

Life-Cycle Assessment of Corn-Based Butanol as a Potential Transportation Fuel

Energy Systems Division

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NOTATION

ABE	acetone, butanol, and ethanol
BC	biochemical
BTX	benzene, toluene, xylene
CEH	Chemical Economics Handbook
CH ₄	methane
CO	carbon monoxide
CO ₂	carbon dioxide
DDGS	distiller's dried grain with solubles
DOE	Department of Energy
EIA	Energy Information Administration
EtOH	ethanol
GHG	greenhouse gas
REET	Greenhouse Gases, Regulated Emissions and Energy Use in Transportation
GV	gasoline vehicles
IPCC	Intergovernmental Panel on Climate Change
K ₂ O	potash fertilizer
LCA	life-cycle analysis
LCI	life-cycle inventory
LDV	light-duty vehicle
LHV	low heating value
MMGY	million gallons per year
N	nitrogen
N ₂ O	nitrous oxide
NG	natural gas
NO _x	nitrogen oxide
P ₂ O ₅	phosphorus fertilizer
PM ₁₀	particulate matter with diameters smaller than 10 micrometers
PM _{2.5}	particulate matter with diameters smaller than 10 micrometers
R&D	research and development
RTO	regenerative thermal oxidizer

SO _x	sulfur oxide
USDA	U.S. Department of Agriculture
VOC	volatile organic compound
WTW	well-to-wheels

UNITS OF MEASURE

Btu	British thermal unit
bu	bushel
g	gram(s)
gal	gallon(s)
kg	kilogram(s)
kW	kilowatt(s)
kWh	kilowatt hour(s)
L	liter
lb	pound(s)
MJ	mega Joule
psi	pounds per square inch
scf	standard cubic feet
wt%	weight percent
yr	year

LIFE-CYCLE ASSESSMENT OF CORN-BASED BUTANOL AS A POTENTIAL TRANSPORTATION FUEL

by

May Wu, Michael Wang, Jiahong Liu, and Hong Huo

ABSTRACT

Butanol produced from bio-sources (such as corn) could have attractive properties as a transportation fuel. Production of butanol through a fermentation process called acetone-butanol-ethanol (ABE) has been the focus of increasing research and development efforts. Advances in ABE process development in recent years have led to drastic increases in ABE productivity and yields, making butanol production worthy of evaluation for use in motor vehicles. Consequently, chemical/fuel industries have announced their intention to produce butanol from bio-based materials. The purpose of this study is to estimate the potential life-cycle energy and emission effects associated with using bio-butanol as a transportation fuel. The study employs a well-to-wheels analysis tool — the *Greenhouse Gases, Regulated Emissions and Energy Use in Transportation* (GREET) model developed at Argonne National Laboratory — and the Aspen Plus[®] model developed by AspenTech. The study describes the butanol production from corn, including grain processing, fermentation, gas stripping, distillation, and adsorption for products separation. The Aspen[®] results that we obtained for the corn-to-butanol production process provide the basis for GREET modeling to estimate life-cycle energy use and greenhouse gas emissions. The GREET model was expanded to simulate the bio-butanol life cycle, from agricultural chemical production to butanol use in motor vehicles. We then compared the results for bio-butanol with those of conventional gasoline. We also analyzed the bio-acetone that is co-produced with bio-butanol as an alternative to petroleum-based acetone. Our study shows that, while the use of corn-based butanol achieves energy benefits and reduces greenhouse gas emissions, the results are affected by the methods used to treat the acetone that is co-produced in butanol plants.

1 INTRODUCTION

Liquid fuel use accounts for the single largest share of petroleum oil consumption in the United States. In 2006, the United States consumed more than 20 million barrels of crude oil per day; 66% of this total was used in the transportation sector. Motor vehicles alone consumed 140 billion gallons of gasoline and 50 billion gallons of diesel in 2006. Gasoline use has increased as a result of the growth in light-duty vehicle (LDV) travel in the past 20 years. The Energy Information Administration projected that transportation fuel use will continue to grow up to 30% by 2030 (Conti 2007).

On the petroleum supply side, the United States relies heavily on foreign oil (13.7 million barrels per day, EIA 2007). The world's most oil-rich region has become extremely unstable, which heightens energy security concerns. Furthermore, competition for petroleum oil has increased dramatically as a result of rapid economic growth in developing countries. Finally, exploration, production, and use of petroleum-based fuels generate greenhouse gas (GHG) emissions, which are the primary cause of global warming, as confirmed in a recent report prepared by the Intergovernmental Panel on Climate Change (IPCC 2007).

Considering the challenges facing the United States in its continued reliance on fossil-based fuels in the transportation sector, many researchers are exploring other alternatives. Finding a liquid transportation fuel that (1) can be produced from domestic resources, (2) is carbon neutral, and (3) has minimal GHG impacts would allow the United States to reduce our dependence on foreign oil and decrease environmental burdens. In a recent State of Union address, the President stated his goal of displacing 20% of gasoline demand by renewable fuels and vehicle efficiency improvement — that translates to 35 billion gallons of biofuels and alternative fuels in 10 years.

Following dramatic growth in the ethanol industry, corn ethanol (EtOH) production reached a record 4.9 billion gallons in 2006. Yet, this total accounts for only 2.3% of the total U.S. gasoline supply (in gallons of gasoline equivalent). Even considering a U.S. Department of Agriculture (USDA) projection that corn ethanol production could reach 12 billion gallons by 2017 (Collins 2007), a large gap remains to be filled by biofuels. Therefore, developments in feedstocks, processing technologies, and new biofuels are urgently needed if the United States is to meet the President's target of 35 billion gallons per year by 2017.

Among potential biofuels, butanol (BuOH) produced from starch has gained visibility in recent years as a replacement for gasoline. Butanol has unique properties as a fuel. The energy content of butanol — 99,840 Btu per gallon (low heating value [LHV]) — is 86% of the energy content of gasoline (on a volumetric basis) and 30% higher than the energy content of ethanol. The low water solubility of butanol could minimize the co-solvency concern associated with ethanol, consequently decreasing the tendency of microbial-induced corrosion in fuel tanks and pipelines during transportation and storage. Butanol is much less evaporative than gasoline or ethanol, making it safer to use and generating fewer volatile organic compound (VOC) emissions. The majority of butanol used as a chemical is produced from petroleum propylene through the Oxo process (in which synthetic gas [syngas] is reacted with propylene), and its ultimate end use is for surface coatings.

The most dominant bio-butanol production process has been acetone-butanol-ethanol (ABE) fermentation. ABE fermentation by *Clostridium acetobutylicum* was the route used to produce butanol during World War II. It was phased out when more economical petrochemical routes emerged. Now, almost all butanol in the world is produced from petrochemical feedstocks. Research interest in developing viable ABE fermentation processes has been rekindled recently as a result of the pursuit of non-fossil-based feedstocks.

In the past 20 years, research and development (R&D) efforts have focused on various aspects of the ABE process. Molecular biology research has achieved major breakthroughs in

strain/mutant development that dramatically improved microbial tolerance to butanol toxicity, which resulted in a significant increase in ABE solvent production yield. Experimental and computational engineering efforts have included designing new schemes to minimize butanol inhibition by using new fermentor configurations, improved downstream processing, and process integration. Huang et al. (2004) reported an experimental process that uses continuous immobilized cultures of *Clostridium tyrobutyricum* and *Clostridium acetobutylicum* to maximize the production of hydrogen and butyric acid and convert butyric acid to butanol separately in two steps. This process reportedly produced butanol at a rate of 4.64 grams per liter of fermentation medium per hour (g/L/h) and used 42% glucose, compared with the up-to-25% glucose use rate in traditional ABE fermentation by *Clostridium acetobutylicum* alone.

In the early, 1990s *Clostridium beijerinckii* BA101 was developed by using chemical mutagenesis together with selective enrichment, which is able to produce twice as much butanol as its parent strain (US Patent 6358717). Extensive studies have been performed to characterize this strain and develop an ABE process with various feedstocks and evaluate technologies for downstream product separation (Qureshi and Blaschek 1999; Parek et al. 1999; Qureshi and Blaschek 2001a and 2001b). Experimental and pilot-scale ABE fermentation processes by this organism resulted in up to 95.1% glucose utilization in fermentation. Using in-situ gas stripping for solvent removal from fermentor minimizes product inhibition and enables higher feed concentration — up to 500g/L of glucose (Ezeji et al. 2004). Solvent production in this process in a fed-batch mode reached 65:35:1 of butanol:acetone:ethanol by weight, which is a significant increase in butanol production from 6:3:1 in conventional ABE process.

Liu (2003) presents an exhaustive survey of major research findings on ABE downstream processing. Recent studies have focused on integration of fermentation and product removal through in-situ gas stripping and fermentation gas recirculation (Qureshi and Blaschek 2000; Qureshi and Blaschek 2001a; Qureshi and Blaschek 2001b; Ezeji et al. 2004; and Ezeji et al. 2005). The latest development includes a DuPont patent (2007) describing a strain that produces butanol from biological feedstocks while minimizing acetone production. Cellulosic feedstock for butanol production has also been reported (Qureshi et al. 2007).

Researchers have employed computer simulations in developing butanol production processes, including ABE fermentation. The earliest efforts in downstream processing simulation of ABE fermentation were reported in Marlatt and Datta (1986) and Dadgar and Foutch (1988). In these studies, simulations were used to evaluate the economics of their processes. More recent studies were published in Liu (2003) and Liu et al. (2004 and 2006). In these studies, downstream processing systems were synthesized, simulated, and optimized in terms of cost. There are comparatively few publications on ABE fermentation process simulation. A corn-to-butanol pathway has been modeled by NRC (Natural Resources Canada, Feb. 2007) recently, on the basis of earlier work of conventional ABE fermentation. The study examined corn-based butanol used as 10% butanol in a gasoline blend to fuel light-duty vehicles. Simulation results for fuel ethanol produced from corn via dry milling, such as those obtained by using USDA's dry mill model (Kwiatkowski et al. 2006; McAloon 2006), are readily available.

Since 1995, with support primarily from DOE's Office of Energy Efficiency and Renewable Energy, Argonne has been developing the **Greenhouse Gases, Regulated Emissions**

and *Energy Use in Transportation* (GREET) model. Argonne released the first version of the model — GREET 1.0 — in June 1996. GREET is a Microsoft® Excel™-based multidimensional spreadsheet model that addresses the well-to-wheels (WTW) analytical challenges associated with transportation fuels (including ethanol) and vehicle technologies. The latest version — GREET 1.7 — is capable of analyzing more than 100 transportation fuel pathways and 75 vehicle/fuel systems (Brinkman et al. 2005). The GREET model has been updated frequently to reflect new feedstocks, processing technologies, fuels, and vehicle systems. For a given vehicle and fuel system, GREET separately calculates:

- Consumption of total energy (energy in non-renewable and renewable sources), fossil fuels (petroleum, natural gas, and coal combined), petroleum, natural gas, and coal;
- Emissions of carbon-dioxide (CO₂) -equivalent GHGs — primarily CO₂, methane (CH₄), and nitrous oxide (N₂O); and
- Emissions of six criteria pollutants: VOCs, carbon monoxide (CO), nitrogen oxides (NO_x), particulate matter measuring 10 micrometers or less (PM₁₀), particulate matter measuring 2.5 micrometers or less (PM_{2.5}), and sulfur oxides (SO_x).

These criteria pollutant emissions are further separated into total and urban emissions.

This study was an attempt to evaluate the potential of the recent ABE process from a life-cycle perspective. This estimate provides a life-cycle analysis (LCA) of the production and use of corn-derived bio-butanol as transportation fuel to displace petroleum gasoline. First, we developed an ABE process simulation model by using Aspen Plus®. We used the energy and mass balance resulting from the Aspen Plus® simulation as a basis for a life-cycle analysis of corn-based butanol production and use. We estimated the life-cycle energy and GHG emissions impacts of corn-based butanol (produced via the ABE process) when used to displace gasoline as a transportation fuel in LDVs. We also performed a “cradle-to-user” analysis for bio-acetone (which is co-produced with bio-butanol) to address the impacts of displacing petroleum-based acetone with the bio-acetone co-product. Merits and shortfalls of such process are discussed in this report.

2 LCA SYSTEM BOUNDARY AND ANALYSIS SCENARIOS

2.1 SYSTEM BOUNDARY

Figure 1 depicts the GREET modeling boundary for this study. The life cycle of bio-butanol is divided into five stages:

1. Corn farming,
2. Corn transportation,
3. Bio-butanol production,
4. Bio-butanol transportation and distribution, and
5. Bio-butanol use in gasoline vehicles (GVs).

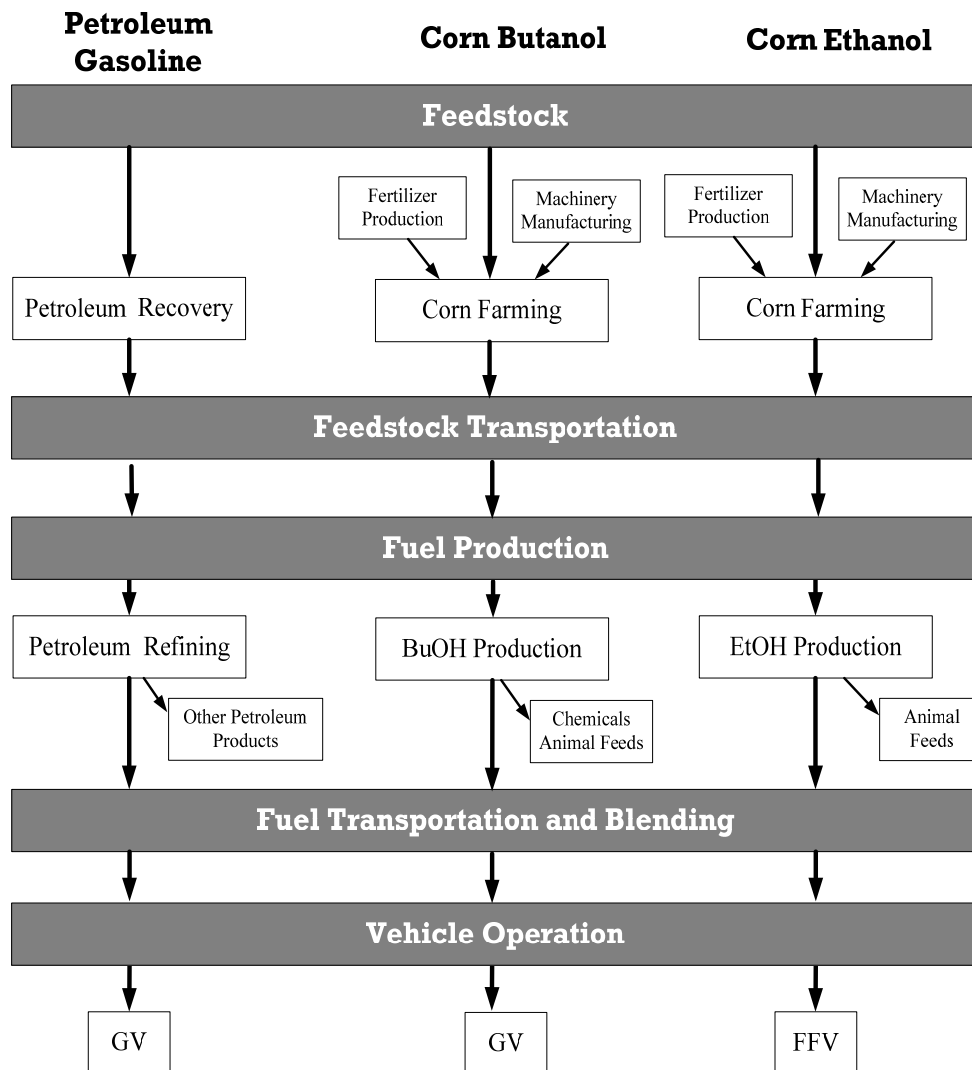


FIGURE 1 Schematic Representation of WTW Analysis System Boundaries for Butanol, Ethanol, and Gasoline

The bio-butanol life cycle begins with the manufacture of fertilizer and farming machinery. Corn farming operations include irrigation, tillage, application of fertilizer, lime, herbicides, and pesticides, and corn harvest. Harvested corn grain is transported via barge, rail, and truck to fuel production facilities, where it undergoes biochemical (BC) processing for fuel production. The demand for heat and power (steam and electricity) from the BC processing is met by grid electricity and natural gas (NG). Liquid fuel is then transported to refueling stations via rail, barge, and truck. We assumed that bio-butanol would be used in unblended form in GVs. The gasoline life cycle, on the other hand, begins with crude oil recovery in oil fields and ends in gasoline combustion in GVs. The timeframe for the analysis is 2010.

2.2 ANALYSIS CASES

This study analyzes a facility that produces 150,000 metric tons of bio-butanol per year, requiring 33 million bushels of corn — equivalent to an 89-million-gallon-per-year (MMGY) corn ethanol dry mill. Corn-derived butanol (bio-butanol) is produced from fermentation that co-produces acetone, butanol, and ethanol (ABE), plus a small amount of fatty acids. The corn-derived butanol is assumed to displace gasoline in GVs on the basis of the similarities in the properties of the two fuels (Table 1).

Because current bio-butanol production technology is still in the early stages of research and development, we assumed a 2010 timeframe for a large-scale demonstration plant. During bio-butanol production, a large amount of acetone is generated as a co-product. Corn-based acetone could displace petroleum-based acetone. We established cases to compare biofuel butanol and biochemical acetone with their petroleum counterparts. For bio-butanol, we conducted a full life cycle (or WTW) analysis; for bio-acetone, we elected a “cradle-to-user” approach because of limited use data available in the open literature. The cradle-to-user analysis includes feedstock farming and transportation, bio-acetone production via ABE process, and acetone transport to user gate. Thus, we established a total of seven cases.

- **Case 1:** Conventional gasoline (baseline fuel).
- **Case 2:** Bio-butanol with natural gas as the process fuel, where bio-acetone is regarded as a chemical to displace petroleum-based acetone and is therefore credited by product displacement. Distiller’s dried grains with solubles (DDGS) and ethanol displace animal feed and gasoline, respectively.

TABLE 1 Properties of ABE Products^a

Product	LHV (Btu/gal)	Density (g/gal)
Acetone	83,127	2,964
Butanol	99,837	3,065
Ethanol	76,330	2,988
Gasoline	116,090	2,819
DDGS	8703 (Btu/lb)	

^a Sources: Acetone and butanol: J.-C. Guibet 1997; ethanol and gasoline: GREET; DDGS (distiller’s dried grains with solubles): Morey et al. 2006.

- **Case 3:** Bio-butanol with natural gas as the process fuel, where acetone and DDGS are regarded as energy products and are thus credited on the basis of the energy allocation method among butanol, acetone, ethanol, and DDGS.
- **Case 4:** Bio-butanol with natural gas as the process fuel, where acetone is regarded as waste and therefore no acetone credit is assigned. DDGS and ethanol displace animal feed and gasoline, respectively.
- **Case 5:** Corn ethanol from dry milling with natural gas as the process fuel, where DDGS is credited by product displacement to displace animal feed (GREET default).
- **Case 6:** Corn ethanol from dry milling with natural gas as the process fuel, where DDGS is regarded as an energy product and is credited on the basis of the energy allocation method between ethanol and DDGS.
- **Case 7:** Cradle-to-user petroleum-acetone (baseline chemical) analysis for examining displacement of petroleum acetone by bio-acetone. Butanol, DDGS, and ethanol are credited by product displacement.

We established a bio-butanol life-cycle framework on the basis of Aspen Plus[®] process simulation and existing GREET, as shown in Figure 1. We adopted feedstock corn farming and transportation values from GREET's corn ethanol pathway. Bio-butanol is produced, together with acetone and ethanol, from a corn dry mill by retrofitting the mill to accommodate the ABE fermentation and separation process. The bio-butanol production process is simulated by using the Aspen Plus[®] model. We approximated the other process steps (grain feed handling, cooking, and DDGS drying) on the basis of a corn dry mill cost model from USDA (Kwiatkowski et al. 2006; McAloon 2006) and results from a recent study (Mueller and Cuttita 2006). Data from these sources and Aspen Plus[®] simulations were then integrated and scaled to obtain the entire bio-butanol plant mass and energy flow. Data from the mass and energy balance of the bio-butanol plant serve as input parameters to the GREET model for the WTW analysis.

We estimated the energy consumption (of both petroleum oil and fossil energy) and the emissions of GHGs (CO₂, N₂O, and CH₄) that occurred over the entire fuel cycle. Energy and emissions were partitioned to all products resulting from the process according to either the displacement or the energy allocation method (see Section 4.3). Finally, we determined fuel transportation and vehicle operation parameters to complete the bio-butanol fuel life cycle. We then compared scenarios for bio-butanol and ethanol produced from conventional corn dry mills to gasoline. Section 4.4 addresses the cradle-to-user analysis of bio-acetone.

3 ASPEN PLUS[®] SIMULATION OF THE ABE PROCESS

The simulation of ABE fermentation and downstream processing was completed by using Aspen Plus[®] and Microsoft Excel[®]. Section 3.1 presents the basis of this simulation, including scope, plant capacity, and product specifications. Section 3.2 presents an overview of the simulated process; upstream raw material processing is also included to provide the context for the simulated process. Mass and energy balances derived from the ABE fermentation and downstream processing simulation are presented at the end of Section 3.3. The results are further integrated into the whole plant to include corn grain pretreatment, saccharification, and DDGS drying. Section 4.1 presents the energy balance of the bio-butanol plant.

3.1 SCOPE AND METHOD

The bio-butanol plant produces butanol from corn via ABE fermentation. Our Aspen Plus[®] simulation is based on two data sources. For the portion of the process upstream from ABE fermentation (i.e., grain pre-treatment, liquefaction, and saccharification), we adopt the results from a USDA Aspen Plus[®] simulation model for a corn dry mill (Kwiatkowski et al. 2006; McAloon 2006), because the upstream results of fermentation would be similar to those of a corn dry mill and can therefore be modeled the same way. For a similar reason, co-product DDGS drying is simulated after the USDA model.

For the second half of the process, including ABE fermentation and downstream processing, the ASPEN simulation was completed on the basis of the research results from a pilot-scale ABE fermentation plant (Ezeji et al. 2003 and 2004) and from literature (Liu 2003; Liu et al. 2004, 2006; Heckl et al. 2006). The production capacity of this plant was set at 150,000 metric tons per year of butanol. The operation runs 315 days per year. Product and by-product specifications were as follows: butanol purity, 99.5% by weight (wt%); acetone purity, 99.5 wt%; and ethanol purity, 99.5 wt%.

3.2 OVERVIEW OF ABE PROCESS

The ABE fermentation simulation describes a process developed by Qureshi and Blaschek (1999; 2001a, b). Acetone, butanol, and ethanol (ABE) are produced by a hyper-butanol-producing strain (*C. beijerinckii* BAI01). Corn is fed into a conventional corn dry mill for conversion to glucose through liquefaction and saccharification. The glucose is fermented to ABE through a fed-batch system. After fermentation, the ABE compounds are removed by means of in-situ gas stripping. ABE products are recovered through molecular sieve adsorption and a three-stage distillation that separates the acetone, butanol, and ethanol. Solids and biomass that are removed from grain processing and fermentation undergo centrifugation and proceed to drying, along with syrup from distillation; DDGS generated from drying is used as animal feed. The following subsections provide brief descriptions of the process for producing butanol from corn. The process consists of three main parts: grain pre-treatment (receiving, liquefaction, and saccharification), fermentation and gas stripping, and downstream processing.

3.2.1 Grain Receiving, Liquefaction, and Saccharification

This section describes of the portion of the conventional dry grind ethanol process that begins with receipt of grain and ends with saccharification, as modeled in the USDA Aspen Plus[®] simulation of the corn ethanol process (Figure 2). We use the data derived from this part of the corn ethanol process in the USDA's 40-mmgy dry mill model to simulate the ABE fermentation process, except we scaled the capacity from 40 MMGY of ethanol to 150,000 metric tons of butanol per year.

Corn brought into the plant site is first separated from finer particles and foreign objects by using a blower and screens. The cleaned, dry corn is ground in a hammer-mill and weighed to control the feed rate to the process. In the liquefaction step, the ground corn is then mixed with water, thermo-stable alpha-amylase, ammonia, and lime in a slurry tank.

A steam injection heater is used to gelatinize the starch, which is then hydrolyzed by the alpha-amylase into oligosaccharides. The stream is then "cooked" and transferred to the saccharification tank, where the oligosaccharides are converted by glucoamylase to glucose at a temperature of 61°C. The slurry is then transferred to an evaporator to concentrate the feed to the desired level for ABE fermentation.

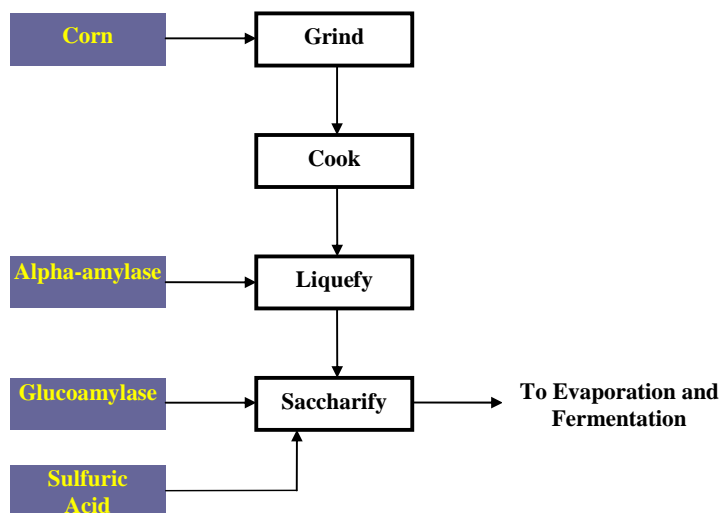


FIGURE 2 Schematic for Grain Receiving, Liquefaction, and Saccharification

3.2.2 Fermentation and In-Situ Gas Stripping

The information in this section is based on the research results from Qureshi and Blaschek (2000; 2001a, b), Ezeji et al. (2004), and Ezeji et al. (2005).

The literature reported that the strain *C. beijerinckii* BA101 can produce butanol in a range of sugar concentrations from 45.4 to 500 g/L. Because typical sugar concentration in fermentation feed is 3–7% (White and Johnson 2003) in a corn ethanol plant, it is desirable to concentrate this stream, which provides a means to integrate the grain processing in corn dry milling with the ABE process we modeled. Further, it could potentially reduce energy demand associated with removing water from ABE products in downstream processing. (Operational issues with respect to the concentrated feed will be discussed later in this section.) The stream that departs from saccharification goes to an evaporator to concentrate the sugar to 430 g/L before entering ABE fermentation. Alternative technologies to provide concentrated feed are available and could be used. Nevertheless, this step represents a large amount of heat demand and a capital cost. Our Aspen Plus[®] simulation begins at this step. The slurry feed generated from evaporation is then cooled to 35°C and introduced to the oxygen-free fermentation vessel, which has been inoculated with *C. beijerinckii* BA101. The temperature is controlled at 35°C, and no pH adjustment is applied during the process.

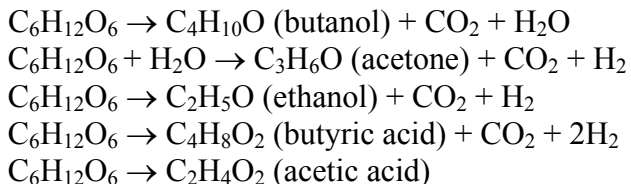
ABE fermentation is operated in a fed-batch mode. ABE production typically starts with a lag phase and gradually increases its rate until the ABE concentration reaches a plateau before it finally decreases (Ezeji et al. 2004). A gas mixture of carbon dioxide (CO₂) and hydrogen (H₂) is also generated from the fermentation. This gaseous mixture is recirculated via a gas pump to maintain a head pressure that ensures the anaerobic environment necessary for the microorganism. ABE products are removed by in-situ stripping from the fermentor by using the gaseous mixture from fermentation. At start-up, the fermentation proceeds for 22 h, until ABE reaches about 5 g/L, and then gas stripping is applied. The ABE vapors that are stripped from the fermentor enter a condenser above the fermentor, and the ABE vapors are cooled to 10°C and condensed to liquids, leaving uncondensed CO₂ and H₂ in the vapor phase to be recirculated. Excessive CO₂ and H₂ are vented to the atmosphere after passing through a CO₂ scrubber. The gas stripping captures most of the butanol, acetone, and ethanol produced during fermentation. The selectivity of the stripping for butanol, defined as

$$[y/(1-y)]/[x/(1-x)],$$

where: x = wt% of butanol in fermentation broth and
 y = wt% of butanol in condensate,

is set at 20 (Qureshi and Blaschek 2001b). Accordingly, about 25 wt% water is present in the condensate; the water will be removed from the product and by-products in the downstream processing stage.

Microbial reaction mechanisms for the conversion of glucose to ABE have not been fully understood and characterized. In principle, the following biochemical reactions could describe the ABE fermentation:



The reactions represent a qualitative measure rather than stoichiometric quantitative relationships for the ABE conversion process. The microbial cell growth was not included in any of the reactions above. In our simulation, the extent of ABE conversion is set according to literature value reported from experimental tests. Glucose utilization is 95.1% (i.e., 4.9% glucose is converted into biomass solids as a result of microbial growth). Butanol, acetone, ethanol, acetic acid, and butyric acid yields are 0.303, 0.155, 0.0068, 0.0086, 0.0084 g/g glucose, respectively (Table 2).

As we noted earlier in this section, integrating the conventional corn ethanol dry mill process with the new ABE process requires closing a gap in the concentration of the sugar feed to the fermentor between the two processes. Feed for the ABE fermentation process contains a sugar concentration of up to eight-fold as high as that of conventional corn ethanol process, which suggests a small footprint for a fermentation and downstream processing unit and, therefore, lower capital expenditure and lower energy demand for downstream separation. However, at such a concentration, the solids could build up to 55% (wt/wt) or higher in the fermentor. In comparison, the level of solids in corn ethanol fermentation is roughly 20% (wt/wt). The level of solids in ABE fermentation broth means increased viscosity, which could result in inhibitory stress on microorganisms and operational difficulties. In addition, feed to a fermentor in a corn dry mill usually contains corn fiber, which could exhibit mass-transfer limitation during gas stripping. The net result could be increased energy consumption for gas stripping or reduced product removal efficiency by stripping. Data in the literature are mostly based upon relatively pure glucose/nutrient feed in which mass transfer may not be limiting. The operability and mass-transfer issues in fermentation for the corn-to-butanol process should therefore be examined carefully. For comparison, we estimated a case with diluted feed to the fermentor (no evaporation), which is similar to the fermentation feed in an existing corn ethanol plant.

Another uncertainty is that ABE fermentation requires a pure form of starch that is similar to starches produced from a wet milling process. Additional steps to purify dry milling starch will be necessary to integrate the dry mill with the ABE fermentation. Unfortunately, at the time of this study, available data were limited to pilot-scale testing, and the corn-to-butanol ABE process is not well established. We did not including starch purification step. Our analysis will be updated once these issues have been addressed and data become publicly available.

3.2.3 Downstream Processing

The liquid fermentation broth from the condenser is subject to a series of distillation operations in which the stream is separated into product, based on their volatilities: 99.5 wt% pure butanol, 99.5 wt% pure acetone, and 99.5 wt% pure ethanol. In a mixture containing

butanol, ethanol, and water, homogeneous ethanol-water azeotrope and heterogeneous water-butanol azeotrope are formed. In descending order of their volatilities, the components in the stream (including the two azeotropes) to be separated by the downstream processing are acetone, azeotrope of ethanol and water, ethanol, azeotrope of water and butanol, water, and butanol. The components in this sequence could plausibly be separated simply by fractional distillation, achieved by various simple and/or complex column configurations, into any two or more subsequences of components at the adjacent components that have sufficiently different volatilities.

The fermentation broth is first fed to the first distillation tower, where a composition cut is made to separate acetone, ethanol, and water from the broth. These components are sent to the top stream, and the butanol (together with a trace amount of water) goes to the bottom stream. The product butanol is 99.5 wt% pure and suitable for transportation fuel use. The top stream is sent to a second distillation tower, where acetone is concentrated, purified, and then sent out from the top. The bottom stream, containing mainly ethanol and water, is subject to further separation in a third distillation tower, where the azeotropic vapor of 94.4 wt% ethanol and 5.3 wt% water (and 2 wt% acetone) is withdrawn from the top and sent to an adsorption unit. The water stream from the bottom is sent back to the fermentor. Water in the top stream is adsorbed in this unit, and ethanol purity in the product stream reaches 99.5% (the minimum purity required for ethanol to be blended with gasoline and used in vehicles).

The adsorption unit consists of two adsorption columns that run cyclically between the adsorption and desorption phases. Molecular sieves are packed in the column as the adsorbents. The sieves consist of a microporous substance designed to separate small polar molecules from larger nonpolar ones via a sieving action. Water molecules are trapped and adsorbed inside the microporous beads, while the ethanol molecules flow around them. Molecular sieves are then regenerated by heat and carrier air. Figure 3 presents the schematic of the adsorption and adsorbent regeneration process.

3.3 PROCESS FLOWSHEET SIMULATED BY ASPEN PLUS[®]

3.3.1 ABE Process Flowsheet

This simulation attempts to address the potential of the new ABE fermentation with an in-situ stripping process, by using the best of the process value reported. The ABE fermentation and downstream processing (separation) model from this study was integrated with the upstream grain processing component of the USDA's corn dry mill model and scaled to the 150,000-metric-ton-per-year bio-butanol production level. Figure 4 shows the Aspen Plus[®] output of the process flowsheet from fermentation to downstream processing. Data for the simulation of fermentation and gas-stripping unit operations are based on the research results from Qureshi and Blaschek (2000; 2001a,b), Ezeji et al. (2004), and Ezeji et al. (2005). Table 2 summarizes the main parameters for fermentation and gas stripping input to the Aspen Plus[®] simulation.

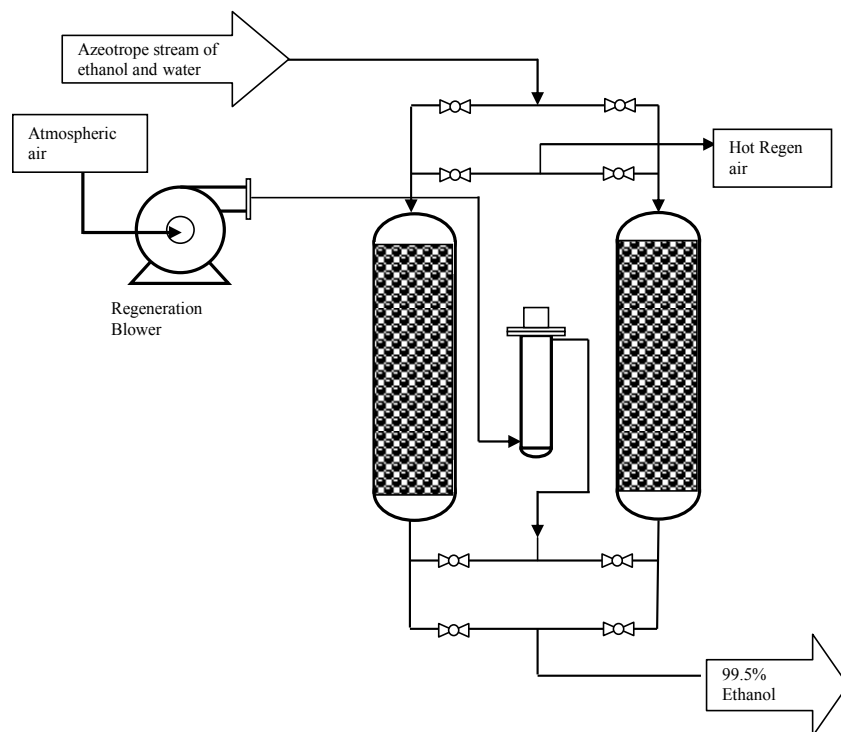


FIGURE 3 Schematic Representation of Adsorption and Adsorbent Regeneration

The downstream processing flowsheet in the simulation is based on the most cost-effective flowsheet rigorously generated from an exhaustive list of plausible processing equipment and unit operations, as described in Liu (2003), Liu et al. (2004, 2006), and Heckl et al. (2006). According to their studies, this optimal flowsheet consists of a gas stripper that isolates a liquid product stream from the fermentation broth; an adsorption unit that removes the majority of water; and a set of distillation columns that purifies the butanol, ethanol, and acetone products. The studies show that the cost of this flowsheet is at least 12.5% lower than that of any other alternative flowsheet. Energy use for the regeneration of the molecular sieve adsorbents is calculated off-line. The calculation, presented in Section 3.3.2, is then incorporated into the simulation by using a Fortran subroutine.

Shortcut methods that highlight the mass and energy balances are chosen for simulating most of the unit operations in the process. Heat integration between the three distillation columns is taken into consideration. Our simulation did not include stream recycling and simple unit operations (such as valves); we also did not examine different distillation column configurations.

The combined Aspen Plus[®] model provides the material balance for the bio-butanol plant, as shown in Table 3. Table 4 lists the yields of acetone, butanol, and ethanol from the bio-butanol plant (in gallon per bushel [gal/bu] of corn). Steam and electricity use for the ABE process (Table 5) indicates that using concentrated feed for ABE fermentation could save 14% of steam needs, in comparison with using existing feed in a dry mill. Among the reductions in steam needs, 75% of those reductions come from distillation. Section 4.1 presents the energy balance for the bio-butanol plant from gate to gate.

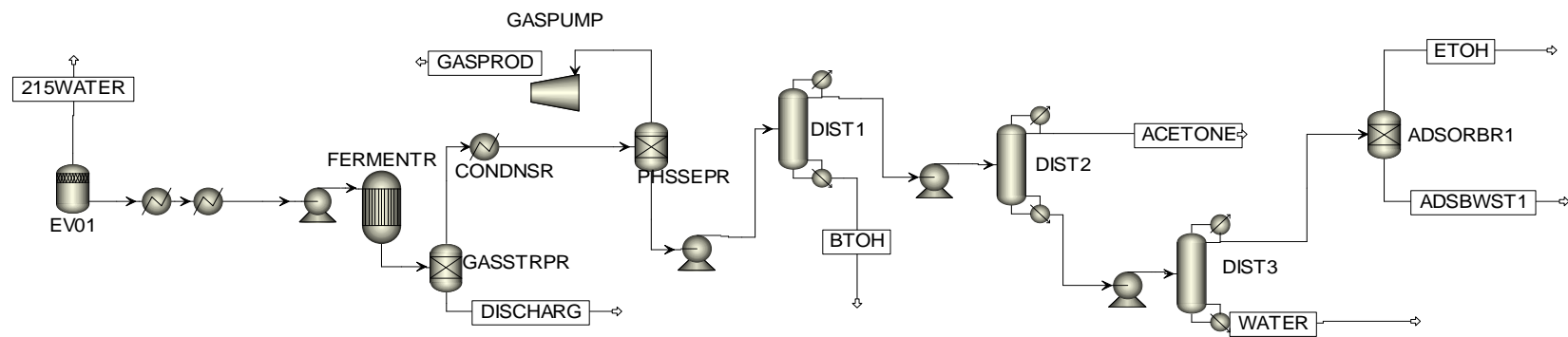


FIGURE 4 Aspen Plus® Output of the Process Flowsheet from Fermentation to Downstream Processing

TABLE 2 Main Input Parameters for Fermentation and Gas Stripping for Aspen Plus® Simulations

Input Parameter	Value Used in the Simulation ^a	
Fermentor operating temperature (°C)	35	
Fermentor operating pressure (atm)	1	
	Acetone	0.155
	Butanol	0.303
	Ethanol	0.0068
Yield (gram/ gram glucose)	ABE (total)	0.465
	Acetic acid	0.0086
	Butyric acid	0.0084
	Hydrogen	0.021
	Carbon dioxide	0.6954
Gas stripping carrier gas	Fermentation gas	
Gas stripping selectivity for butanol	20.0	
Condensation temperature (°C)	2	

^a Sources: Ezeji et al. (2004); Qureshi et al. (2001b)

TABLE 3 Material Balance of Bio-Butanol Plant

Parameter	Value	Source
Feed grain moisture content (%)	15	USDA dry mill model (Kwiatkowski et al. 2006; McAloon 2006)
Corn grain feed rate (lb corn/h)	237,338	Aspen Plus® results scaled up from USDA dry mill model (Kwiatkowski et al. 2006; McAloon 2006)
Glucose feed rate to fermentor (lb/h)	154,871	Aspen Plus® simulation (this study)
Production (lb/h)		Aspen Plus® simulation (this study)
Acetone	23,997	
Butanol	42,728	
Ethanol	1,032	
DDGS	73,816	
DDGS moisture content (%)	11	

TABLE 4 Yields of Acetone, Butanol, and Ethanol from Bio-Butanol Plant

Product	Yield (gal/bu corn)	Energy (Btu/bu corn)	Energy Output Share (%)
Acetone	0.868	69,525	31.4
Butanol	1.495	149,267	67.4
Ethanol	0.037	2,828	1.2
Total	2.4	221,621	100

TABLE 5 Process Fuel Use for ABE Fermentation and Downstream Processing

Process Step	Steam (Btu/h)	Electricity (kW)	Diluted Sugar Feed to Fermentor ^a Steam (Btu/h)
Evaporator	278,653,091		0
Fermentor agitator		192.73	
Condenser		3105.40	
Gas pump		61.04	
Gas stripper	1,307,400		1,412,700
Adsorption feed pump		0.24	
Distillation Column 1	43,220,100		68,173,300
Distillation Column 2	62,665,700		374,388,000
Distillation Column 3	5,730,860		10,891,300
Distillation 2 feed pump		0.40	
Distillation 3 feed pump		0.03	
Adsorbent regeneration	-729,205	237.33	-729,205

^a Existing fermentation feed, such as those from corn dry mill used for ABE fermentation.

3.3.2 Estimate of Energy Use for Adsorbent Regeneration

The heat use for the regeneration of adsorbents is calculated as the total amount required to bring the system — which includes the adsorption column, the molecular sieves, adsorbed water, and the carrier gas — to a temperature of 500°F. An electric heater provides the energy requirement for adsorbent regeneration. The system is cooled by exchanging the heat with the process streams fed to the distillation towers (assuming a loss factor of 10%). Therefore, the energy used to cool the system is not taken into account. The weight of water that the molecular sieves adsorb is set at 22% of the weight of the molecular sieve. The peak concentration of water in the carrier air is set at 1.7 wt%. The adsorption and regeneration cycle time is set at 8 h. The amount of heat required to bring the column to the specified temperature is calculated by using a method based on logarithmic mean temperature difference (LMTD) and the scaling of experimental data. The radiation loss factor for heater is set at 5%. Other major parameters for the calculation are listed in Table 6.

TABLE 6 Parameters for Calculating Energy Use for Adsorbent Regeneration

Parameter	Water Adsorbed		Adsorption Column	Carrier Gas — Air
	Inside Molecular Sieves	Molecular Sieves		
Amount (lb/h)	55.6	2,020.0	n/a	3,333.0
Cp (btu/lb/°F)	1.0	0.2	n/a	0.2
T1 (°F)	175.0	175.0	175.0	175.0
T2 (°F)	500.0	500.0	500.0	500.0
ΔT (°F)	325.0	325.0	325.0	325.0
Q (Btu/h)	18,053.8	150,995.0	343,706.1	258,890.8
Total (Btu/h)	810,227.9			

4 BIO-BUTANOL LIFE-CYCLE ASSESSMENT

4.1 BIO-BUTANOL PLANT ENERGY REQUIREMENTS

We assume that the bio-butanol plant uses natural gas as process fuel to generate steam and purchases electricity from the grid. Our process fuel estimate for the butanol plant is based on three sources: (1) the Aspen Plus[®] simulation of ABE fermentation and downstream processing from this study, (2) a recent study by Mueller and Cuttica (2006) of process fuel use in corn ethanol dry mills, and (3) the USDA corn dry mill model (Kwiatkowski et al. 2006; McAloon 2006). Aspen Plus[®] results from this simulation generate process fuel use values for ABE fermentation and downstream processing (Table 5). Considering the similarity in upstream grain processing between corn ethanol and corn butanol process in this study, we adopted the grain processing and DDGS drying steps from USDA dry mill model, scaling-up the corn feed for the bio-butanol plant. Thus, the heat and power needs in the rest of the plant (for cooking, the regenerative thermal oxidizer [RTO], and DDGS drying) are based on sources (2) and (3).

An estimate of process fuel (natural gas) use for cooking, DDGS drying, and RTO in the corn butanol plant was based on the amount of corn feed processed in the following steps. We first converted the energy input per gallon of ethanol to energy input per bushel of corn feed at a yield of 2.72 gallons of denatured ethanol per bushel of corn. We then converted this value to energy use per gallon of bio-butanol, with a bio-butanol yield of 1.50 gallons per bushel of corn (Table 4) for each process step above. In a conventional corn ethanol dry mill, water is removed from WDG (solids from grain processing) and syrup (solids from distillation) at the drying step and from ethanol via distillation. The ABE fermentation process described in this study partially removes water before fermentation to concentrate feed sugar content. Therefore, it is likely that less water will be removed at downstream processing and DDGS drying, which means lower energy demand. Another parameter that has not been fully evaluated and reported is DDGS yield from the corn-to-butanol ABE process and its quality. We assume equivalent heating demands for DDGS drying in the ethanol plant and in the butanol plant. Table 7 details the calculations of natural gas use in the bio-butanol plant. This steam demand is met by using a natural-gas-fired steam boiler with 80% efficiency to produce 150-psi, medium-pressure steam.

Electricity demand for the bio-butanol plant was estimated in a similar way. According to the ethanol plant study by Mueller and Cuttica (2006), the average electricity use in corn ethanol plants is 0.75 kWh per gallon of ethanol, which agrees with the value estimated by an ethanol plant designer (Roddy 2006), while it is slightly higher than the 0.73 kWh per gallon of ethanol suggested by the USDA model. We used the former estimate in this analysis to reflect the current industry average. Electricity used for fermentation and distillation in the corn ethanol plant was displaced by that for ABE fermentation and downstream processing. The power consumption value was converted from per gallon of ethanol to per gallon of butanol via per bushel of corn on the basis of 2.72 gallons of EtOH/bushel and 1.50 gallons of bio-butanol/bushel. Table 8 summarizes the major assumptions and data sources for power use in the bio-butanol plant.

TABLE 7 Thermal Energy Requirements in Bio-Butanol Plant

Process Steps	EtOH Plant NG Required (Btu/gal denatured EtOH)	BtOH Plant NG Required Based on Feed Corn (Btu/bu corn) ^c	BtOH Plant NG Required Based on BtOH (Btu/gal BtOH) ^d
Cooking	10,013 ^{a,b}	27,236	18,216
Dryer and RTO ^e	10,830	29,458	19,703
ABE fermentation ^f and processing			77,195
BtOH plant total			115,114

^a Source: Mueller (2006). 23.1% total process fuel for cooking; 26.5% for EtOH processing. Therefore, cooking fuel use is $23.1\% / (23.1\% + 26.5\%) = 46.57\%$ of total fuel used in ethanol processing (excluding DDGS drying).

^b The total thermal fuel requirement for cooking, fermentation, and distillation is 21,500 Btu/gal denatured EtOH in a 100-MMGY ethanol dry mill. Source: Mueller and Cuttica (2006). NG needed for cooking is $46.57\% \times 21,500 \text{ Btu/gal} = 10,013 \text{ Btu/gal EtOH}$.

^c Assumed corn ethanol yield: 2.72 gal/bu (denatured).

^d Corn butanol yield: 1.50 gal/bu of corn.

^e Source: Mueller and Cuttica (2006).

^f Aspen Plus[®] results from this study includes heat for evaporation, fermentation, distillation, and gas stripping.

TABLE 8 Electricity Consumption in Bio-Butanol Plants

Item	EtOH Plant Electricity Required (kWh/gal EtOH)	BtOH Plant Electricity Required Based on Feed Corn (kWh/bu)	BtOH Plant Electricity Required Based on BtOH (kWh/gal BtOH ^a)
EtOH plant ^b	0.75	2.04	
EtOH plant, excluding fermentation and distillation	0.68 ^c	1.84	1.23
ABE fermentation and separation			0.53 ^d
BtOH plant total			1.76

^a Converted from kWh/bu to kWh/gal BtOH, with a corn butanol yield of 1.50 gal/bu.

^b Source: Mueller and Cuttica (2006). Converted to per bushel with an assumed corn ethanol yield of 2.72 gal denatured ethanol/bu.

^c Calculated on the basis of USDA dry mill model: fermentation requirement 0.06 kWh/gal EtOH and 0.01 kWh/gal for distillation are subtracted from 0.75 kWh/gal EtOH.

^d Electricity needs from ABE fermentation and separation. Aspen Plus[®] results from this study.

Scale-up from pilot test to full-scale commercial production could change the yield and energy consumption. These factors affect the overall bio-butanol production and energy use estimates.

4.2 BUTANOL LIFE-CYCLE PARAMETERS

Bio-butanol in this study is produced from corn. It would be economical for the bio-butanol plant to be built near corn farms to reduce transportation costs. Operations associated with corn farming and feedstock transportation would be similar to those for corn. Bio-butanol produced from corn will displace gasoline; therefore, transportation, storage, and distribution of bio-butanol would be similar to those of ethanol. Table 9 presents key assumptions and GREET inputs for the bio-butanol life-cycle analysis. Electricity for the bio-butanol plant is supplied from the U.S. electric generation mix (Table 10).

TABLE 9 GREET Input Parameters for Corn Butanol WTW Analysis: Corn Farming, Transportation of Corn and Butanol, and Vehicle Operation

Parameters	Assumptions
Corn yield (bu/harvested acre)	158
Ratio of harvested acreage to planted acreage	0.9
Fertilizer use (g/bu)	N = 420, P ₂ O ₅ = 149, K ₂ O = 174 ^a
CO ₂ emissions from potential land use changes of farming (g/bu)	195
Lime use (g/bu)	1,202
Corn transportation mode and distance (mi)	
Truck (100%)	50
Butanol transport and distance (mi)	
Barge (40%)	520
Rail (40%)	800
Truck (20%)	110
On-road fuel economy of LDVs fueled with bio-butanol (mi/gal gasoline equivalent)	24.8

^a N = nitrogen; P₂O₅ = phosphorus fertilizer; and K₂O = potash fertilizer.

To clearly show the energy and emission effects of bio-butanol vs. gasoline, we assumed in this study that bio-butanol is used in pure form in GVs and that butanol could achieve the same fuel economy per gallon gasoline equivalent as gasoline-powered GVs (Table 9). WTW results are expressed in a per-million-Btu fuel matrix for comparison. In reality, bio-butanol may be used in various gasoline blends. The per-million-Btu base system is more appropriate from a fuel supply perspective. Because energy and emission results are presented in Btu or grams per million Btu of fuel produced and used, the effects of differences in fuel economy are removed.

TABLE 10 U.S. Average Electricity Generation Mix Used in this Study^a

Source	Percent of Total
Residual oil	2.7
Natural gas	18.9
Coal	50.7
Nuclear power	18.7
Biomass	1.3
Others	7.7

^a Source: GREET, year 2010

4.3 CO-PRODUCT CREDIT

During bio-butanol production, several co-products are generated along with butanol — these include acetone, DDGS, a small amount of ethanol, fatty acids (butyric acid and acetic acid), and H₂ gas. On the scale that we analyzed, acetone is the major co-product of the bio-butanol plant, with 82,000 metric tons produced per year. Acetone contributes to more than one-half (by weight) of the butanol production. The bio-butanol plant also generates 253,600 metric tons of DDGS (11% moisture) per year — the second large co-product. The yield of ethanol is relatively small (Tables 3 and 4) (similar to the level of fatty acid mixtures). Ethanol yield from ABE fermentation accounts for 1.5% of total ABE (acetone, butanol, and ethanol) by weight and only 1.2% by energy content (Btu/bu of corn) (Table 4). Although the fatty acids could be separated, further purified from the liquid discharge stream, and sold for use in the chemical market, the separation step has not yet been tested with ABE fermentation. In this Aspen Plus[®] simulation, the fatty acids were not separated and purified, and so they were not treated as co-products.

Significant amounts of H₂ and CO₂ gas were produced from fermentation; these gases were used internally for gas stripping and then for maintaining anaerobic conditions for ABE fermentation. The H₂ could be separated as a fuel product if high-purity nitrogen gas is used in place of fermentation gas. However, using such nitrogen gas to maintain anaerobic conditions and for stripping in large-scale operation could be cost prohibitive. Further studies to evaluate the engineering economics of alternative approaches for process operation while economically producing bio-butanol and hydrogen would be beneficial. In this initial attempt to address the life cycle of bio-butanol, H₂ was not considered as a co-product.

We partitioned total energy and emissions into bio-butanol and the co-products by using two methods: product displacement and energy allocation. Co-product displacement (Case 2) is based on the concept of displacing the current product with the new product. In this case, bio-acetone is regarded as a renewable chemical. The energy consumed and the emissions that occur during bio-acetone production displace the energy and emissions associated with petroleum-based acetone production. Energy and emission accredits from the acetone displacement are

assigned to bio-acetone. Similarly, DDGS generated from corn butanol production contains 26.7% protein by weight, which is close to the amount of protein contained in the DDGS from the corn ethanol process. With the assumptions that the nutritional values of DDGS from the two processes are similar, the DDGS from the bio-butanol plant displaces traditional animal feed (soy protein and corn), the production pathway of which is already in place in GREET.

The limitation of using the displacement method for the bio-butanol life-cycle analysis is the large amount of acetone that is co-produced with butanol. While the main product — butanol — accounts for 63% (wt/wt) of the total product yield (acetone, butanol, and ethanol), acetone accounts for 35% (wt/wt) (Table 3). Our previous study (Wu et al. 2005) suggested that when the share of energy co-products increases, the co-product displacement method could yield misleading results. Therefore, other partitioning methods, such as energy allocation, should be examined.

For Case 3, we applied the product energy allocation method to co-products, in which emission and energy burdens are allocated among products according to their energy output shares from the bio-butanol plant. In the energy allocation method, shares of output product energy for each product are determined according to the heating value. Energy use and associated emissions from bio-butanol production and from upstream feedstock production and transportation activities are partitioned among acetone, butanol, ethanol, and DDGS on the basis of their corresponding energy shares. This approach treats all energy products from the production process as equal, regardless of the form and quality differences among them. It also implies that all four products are energy products. The energy allocation method is applicable to this case because, of the ABE products, both butanol and ethanol are liquid fuels. Although acetone is normally regarded as a chemical solvent and feedstock, its energy content (in LHV) is, in fact, in between that of butanol and ethanol (Table 1). Furthermore, DDGS has a LHV of 8,703 Btu/lb and can be used as a solid fuel for ethanol plant operations. Several ethanol plants are currently exploring DDGS combustion or gasification, such as Corn Plus, to provide heat and power. Although the fuel quality of DDGS is lower than that of the liquid fuels, considering its large quantity (Table 3), use of DDGS for process heat brings energy savings and yet relaxes pressure on the already stagnant DDGS market. Table 11 presents energy shares based on product energy (in Btu) content.

TABLE 11 Co-Product Energy Partitioning by Energy Allocation^a

Bio-Butanol	Bio-Acetone	DDGS	Bio-Ethanol
40%	19%	40%	0.01%

^a Based on energy content.

We also established a case to consider the impact of overproduction of acetone (Case 4). In this case, an overabundance of acetone produced by a large-scale butanol industry would flood the acetone market, consequently losing its commercial value. Case 4 is the same as Case 2, except that it treats acetone as a waste stream (i.e., corn-acetone is not credited). This case provides an extreme scenario for bio-butanol.

4.4 CRADLE-TO-USER ASSESSMENT OF PETROLEUM ACETONE AND DISPLACEMENT

4.4.1 Petroleum Acetone and Feedstocks Production

To evaluate the energy and emissions benefits of producing bio-acetone in a corn butanol plant, we performed a cradle-to-user analysis of petroleum-based acetone — from feedstock extraction to acetone delivery to the user site. Acetone is almost exclusively produced via cumene peroxidation, as a co-product with phenol. Its main use is as a chemical intermediate in the manufacture of acetone cyanohydrin for methyl methacrylate, biphenol A, and adol chemicals. Direct solvent use accounts for about 30% of world demand for acetone.

A synthetic process based on hydrocarbons or derivatives is now accounted for all acetone production in the United States and nearly all production in other countries. In this process, acetone is co-produced with phenol from cumene. The yield of acetone from this process averages 2.21 units of cumene per unit of acetone by weight (Camara-Greiner 2005). Cumene is produced via alkylation of benzene with propylene under elevated temperatures and pressures in the presence of a catalyst. Upstream from cumene production, benzene is produced principally through a catalytic reforming from naphtha in a BTX (benzene, toluene, and xylene) process. The other feedstock for cumene, propylene, is one of a half dozen products from crackers receiving raw hydrocarbon (naphtha) from oil refineries, as well as natural gas. Figure 5 presents a schematic of cradle-to-user petroleum acetone production.

4.4.2 Assumptions and Data Sources

The cradle-to-user analysis system boundary for petroleum acetone includes resource extraction, feedstock production, acetone production, process fuel production, and associated transportation. Our petroleum acetone production data are based on the life-cycle inventory (LCI) of Eco-Profile (Boustead 2005).

Eco-Profile Reports compiled average industry data and assembled detailed environmental data for various petrochemical processes. We noted system boundary differences in the transportation and upstream fuel production stages between the Eco-Profile and the GREET database. To ensure a consistent system boundary for all seven cases with current GREET biofuel pathways, we selected feedstock production (under category “feedstock energy” in Eco-Profile) and the amount of process fuel used in production of acetone feedstocks and acetone (under category “energy content of delivered fuel” in Eco-Profile) to arrive at our energy estimate for petroleum acetone. The GREET default energy values were used for upstream fuel production (oil extraction, refining, and transportation), transport of feedstocks, and transport of acetone to users. Direct emissions from production processes (under category “process” in Eco-Profile) from Eco-profile were used for our petroleum acetone cradle-to-user estimate. Emissions associated with upstream fuel production and all transportation activities were based on GREET values. Table 12 presents data sources for each life-cycle step in petroleum acetone production.

TABLE 12 Assumptions and Data Sources of Cradle-to-User Petroleum Acetone

Cradle-to-User Stage	Data Sources
Crude extraction for process fuel Crude transport for process fuel Oil refining and transport for process fuel	GREET 1.7
Cumene transport ^a	GREET 1.7
Acetone production (life-cycle value) ^b	Eco-Profile

^a Benzene and propylene were assumed to be captive. Acetone is for captive use in the acetone production facility to produce acetone cyanohydrin, biphenol A, and adol chemicals. Cumene is transported to acetone production facility.

^b Cumene production value is not available.

The hypothetical corn butanol plant is located in the U.S. Corn Belt to reduce corn transportation costs. We assumed that acetone produced from the corn butanol plant would displace petroleum acetone produced in the region of Petroleum Administration for Defense Districts (PADD) II (EIA 2004). PADDs were delineated during World War II to facilitate oil allocation. PADD II includes 14 Midwest states and overlaps with the Corn Belt where most corn-based plants would operate. We identified the mass flow for cumene and acetone production and transportation in PADD II on the basis of a Chemical Economics Handbook (CEH) Marketing Research Report (Camara-Greiner 2005). In this region, 85% of total cumene is produced from captive benzene and propylene (that is, benzene and propylene are produced and consumed on-site). The cumene is purchased by and subsequently transported to the acetone producer.

Major assumptions for cradle-to-user analysis of petroleum acetone are listed below:

- Process fuels used in the acetone pathway are electricity, oil, and natural gas.
- Electricity is purchased from the grid with the U.S. average generation mix (Table 10).
- Cumene production feedstocks (benzene and propylene) are captive in the refinery, so no transportation is associated with these feedstocks.
- The acetone production facility purchases 100% of feedstock cumene.
- Cumene needs for the acetone producer is estimated on the basis of the mass unit ratio of 2.21 units of cumene per unit of acetone (Camara-Greiner 2005).

- Cumene is transported to the acetone production facility an average distance of 323 miles in a 1,028-Btu/ton-mi Class 8 diesel truck.

Table 13 presents the heating values used in Eco-Profile and GREET. In this assessment, energy data are expressed in LHV of Btu or kWh/kg acetone produced. When there was a discrepancy in LHV between Eco-Profile and GREET for same fuel or chemical, the GREET value was selected to ensure consistency with the baseline fuel pathways of petroleum gasoline and corn ethanol. The energy data from Eco-Profile are converted according to the ratio of LHV Eco-Profile/LHV GREET (Table 13).

TABLE 13 Low-Heating-Value Comparison for this Study^a

Fuel	GREET (Btu/gal, Btu/scf)	Eco-Profile (MJ/kg)	Eco-Profile (Btu/gal, Btu/scf)	Ratio LHV Eco/GREET
Fuel oil	140,353	40.5	144,176	1.03
NG	983	48.16	1,005	1.02

^a Unit for fuel oil is Btu/gal; unit for natural gas is Btu/scf.

4.4.3 Petroleum Acetone Displacement

We assumed that the corn-based butanol plant would be built near a corn farm in the Midwest PADD II region and operated at a production scale of 150,000 metric tons of bio-butanol per year. With a mass production ratio of 0.56 lb of bio-acetone per pound of bio-butanol, this facility could yield 82,461 metric tons of bio-acetone annually — 16% of the total acetone production in PADD II and 4% nationwide. We assumed that bio-acetone would be transported to acetone consumers via train (500 miles) and truck (100 miles) within PADD II.

In the co-product displacement approach (Case 2), petroleum acetone is displaced by corn-based acetone from cradle to user. The displacement is carried out in the following sequence: the cradle-to-gate results of petroleum acetone (as illustrated in Figure 5) were first subtracted from the WTW results of bio-butanol, and then the energy or emissions values associated with bio-acetone transportation from the bio-butanol plant to the acetone user were added.

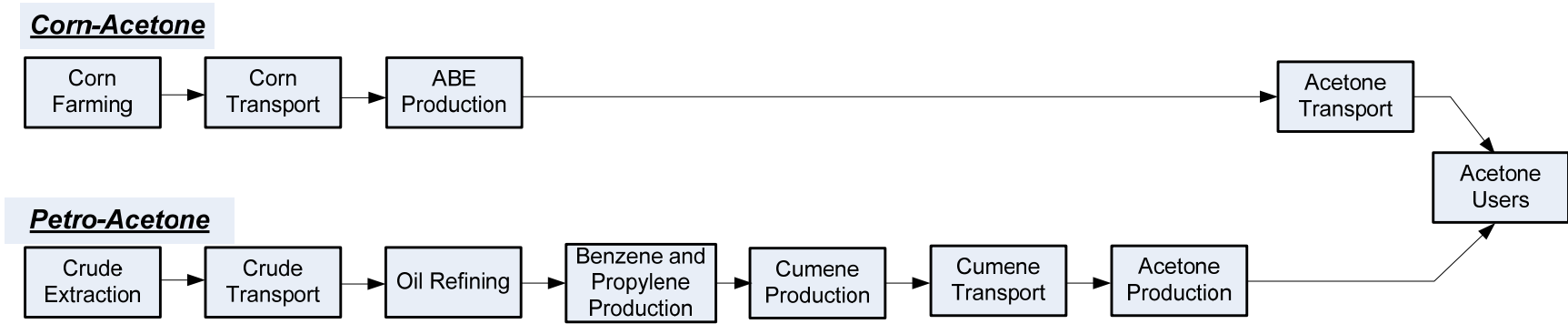


FIGURE 5 System Boundaries for Cradle-to-User Pathway of Fossil-Based Acetone and Corn-Based Acetone

5 RESULTS AND DISCUSSION

5.1 ENERGY CONSUMPTION AND GHG EMISSIONS

Corn-derived butanol achieves substantial fossil energy savings (39–56%) compared with gasoline ([Cases 3 and 2], Figure 6) on a life-cycle basis. In Cases 2 and 3, bio-butanol production contributes to a positive energy balance (defined as fossil energy used in gasoline production minus fossil energy used in bio-butanol production). Without acetone credit as in Case 4, in which acetone is regarded as a waste, bio-butanol production is not an option for fossil energy savings.

The primary fuel consumed in the bio-butanol life cycle is natural gas, followed by petroleum oil and coal (Figure 6). Although electricity generation uses 50% of coal (Table 10), the amount of electricity required is relatively small (Table 8), and so only 9–17% of total fossil energy use is from coal (Cases 3 and 2). A life-cycle fossil energy breakdown (Figure 7) indicates that about three-fourths of the fossil fuel is spent in the butanol production plant (73%). Corn cultivation accounts for a total of 23% of WTW fossil energy (12% for agricultural chemical and fertilizer manufacturing and 11% for farming operations). In the butanol plant, the majority of natural gas demand comes from the process steam requirement (Table 5), which leads to 115,000 Btu per gallon of butanol produced — approximately three times that of corn ethanol production before co-products are allocated. As we pointed out earlier, this estimate tends to be conservative because it did not reflect the lower heating requirement for DDGS drying in the bio-butanol plant. The water requirement in biological fuel production drives the energy balance in the plant. A higher concentration of product in fermentation reduces energy needs for product concentrating in subsequent process steps. Historically, improvement of ethanol concentration in a fermentor from ~8% in 1980s to 20% at present demonstrates, in part, the lower energy cost in ethanol plant operation. The ABE fermentation process evaluated in this study achieved a concentration of 19% (wt/wt) of total solvents (ethanol, butanol, and acetone) in a fermentor. With rapid in-situ removal of solvent by gas stripping, the process is able to increase feed concentration to improve production rate while minimizing butanol inhibition. Although using concentrated feed in fermentation effectively reduces about 14% of the steam requirement (Table 5), solids concentration in the fermentor — an important issue in process development and operation — remains a constraint.

Vehicles fueled by bio-butanol achieve small to moderate reductions in GHG emissions relative to gasoline vehicle on a WTW basis in Cases 2 (8%, displacement) and 3 (32%, energy allocation) (Figure 8). For every million Btu of bio-butanol used in place of one million Btu of gasoline, 8–32 kg of GHG emissions could be avoided (Cases 2 and 3). The GHG emissions profile for the bio-butanol production option in this study is similar to that of corn ethanol. Of total GHG emissions in the bio-butanol WTW cycle, over 70% by weight of the GHGs are from CO₂, less than 5% is from methane, and the remaining 18–21% is from N₂O (Figure 9). Natural gas consumption in butanol plant is the major cause of GHG emission.

We assumed that vehicles fueled by bio-butanol would offer performance similar to that of vehicles fueled by gasoline. We have not found any vehicle testing data to confirm this

assumption. Vehicle testing with butanol should be conducted to evaluate butanol's performance in vehicles under realistic driving conditions.

5.2 EFFECT OF ACETONE CO-PRODUCT CREDIT

Energy partitioning for co-products has a significant effect on overall energy use and associated GHG emissions. The three cases that we examined (2, 3, and 4) presented different options for acetone. When acetone is regarded as a fuel, and credit is allocated on the basis of product energy content (Case 3), the WTW analysis yields moderate fossil energy and GHG emissions benefits for bio-butanol. When acetone is used as a renewable chemical to displace petroleum acetone via the displacement method (Case 2), the results of analysis show 17% savings in fossil fuel (Figure 6) and small reductions in GHG emissions (Figure 8). However, treating acetone as a waste stream (Case 4) resulted in an increase of almost one million Btu in fossil energy and 40,000 g of GHG emissions (compared with gasoline) for each million Btu of bio-butanol produced. The difference is largely attributable to the acetone credit. Feedstocks for petroleum-based acetone production (propylene and benzene [Figure 5]) are produced from naphtha and natural gas — 100% fossil feedstock (Lacson et al. 2005). Another factor is the high yield of acetone from the ABE process: 0.56 lb acetone per pound of butanol. These two factors suggest that a significant portion of fossil energy use in petroleum acetone production will be regarded as a credit when bio-acetone displaces fossil acetone, which eventually leads to a small fossil energy value (Figure 6).

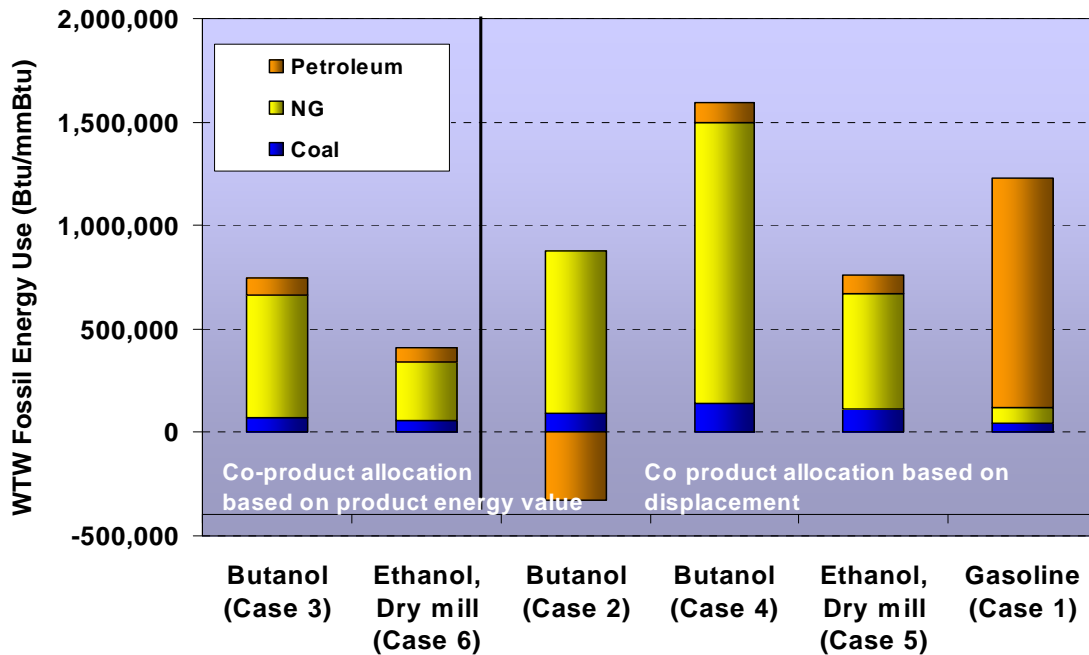


FIGURE 6 Well-to-Pump Fossil Energy Breakdown for Bio-Butanol and Corn Ethanol Compared with Gasoline, Using Different Co-Product Allocation Methods (negative value indicates fossil energy avoided)

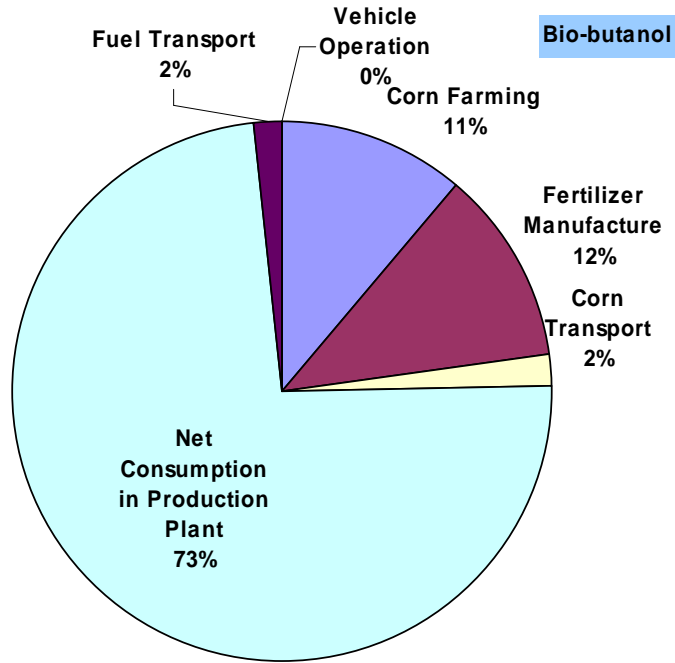


FIGURE 7 Breakdown of Fossil Energy Use in Various Stages of Fuel Life Cycle for Corn-Based Butanol (Case 3)

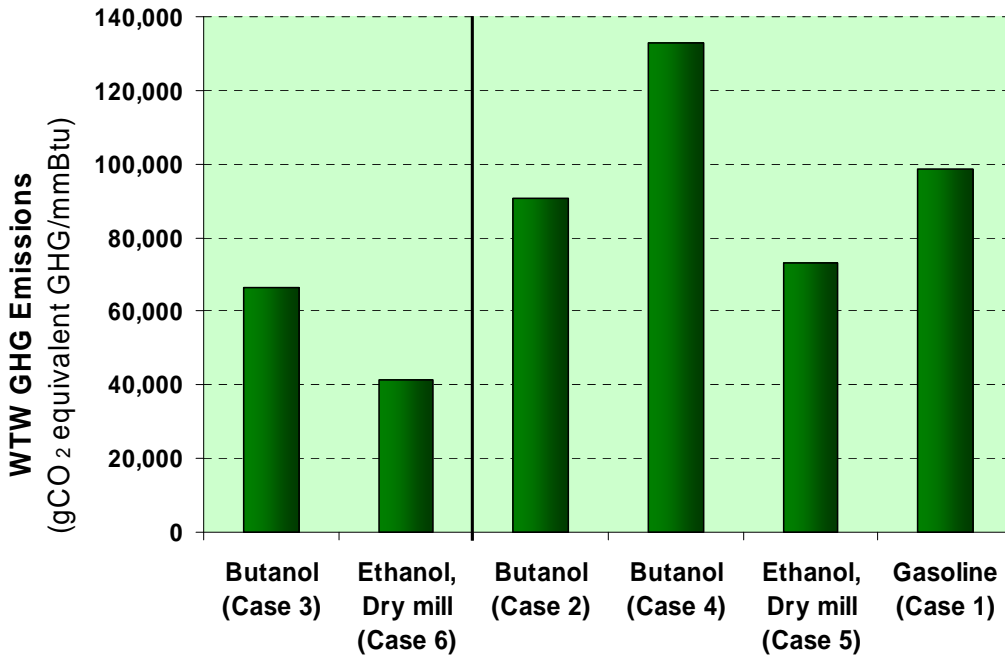


FIGURE 8 Life-Cycle GHG Emissions of Bio-Butanol and Ethanol Compared with Gasoline, Using Different Co-Product Allocation Methods

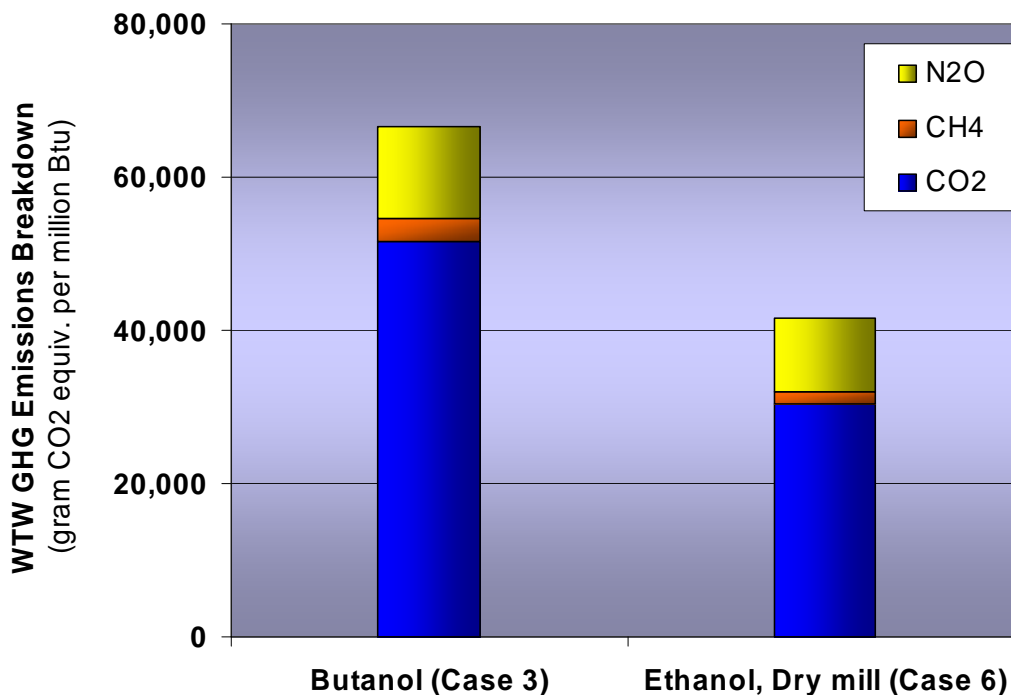


FIGURE 9 Life-Cycle GHG Emission Breakdown for Bio-Butanol and Ethanol (Energy Allocation)

The displacement method provides significant benefits in terms of reductions in the use of fossil energy (Figure 6), but relatively small reductions in GHG emissions (Figure 8). The main reason for this phenomenon is that petroleum acetone production extracts carbon from a fossil resource and transforms the carbon to another bounded form (chemical), with net GHG emissions generated from consumption of the process fuel. In its life cycle, petroleum acetone is primarily used as a chemical/feedstock with a fraction as solvent. Although a small amount of carbon embedded in petroleum acetone may escape to the atmosphere through volatilization during product application (i.e., use as solvent), the majority ultimately ends up as a solid/liquid chemical in a bound form rather than being emitted to the air as CO₂. By displacing petroleum acetone with bio-acetone in this case, the life-cycle reductions in fossil energy use do not translate to benefits in terms of GHG emissions.

5.3 COMPARISON OF BIO-BUTANOL WITH CORN ETHANOL

The ABE process simulated in this study appears to be as efficient in producing acetone, butanol, and ethanol on a weight basis as current corn dry mills (Table 14). Measured by gallon or gram of ABE, the yields from the ABE process are similar to ethanol yields from a conventional dry mill. As a rule of thumb in ethanol produced from corn dry milling, one-third of the feed mass goes to ethanol, one-third is left in DDGS, and one-third is emitted as CO₂. The

TABLE 14 Acetone, Butanol, and Ethanol Outputs from Corn Compared with Ethanol from Conventional Corn Mills

	Corn Butanol Plant				Ethanol from Corn Dry Mills
	Acetone	Butanol	Ethanol	Total	
Btu/bu corn	69,525	149,267	2,828	221,620 (with acetone); 152,095 (without acetone)	198,458
Gal/bu corn ^a	0.87	1.50	0.04	2.40	2.60
gC/g corn ^b	0.074	0.137	0.003	0.214	0.172

^a Un-denatured.

^b Based on dry corn feed.

ABE process examined in this study follows almost the same rule: one-third of the feed mass ends up in the products (acetone, butanol, and ethanol), one-third remains in DDGS, and about one-third (30%) is emitted as CO₂ (Table 15) (the remaining ~3% ends up in fatty acids [butyric and acetic acids] and losses).

Because acetone is not used as a fuel at present, net fuel production (butanol and ethanol) is small. A typical dry mill can deliver 2.72 gal/bu of fuel ethanol, or 2.6 gal/bu of undenatured ethanol, which is ~1.1 gal more than the butanol and ethanol yield together from the ABE process (1.54 gal/bu) (Table 14). On the other hand, butanol contains 30% more energy (LHV) than ethanol (Table 1) by volume. When we take fuel energy yield into consideration, each bushel of corn could generate nearly 152,000 Btu of liquid fuels from the ABE process (butanol and ethanol together), while the same bushel delivers 198,000 Btu of liquid fuels (undenatured ethanol) from the conventional ethanol dry mill (46,000 Btu more than the bio-butanol option). Hence, from a liquid fuel production perspective, the ABE process option does not offer an increase in renewable fuel production, in comparison with conventional corn ethanol production.

Process fuel use for ABE production could be a major hurdle, as indicated in Table 16. A bushel of corn requires 82% more steam and 34% more electricity to produce ABE from a bio-butanol plant than to produce ethanol from a corn dry mill. If the first corn butanol plant is built from an existing corn dry mill that has been retrofitted, the implication is that operation cost will be high. To build a new corn butanol plant, capital cost may be lower because of the reduced footprint in fermentation and downstream processing relative to the existing dry mill, but the plant would have increased process fuel cost — especially given the current price for natural gas.

TABLE 15 Co-Product Yields (g/g corn)

Acetone, Butanol, Ethanol	DDGS	CO ₂
0.34	0.33	0.30
Acetone: 0.119		
Butanol: 0.212		
Ethanol: 0.005		

TABLE 16 Process Fuel Use in Bio-Butanol and Ethanol Production Plant

Fuel	Bio-butanol Plant	Ethanol Dry Mill	Ratio of Butanol to Ethanol
Natural gas (Btu/bushel of corn)	172,108	94320	1.82
Electricity (kW/bushel of corn)	2.63	1.97	1.34

Another concern is the feedstock supply for bio-butanol. The current ABE process shares the same starch-based feedstocks with conventional corn ethanol. Development of bio-butanol through the ABE process could take limited feedstocks away from conventional corn ethanol production. R&D efforts in bio-butanol may need to be directed toward identifying new feedstocks and process technologies. In fact, Qureshi (2007) recently reported on a study using cellulosic biomass as feedstock for bio-butanol production via the ABE process. Because ABE fermentation is from glucose, the results of ongoing R&D on cellulosic pretreatment for cellulosic ethanol could be applied to the ABE process.

5.4 CRADLE-TO-USER COMPARISON OF BIO-ACETONE WITH PETROLEUM ACETONE: ISSUES AND CONCERNS

Use of bio-acetone to displace petroleum acetone shows promising energy and environmental benefits (Figure 10), from a life-cycle perspective. Conventional acetone production is a fossil-energy-intensive process. By producing acetone from corn, manufacturers could save a significant amount of total fossil energy — up to 71% relative to petroleum-based acetone. The renewable acetone achieves energy savings of 91% for petroleum and 58% for natural gas. Figure 11 further shows the life-cycle fossil energy distribution between the two. The majority of fossil energy use shifts from feedstocks (57%) in the petroleum acetone production process to acetone production (70%) in the corn acetone production process.

Bio-acetone in this study is produced from corn — a renewable agricultural resource that absorbs atmospheric CO₂ during its growth. The carbon in CO₂ is converted to organic carbon in the corn and is further transformed and embedded in acetone through the ABE process. Therefore, we allocated a renewable carbon credit to bio-acetone for the carbon embedded in corn. As illustrated in Figure 12, a net carbon sequestration would occur from cradle to user. GHG emissions would be much higher — about 500 g/lb acetone produced, if the carbon in acetone is from non-renewable sources.

Although bio-acetone production results in positive WTW energy benefits and decreased GHG burdens, several issues and concerns need to be addressed. In 2005, a total of 1.9 million metric tons of acetone was produced in the United States (Camara-Greiner 2005). PADD II, which overlaps with the U.S. corn belt, would most likely to be the location for corn-based

butanol plants. Production of petroleum acetone in this region in 2005 was 505,000 metric tons, representing 26% of total U.S. production. If bio-acetone were produced from a single simulated bio-butanol plant located in this region, the volume of bio-acetone would be about 16% of the total petroleum acetone production in the region and 4% nationwide. Furthermore, assuming that total bio-butanol production levels could reach a quarter of the production level of corn ethanol of 4.9 billion gallons (2006), the amount of corn feed used for bio-butanol production could generate 676 million gallons of bio-butanol and 391 million gallons (1.2 million metric tons) of bio-acetone. At this production scale, the acetone market would be flooded with both bio- and petroleum acetones, dramatically decreasing the market value of acetone. Thus, one may argue that acetone should be treated as a waste stream (as we did in Case 4). Aside from the fossil energy and GHG benefits (within WTW analysis boundaries) that may result from the production of bio-butanol, we should consider the emission of liquid acetone into the environment if acetone is treated as a waste stream. On the basis of a value of 0.074 g of carbon generated in acetone from each gram of corn, if all of the carbons contained in acetone were converted to gaseous CO₂, approximately 6,900 g of CO₂ could be emitted to the atmosphere per bushel of processed corn. Acetone-containing water in such high volumes could become a major source of atmospheric VOC and CO₂ emissions.

Unfortunately, the outlook for replacement of petro-chemicals with bio-chemicals is far from clear. Petroleum acetone is currently generated as a by-product during phenol production from cumene. On average, 0.61 lb of acetone is obtained per pound of phenol produced (SRI Consulting 2005). The United States consumed \$2.1 million metric tons of phenol in 2004 (SRI Consulting 2007). Worldwide, the consumption of phenol grows at a rate of 4.1% per year. As demand for phenol continues to rise, petroleum acetone will be produced with or without the presence of bio-acetone. In the ABE process studied, the bio-acetone is also a co-product. New technologies/processes that significantly reduce the acetone that results from phenol and ABE production are therefore needed. In fact, at the time of this study, DuPont was making considerable progress in molecular biology, which led to a patent award for a recombinant bacterium that produces butanol exclusively from biological feedstocks (DuPont 2007). Other potential research directions include exploring the use of acetone as a fuel blend and as a feedstock for new chemicals.

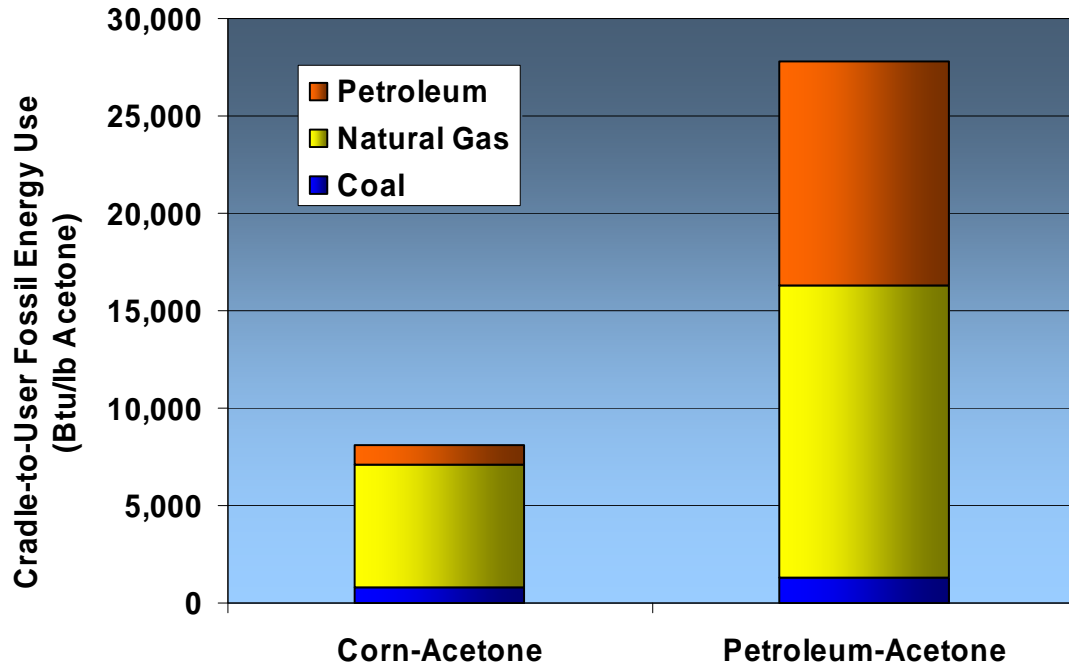
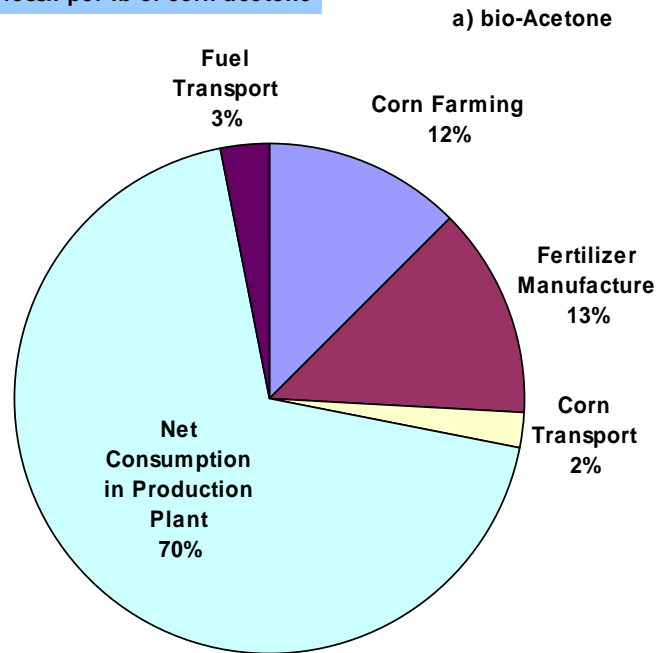


FIGURE 10 Fossil Energy Use Based on the Production of Bio-Acetone Compared with Fossil Energy Use Based on the Production of Petroleum Acetone

8127 Btu of fossil per lb of corn acetone



27818 btu of fossil per lb of acetone

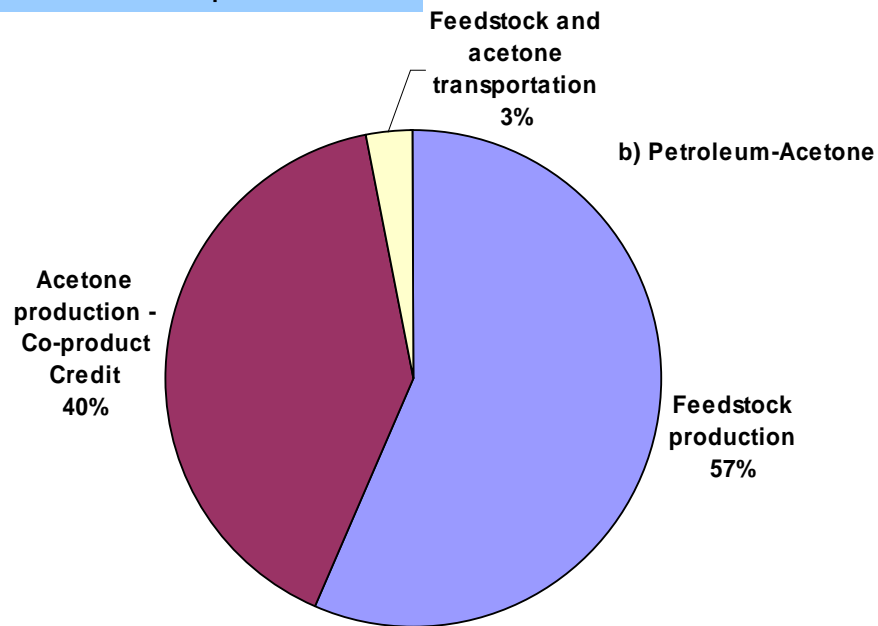


FIGURE 11 Fossil Energy Consumption Breakdown for (a) Bio-Acetone and (b) Petroleum Acetone

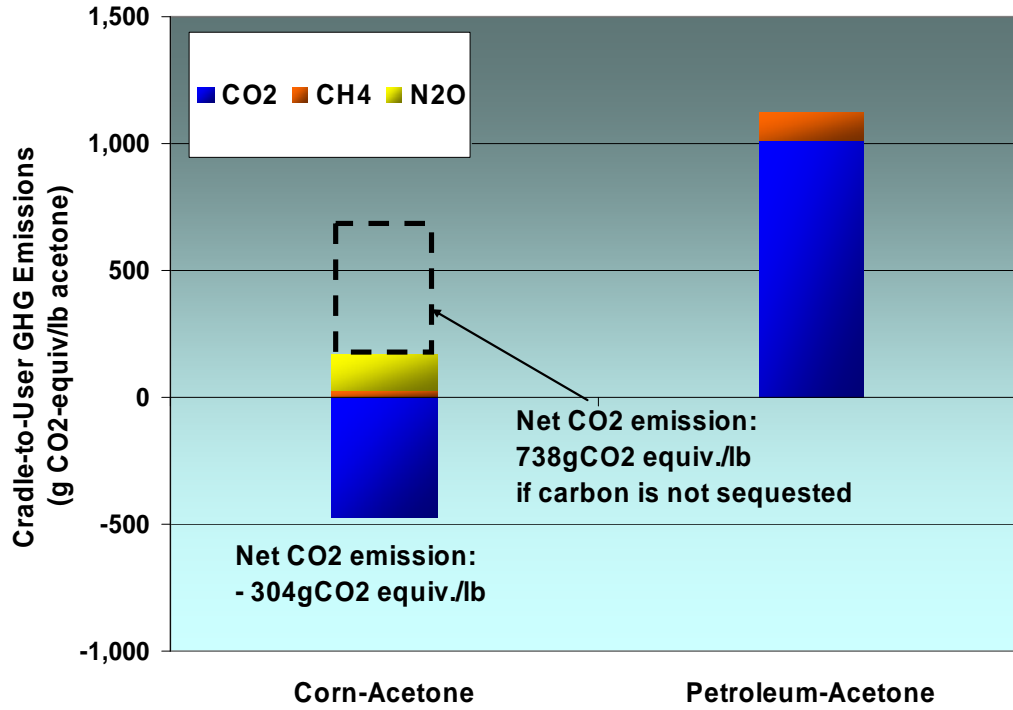


FIGURE 12 GHG Emissions Generated or Avoided by Bio-Acetone Production Compared with Petroleum Acetone Production

6 CONCLUSIONS

Our conclusions, based on the results of our study, include the following:

- Corn-based butanol, produced by means of the current ABE process, could offer substantial fossil energy savings and moderate reductions in GHG emissions relative to petroleum gasoline on a WTW basis, when co-products are credited by energy allocation.
- The energy benefits associated with bio-butanol are significant when co-product corn-acetone is credited with displacement method.
- When acetone is credited by energy allocation, life-cycle energy benefits for corn butanol are less promising than those of corn ethanol generated from conventional dry milling processes. GHG emissions generated from bio-butanol life cycle are higher than those generated from corn ethanol.
- From a liquid fuel production standpoint, the ABE process examined may not be as effective as conventional corn ethanol production in that it produces less liquid fuel (on an energy basis) per bushel of corn than the corn ethanol process, in addition to increased process fuel use in the production plant.
- The impacts of corn-acetone (produced via the ABE process) on the acetone market need to be carefully examined, and new uses for bio-acetone need to be explored.

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APPENDIX

APPENDIX

A1 PARAMETERS FOR CORN BUTANOL LIFE-CYCLE ANALYSIS

Corn Farming

<i>Energy Use</i>	22,500 Btu/bu	GREET corn-EtOH pathway
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Fertilizer Use

Nitrogen:	420 g/bu	GREET corn-EtOH pathway
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P ₂ O ₅ :	149 g/bu	GREET corn-EtOH pathway
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K ₂ O:	174 g/bu	GREET corn-EtOH pathway
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CaCO ₃ :	1,202 g/bu	GREET corn-EtOH pathway
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Pesticide Use

Herbicide:	8.10 g/bu	GREET corn-EtOH pathway
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Insecticide:	0.68 g/bu	GREET corn-EtOH pathway
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Corn Transportation*From Field to Stacks*

Truck

Share:	100%	GREET corn-EtOH pathway
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Distance:	10 mi	GREET corn-EtOH pathway
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From Stacks to Plants

Truck

Share:	100%	GREET corn-EtOH pathway
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Distance:	40 mi	GREET corn-EtOH pathway
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Butanol Production*Energy Use*

Thermal Energy	115,114 Btu/gal BuOH	see report
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Electricity	1.76 kWh/gal BuOH	see report
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Yield

Butanol	1.50 gal/bushel	see report
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Acetone	3.80 lb/gal BuOH	see report
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DDGS	11.66 lb/gal BuOH	see report
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Butanol Transportation and Distribution*Transportation*

Barge

Share:	40%	see report
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Distance:	520 mi	see report
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Rail

Share:	40%	see report
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Distance:	800 mi	see report
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Truck

Share:	20%	see report
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Distance:	110 mi	see report
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Distribution

Truck

Share:	100%	see report
Distance:	30 mi	see report

Butanol Combustion in Vehicles

On-Road Fuel Economy:

24.5 mi/gal	see report
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A2 PARAMETERS FOR PETROLEUM-BASED ACETONE ANALYSIS*Energy Use**Energy Used as Process Fuel*

Electricity:	0.31 kWh/kg acetone	see report
Oil:	9,337 Btu/kg acetone	see report
NG:	10,678 Btu/kg acetone	see report

Energy Used as Feedstock

Oil:	12,961 kWh/kg acetone	see report
NG:	18,908 kWh/kg acetone	see report

Cumene Transportation

Truck

Share:	100%	
Distance:	323 mi	see report
Fuel economy:	5.0 mi/gal	see report

A3 TRANSPORTATION FOR CORN-ACETONE*Rail*

Share:	100%	see report
Distance:	500 mi	see report

Truck

Share:	100%	see report
Distance:	100 mi	see report

A4 FUEL SPECIFICATIONS*Butanol*

Low heating value	99,837 Btu/gal
Density	3,065 g/gal
Carbon content	65%

Acetone

Low heating value	83,127 Btu/gal
Density	2,964 g/gal
Carbon content	62%



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