Assessment of feasibility and benefits of replacing bioethanol with biobutanol in the transportation fuels industry

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Abstract

In recent years there has been a strong drive towards transitioning the transportation fuels market to a sustainable alternative. Biofuels has emerged as one of the solutions and is receiving a great deal of focus in research, industry, and politics. Ethanol is currently the most popular biofuel, but butanol has been acknowledged as a superior alternative in several regards. In this paper, the chemical and physical properties of butanol are compared to ethanol and gasoline. In addition, the feasibility of a butanol-based economy is assessed in terms of available supply, compatibility in spark ignition engines in terms of performance and emissions, and ability to easily transport, store, and dispense the fuel. Life cycle assessments of biobutanol are also reviewed, which ultimately suggest that butanol has the potential to be a sustainable alternative. However, the yield of biobutanol production via ABE fermentation, the primary process currently utilized to produce the fuel, is low. Additional research is required to improve upon the ABE fermentation process, or perhaps to develop and implement an alternative process such as a thermochemical route.

Introduction

As a result of the adverse effects of burning gasoline and utilizing fossil fuels for energy there is a strong drive towards transitioning the transportation fuels market to a more sustainable alternative. Various technologies that could improve the issue include electric vehicles, fuel cells, and biofuels. Since the transportation industry relies on internal combustion engines, biofuels are receiving considerably more focus from researchers in the field and governments are creating and updating related policies [1]. In the United States, the Environmental Protection Agency (EPA) updates a Renewable Fuel Standard (RFS) annually, which mandates the total volume of renewable fuels that must be blended into transportation fuels across the US [2], based off of projections in the Clean Air Act [3]. The 2013 RFS mandated a volume of 16.55 billion gallons of renewable fuels, 2.75 billion gallons of which were dedicated to advanced biofuels (cellulosic biofuel, imported sugarcane ethanol, etc.) [3]. The Energy Independence and Security Act (EISA) expanded the RFS in 2007, which states that by 2022 36 billion gallons of renewable fuels are required to be in the US market [2], [4]. Prior to focusing on whether or not this volume will be met, attention should be directed towards which particular biofuel should provide the majority of this amount.

Ethanol has historically been the predominant biofuel in the transportation fuels industry; however, butanol is emerging as an alternative with great potential. The purpose of this paper is to assess the advantages and disadvantages of biobutanol, as well as to explore the feasibility of this transition, in terms of production, transportation, storage, and compatibility in spark ignition engines.

Properties of Biobutanol and Bioethanol

Although bioethanol has historically been the predominant biofuel, biobutanol is emerging as an alternative with great potential. It has several properties that make it a superior alternative to ethanol as a transportation fuel. The most significant of these properties is its energy density, which is approximately 27% greater than that of ethanol. This relates to improved fuel consumption and mileage for vehicles run on butanol blends as opposed to ethanol. Table 1 compares additional properties of butanol, ethanol, and gasoline, demonstrating the extensive benefits of butanol.

The most significant disadvantage of biobutanol as a transportation fuel is its low production rate [4]. Biobutanol is most commonly produced via acetone butanol ethanol (ABE) fermentation, during which all three products are produced. The yield of butanol produced from this process has been reported to be 10-30 times lower than a typical yeast fermentation process to produce ethanol [4]. A survey performed by Argonne National Laboratory found the difference to be less extreme, however, with the yield of corn ethanol from yeast fermentation and n-butanol from ABE fermentation being 0.30 kg biofuel per kg corn and 0.11 kg biofuel per kg corn, respectively [5]. This limitation on yield is the result of the inhibition of cell growth by the butanol produced in the fermentation reaction when its concentration reaches 1-2% [6], [7], [8].

Another shortcoming with the production of biobutanol is the high consumption of energy required for purification of the by-products, since the fermentation produces large quantities of acetone and ethanol in addition to the butanol [9]. However, the acetone and ethanol produced should not be considered as waste products; they can still be utilized for other purposes, and treated as co-product credits when considering a life cycle assessment [9].

Feasibility of a Butanol-Based Economy

In terms of feasibility of replacing bioethanol with biobutanol as a transportation fuel, one major aspect that must be considered is whether or not the industry will be capable of producing adequate amounts of biobutanol. An immediate jump might not be possible, however there are a number of companies already focusing on biobutanol production. Major industrial companies include Butalco, Cathay Industrial Biotech, Cobalt Technologies, Green Biologics, TitraVitae Bioscience, and METabolic Explorer [10]. Butamax™ Advanced Biofuels, a joint venture between DuPont and BP, is another company heavily involved in the biobutanol industry. They have a commercial demonstration facility that began production in 2010, and are planning a full-scale commercial production plant for 2014 [14].

Another area that is important to the feasibility of a biobutanol-based economy is the transportation of the biofuel from refiner to retail sites. Since biobutanol is non-corrosive and does not readily absorb water, it is expected that biobutanol can easily be transported using the already existing pipeline infrastructure [10], [11]. In terms of blending facilities, storage tanks, and retail station pumps, Butamax™ claims that biobutanol will be compatible with all of these [14]. In addition, Underwriters Laboratories, an independent organization focused on product safety testing and certification, performed a technical review on isobutanol as a joint project with Butamax™. They announced in 2013 that fuel storage and dispensing equipment that is currently used and certified for use with gasoline can also be used safely and effectively with biobutanol blends up to 16% [15], [16].

In 2013, an ASTM Standard (D7862) was published for biobutanol blends to be used as transportation fuel [17], highlighting the potential for this compound [18]. This standard defines the performance and quality requirements and test methods to be used for biobutanol blends of 1-

12.5%; the upper limit is based on US regulation limits as opposed to performance. These requirements are summarized in Table 2. This standard ultimately provides a fuel quality standard that can be used to govern butanol use as a transportation fuel and is expected to promote commercialization of biobutanol as a transportation fuel [18].

Compatibility issues of biobutanol in modern vehicle engines as well as emissions have received moderate attention. There have been a great deal of studies performed that examine the effects of butanol on engines, both cooperative fuel research (CFR) engines, which are the engines used for testing and research in regards to fuel performance in an internal combustion engine (IC) [19], and IC engines themselves. Yacoub et al. found that n-butanol is more prone to generating combustion knock than gasoline. In addition, alcohol-gasoline blends cause lower carbon monoxide emissions than gasoline, but leads to larger unburned alcohol emissions [20]. Szwaja and Naber also examined combustion characteristics using n-butanol in a CFR; they ultimately concluded that n-butanol is capable of replacing gasoline, either completely or as a butanol/gasoline blend, when considering combustion and energy density properties [4], [21].

Many studies have also been performed on spark ignition (SI) engines. Wallner et al., for example, performed tests on 10% butanol, 10% ethanol, and pure gasoline to measure emissions, performance, and combustion. They found that combustion stability, carbon monoxide, and hydrocarbon emissions were relatively similar between the fuels. 10% ethanol was found to be less prone to knock than the other two fuels and NOx emissions were found to be the lowest with 10% butanol. They ultimately concluded that, based on their experimental results, 10% butanol can replace 10% ethanol without negatively affecting emissions or combustion stability [22].

Based on various papers reporting combustion in SI engines, Jin et al. summarized that knocking tendency and combustion durations of n-butanol, both pure and blends, are similar to that of gasoline. In terms of performance, engine power is maintained for butanol blends less than 20%. The use of butanol was also suggested to reduce CO, THC, and NOx, depending on the engine design and operating conditions, but increases the amount of unburned alcohol emissions, in comparison to gasoline. Aldehyde emissions, namely formaldehyde, is also high for n-butanol [4].

In a more recent study, Ratcliff et al. tested 16% ethanol, 17% n-butanol, 21% isobutanol, and 12% isobutanol plus 7% ethanol gasoline blends. The fuels were tested in a light duty vehicle (2009 Honda Odyssey) using triplicate LA92 cycles (California Unified Cycle). They discovered that there was no statistically significant difference in NOx or non-methane organic gas emissions between the blends, but that CO emissions was the lowest in the ethanol blend. In addition, the butanol blends showed the greatest amount of carbonyl emissions. The statistically significant effects on emissions of chemicals that are currently regulated in the US include a 60% increase of formaldehyde emissions from isobutanol and 29% decrease in CO emissions from 16% ethanol, both compared to conventional gasoline. However, both butanol isomers tested resulted in approximately 20% lower amounts of unburned alcohol emissions than ethanol [23]. A lot of the data related to emissions from engines run ethanol versus butanol conflicts with each other. This is likely a result of the large degree of variability between engines, vehicles, and operating conditions.

There are a few cases where vehicles have been driven on pure butanol with no modifications needed, although these reports are not located in peer-reviewed journals. In one case, a 1992 Buick made a 10,000 mile trip across the US run on butanol; no modifications to the car were required for this trip. Large reductions in hydrocarbon, carbon monoxide, nitrogen oxides, and carbon dioxides were reported, as well as a gas mileage of 20-26 mpg [24]. In addition, Butamax™ fueled over 5,000 vehicles with 24% biobutanol blends during the 2012 Olympic Games; a UK demonstration was also held in which 250,000 vehicles were filled up and drove 80 million miles without any performance compromised [25]. Butamax™ also claims that biobutanol can be used at blends higher than 16% without requiring engine modifications, and that up to 16% volume there is no reduction in performance, durability, or emissions. These are all significant accomplishments, although they must be addressed with caution as these claims do not appear to be backed up with publicly available information [14].

Life Cycle Analyses

Since the most significant disadvantage of biobutanol is its low production yield via current technology, a great deal of research is going into improving the production process. Currently, the majority of this research is focused on improving the ABE fermentation process. This includes genetic manipulations, metabolic engineering [5], the use of separation technology to remove the butanol from the broth during fermentation [8], and the use of surfactants hold the butanol inside micelles [7], among others. Pfromm *et al.* has suggested that the ABE process must improve by 74% to allow the yield of biobutanol to be equivalent to that of ethanol production [5], which could be a difficult feat for ABE fermentation.

Swana et al. analyzed the net energy production of bioethanol and biobutanol. They reported a net energy generation of 6.53 MJ/L for corn-to-biobutanol conversion, while corn-to-bioethanol was only 0.4 MJ/L [1]. However, they only considered a “well-to-product” life cycle assessment. Wu et al. also performed a life cycle analysis on biobutanol production, in which they determined that it results in a 39-56% reduction in fossil energy usage in comparison to conventional gasoline, as well as a 32-48% reduction in greenhouse gases. It was also noted, however, that corn ethanol is suspected to boast even larger reductions [26]. Pfromm et al. also assessed the lifecycle of biobutanol, and suggested that the energy yield of n-butanol is approximately half of that of ethanol when produced from ABE fermentation and yeast fermentation, respectively. They further analyzed the production process and determined that a fermenter must be 4 times the size to produce a comparable yield of n-butanol in comparison to ethanol production, thus increasing capital costs immensely [5].

Tao et al. performed a more detailed "field to wheel" life-cycle assessment (LCA) on cellulosic isobutanol, n-butanol, and ethanol, all produced via fermentation [9]. The energy return on investment (EROI) was calculated based on the ratio of energy in the biofuel to energy consumed during the production. Although the yield of butanol production via ABE fermentation is significantly lower than that of ethanol, the by-products produced can be treated as co-product displacement credits, thus increasing the EROI. The field to wheel analysis determined that the 3 biofuels have comparable EROI, in the range of 1.4 – 1.5 MJ/MJ. Note, however, that if excess electricity produced by the biorefineries can be sold to the grid, electricity credits can also be considered, increasing this metric to 2.2 – 2.8 MJ/MJ. The LCA also suggests that butanol, both normal- and iso-, result in greater greenhouse gas emissions than ethanol, but n-butanol requires the smallest amount of fossil energy. All of this data is summarized in Table 3 [9].

This data is promising when it comes to the feasibility of replacing bioethanol with biobutanol, from a net energy perspective. It also highlights the great potential of biobutanol, since the EROI is comparable with ethanol despite its low yield. Further advancement in biobutanol production could greatly enhance the EROI of the component, thus improving its strong potential in the fuel industry. In addition, the butanol in this study assumes the ABE fermentation route. However, non-biochemical routes are also possible. For example, Okoli and Adams have developed a thermochemical route for the production of biobutanol from lignocellulosic biomass, which theoretically has a yield of 44%, but has yet to be demonstrated [27]. Systems using the thermochemical route may be able to reduce the energy consumption and costs of the separations step and significantly improve upon the ABE route.

Conclusions

Although ethanol is the predominant biofuel currently in the transportation fuels market, there is a great deal of data supporting the immense potential for biobutanol as a preferable alternative. Butanol has a number of chemical and physical properties making it a superior alternative to ethanol. In addition, several studies have suggested that biobutanol is compatible in the spark ignition engine and a switch from ethanol to butanol will not affect engine performance. In terms of vehicle emissions, however, there is conflicting data regarding the effects of utilizing butanol versus ethanol.

There is promising evidence related to the life cycle and energy return on energy invested of biobutanol, suggesting that this chemical may have the potential to be a sustainable alternative for the automotive fuel industry. The major drawback, however, is the low yield of butanol production via ABE fermentation. Therefore additional research is required to improve the yield of butanol production before butanol can have great success in the biofuels industry. A lot of research is going into methods to improve ABE fermentation, however perhaps a thermochemical route may be more promising.

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Tables

Table 1. Comparison of butanol, ethanol, and gasoline properties.

Property	Butanol	Ethanol	Gasoline	Implications
Energy Return on Energy Invested	1.4 – 1.5 [9] (cellulosic)	1.5 [9] (cellulosic)	18 [9] (2005)	- EROEI is comparable between butanol and ethanol, but is still low compared to gasoline
Volumetric energy density (MJ/L)	27 - 29 [6]	19.6 [6]	32 [6]	- Butanol has higher energy density than ethanol; closer to gasoline [10] - Higher energy density reduces fuel consumption and improves mileage [4]
Miscibility in gasoline	High [10] [11] [4]	Low, relative to biobutanol	NA	- High miscibility allows fuel to blend with gasoline at any ratio [4], [10], [11]
Water solubility at 25°C (%)	9.1 [11]	100.0 [11]	< 0.01 [11]	- Low solubility in water reduces the spread of spills into groundwater [11] - Biobutanol has much lower risk of phase separation if the biofuel/gasoline blend comes into contact with water [4], [12], [9] - Allows biobutanol, unlike ethanol, to be transported via pipeline [4]
Anti-Knock Index (Octane at Pump)	87 [13]	113 [13]	86 - 95 [6]	- AKI of butanol is more comparable with gasoline [13] - Fuel economy not largely affected with butanol/gasoline blends [11], [6]
Reid Vapour Pressure (RVP) of 10% blends in gasoline (psi)	6.4 [11]	20 [11]	Summer: <7.8 Winter: <15 [11]	- RVP of gasoline is regulated; low RVP lowers emissions via fuel evaporation from tank [9] - butanol allows the use of less expensive octane enhancers [11] (lower RVP generally relates to higher cost components in blend) - butanol can prevent requirement for summer and winter blends - Lower volatility reduces occurrence of cavitation [4]
Heat of Vapourization (MJ/kg)	0.43 [6]	0.92 [6]	0.36 [6]	- Lower HOV relates to less ignition problems and easier to start engine in cold weather [4]
Flammability Limit (volume % in air)	1.4 – 11.2 [4]	4.3 – 19 [4]	0.6 – 8 [4]	- Comparable flammability between both alcohols and gasoline
Viscosity at 40°C (mm^2/s)	2.63 [4], [6]	1.08 [4], [6]	0.4 – 0.8 [4], [6]	- Higher viscosity reduces wear on fuel pumps but could potentially lead to buildup of material in the engine [4]
Corrosivity	Low relative to ethanol [4], [12]	High [12]	Low	- High corrosion risk with ethanol causes problems with storage and transportation [12]

Table 2. Performance requirements of butanol to be blended with gasoline established by ASTM Standard D7862.Adapted from [17].

Property	Limit
Butanol, volume %, min	96.0
Methanol, volume %, max	0.4
Water content, volume %, max	1.0
Acidity (as acetic acid), mass % (mg/L), max	0.007
Inorganic chloride, mg/kg (mg/L), max	8
Solvent-washed gum, mg/100 mL, max	5.0
Sulphur, mg/kg, max	30
Existent sulphate, mg/kg, max	4

Table 3. Life cycle metrics of biofuels. GGE=gasoline gallon equivalent basis. Adapted from [9].

Metrics		N-Butanol	Isobutanol	Ethanol
GHG emissions	kg CO_2-eq/GGE	6.9	7.0	6.5
Fossil energy input	MJ/GGE	67	75	69
EROI	MJ/MJ	1.5	1.4	1.5