on a large scale.

We will here use the industrially confirmed yield of 34 wt% of solvents relative to the mass of starch in the incoming corn producing a mass ratio of 6/3/1 n-butanol/acetone/ethanol to compare ABE fermentation to current state of the art bio-ethanol production from dry-milled corn using yeast. The gases evolved from ABE fermentation are estimated here as 1.5 times the mass of solvents produced composed of 60 vol% CO_2 and the balance hydrogen [9]. The humid hydrogen/CO_2 gas mixture issuing from the fermentation could be separated to recover a small amount of hydrogen but this is not the focus here and likely will not be cost effective.

Genetic manipulations and metabolic engineering to improve biomass fermentation to butanol

In the traditional and historic batch ABE process, *C. acetobutylicum* produce some hydrogen, carbon dioxide, acetate, and butyrate during the initial growth phase, resulting in decreasing pH. *Clostridium* spp. secrete enzymes that facilitate the breakdown of polymeric carbohydrates such as starch into monomers that can be transported into the cells using the phosphoenolpyruvate-dependent phosphotransferase system (PTS) for glucose and non-PTS mechanism for galactose. As the batch culture enters the stationary phase, a metabolic shift to solventogenesis occurs with the assimilation of the acids and concomitant release of n-butanol, acetone and ethanol. The biochemical pathways followed in *Clostridia* are fairly well described [24]. However, the

multiple metabolic pathways and two stage nature of ABE fermentation still prevent a clear and conclusive calculation of maximum theoretical yield.

The two primary solventogenic *Clostridium* organisms that have been investigated for the production of n-butanol are *C. acetobutylicum* ATCC 824 and *Clostridium beijerinckii* NCIMB 805212. The hyper-butanogenic *C. beijerinckii* BA101 strain was generated by chemical mutagenesis from *C. beijerinckii* NCIMB 8052 [25]. *C. beijerinckii* BA101 has enhanced capability to utilize starch and tolerates 0.017 to 0.021 kg n-butanol per liter of fermentation broth [26]. Various agricultural residues, such as corn stover, corn fiber and fiber-rich distillers dried grains and solubles (DDGS) as substrates have been reported as substrate for this strain [27]. Though pentoses and hexoses were used concurrently for n-butanol production, the highest concentration of n-butanol was produced when cellobiose was used, whereas the least amount of n-butanol was produced using galactose [26]. Fermentation inhibitors such as furfural, hydroxymethyl furfural (HMF), acetic, ferulic, glucuronic and phenolic compounds are generally formed during pretreatment of fiber-rich cellulosic biomass. Of these, furfural and HMF are not inhibitory to *C. beijerinckii* BA101; however, even 300 g of ρ-coumaric and ferulic acids per m^3 fermentation broth reduced n-butanol production significantly [27].

The current bio-butanol production using the existing *Clostridium* spp. suffers compared to yeast-based bio-ethanol from low final n-butanol titer, low yield, and low productivity (longer fermentation times). Recombinant DNA technology along with traditional mutagenesis and selection has been employed to modify targeted metabolic pathways in the solventogenic *Clostridium* spp. [25]. For example, Tummala et al. [28] used antisense RNA to downregulate the enzymes in the acetone formation pathway. Even though lower levels of acetone formation were achieved there was no redirection of carbon flux towards n-butanol synthesis. The solvent tolerance was similar to ABE fermentation and this is perhaps not surprising due to the physical impact of the solvent butanol on organisms. Butanol will dissolve cell membranes and the low saturation concentration of n-butanol in water (about 8wt%) leads to high and lethal thermodynamic activity already at butanol concentrations that are modest compared to concentrations in ethanol fermentation.

Recently, genetically engineered *E. coli* has been reported for production of butanol and other higher alcohols from glucose in a laboratory medium containing antibiotics [29,30]. The

reported yield of iso-butanol, however, appears to have been only about 50% of the yield of ABE fermentation to n-butanol when the number of carbon atoms transferred from the feedstock to the biofuel is compared. In addition, the ABE yield is proven on the industrial scale using corn while the reported engineered *E. coli* yield is for glucose in a carefully constructed medium at the bench scale.

The draft genome sequence data for *C. beijerinckii* 8052 was recently made available by the Department of Energy (DOE) Joint Genome Institute [31]. Availability of genomic information will enable examination of global gene expression during acidogenesis and solventogenesis. The potential for utilization of various carbon sources and complete understanding of the mechanism for sugar transport, regulation of butanol production, and butanol tolerance might be determined from the genetic information to ultimately produce improved second-generation strains. However, these achievements are certainly years in the future, especially considering the need to improve the yield of ABE fermentation to n-butanol by on the order of a factor of two compared to bio-ethanol via yeast (see below).

Processing issues

Figure 1 shows a schematic overview of yeast-based and *Clostridium* spp.-based biofuel production from corn.

Corn pre-processing and limits on the feedstock concentration in the fermenter

The mechanical processing of corn will be assumed to be identical for ethanol or n-butanol production. After milling in a hammer mill, water is added to produce a corn mash. The water content of the mash going to the fermenter must match the ability of the fermentation in question to convert starch to solvents and byproducts (gases), and to tolerate the solvents produced, in addition to conversion of some starch to biomass (microorganisms). Once the limiting biofuel concentration in the fermentation broth is reached valuable starch would otherwise be left unused since fermentation ceases.

Enzymes are used in industrial practice to convert the starch in corn to sugars before fermenting to ethanol by yeast. This is not practiced when ABE fermentation is performed [9] and fermentation of solubilized starch from corn without enzymatic pre-processing by ABE fermentation is explicitly documented [19]. ABE fermentation proceeds readily on mash with no enzyme addition and saccharification appears to be of no additional value [32]. This simplifies

the corn processing for ABE fermentation and reduces the cost. A partial hydrolysis using sulfuric acid (later neutralized) has been proposed for ABE fermentation [20], but this is only conceptual and not supported by industrial experience.

For ABE fermentation, ground corn is suspended in water at 8-10wt%. In ethanol fermentation 25-30wt% corn in water can be used due to the higher final titer for ethanol. Much less corn per fermenter volume can therefore be used in ABE fermentation since the ABE products inhibit fermentation already at relatively low concentration (about 2wt% for ABE as compared to up to 15wt% for ethanol).

Practical issues of ABE fermentation compared to fermentation using yeast

ABE fermentation using *C. acetobutylicum* was historically the first large scale fermentation process that required rather stringent aseptic conditions due to potential contamination by aerobic bacteria early in the fermentation, and contamination by acid-producing anaerobic organisms later in the fermentation. Yeast fermentation on the other hand can be performed with the most rudimentary equipment and minimal cleanliness. The requirements for aseptic operation for ABE resulted in the historic development of the now familiar steel fermentation vessel that is steam sterilized under pressure. Aseptic inoculation of large steel vessel fermenters was another important achievement to enable the early ABE industry. These developments for aseptic operation also paved the way for industrial penicillin production [33].

Contamination issues are considered serious in ABE fermentation and can lead to extended shutdowns and costly cleanup [8]. Occasional "acid crash" is known as a failure of an ABE fermentation batch to switch from the initial acidogenic to the solvent-producing stage. This results in complete loss of a fermentation batch.

Fermentation with yeast does not require stringent sterility due to the vigorous growth of yeast which out-competes many other organisms, and the low pH of the operation. ABE fermentation on the other hand has been reported to be subject to infection by bacteriophages [13] which is not an issue in yeast fermentation. Steam sterilization (perhaps at pressures on the order of 202 kPa [32]) and the required pressure- and heat resistant vessels, piping, fittings, and armatures are employed for ABE fermentation, but not for yeast fermentation. Yeast can be obtained in a convenient form from industrial suppliers, while inoculum for the ABE fermentation would likely have to be carefully produced by stepwise scale up from microbial cultures on site.

Various strains should be available on-site for ABE fermentation to switch in case of phage infection. An ABE facility would essentially have an on-site microbiology department. The foregoing special needs for ABE fermentation indicate increased capital and operating costs vis-à-vis yeast-based bio-ethanol.

Impact of the final ethanol or n-butanol concentration in the fermenter on the productivity and capital cost

Ethanol is completely miscible with water and final ethanol concentrations in industrial fermenters may reach 15 wt%. n-butanol, on the other hand, is not completely miscible with water and phase separates into an ethanol-rich and an n-butanol-rich phase above about 8wt% n-butanol in water (20°C). The final n-butanol concentrations in batch ABE fermentation are perhaps less than one third of the n-butanol solubility in water. It is unlikely that this can be increased significantly since n-butanol is an excellent solvent and will physically dissolve biological membranes, even disregarding biological toxicity. Exposure of an organism to 8 wt% n-butanol in water is thermodynamically equivalent to pure butanol exposure. Ethanol fermentation reaches about 15wt% (or ~7% of saturation) while ABE fermentation appears to reach generally about 2wt% n-butanol (~25% of n-butanol saturation).

The low final n-butanol concentration directly translates to a need for increased fermenter volumes to produce equivalent amounts of n-butanol per time compared to ethanol. There have been attempts to deal with the low final concentration of n-butanol in batch ABE fermentation by removing n-butanol selectively from ABE fermentation broth during fermentation through extraction or membrane separation [26] (see also Figure 1). Extraction methods introduce additional chemicals while issues with membrane separations include costly electrical energy to maintain a partial pressure driving force and achievement of sufficient selectivity for n-butanol. Both approaches have only been tested at small pilot scale, at best. These techniques, if developed to the industrial scale, may address the low final butanol concentrations to some extent, but they do not address the low yield of LHV per mass of feedstock that plagues ABE fermentation compared to yeast-based fermentation to ethanol. Longer fermentation times for ABE versus yeast-based fermentation (about 55 hours vs. 45 hours [9]) further exacerbate ABE's capital costs when compared to those of bio-ethanol on an equal LHV production per time basis.

To illustrate the foregoing, we shall assume that an existing yeast-based bio-ethanol plant is converted to ABE fermentation. Due to the lower volumetric productivity and longer fermentation time of ABE fermentation only about 25% of the LHV that could be produced as ethanol via yeast would be produced if the fermenter volume of this existing facility was used for ABE fermentation. The need for significant investment to achieve sterile operation and handle inoculum preparation is of course also important for this hypothetical process conversion.

Downstream separation issues

The relatively low concentration of ABE solvents in fermentation broth from conventional batch fermentation (~ 2wt%) compared to ethanol in yeast fermentation broth (~ 15 wt%) and the high normal boiling point of n-butanol (117ºC) relative to water (100ºC), and water relative to ethanol (78ºC) set ABE fermentation apart from bio-ethanol production by fermentation as far as downstream purification is concerned. The focus for ethanol/water separation is on evaporation of the volatile minority component, ethanol. While liquid water and ethanol are miscible in all proportions, the n-butanol/water system shows a hetero-azeotrope which perhaps must be taken advantage of to avoid the severe energy penalty of evaporating the majority component low-boiling (relative to n-butanol) water. This means that traditionally a first separation step for n-butanol separation from fermentation broth was a steam stripper where large amounts of water and most of the acetone and ethanol were evaporated for later recovery of the acetone and ethanol products. The water/n-butanol immiscibility is later exploited by routing the remaining n-butanol/water mixture (bottoms of the initial column) to a combination of two distillation columns and a decanter to recover fuel-grade n-butanol [34].

Scope of this work

First a comparison will be made for corn-based ethanol production in a state-of-the-industry process with industrial-scale data for ABE fermentation via the organism *C. acetobutylicum*. This will be followed by dynamic economic modeling.

A second comparison will then be attempted for the hypothetical fermentation of both C5 and C6 sugars from the cellulosic feedstock switchgrass to ethanol (based on an advanced yeast, research/pilot level data available only) or n-butanol (ABE fermentation).

Benchmarks of needed improvements are then estimated.

Results

Generic flowcharts of corn processing to bio-ethanol or bio-butanol are shown in Figure 1. The two processes are first compared for corn as feedstock using industrial-scale data, and are then compared for the hypothetical use of switchgrass.

Base case corn based bio-ethanol process

The base case will be a yeast fermentation-based bio-ethanol facility producing 149 Gg of pure ethanol per year with 360 days of operation per year (Figure 2). This implies 1.37 Gg of corn (16wt% water) per day of operation to be processed for the corn base case (compositions and flows see Table 2). Starch is by far the majority component (>70wt%) of corn both by mass and by the fraction of carbon atoms in starch compared to the carbon atoms in the whole kernel.

Comparison of ABE fermentation and yeast based fermentation to produce liquid fuels from corn

Figure 3 shows the carbon balance for ABE fermentation based on the incoming carbon in starch. Compared to ethanol production, an additional distillation column is needed to perform the acetone/ethanol split for ABE so that fuel ethanol becomes available as is assumed and credited here. Combined ethanol and n-butanol is considered as fuel produced from ABE fermentation to give the most favorable comparison with only ethanol from the traditional fermentation using *S. cerevisiae* (Figure 2).

The LHV yield per mass of corn is significantly lower for ABE fermentation (Table 3). Reasons include that the ABE fermentation converts a substantial amount of carbon to acetone which cannot be used as a fuel, that ABE fermentation produces relatively more CO_2 than yeast fermentation, and that more starch remains unfermented.

The LHV yield of the ABE process would have to increase by 74% (with the current ABE LHV yield taken as 100%) to equal the yeast based bio-ethanol process. This would mean to increase the n-butanol yield from about 0.11 to 0.19 kg n-butanol per kg corn to break even with state of the art bio-ethanol facilities assuming a constant 6/3/1 solvent split (see above). It is important that this improvement must be shown on actual corn mash from an industrial corn dry mill process, not on an artificial substrate such as pure glucose in a carefully constructed, complex, and costly medium in a well-controlled laboratory environment. No data appears to be

available that would indicate that such an improvement is likely in the near future at the industrial scale (see Background).

Overall economic modeling of corn fermentation to ethanol vs. ABE fermentation of corn

The software used for the system dynamic modeling of the bio-ethanol production process using yeast and the bio-butanol production process using ABE fermentation is iThink (isee systems Inc., Lebanon, NH). The advantage of this tool is its transparency about the assumptions being used in the analysis and ease of altering these assumptions to test the model's robustness. The techno-economic model captures the foregoing assumptions about conversion rates and LHV yields as well as operation costs and market price conditions for the products from the two processes.

The interest of the U.S. government in the production of bio-ethanol has resulted in the implementation of a $0.14 per liter subsidy directed at blenders. This subsidy is expected to end in 2010 and whether it will be renewed or terminated is a policy uncertainty. Currently, however, there is no such policy support for the production of bio-butanol, implying that there are inherent economic disadvantages embedded in a switch from ethanol production to n-butanol production. The ensuing analysis considered two scenarios about the subsidy: removed when its term expires in 2010; allowed to continue at the same level after 2010.

The literature indicates that the current yield of n-butanol per kg of starch can perhaps be increased over time. Therefore, we have assumed a linear growth in yield of 0.76% beginning in 2010, which, while a very aggressive growth rate in yield given the historical performance of yield of ABE fermentation over about nine decades, incorporates potential technological improvements into the model. Table 4 shows the cost and price assumptions of the different inputs and outputs.

We assumed that all the outputs from the ABE process are sold at their prevailing market prices. However, having assumed that the by-products such as distillers' grain and carbon dioxide from the ABE and yeast ethanol production processes are indistinguishable, they were ignored in further comparisons. Using U.S. Department of Energy historical data and assumptions about prices, demand and supply trends, as well as information from industry, we projected these prices over 20 years, from 2007 (base year) to 2027 (Figure 4). In these projections, we assumed that n-butanol and acetone prices are consistently higher than that of

ethanol given the historical market trends. The average acetone price over the 20 years was about $0.92 per kg with a standard deviation of about $0.07 per kg compared to ethanol at $0.59 per kg and $0.07 and n-butanol at $0.77 per kg and $0.06 per kg respectively.

Despite assuming a higher price for n-butanol, including the revenues from acetone and ethanol emanating from the ABE process and allowing more significant process improvement, Figure 5 shows for example that converting an ethanol plant into an n-butanol production facility is not a profitable venture, even over the long run. The results show that although ethanol production becomes profitable again in 2022 after removing the subsidy in 2010, its net present value is $-26 million over the 20 years at 8.5 percent discount rate. On the other hand, reinstating the subsidy yields a net present value of $116.4 million over the same period and at the same rate. The net present value of net revenues for the ABE process is $-306.6 million, making it almost 12 times more unprofitable than continuing with the production of ethanol without the subsidy.

Although n-butanol transportation is reputed to be compatible with existing pipeline systems, the need to build processing facilities within proximate distances of feedstock implies investing about $1 million per km to move the n-butanol by pipeline. Assuming an average pipeline construction cost of $1 million per km with a 20-year depreciation, and pipeline transportation cost of $0.005 per kg compared with overland transportation cost of $0.027 per kg, the ABE process is still not competitive against the yeast-based ethanol process. The ABE process's lack of competitive advantage was found to be robust under numerous plausible assumptions about prices, operation costs and yield improvements. Therefore, based on the technical and economic simulation assumptions used in this study, the production of n-butanol is likely unattractive when compared with traditional yeast-based ethanol production from corn for transportation fuel despite the often cited higher LHV per kg fuel for n-butanol when compared to ethanol.

Switchgrass as feedstock for bio-butanol vs. bio-ethanol

The EISA mandates include very substantial biofuel production goals from cellulosic feedstocks (second-generation biofuels). Cellulosic feedstocks such as corn stover, wheat straw, and switchgrass are considered promising for production of liquid biofuels [35]. ABE fermentation may be thought to have an advantage here since it has been reported that not only

C6 sugars (from hydrolyzed cellulose) but also C5 sugars (from hemicellulose) may be fermented to mainly n-butanol using *Clostridium* spp. [30].

Industrial scale data of fermentation-based ethanol production from switchgrass using both C5 and C6 sugars is not publicly available. Yeast strains developed at Purdue University and licensed by Iogen Corp. are perhaps promising for industrial scale fermentation of both C5 and C6 sugars to ethanol from hydrolyzed cellulosic feedstock [36]. Sedlak and Ho's value of 0.41 kg ethanol per kg of combined C5 and C6 sugars fed will be used together with a switchgrass composition (dry) of 33.45wt% cellulose and 26.51wt% hemicellulose (balance lignin and other non-fermentables). It will be assumed that all of the cellulose and hemicellulose is depolymerized to glucose (C6) and xylose (C5) during pre-treatment and all the resulting sugars are available for fermentation to either ethanol or ABE solvents without significant inhibition of the fermentation.

Base case switchgrass bio-ethanol process

As above, the base case will be an advanced yeast fermentation based bio-ethanol facility producing 149 Gg of pure ethanol per year with 360 days of operation per year. With the yield and switchgrass composition shown above about 1,689 tonnes of switchgrass (dry) will need to be processed per day (> 600,000 tonnes per year).

Comparison of ABE fermentation and yeast based fermentation to produce liquid fuels from switchgrass

Comparison of Figure 6 and Figure 7 shows that ABE fermentation of switchgrass again is not competitive when comparing laboratory data for an advanced yeast with ABE fermentation under the assumptions above. Other organisms to convert C6 and C5 sugars to ethanol have been proposed, but this has only been shown at the laboratory scale and with long fermentation times [37]. Modified yeast to ferment both C5 and C6 sugars are under development in other research groups in addition to Ho and coworkers [36].

Overall economic modeling of switchgrass fermentation to ethanol vs. ABE fermentation of switchgrass

Large scale industrial experience of switchgrass production, harvest, transport, storage, and conversion to a biofuel via fermentation on a thousand tonne per day per facility scale is lacking at this time. Therefore economic modeling would entail a great deal of uncertainty and the

economic outlook is perhaps best represented by the yield figures shown above. One would conclude that ABE fermentation of C5 and C6 sugar from switchgrass is not competitive to fermentation of the same sugars by an advanced yeast.

Discussion

The analysis executed above based on carbon mass balances, LHV, and dynamic economic modeling shows that for available industrial-scale performance data n-butanol as a biofuel is not competitive from corn or a cellulosic feedstock. The low LHV yield of *Clostridium* spp. based fermentation to n-butanol (and ethanol) is crucial as long as feedstock costs are a significant portion of the cost to produce the fuel. The yield gap between state-of-the-art bio-ethanol production and bio-butanol is very significant, and bio-butanol would have to not only pull even but exceed bio-ethanol's LHV yield significantly to provide motivation for the relatively challenging fermentative n-butanol production process.

One could perhaps argue that ABE fermentation products can be sold as chemicals, which was the basis of the n-butanol industry early in the 20th century. The impact of increased n-butanol production on the market price however has to be carefully scrutinized and n-butanol as a chemical was not the focus here.

Conclusions and Outlook

It is acknowledged that all fundamental arguments (such as feedstock limitations, food vs. fuel, etc.) against the production of ethanol from biomass apply equally (or even more so, see below) to fermentation derived n-butanol assuming the current state of technology.

Production of fuel n-butanol via ABE fermentation of biomass does not seem advantageous at this time compared to bio-ethanol. The main reason is the low yield of fuel lower heating value per mass of biomass processed from the ABE fermentation, and additionally the low productivity per fermenter volume and time, compared to ethanol production via fermentation. The economic disadvantage remains even when the acetone and the ethanol from the ABE process are assumed to be sold at market prices in addition to the n-butanol. The touted advantage of transportation of n-butanol using existing pipelines is limited due to the relatively limited production volume and location of necessarily often remote biofuel facilities. Biomass transportation cost and energy needs preclude heavily centralized processing. Although metabolic and genetic engineering may

alleviate some or all of these disadvantages, this is perhaps years into the future and success of this basic research on the industrial scale is by no means guaranteed.

Given the prevailing disadvantages of the ABE process, it would seem that investing resources in reducing the fossil fuel energy demand (and thereby water demand [38]) and other more easily accessible aspects of ethanol production would perhaps yield higher net economic and environmental benefits compared to developing bio-butanol. Low yield, low titer, strict sterility requirements, phage infection risks, and downstream separation issues are a fairly formidable collection of obstacles for bio-butanol absent great advances in robust and industrial-scale microbiology of the process.

The yield as lower heating value (for fuel) per mass of biomass processed would have to be more than doubled to make n-butanol production via *Clostridium* spp. attractive compared to bio-ethanol, considering the significantly more complex fermentation for bacteria-based n-butanol vs. yeast-based ethanol.

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Figures

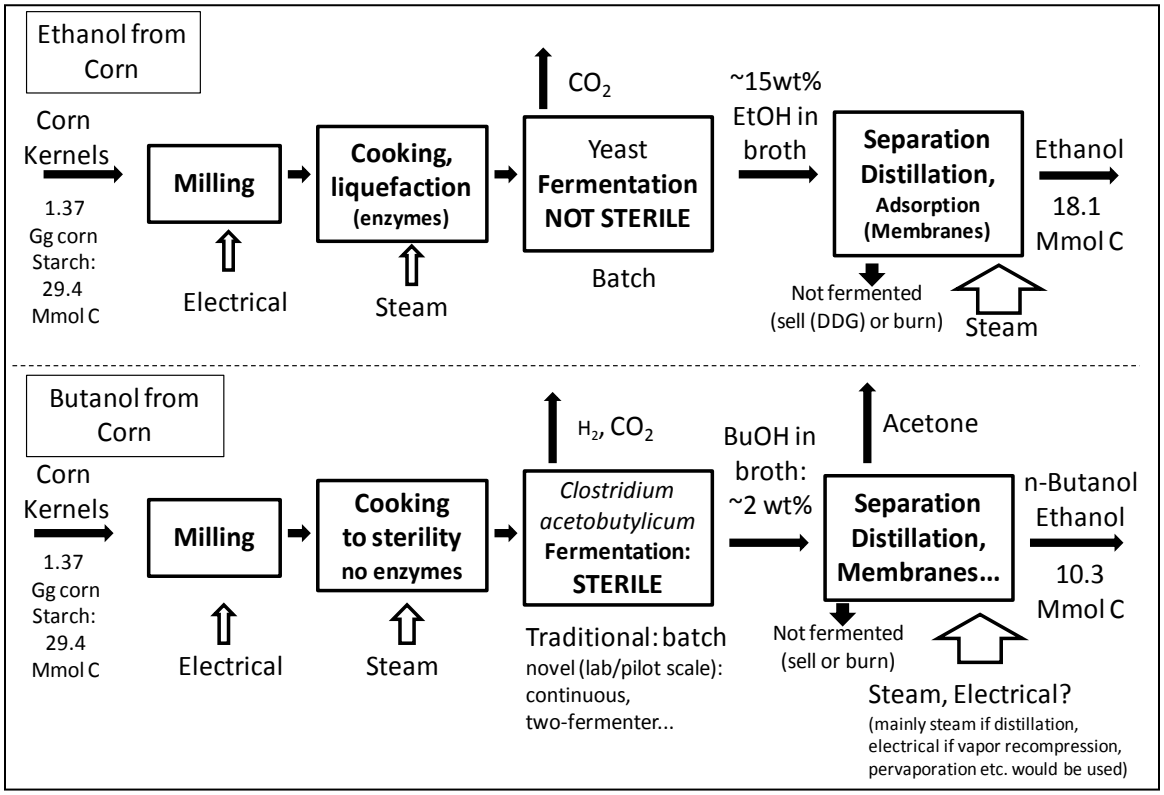

Figure 1: Overview flowcharts for bio-ethanol and bio-butanol via corn fermentation (detailed carbon balances below). Carbon flows are schematically indicated (solid arrows). Energy flows (outlined arrows) are shown roughly proportional (arrow width) to the energy. No enzymes are added for pre-processing for ABE fermentation. Both n-butanol and ethanol from ABE fermentation via *Clostridium* spp. are credited as fuels. Some research and development approaches are noted for n-butanol fermentation and separation where applicable. (360 days of operation per year assumed)

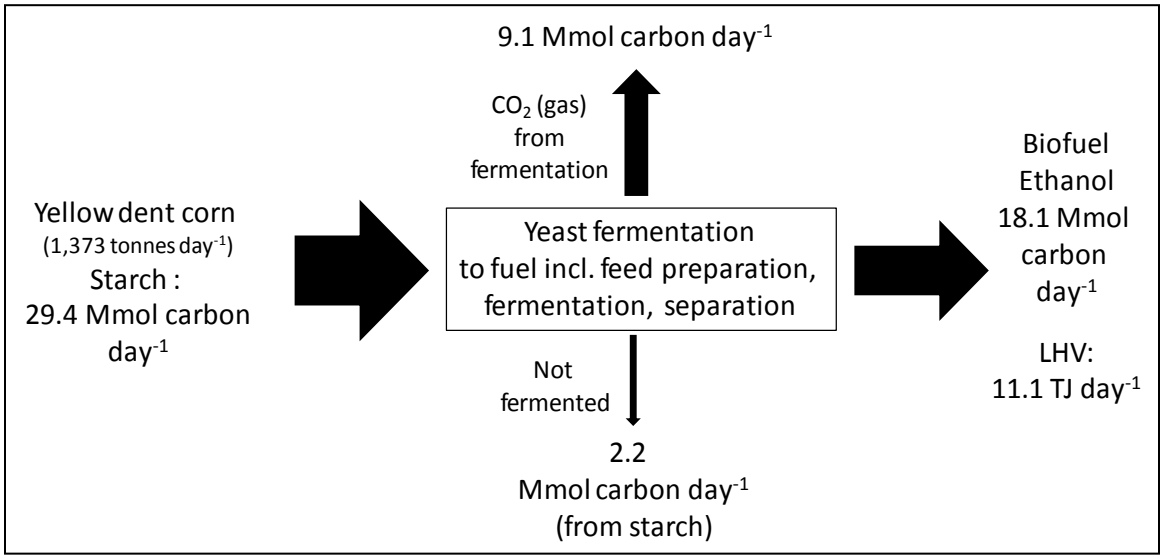

Figure 2: Carbon balance based on the starch fraction of 1,373 tonnes of yellow dent corn (16wt% water) fermented per day by yeast. Yield is assumed at 0.30 kg pure ethanol per kg corn. 100% recovery of ethanol from fermentation broth is assumed. One mol CO_2 per mol of ethanol is assumed. Arrow thicknesses are roughly proportional to the carbon mass flows.

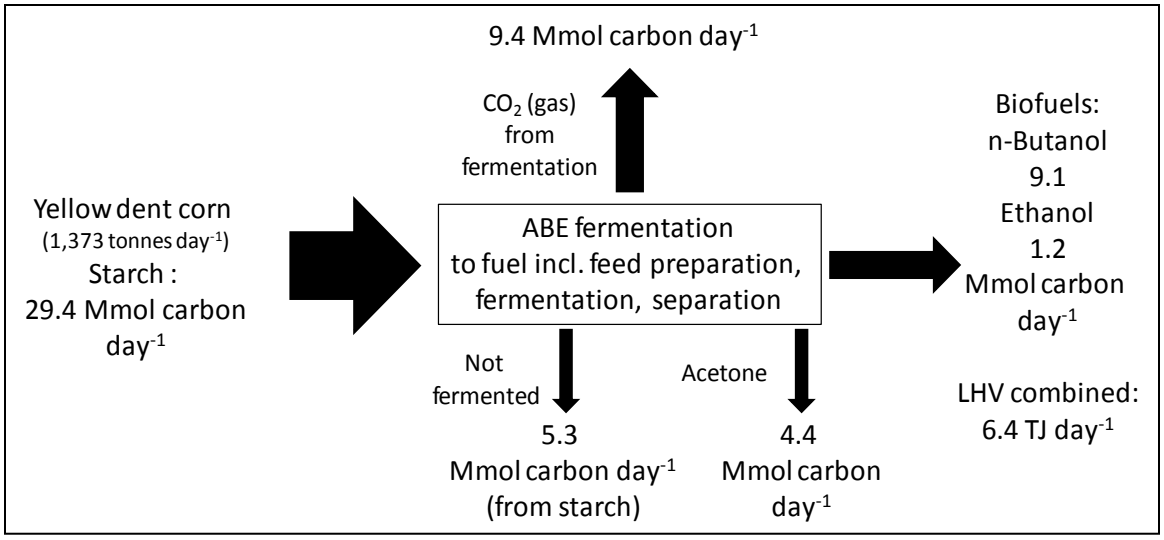

Figure 3: Carbon balance based on the starch fraction of 1,373 tonnes of yellow dent corn (16wt% water) fermented per day by ABE fermentation. Yield is assumed at 0.11 kg pure n-butanol per kg corn (50% of carbon atoms from starch go to solvents). 100% recovery of solvents from fermentation broth is assumed. One mol CO_2 per mol of ethanol is assumed. Arrow thicknesses are roughly proportional to the carbon mass flows.

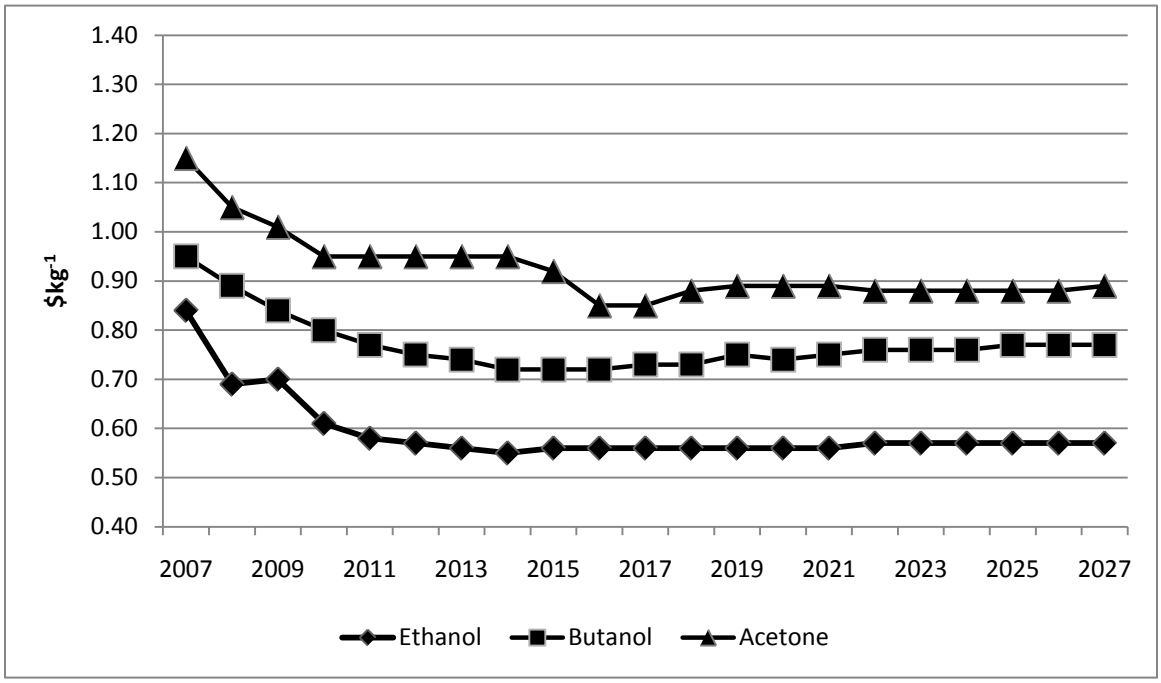

Figure 4: Projected product prices based on expected future market conditions and historical trends.

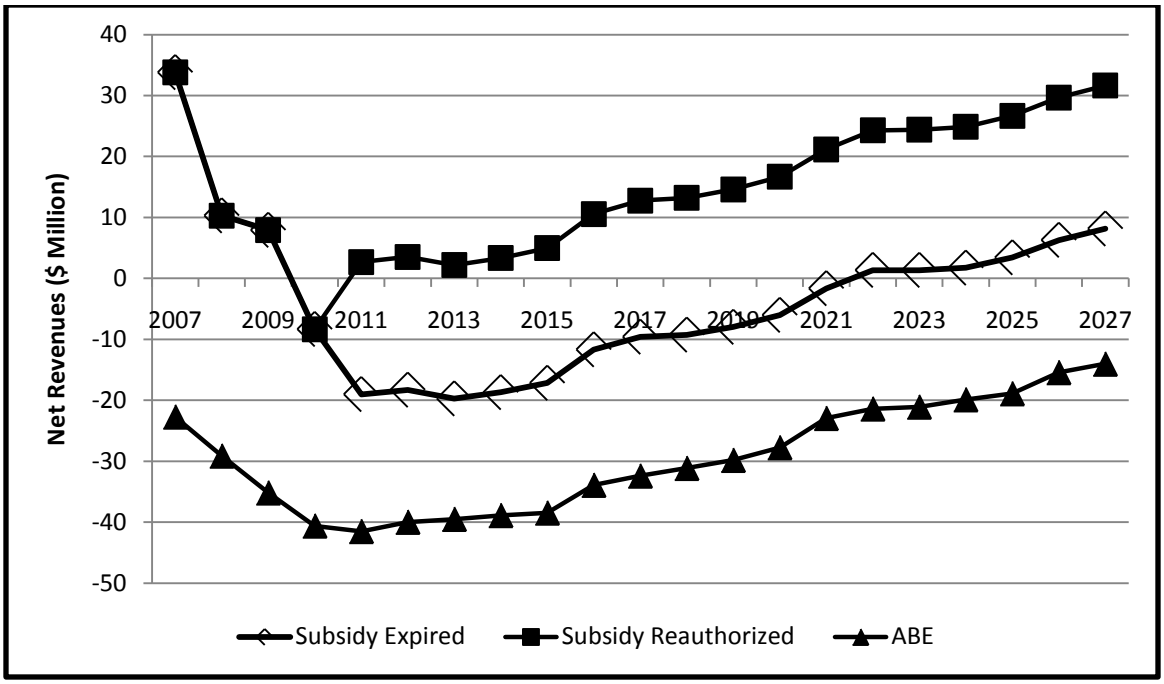

Figure 5: Net revenue under alternative production technologies and subsidy scenarios.

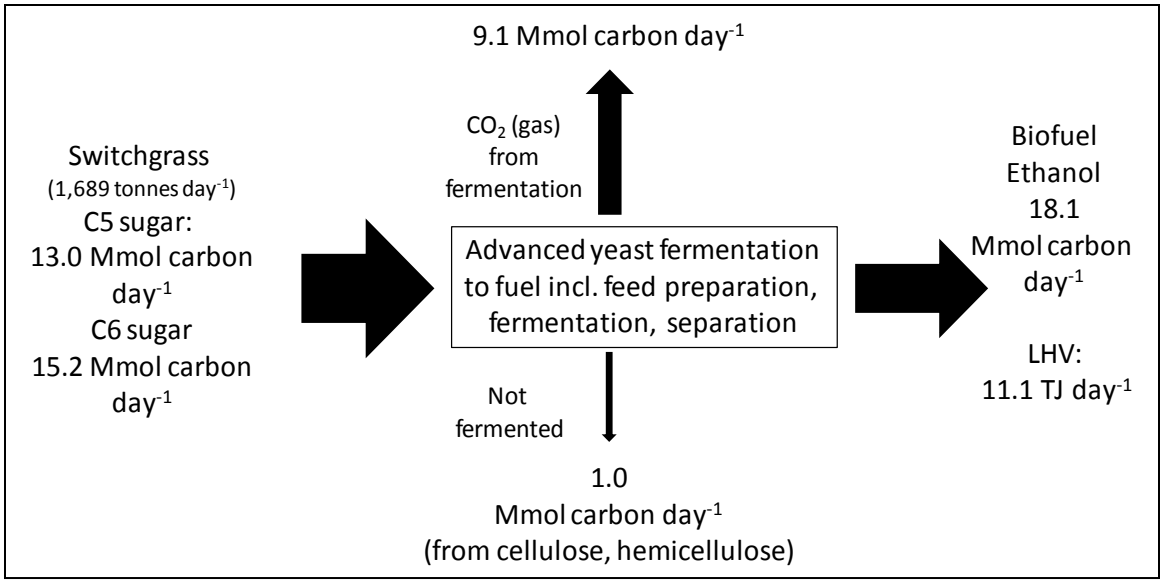

Figure 6: Carbon balance based on the C5 and C6 fraction of 1,689 tonnes of switchgrass (dry) fermented per day by an advanced yeast [36]. One mol CO_2 per mol of ethanol is assumed. Arrow thicknesses are roughly proportional to the carbon mass flows.

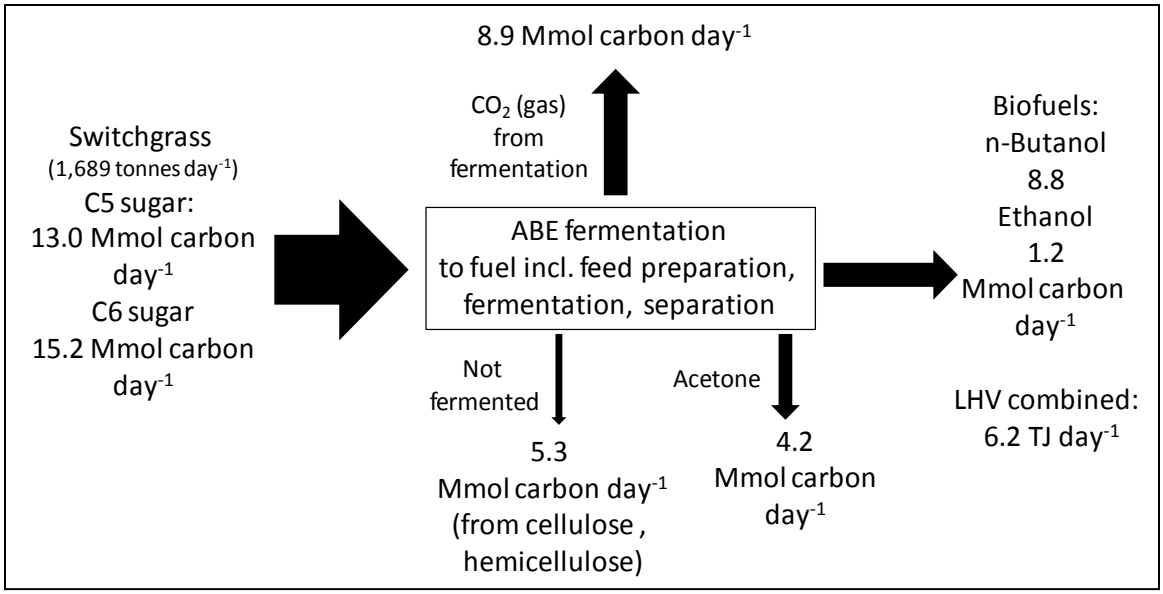

Figure 7: Carbon balance based on the C5 and C6 fraction of 1,689 tonnes of switchgrass (dry) fermented per day by ABE fermentation. The same yield as above for fermentation of starch from corn is here applied to fermentation of the C5 and C6 sugars (50% of carbon atoms from C5 and C6 sugars go to solvents). 100% recovery of solvents from fermentation broth is assumed. One mol CO_2 per mol of n-butanol is assumed. Arrow thicknesses are roughly proportional to the carbon mass flows.

Tables

Table 1: Density and lower heating value (LHV) of fermentation products and gasoline for reference.

	Density [15] Mg m^{-3} at 20°C	LHV kJ g^{-1}
n-Butanol	0.81	33.4*
Ethanol	0.79	27.0*
Acetone	0.79	28.7*
Hydrogen		121.5 [16]
Gasoline	0.72-0.78 [17]	43.4 [16]

*LHV = (Heat of Combustion) – (enthalpy of evaporation of water formed during combustion, at 100 kPa); data from [15].

Table 2: Baseline composition and component mass flows of yellow dent corn. The base case assumes that 1.373 Gg of corn (16wt% water, as is) are processed per day of operation to reach 149 Gg as pure ethanol produced per year (assuming a yield of 0.30 kg pure ethanol per kg corn).

	Mg day^{-1}	wt%	wt% (dry basis)	Mg of carbon day^{-1}	mol carbon day^{-1}	wt% of carbon in corn
Water	219.6	16.0	0	-	-	-
Starch	837.3	61.0	73	352.2	$2.94\ 10^{7}$	67.69
Oil	52.2	3.8	5	41.2	$3.43\ 10^{6}$	7.92
Protein	109.8	8.0	10	58.7	$4.89\ 10^{6}$	11.28
Fiber	153.7	11.2	13	68.2	$5.68\ 10^{6}$	13.11

Table 3: Overall comparison of fermentation of corn to ethanol by yeast or to the fuels n-butanol and ethanol by *C. acetobutylicum* (ABE fermentation).

Yeast: ethanol	***C. acetobutylicum*: n-butanol+ethanol**
18.1 Mmol C day^{-1}	10.3 Mmol C day^{-1}
1,893 hm^3 y^{-1} (20°C)	761 hm^3 y^{-1} (n-butanol, 20°C) 129 hm^3 y^{-1} (ethanol, 20°C)
4.0 PJ(LHV) y^{-1}	2.3 PJ(LHV) y^{-1}

Table 4: Base production cost assumptions on output basis.

Item	$ kg^{-1} (Product)	
	Ethanol	N-butanol
Feedstock (corn)	0.380	1.853
Microorganisms & chemicals	0.072	0.085
Labor	0.011	0.050
Utilities	0.072	0.338
Overhead (Admin, etc.)	0.016	0.016
Total	**0.550**	**2.342**